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(54) **THERMOREVERSIBLE RECORDING MATERIAL, PRODUCTION THEREOF, AND THERMAL RECORDING MEDIUM.**

(57) A thermoreversible recording material which can reversibly repeat transparent and opaque states according to temperature history and gives a thick thermoreversible recording layer having a good contrast between transparent and opaque states and a high sensitivity. The material comprises a low-molecular organic compound dispersed in a polymer resin, which compound has both a proton-donating group (A) and a proton-accepting group (B) in its molecule, forms a dimer (C) at the transition point (T1) thereof, and separates into the monomer at a temperature (T2) higher than the T1.

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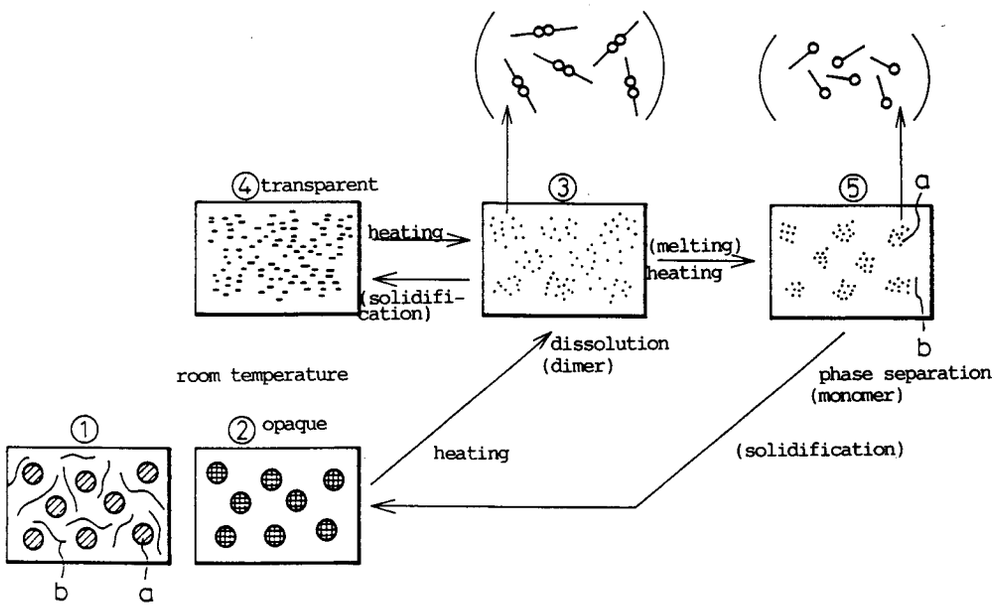
Fig.1


④transparent
heating
(solidifi-
cation)
③
(melting)
heating
⑤
a
b
dissolution
(dimer)
phase separation
(monomer)
room temperature
①
②opaque
heating
(solidification)
b
a

TECHNICAL FIELD

This invention relates to a thermo-reversible recording material, its production method, and thermo-sensitive recording medium. More particularly, it relates to a thermo-reversible recording material capable of reversibly repeating a transparent state and an opaque state upon heating, its production method, and a thermo-sensitive recording medium.

BACKGROUND ART

An example of thermo-reversible recording materials according to the prior art which is composed of dispersed an aliphatic acid in a vinyl chloride type resin matrix, and utilizes the property that the crystalline state of the aliphatic acid reversibly changes in accordance with a temperature change.

The structure of this thermo-reversible recording material and its production method are described, for example, in KOKAI (Japanese Unexamined Patent Publication) Nos. 57-82086, 57-82087, 57-82088 and 63-132089. Hereinafter, a production method of this thermo-reversible recording material will be explained.

docosanoic acid (behenic acid)	0.25g (14 wt%)
polyvinylidene chloride/acrylonitrile copolymer (salan resin "R-200", a product of Asahi Kasei)	1.5g (86 wt%)

After the mixture of the compounds described above is sufficiently dissolved in 8.0g (450 wt%) of tetrahydrofuran as a solvent, and the resulting solution is coated to a 120 μm-thick mylor film (polyester film) by casting. The solvent is evaporated at 50 °C, and a 15 μm-thick film-like thermo-reversible recording material is formed.

Fig. 14 is a schematic view showing the thermo-reversible recording material of the prior art under various conditions. In the drawing, ① represents the state where dedocosanoic acid 2 and the polyvinylidene chloride/acrylonitrile copolymer 4 are dispersed in tetrahydrofuran; ② represents the state of the thermo-reversible recording material at room temperature T; ③ represents the state of the thermo-reversible recording material at 90 °C higher than the melting point of a low molecular weight organic compound in the thermo-reversible recording material; ④ represents the state of the thermo-reversible recording material when it is returned from the state ③ to room temperature, and ⑤ represents the state of the thermo-reversible recording material when it is heated to 110 °C from the state ④ .

However, the thermo-reversible recording material according to the prior art described above is white and translucent, and when hand-writing is made on this recording material using a heat pen having a distal end at 90 °C (not shown in the drawing), the hand-written portion changes to the transparent state (the state ④ in Fig. 14), and a thin transparent character can be written on a white base. However, since the contrast between transparency and opaqueness is not sufficient, the character is not clear and is difficult to identify. A light transmission factor of the white base is 78% and that of the transparent portion is 84%. In other words, the difference of these transmission factors is only about 6%. Next, when this thermo-reversible recording material according to the prior art is placed into a hot blast oven kept at 110 °C (not shown in the drawing), the transparent portion becomes turbid and the returns to the original translucent state as a whole (the state ② in Fig. 14). When this procedure is repeated several times, however, the contrast becomes progressively lower.

When a sample of the conventional thermo-reversible recording material in the white translucent state and another in the transparent state are observed through an electron microscope, it is found that the particles of docosanoic acid are extremely small and are almost in the dissolved state. In other words, since the conventional production method uses a solvent such as tetrahydrofuran, which easily dissolves the low molecular weight organic compound such as docosanoic acid, the low molecular weight organic compound does not assume a dispersion state where it forms the very small particles. For this reason, the molecules of docosanoic acid already exist individually in the single molecule state in the polymer chains of the polyvinylidene chloride/acrylonitrile copolymer at the time of film formation, and do not form fine particles. Accordingly, a sufficient scattering of light does not occur and a sufficient opaque state cannot be attained.

If the thickness of the thermo-reversible recording layer is increased, the contrast between transparency and opaqueness can be improved to some extent, but this method promotes a reduction in sensitivity, which is another problem. When the thermo-reversible recording material is applied to a magnetic card that includes a magnetic recording layer between a support of the magnetic card and the thermo-reversible recording layer and has printable surfaces on both of its sides, magnetic data cannot be read out,

particularly when the distance between the thermo-reversible recording layer and a magnetic head has increased. Accordingly, it has been necessary to further reduce the thickness of the thermo-reversible recording layer.

Accordingly, there has not been available a thermo-reversible recording material that has a small film thickness, a sharp contrast between transparency and opaqueness and a high degree of sensitivity.

The present invention is directed to provide a thermo-reversible recording material that has a sharp contrast between a transparent state and an opaque state, even though it has a small film thickness, and has a high degree of sensitivity, and a method of supplying such a thermo-reversible recording material.

DISCLOSURE OF THE INVENTION

The problems described above can be solved by the following thermo-reversible recording material.

In other words, in a thermo-reversible recording material containing a low molecular weight organic compound dispersed in a polymer resin capable of reversibly repeating a transparent state and an opaque state in accordance with its heat history, the present invention uses a thermo-reversible recording material characterized in that the low molecular weight organic compound contains both a proton donor group (A) and a proton acceptor group (B) in one molecule thereof, forms a dimer at a transition temperature T1 of the low molecular weight organic compound, and separates into a monomer at a temperature T2 higher than the transition temperature T1. The present invention can be accomplished in the following three modes.

In the first mode, two molecules of the low molecular weight organic compound (a) form a dimer by a hydrogen bond at the transition temperature T1 of the low molecular weight organic compound, and is dissolved in the polymer resin (b). The thermo-reversible recording material undergoes phase separation from the polymer resin (b) at a temperature T2 higher than the transition temperature T1.

In the second mode, the low molecular weight organic compound (c) is dispersed in dot form in the polymer resin (d), and the polymer resin (d) is not compatible with the low molecular weight organic compound (c) at the transition temperature T1 of the low molecular weight organic compound (c) but retains the dot form.

Finally, in the third mode, the polymer resin (f) forms a three-dimensional network structure, and the low molecular weight organic compound (e) exists in continuous phase form inside the polymer resin (e). The polymer resin (f) is not compatible with the low molecular weight organic compound at the transition temperature T1 of the low molecular weight organic compound (e) but retains its three-dimensional network structure.

The term "transition temperature" used herein means a temperature lower by 5 to 15 °C than the melting point of the low molecular weight organic compound.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic view of a thermo-reversible recording material showing the principle of the present invention (1).

Fig. 2 is a schematic view of a thermo-reversible recording material showing the principle of the present invention (2).

Fig. 3 is a schematic view of a thermo-reversible recording material showing the principle of the present invention (3).

Fig. 4 is a graph showing the degree of transparency of the thermo-reversible recording material of the present invention in accordance with temperature.

Figs. 5a-5d are sectional views of a display panel in the first embodiment of the present invention.

Figs. 6a-6b are sectional views of the display panel in the second embodiment of the present invention.

Figs. 7a-7b are sectional views of an OHP sheet in the third embodiment of the present invention.

Fig. 8 is a sectional view of a thermo-sensitive sheet in the fourth embodiment of the present invention.

Fig. 9 is a sectional view of a magnetic card in the fifth embodiment of the present invention.

Fig. 10 is a sectional view of a magnetic card in the sixth embodiment of the present invention.

Fig. 11 is a sectional view of a dimmer film in the seventh embodiment of the present invention.

Fig. 12 is a sectional view of dimmer glass in the eighth embodiment of the present invention.

Fig. 13 is a structural view of a low molecular weight organic compound forming a dimer of the present invention.

Fig. 14 is a schematic view of a thermo-reversible recording material showing the principle of a prior art example.

Figs. 15a-15b are IR charts showing that the low molecular weight organic compound in the present invention is converted to a dimer.

Fig. 16 is a schematic view of a two-molecule arrangement of the low molecular weight organic compound in the present invention.

Fig. 17 is a TEM (Transmission Electron Microscope micrograph (20,000 times) of a thermo-reversible material (transparent state) in the second embodiment of the present invention.

Fig. 18 is an X-ray diffraction diagram (in a sectional direction) of the thermo-reversible material in the second embodiment of the present invention.

Fig. 19 is an X-ray diffraction diagram (in a front face direction) of the thermo-reversible material in the second embodiment of the present invention.

Fig. 20 is an explanatory view explaining a thermo-reversible mechanism of the thermo-reversible material in the second embodiment of the present invention.

Fig. 21 is a schematic view of a one-molecule arrangement of the low molecular weight organic compound.

BEST MODE FOR CARRYING OUT THE INVENTION

The basic principle of the thermo-reversible recording material of the present invention utilizes the property that the molecules of a low molecular weight organic compound as one of the components of the thermo-reversible recording material causes a reversible change between a dimer and a monomer. Fig. 13 shows a structural formula of a low molecular weight organic compound that forms the dimer of the present invention. When the low molecular weight organic compound is kept at a transition temperature T_1 °C (lower by 5 to 15 °C than a melting point), the molecules of this low molecular weight organic compound have both a proton donor group and a proton acceptor group, and since these groups cause a hydrogen bond as shown in the drawing, the low molecular weight organic compound has the property of association (is converted to a dimer) by two molecules. When the compound is returned to room temperature (T), the compound exhibits the characteristic feature in that it is solidified while forming the dimer. [This is evidenced by the fact that the peak of 1,737 cm^{-1} as the absorption of a carbonyl group is found to shift to a lower frequency side as a result of IR analysis as shown in Fig. 15. (The absorption of the carbonyl group after the association of the two molecules appears at 1,701 cm^{-1}).] When the low molecular weight organic compound is held at a temperature T_2 °C higher than its melting point, the compound is completely molten and the activity of the molecules becomes so active that the compound can no longer exist as the dimer but is decomposed to monomers. Therefore, various forms of behaviour such as the change of an apparent polarity of the molecules to hydrophilicity, various molecular arrangement and crystal directions at the time of crystallization, the change of a refractive index, and so forth, occur. In this way, the transparent state and the opaque state are reversibly attained by utilizing the characteristic property in that the low molecular weight organic compound can assume two forms of the dimer and the monomer depending on the temperature history imparted thereto, that is, dissolution due to the change of the apparent polarity, the phase separation phenomenon, anisotropy of the molecular arrangement and crystal, the change of the refractive index, and so forth.

Three modes of the thermo-reversible recording material of the present invention provide the following action by utilizing the properties described above.

To begin with, in the first mode, when the thermo-reversible recording material is held at a temperature lower by 5 to 15 °C than the melting point of the low molecular weight organic compound a (at the transition temperature), the low molecular weight organic compound a forms the dimer by the hydrogen bond, commonly shares the polar groups and assumes the form in which a hydrophobic group faces outward.

Therefore, the apparent polarity becomes more hydrophobic, and when a surrounding polymer resin b having a polarity approximate to this polarity is used, the low molecular weight organic compound is dissolved, and permeates, between the polymer chains, so that the recording material becomes transparent (③), and even when the recording material is returned to room temperature, this state is maintained (④). On the other hand, when the thermo-reversible recording material is held at a temperature higher than the melting point of the low molecular weight organic compound, the motion of the low molecular weight organic compound becomes so vigorous that the hydrogen bond forming the dimer is cut off and the dimer changes to monomers. Therefore, the polarity becomes more hydrophilic and comes off from the polarity of the polymer resin. Accordingly, phase separation takes place and the low molecular weight organic compound again aggregates (⑤), and when the recording material is returned to room temperature, the low molecular weight organic compound is converted to fine particles, and the recording material becomes opaque (②).

Next, in the second mode, when the low molecular weight organic compound is heated to a temperature lower by 5 to 15 °C than the melting point, it is converted to the dimer as shown in Fig. 2. However, since the polymer resin d is not compatible with the low molecular weight compound c, the fine particles do not change their shapes but the internal molecular arrangement changes. In other words, the low molecular weight organic compound forms the dimer with the neighboring molecules and takes the two-molecule arrangement as shown in Fig. 16, and the axes of the molecules are aligned in a direction perpendicular to the film surface (③), and when the compound is returned to room temperature, crystallization proceeds under this state (④), which is shown in a TEM micrograph (20,000X) of Fig. 17. It can be recognized from this micrograph that the fine particles of the low molecular weight organic compound are from about 0.3 to about 0.5 μm, and a stripe structure with a pitch of about 60Å parallel to the film surface is recognized inside the particles. This 60Å pitch is in agreement with the alignment length of the two molecules of the low molecular weight organic compound shown in Fig. 16, and it can be understood from this fact that the molecules are converted to the dimers and are aligned. As to the direction of the molecules, the result of the X-ray diffraction suggests that the axes of the molecules are aligned perpendicularly to the film surface because the diffraction peak of a diffraction angle of 5.75° (face interval 15.9Å) of the samples (a) and (c) in the transparent state appears only in the direction of the section (EV) but does not appear in the direction of the surface (TV). It is believed, therefore, that the incident light is easily transmissible, and if the refractive index is brought into conformity with that of the polymer resin, the recording material exhibits transparency. On the other hand, when heating to a temperature higher than the melting point of the low molecular weight organic compound, the crystal is liquefied, and the activity of the molecules becomes so active that the compound can no longer exist as the dimer but is separated into the monomers. The molecules of the low molecular weight organic compounds move while facing in various directions (⑤), and when the temperature is lowered to room temperature in this state, the molecules are crystallized in a state where the one-molecule arrangement shown in Fig. 21 and the two-molecule arrangement shown in Fig. 16 exist in mixture, and the molecules are crystallized while facing in various directions and a large number of fine crystals are formed (②). This is evidenced from the fact that the diffraction peak at the diffraction angle of 5.75° (face interval 15.9Å) of the opaque sample (b) does not exhibit a big difference between the direction of the section and the direction of the surface in the X-ray diffraction data shown in Figs. 18 and 19. It is believed that the incident light is irregularly reflected when passing through the recording material and the material becomes white and opaque. Fig. 20 is a model of the thermo-reversible mechanism described above.

Finally, in the third mode described already, the polymer resin g formed by the polymerization of the monomer or the oligomer f assumes a three-dimensional network structure (sponge-like structure; Fig. 3- ②), and the low molecular weight organic compound e exists while forming a continuous phase but not in dot form (②), and when the transition temperature of the low molecular weight organic compound is increased, the low molecular weight organic compound is converted to the dimer, and is arranged in the two-molecule arrangement perpendicularly to the film surface in the same way as in the second embodiment described above, as shown in Fig. 16 (③), and even when the temperature is returned to room temperature, this organic compound is crystallized in a state to similar (④). Accordingly, incident light is easily transmissible, and when the refractive index is brought into conformity with that of the polymer resin, the recording material exhibits transparency. On the other hand, when heated to a temperature higher than the melting point of the low molecular weight organic compound, the activity of molecules becomes so vigorous that the low molecular weight organic compound can no longer exist as the dimer but is separated into the monomers. As a result, the low molecular weight compound moves while facing various directions (⑤). When the temperature is returned to room temperature, the molecules crystallize while facing various directions and a large number of fine crystals are formed (②). When incident light passes through the molecules, it is reflected irregularly, and the recording material appears white and opaque.

EMBODIMENTS

Hereinafter, embodiments of the present invention will be explained more definitely with reference to the drawings.

Figs. 1 to 4 are schematic views and a graph showing the state of the thermo-reversible recording material of the present invention under various conditions. In these drawings, reference numerals ① to ⑤ represent the following state, respectively:

① the state where the low molecular weight organic compound and the polymer resin are uniformly dispersed in a solvent;

② the state of the thermo-reversible recording material at room temperature T;

③ the state of the thermo-reversible recording material at the transition temperature T1 of the low molecular weight organic compound in the thermo-reversible recording material;

④ the state of the thermo-reversible recording material when the state ③ is returned to room temperature T;

5 the state of the thermo-reversible recording material when heated to a temperature T2 higher than the temperature T1 from the state ④.

[FIRST EMBODIMENT]

The first embodiment of the present invention is the application of this invention to a display panel, which utilizes the mode shown in Figs. 1 and 4. Fig. 5 shows a sectional view of the display panel.

stearic acid amide a	15 wt%
polymethyl methacrylate b	85 wt%
toluene/MEK = 7/3	400 wt%

The components described above were uniformly dispersed using a sand mill. At this time, methacrylate was dissolved in toluene/MEK = 7/3 as the solvent, but stearic acid amide a not soluble in toluene/MEK = 7/3 was so arranged as to be uniformly dispersed in toluene/MEK = 7/3 (state of Fig. 1 ①). Next, the solution described above was coated on a 100 μm-thick polyester film by casting, and toluene/MEK = 7/3 as the solvent was evaporated at 60 °C, thereby providing a thermo-reversible layer 11 consisting of a 10 μm-thick white opaque thermo-reversible recording material according to the first mode (the structure shown in Fig. 1) of the present invention (state shown in Figs. 1 and 4- ②).

In Fig. 5(a), "Aronix UV-3333" (a one-liquid type UV-curable acrylic resin, a product of Toa Gosei) was coated to a thickness of 5 μm on the surface of the resulting thermo-reversible recording layer 11, and was cured by UV (ultraviolet rays) to form a protective film 13.

Next, the polyester film 12 described above was bonded to a steel board 14 having the surface thereof colored in black, to complete a display panel.

In Fig. 5(b), when hand-writing was effected by a heat pen 15 having the tip thereof at 100 °C, stearic acid amide a dissolved and permeated the molecular chains of polymethyl methacrylate b because the molecules of stearic acid amide a at the contact portion of the heat pen 15 formed the dimer by the hydrogen bond and polymethyl methacrylate b (polymer resin) had solubility approximate to that of stearic acid amide a at this time (state ③ of Figs. 1 and 4).

When the heat pen left thereafter the display panel, stearic acid amide a was solidified while being dissolved and permeated the molecular chains of the polymer, and consequently, the thermo-reversible recording material changed to a transparent state (state ④ in Figs. 1 and 4), and a black character could be clearly printed, as if the character were written by a black marker on a white board. Though a black sheet existed at the back of a white portion, the latter was hardly affected by the former, and a black-and-white contrast was very sharp because of the high degree of whiteness.

In Fig. 5(c), when an iron type erasing hot plate 16 at 120 °C was brought into contact with the display panel, the motion of stearic acid amide a was activated. Since the hydrogen bond forming the dimer was cut off and the dimer changed to the monomer, solubility also changed, and came off from the solubility of polymethyl methacrylate b. As a result, stearic acid amide a was converted to fine particles (state ⑤ in Figs. 1 and 4), and when the thermo-reversible recording material was returned to room temperature, the transparent portion became turbid, and the recording material returned to the original white base as a whole and the character disappeared (to the state ② in Figs. 1 and 4). Even after this procedure was repeated 500 times, printing could be effected problem free.

Fig. 5(d) shows an example of a planar heat generator 17 when disposed on a steel board 14 in Fig. 5-(a) and used for erasing.

Next, a sample of the thermo-reversible recording material in the white (opaque) state and a sample in the transparent state were observed by an electron microscope. It was found that, in the case of the white state, fine particles of about 0.2 to 1.0 μm of stearic acid amide a were distributed, and in the case of the transparent state, stearic acid amide a was dissolved and permeated the molecular chains of polymethyl methacrylate b and hence, the particles existed in a distinct state. The light transmission factor was 80% in the transparent state and 60% in the opaque state.

[SECOND EMBODIMENT]

Two kinds of thermo-reversible recording materials were obtained in the same way as in the first embodiment except that the proportion of stearic acid amide a and polymethyl methacrylate b was changed. The proportion and characteristics of these two kinds of thermo-reversible recording materials as the second embodiment are tabulated in Table 1.

Table 1

Example	stearic acid amide (wt%)	PMM* (wt%)	particle size (μm)	transparent (**)	opaque (**)	contrast
1	15	85	0.2 - 1.0	80	60	fair
2 sample 1	8	92	0.1 - 1.0	80	69	fair
2 sample 2	38	62	0.5 - 5	77	72	fair

*: polymethyl methacrylate
**: light transmission factor (%)

As a result Example 1 having the proportion of stearic acid amide a to polymethyl methacrylate b = 15:85 provided the highest contrast.

It was believed that the proportion of stearic acid amide a to polymethyl methacrylate b of 5:95 to 40:60 was suitable and a higher contrast could be obtained when 5 to 40 vol% of the low molecular weight organic compound on the basis of the total volume was contained.

In order to obtain a sufficient contrast, the relation of the light transmission factor between the transparent state and the opaque state must be such that the light transmission factor in the opaque state is not greater than 75% and the difference in the light transmission factor between the transparent state and the opaque state must be at least 5%, for, when the light transmission factor in the opaque state is greater than 75%, the contrast is not sufficient because the color of a colored support that is generally disposed in the background can be seen through, and if the difference in the light transmission factor in the transparent state is less than 5%, the difference of the change is so small that a sufficient contrast cannot be obtained.

The production method of the thermo-reversible recording material of the first embodiment (the structure shown in Fig. 1) of the present invention can be attained by uniformly and finely dispersing the low molecular weight organic compound a in a solvent not dissolving the low molecular weight organic compound a but dissolving the polymer resin b, forming a film by casting, and drying the solvent. In the film after drying, the low molecular weight organic compound a is finely dispersed in the polymer resin b, and the film is in the opaque state.

The optimum particle size of the low molecular weight organic compound a is from 0.1 to 5 μm so as to obtain a high contrast. The particle size below this range approaches the wavelength of light, and the light scattering capability becomes insufficient. In contrast if the particle size exceeds this range, the light scattering capability drops, because a large number of particles cannot be retained per unit volume.

Examples of the polymer resin b used in the first embodiment (the structure shown in Fig. 1) of the present invention includes polyacrylates, polymethacrylates, polystyrene, methyl methacrylate-styrene copolymers, acrylonitrile-styrene copolymers, styrene-butadiene copolymers, acrylonitrile-acrylate-styrene copolymers, polymethyl pentene, transparent ABS resins, polycarbonates, silicon resins, polyvinyl butyral, polyvinyl formal, ethyl cellulose, methyl cellulose, cellulose acetate, nitrocellulose, polyvinyl alcohol, polyacrylic acid, polyacrylamides, starch, gum arabic, styrene-maleic acid copolymers, gelatin, polyvinyl acetate, ethylene-vinyl acetate copolymers, ethylene-vinyl acetate partially saponified compounds, vinyl chloride, vinyl acetate copolymers and polyvinyl chloride. More preferred polymer resins are polymethacrylates, ethyl cellulose, vinyl chloride-vinyl acetate copolymers and polyvinyl chloride.

To further enhance the contrast, it is effective to render the color of the background color layer difficult to transmit when the recording material is opaque. Therefore, the thermo-reversible recording material is disposed in advance on a transparent support, and the back side of this transparent support is bonded to a colored support through a spacer, such as inorganic or organic particles having a particle size of 1 to 500 μm, a fiber or a resin printed dot pattern so as to separate the thermo-reversible recording layer from the colored support. According to this arrangement, reflected light from the color support is not directly incident into the thermo-reversible recording layer but is scattered once on the back side of the thermo-reversible

recording layer to lower the transmission factor. In this way, the color of the colored layer is rendered difficult to transmit and eventually, the contrast can be improved.

Next, the third embodiment, wherein a spacer is disposed on the display panel of the first embodiment, will be explained.

[THIRD EMBODIMENT]

The third embodiment of the present invention represents the application of the present invention to a display panel having a spacer, and is shown in Fig. 6.

In Fig. 6(a), urea resin particles 18 having a particle size of about 500 μm were sandwiched between a polyester film 12 having a thermo-reversible recording layer 11 and protective layer 13 and obtained in the first embodiment, and a steel board 14 having a black colored layer 14a on the surface thereof, and a film 12 and a steel board 14 were bonded by a sealant so as to produce a display panel similar to that of the first embodiment. In Fig. 6, reference numeral 19 denotes the sealant.

When hand-writing was effected on the display panel by a heat pen (not shown in the drawing) having a distal end heated to 100 °C, a portion of the panel changed to a transparent state and a clear black character was printed on the white base. The degree of whiteness could be improved much more than in the first embodiment, and the contrast became higher. Table 2 comparatively tabulates the reflection density of the first and third embodiments.

Table 2

Example	spacer	reflection density*		contrast
		white	black	
1	nil	0.3	1.4	fair
2	yes	0.1	1.4	excellent

*: measured by Macbeth illuminometer

In the third embodiment, the space was disposed between the thermo-reversible recording material and the black base of the background as shown in Fig. 6(b). Therefore, reflected light from the back was once scattered and then allowed to be incident into the recording layer, and the degree of whiteness could be improved without an adverse influence from the back.

The display panel described in the first and third embodiments can be used for a black board, a white board, an OA board, an information board, a public notice board, etc., which can make these boards clean and save labor, and when combined with a personal computer or the like, the display panel can produce an automatic drawing, and is extremely convenient.

The polyester film, the steel board, etc., are used as the support below the thermo-reversible recording material, but it is also possible to use various other members such as a film, a resin board, paper, a metal sheet, glass, a composite material, and so forth. These supports must be colored in colors other than white. The colored layer may be disposed on the surface, or the support itself may be colored. In the case of a transparent support, the back may be colored. A black or a silver type is preferred so as to obtain a high contrast.

[FOURTH EMBODIMENT]

The fourth embodiment represents the application of the present invention to an OHP sheet, and utilizes the modes shown in Figs. 2 and 4. Fig. 7 shows a sectional view of the OHP sheet.

First of all, the following components, not shown in the drawing, were uniformly dispersed by a sand mill [the state ① in Fig. 2]:

ethyl alcohol condensate c of octadecyl monoisocyanate	25 wt%
acryl oligomer (tetraethyleneglycol diacrylate)	71 wt%
benzophenone d	4 wt%
toluene	300 wt%

The solution described above was coated on a 120 μm-thick polyester film 22 by casting, and a toluene solvent was evaporated at 60 °C. Next, curing was carried out by irradiating UV (ultraviolet) rays, and a thermo-reversible recording layer 21 consisting of a 15 μm-thick white opaque thermo-reversible recording material according to the second mode (the structure shown in Fig. 2) could be obtained (the state ② shown in Figs. 2 and 4).

In Fig. 7(a), a 20 μm-thick polyethylene naphthalate film was bonded to the surface of the thermo-reversible recording layer 21, obtained as described above, to form a protective film 23 and to thus obtain an OHP (overhead projector) sheet.

When printing was effected on this sheet by using a heat pen 24 having a distal end of 90 °C or a thermal printer (not shown in the drawing), the molecules of the low molecular weight organic compound c in the thermo-reversible recording material at the printed portion thereof formed the dimers (the state ③ in Figs. 2 and 4), and when the temperature of the printed portion was returned thereafter to room temperature, the molecules forming the dimer were as such solidified, so that the refractive index of the low molecular weight organic compound c became substantially equal to that of the acrylic resin d. As a result, the thermo-reversible recording material at the printed portion changed to a transparent state (the state ④ in Figs. 2 and 4), and a clear transparent character could be drawn on the white base and when the character was projected by an OHP, an extremely clear negative image could be projected.

Next, when the thermo-reversible recording material was passed through a heat roller (not shown) at a higher temperature of 110 °C to erase the character, the molecules c forming the dimer returned to the monomer (the state ⑤ in Figs. 2 and 4), and when the temperature was returned to room temperature, the molecules c were solidified while remaining as the monomer. Due to the difference of the refractive index between the low molecular weight organic compound c and the acrylic resin d, the transparent portion became turbid, and the thermo-reversible recording material returned to the original white state as a whole and the character disappeared (the state ② in Figs. 2 and 4). This OHP sheet could be used problem free even after re-writing was repeated 500 times.

As described above, the OHP sheet could be formed directly using the thermal printer, and the OHP sheet could be used after correction or by erasing. Therefore, the sheet could be used without waste.

Incidentally, ordinary polyethylene terephthalate, acetyl cellulose, etc., can be used for the transparent support, such as a polyester film.

Next, when a sample of the thermo-reversible recording material in the white (opaque) state and another in the transparent state were observed through an electron microscope, it was found that fine particles of the condensate c having a particle size of about 0.2 to about 4.0 μm were distributed in the case of the white state, and the particles also existed in distinct from in the case of the transparent state and only transparency increased in the latter case. The light transmission factor was 87% in the transparent state and 60% in the opaque state.

A thermo-reversible recording material of Comparative Example 1 shown in Table 3 was obtained in the same way as in the fourth embodiment except that acetone was used in stead of toluene as the solvent.

Table 3

Example	low molecular weight organic compound c (wt%)	acryl oligomer benzophenone (wt%)	solvent	particle size (μm)	trans-parent*	opaque*	contrast
4	25	75	toluene	0.2 - 4.0	87	60	fair
Com. Ex. 1	25	75	acetone	< 0.1	82	77	insuffic ient

*: light transmission factor (%)

As a result, the low molecular weight organic compound was easily soluble in acetone and was not dispersed to a suitable particle diameter during the film formation process. Since the dissolved state of below 0.1 μm existed, the light transmission factor when the recording material was made opaque was so great that a contrast could not be obtained.

The polymer resin used in the second mode (the structure shown in Fig. 2) of the present invention preferably is not compatible with the low molecular wight organic compound, and a curing type resin is

used. When a thermoplastic resin is used, those resins that are not compatible with the low molecular weight organic compound are used. Micro-capsules of the resins not compatible with the low molecular weight organic compound may be prepared in advance and may be then dispersed in the thermoplastic resin.

Examples of the curing type resin are a phenol resin, a urea resin, a melamine resin, an unsaturated polyester resin, an epoxy resin, a silicone resin, a urethane resin, an acrylic resin, and so forth. The production method of the thermo-reversible recording material at this time comprises adding a polymerization initiator to the low molecular weight organic compound and the oligomer or the monomer, uniformly dispersing the initiator, coating the dispersion on the support and polymerizing the dispersion by heat, light or electron beams.

The condition of the light transmission factor, the particle size and the blend proportion when the low molecular weight organic compound forms the fine particles, for obtaining a high contrast, are the same as those of the first mode (the structure shown in Fig. 1) of the present invention.

[FIFTH EMBODIMENT]

The fifth embodiment represents the application of the present invention to a thermo-sensitive sheet, and is shown in Fig. 8.

In Fig. 8, a thermo-sensitive sheet was formed by forming the thermo-reversible recording layer 21 and the protective film 23 of the fourth embodiment on 80 μm-thick black colored coating paper 24.

When printing was made on this paper by using a thermal printer (not shown) of a word processor, "OASYS 30 ms" of Fujitsu Corporation (trade name) at 90 °C, a black character was clearly printed on the white base, and when this paper was clamped and passed through heat rollers at 100 °C (not shown), the character disappeared.

In other words, when the rewriting type thermo-sensitive sheet of the present invention is used in place of conventional thermo-sensitive paper, it can reduce the amount of paper wasted. Furthermore, when it is used in place of hand-written memorandum, throw-away type applicantation forms and slips, etc., the thermo-sensitive paper of the invention can be used repeatedly, and the amount of paper consumed can be reduced.

In the present invention, the support uses a film colored in colors other than white, paper and a sheet made of other composite materials, and the thermo-reversible recording material is disposed on the support. Furthermore, the heat-resistant protective layer or protective film is disposed on the recording material. The recording material can be used in the form of either a roll or cut paper.

When the thermo-reversible recording material is set and used with an output thermal printer of a personal computer or a word processor, printed paper is first printed out for the purpose of correction, and unnecessary portions are erased, so that the recording material can be used many times very conveniently. When the thermo-reversible recording material is used for a facsimile, the amount of waste can be reduced because it has been a customary practice to keep a copy for preservation and to discard the original.

As to the spacer, the same technique as that of the third embodiment can be applied, as well.

[SIXTH EMBODIMENT]

The sixth embodiment represents the application of the present invention to a magnetic card. This embodiment uses the mode shown in Figs. 2 and 4, and Fig. 9 is a sectional view of the magnetic card. First, the following components were prepared:

stearic acid	20 wt%
gelatin	5 wt%
ethyl cellulose	75 wt%
ethyl alcohol	400 wt%

Stearic acid was encapsulated into micro-capsules by an aqueous gelatin solution, and the resulting micro-capsules were added to an ethyl alcohol solution of ethyl cellulose to prepare a dispersion (the state ① of Fig. 2). The dispersion was coated to a magnetic recording surface 32 of a magnetic card 32 by casting and was dried at 65 °C, thereby providing a thermo-reversible recording layer 31 consisting of a white and opaque thermo-reversible recording material of the second mode (the structure shown in Fig. 2) of the present invention.

In Fig. 9, "Alonix UV-3333" (one-liquid type UV-curable acrylic resin, a product of Toa Gosei) was coated to a thickness of 5 μm on the surface of the thermo-reversible recording layer 31 obtained as described above, and was cured by UV (ultraviolet) rays to form a protective film 33.

When printing was effected on this thermo-reversible recording material by a thermal printer (not shown) of a card writer of Fujitsu Corporation at 80 °C, the molecules of the low molecular weight organic compound, i.e., stearic acid, at the printed portion formed the dimer (the state ③ in Figs. 2 and 4), and when the temperature of the printed portion returned thereafter to room temperature, the molecules forming the dimer were solidified. As a result, the refractive index of stearic acid became substantially equal to that of ethyl cellulose, the thermo-reversible recording material at the printed portion changed to a transparent state (the state ④ in Figs. 2 and 4), and a black character could be printed clearly on the white base. Though the black magnetic recording layer 34 existed at the back of the white color portion, the white color portion was hardly affected by the former, and the black-and-white contrast was extremely high because the degree of whiteness was high.

Next, when the thermo-reversible recording material was clamped and passed through heat rollers (not shown) at 110 °C, the molecules forming the dimer returned to the monomer (the state ⑤ in Figs. 2 and 4), and when the temperature returned to room temperature, the monomer was solidified. Accordingly, due to the difference of the refractive index between stearic acid and ethyl cellulose, the transparent portion became turbid and the recording material returned to its original white base as a whole. Thus, the character disappeared (the state ② in Figs. 2 and 4), and when this procedure was repeated 500 times, printing could be effected problem free.

In the sixth embodiment, a display can be made on the back by the thermo-reversible recording layer by effecting a printing on the surface of the magnetic card. However, since the thermo-reversible recording layer was disposed on the magnetic surface, the film thickness had to be kept within 10 μm so as to ensure magnetic reading.

Next, when a sample of the thermo-reversible recording material in the white (opaque) state and another sample in the transparent state were observed through an electron microscope, it was found that fine particles of stearic acid having a particle size of about 0.4 to about 0.8 μm were distributed with an extremely small particle size distribution width in the case of the white state, while the particles existed in a very distinct form in the case of the transparent state, and the micro-capsules were completed protected. The light transmission factor was 88% in the transparent state and 58% in the opaque state.

Micro-encapsulation was carried out by a known method; the material for encapsulating the low molecular weight organic compound must be insoluble with the low molecular weight organic compound, the gelatin, polyvinyl alcohol, and so forth, are used for this purpose. The polymer resin for holding the micro-capsules is one of the afore-mentioned thermoplastic resins. However, the refractive index of the micro-capsules must be brought into conformity with that of the polymer resin.

[SEVENTH EMBODIMENT]

The seventh embodiment represents the application of the present invention to a magnetic card by modifying the sixth embodiment, and is shown in Fig. 10.

In Fig. 10, a blue colored layer 35 was disposed on the surface of a magnetic card 32 opposite to the magnetic recording surface, and the thermo-reversible recording layer 31 and the protective film 33 of the sixth embodiment were disposed on the blue colored layer 35.

When printing was effected by a thermal printer (not shown) of a card writer of Fujitsu Corporation at 80 °C, a blue character could be printed clearly on the white base. When the thermo-reversible recording material was clamped and passed through heat rollers (not shown) at 110 °C, the character disappeared.

Though the blue colored layer existed at the back of the white color portion, the white color portion was hardly affected by the former, and since the degree of whiteness was extremely high, the contrast was satisfactory.

When the re-writing type is employed for inputting data to the magnetic card, the magnetic card can correct wrong data input, can cope with a large number of input items, and can be applied to novel applications, such as re-writable information, public notification services, and so forth.

As to the spacer, the same technique as that of the third embodiment can be employed.

[EIGHTH EMBODIMENT]

The eighth embodiment represents the application of the present invention to a dimmer film, and utilizes the mode shown in Figs. 3 and 4. Fig. 11 is a sectional view of the dimmer film.

erucic acid amide e	50 wt%
polyester polyol ("Takeluc U-53" of Takeda Yakuhin)	35 wt%
polyisocyanate f ("Takenato D-160N" of Takeda Yakuhin)	15 wt%
toluene	100 wt%

The components listed above were uniformly dispersed by a sand mill (the state ① of Fig. 3), and were coated to a 120 μm-thick polyester film 42. Toluene as the solvent was evaporated at 60 °C, and curing was then carried out by UV (ultraviolet) rays, thereby providing a thermo-reversible recording layer 41 consisting of a 7 μm-thick, white and opaque thermo-reversible recording material (the structure shown in Fig. 3) of the third mode of the present invention (the state ② in Fig. 3).

In Fig. 11, a 20 μm-thick polyethylene naphthalate film 42 was bonded to the surface of the thermo-reversible recording layer 41 obtained as described above to form a protective film 43.

Next, a transparent heat-generating sheet 45 (a transparent film heater, a product of Gunze) obtained by applying a transparent resistor pattern on a 100 μm-thick polyester film was sandwiched between, and integrated with, the polyester film 42 and the heat-resistant protective film 44, and cables were fitted so that a current could be applied. Furthermore, a circuit was so arranged as to change over a voltage and switch the heat generating temperature to two stages. In this way, the dimmer film of the present invention was produced.

When a current was applied to the dimmer film and the heat-generating sheet was heated to 90 °C, the molecules of erucic acid amide e in the thermo-reversible recording material formed the dimer (the state ③ in Figs. 3 and 4). Thereafter, when the temperature of the heat-generated portion returned to room temperature, the molecules forming the dimer were solidified, and the refractive index of erucic acid amide e became substantially equal to that of the polyester polyol/polyisocyanate cured product f. Accordingly, the thermo-reversible recording material at the heated portion became transparent (the state ④ shown in Figs. 3 and 4), and the dimmer film became transparent.

Next, heat generation was made at 100 °C by changing over the switch, the molecules e forming the dimer returned to the monomer (the state ⑤ shown in Figs. 3 and 4), and when the switch was cut off and the temperature returned to room temperature, the monomer was solidified. Due to the difference of the refractive index between the erucic acid amide e and the polyester polyol/polyisocyanato cured product f, the transparent portion became turbid and thermo-reversible recording material became opaque as a whole (the state ② shown in Figs. 3 and 4). When this procedure was repeated 500 times, no problem occurred.

Next, a sample of the thermo-reversible recording material in the white (opaque) state and another sample in the transparent state were observed through an electron microscope, the fine continuous phase structure of the erucic acid amide e was distributed in a complex manner in the case of the white state, and the polymer urethane f formed a three-dimensional network structure (sponge-like structure) inside the erucic acid amide e. This structure also existed as such in the case of the transparent state, and only transparency increased. The light transmission factor was 90% in the transparent state and 55% in the opaque state.

The difference from the second mode (the structure shown in Fig. 2) of the present invention remains whether the low molecular weight organic compound exists in dot-like form or has a continuous phase. In the first and second modes of the present invention, the low molecular weight organic compound occupies 5 to 40 vol% of the composition of the thermo-reversible recording material and the optimum particle size is 0.1 to 5 μm. In the third mode of the present invention, the low molecular weight organic compound occupies 30 to 80 vol% in the structure of the thermo-reversible recording material, and forms the continuous phase. The principle of transparency and opaqueness is also analogous in the case of the continuous phase, and similar functions are provided. However, the difference resides in that, since the continuous phase has a greater light scattering capacity, a greater contrast can be obtained. Accordingly, the same contrast can be obtained by a smaller film thickness.

[NINTH EMBODIMENT]

The ninth embodiment represents the application of the present invention to dimmer glass, and is shown in Fig. 12.

In Fig. 12, the dimmer film obtained in the eighth embodiment was sandwiched between two glass sheets 46 through polyvinyl butyral to produce dimmer glass, and when this was fitted to transparent glass, it was necessary to turn on the switch only when it was desired to switch the transparent state and the opaque state. Therefore, unlike the conventional liquid type where the current always had to be fed to attain

the transparent state, this dimmer glass was much more convenient.

It is possible to use the dimmer film and dimmer glass in place of a curtain or glass and to return to the state only when necessary. However, this is very expensive because liquid crystal is used. According to the present invention, production can be extremely economically. Furthermore, there is the advantage that voltage need not always be applied to attain the transparent state.

The following compounds can be cited as examples of the low molecular weight organic compounds that can be used in the present invention.

First, it is the first condition to apply heat when switching from the opaque state to the transparent state. Therefore, the melting point of the low molecular weight organic compound must be higher than room temperature. Therefore, higher aliphatic acid amides, higher alcohols, saturated and unsaturated aliphatic acids, amino acids and low molecular weight urethane can be illustrated as low molecular weight organic compounds having a melting point not lower than 40 °C.

Examples of the higher aliphatic acid amides include lauric acid amide, myristic acid amide, palmitic acid amide, stearic acid amide, docosanoic acid amide, arachidic acid amide, oleic acid amide, erucic acid amide, elaidic acid amide, linolic acid amide, linolenic acid amide, ricinoleic acid amide, stearylstearic acid amide and distearylstearic acid amide.

Examples of the higher aliphatic acids include lauric acid, myristic acid, palmitic acid, stearic acid, docosanoic acid, and arachidic acid.

An example of amino acids is glutamic acid.

Examples of low molecular weight uretanes include alcohol condensates of hexamethylene diisocyanate, alcohol condensates of xylenediisocyanate, and actyl monoisocyanate.

Finally, a comparison of contrasts under various conditions between the first, fourth, sixth and eighth embodiments and the prior art example is illustrated in Table 4.

Table 4

Example	low molecular weight organic compound (wt%)	polymer resin (wt%)	particle size (μm)	trans-parency*	opaque-ness*	contrast
1	15	85	0.2 - 1.0	80	60	fair
4	25	75	0.2 - 4.0	87	60	fair
6	20	80	0.4 - 0.8	88	58	fair
8	50	50	continuous phase	90	55	fair
Conventional Example	14	86	< 0.1	84	78	inferior

*: light transmission factor (%)

As described above, in the thermo-reversible recording material repeating the transparent state and the opaque state in accordance with the temperature change, this embodiment uses a solvent not dissolving the low molecular weight organic compound, and a polymer resin having solubility approximate to the solubility of the low molecular weight organic compound at the melting point of the latter, or uses a polymer resin not compatible with the low molecular weight organic compound when the latter is dissolved at the melting point, encapsulates the low molecular weight organic compound into micro-capsules, sets the particle size of the low molecular weight organic compound to dot form of 0.1 to 5 μm, depending on the proportion of the low molecular weight organic compound to the polymer resin, and can convert the low molecular weight organic compound to the continuous phase. Accordingly, this embodiment can obtain a high contrast.

Since this embodiment used the protective film on the thermo-reversible recording material, the thermo-reversible recording material could be protected from damage and stain, and fusion with the heat pen, so that its service life could be improved drastically. A resin not having a softening point, or having a softening point not lower than 150 °C, and having a light transmission factor of at least 65% was used as the protective film. This film could be attained by coating a cross-linkable resin such as a heat-setting resin, a photo-curable resin or an electron beam-curable resin and curing the resin, or coating a thermoplastic resin having a softening point of not lower than 150 °C or by laminating a film. Examples of the thermoplastic resin film are polyethylene terephthalate, polyethylene naphthalate, polyether ether ketone, polycarbonate, polyimide, and so forth.

Since the present invention is constituted as described above, the opaqueness factor is high and the base is not translucent. Therefore, the degree of whiteness is high, and it is possible to obtain clear display even when viewed from a remote location. Since the film thickness can be reduced, a recording having a higher degree of sensitivity and response than the prior art can be carried out.

INDUSTRIAL APPLICABILITY

As described above, the products applying the thermo-reversible recording material of the present invention can eliminate waste, and greatly contribute to the automation of display and labor, and utilization will increase in future in the fields of "display", "recording" and "dimming", as energy, is saved counter-measures against environmental pollution, are provided and automation, can be ensured.

Claims

1. A thermo-reversible recording material containing a low molecular weight organic compound dispersed in a polymer resin capable of repeating reversibly a transparent state and an opaque state in accordance with a temperature history, characterized in that said low molecular weight organic compound has both a proton donor group (A) and a proton acceptor group (B) inside one molecule thereof, forms a dimer (C) at a transition temperature T1 thereof, and separates into a monomer at a temperature T2 higher than said temperature T1.

2. A thermo-reversible recording material according to claim 1, wherein said low molecular weight organic compound (a) is dissolved in said polymer resin (b) at said transition temperature T1, and undergoes phase separation from said polymer resin (b) at a temperature T2 higher than said temperature T1.

3. A thermo-reversible recording material according to claim 1, wherein said low molecular weight organic compound (c) is dispersed in dot-like form in said polymer resin (d), and said polymer resin (d) is not compatible with said low molecular weight organic compound (c) but maintains the dot-like form at said transition temperature T1 of said low molecular weight organic compound (c).

4. A thermo-reversible recording material according to claim 1, wherein said polymer resin (f) forms a three-dimensional network structure; said low molecular weight organic compound (e) exists in said polymer resin (f) in a continuous phase, state and said polymer resin (f) is not compatible with said low molecular weight organic compound (c) but maintains the three-dimensional network structure at said transition temperature T1 of said low molecular weight organic compound (e).

5. A thermo-reversible recording material according to claim 3, wherein said low molecular weight organic compound is dispersed in the form of micro-capsules in said polymer resin.

6. A production method of said thermo-reversible recording material according to claim 2 or 3 comprising:

a step of preparing a mixed solution containing said low molecular weight organic compound (a) having both said proton donor group (A) and said proton acceptor group (B) inside one molecule thereof, said polymer resin (b) and a solvent;

a step of preparing a dispersion for dispersing said low molecular weight organic compound in said solvent;

a step of coating said dispersion on a support (12); and

a step of drying said dispersion and obtaining said thermo-reversible recording material;

wherein said solvent is a non-solvent or a lean solvent of said low molecular wight organic solvent, but dissolves said polymer resin (b).

7. A production method of a thermo-reversible recording material according to claim 6 that further comprises:

a step of dispersing a solution containing said low molecular weight organic compound, an oligomer or a monomer or said oligomer and said monomer, and a polymerization initiator;

a step of coating said dispersion on said support; and

a step of polymerizing said oligomer or said monomer, or said oligomer and said monomer, to obtain said polymer resin.

8. A production method of a thermo-reversible recording material according to claim 6 that further comprises:

a step of encapsulating said low molecular weight organic compound into micro-capsules;

wherein said low molecular weight organic compound is dispersed in said polymer resin.

9. A thermo-sensitive recording medium including a recording layer (11) made of said thermo-reversible recording material according to claim 1 disposed on a support, characterized in that said recording layer (11) is caused to reversibly change between a transparent state and an opaque state by heat-generating means (15).

10. A thermo-sensitive recording medium according to claim 9, wherein a protective layer (13) is disposed on the surface of said thermo-reversible recording material.

11. A thermo-sensitive recording medium according to claim 9, wherein a distance (18) is maintained between said thermo-reversible recording layer (11) and a colored layer (14).

Fig.1

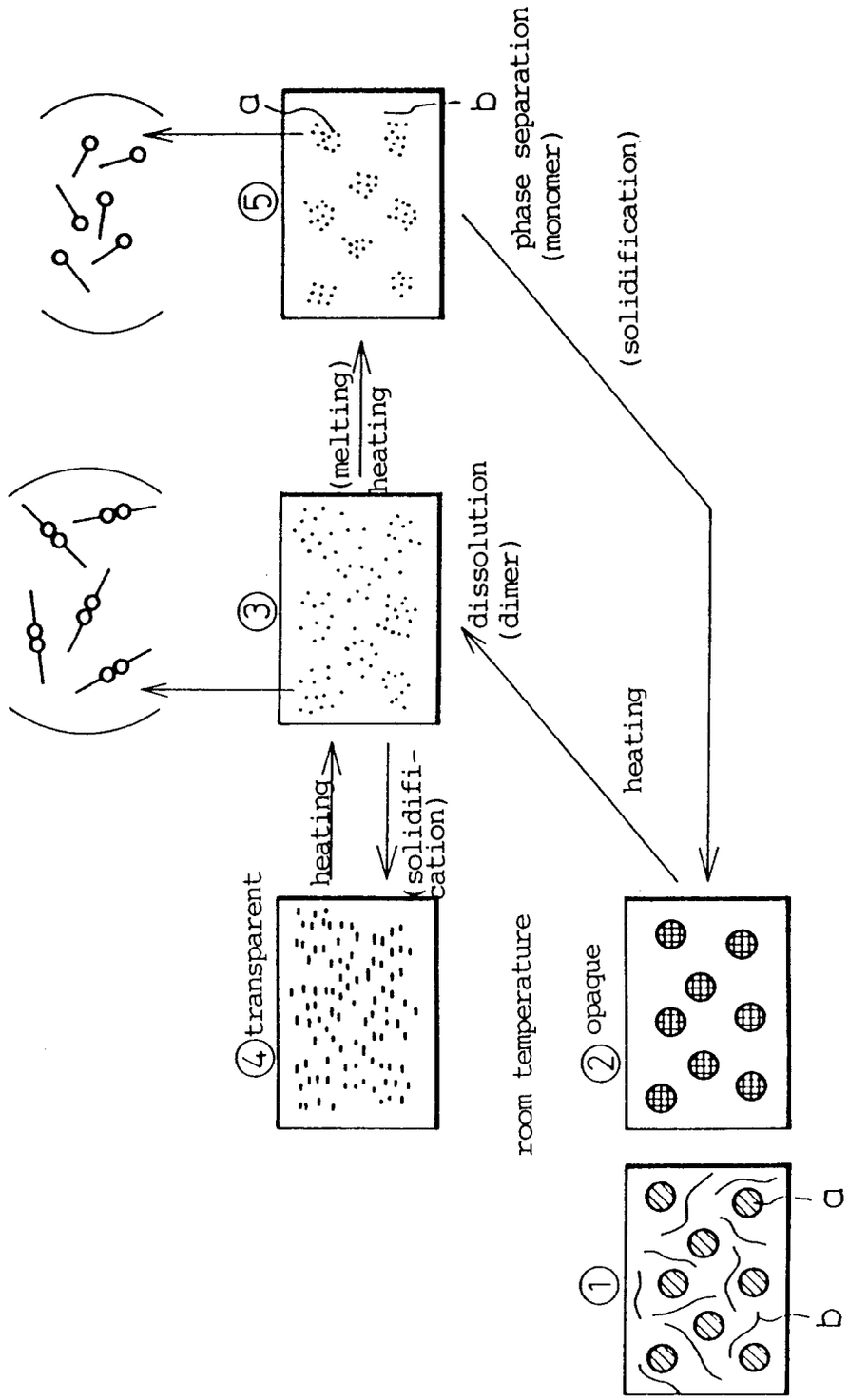
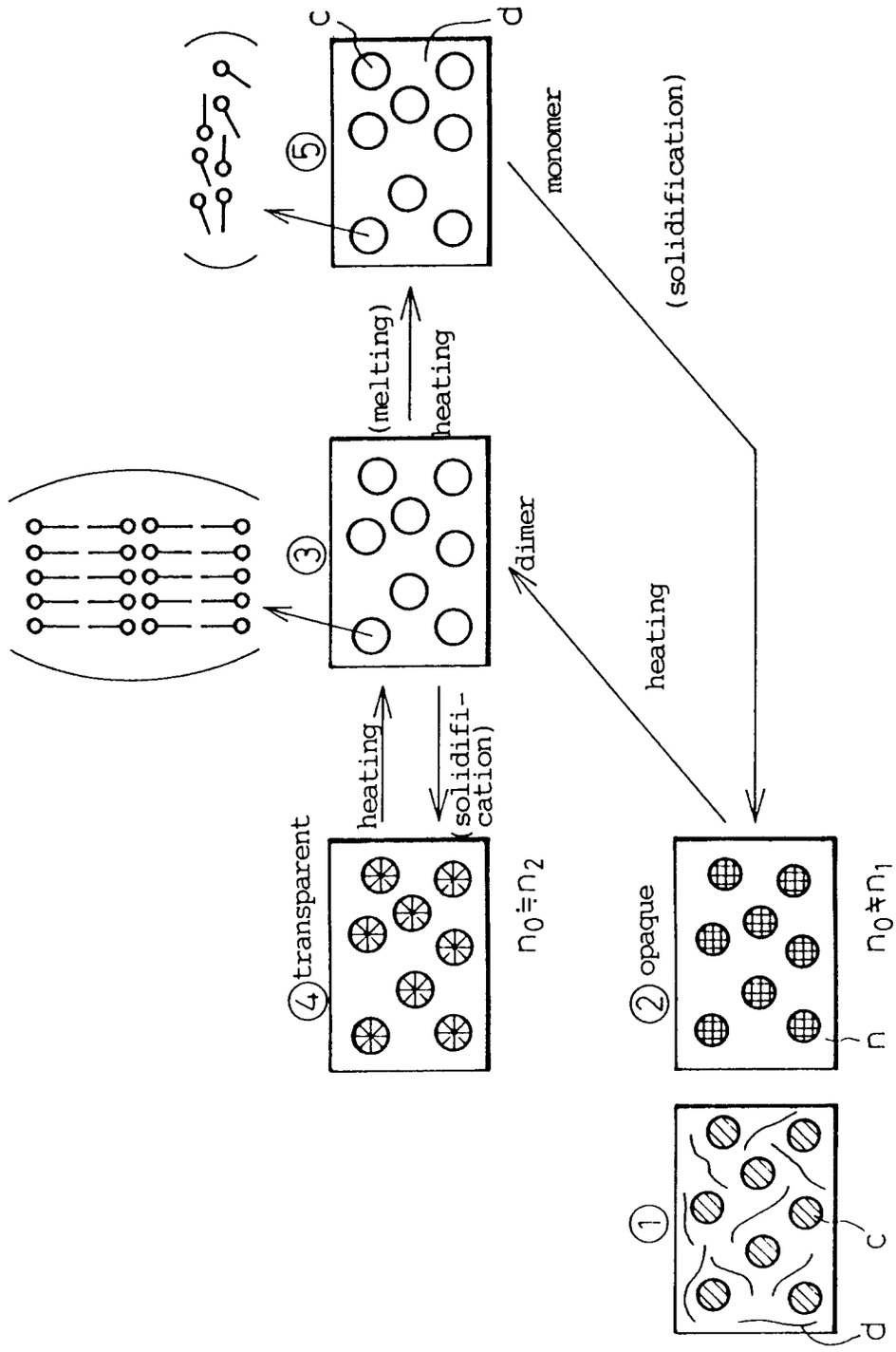

phase separation
(monomer)
(solidification)
a
b
⑤
(melting)
heating
dissolution
(dimer)
③
heating
(solidifi-
cation)
④transparent
heating
room temperature
②opaque
①
a
b

Fig.2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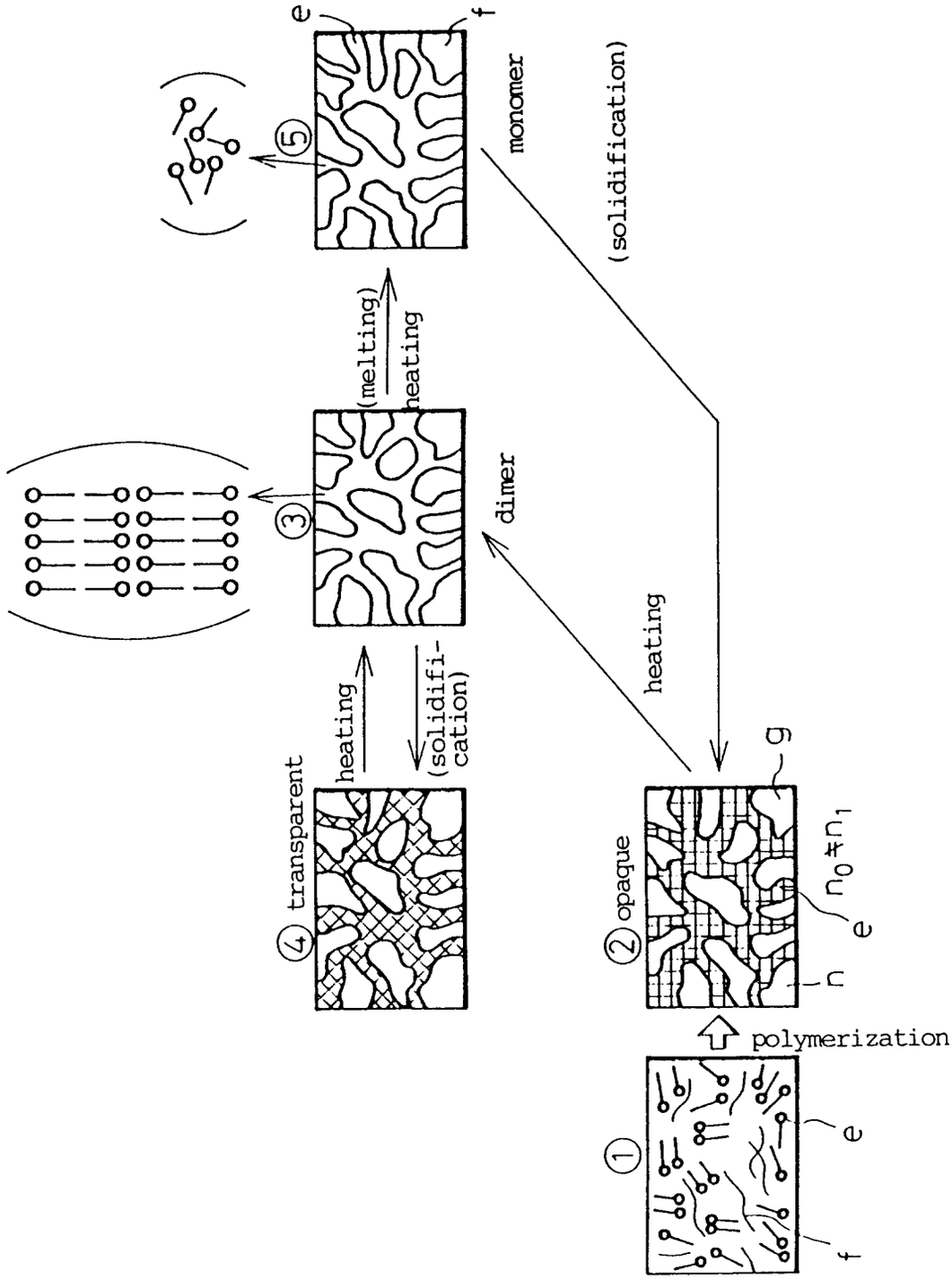
d
⑤
monomer
(solidification)
(melting)
heating
③
dimer
heating
heating
(solidifi-
cation)
④ transparent
$n_0 \doteqdot n_2$
② opaque
$n_0 \neq n_1$
n
①
c
d

Fig.3


e
f
monomer
(solidification)
⑤
(melting)
heating
③
dimer
heating
(solidifi-
cation)
④ transparent
heating
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② opaque
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polymerization
①
e
f

Fig.4

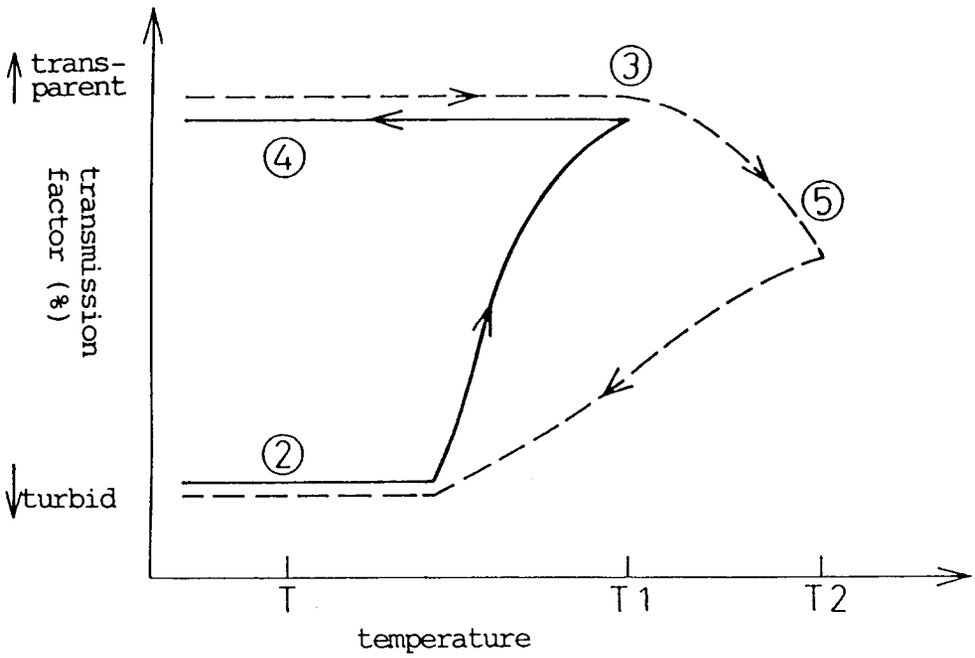

trans-
parent
transmission
factor (%)
turbid
③
④
⑤
②
T
T1
T2
temperature

Fig.5a

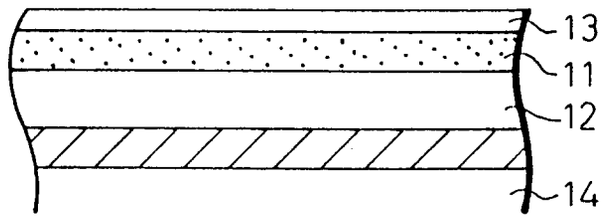


Fig.5b

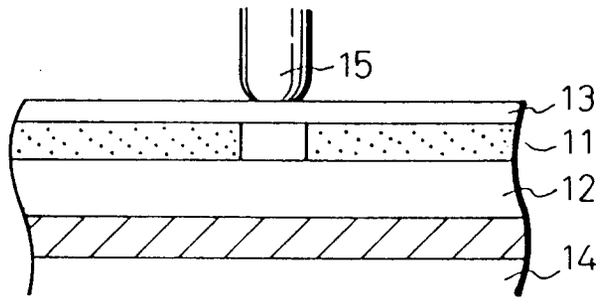


Fig.5c

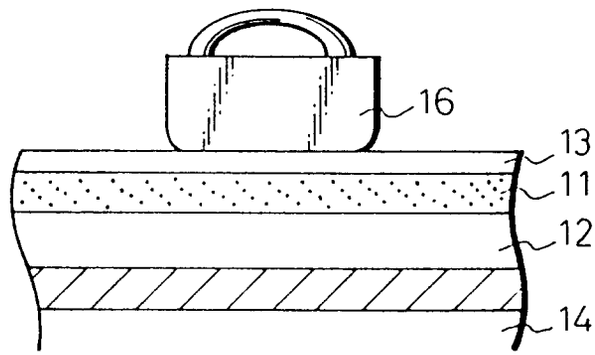


Fig.5d

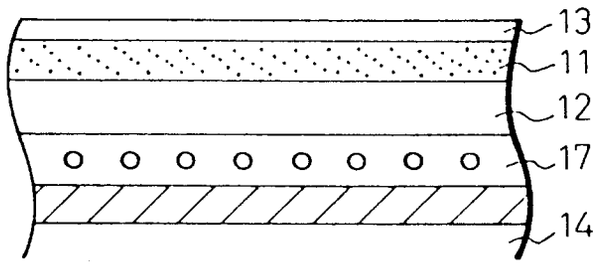


Fig.6a

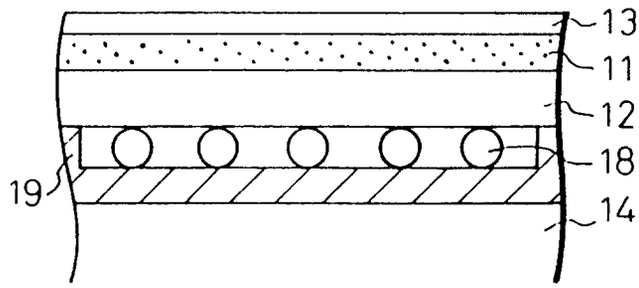


Fig.6b

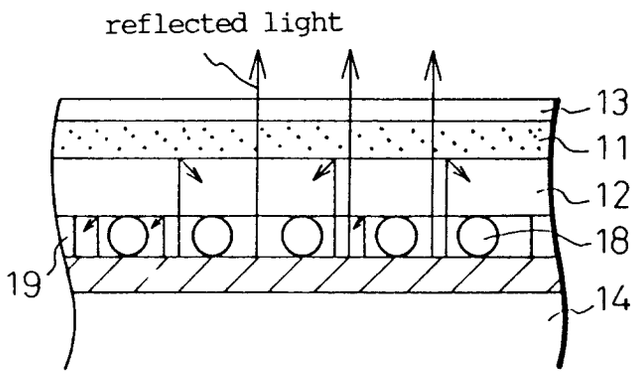


Fig.7a

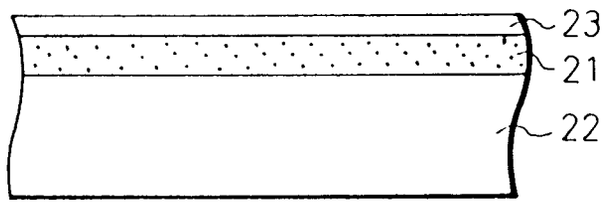


Fig.7b

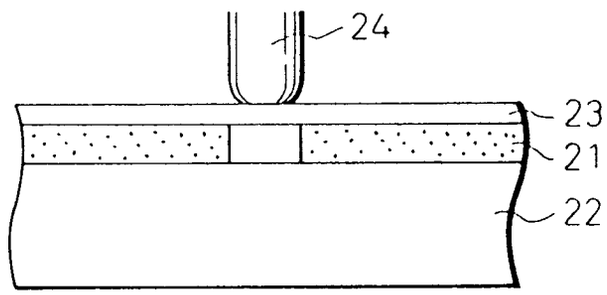


Fig.8

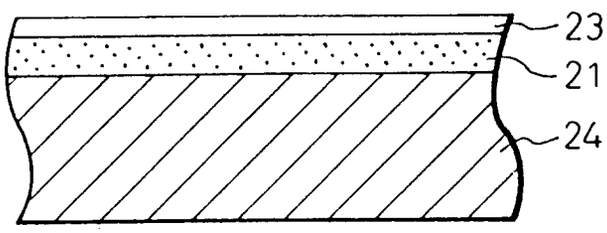


Fig.9

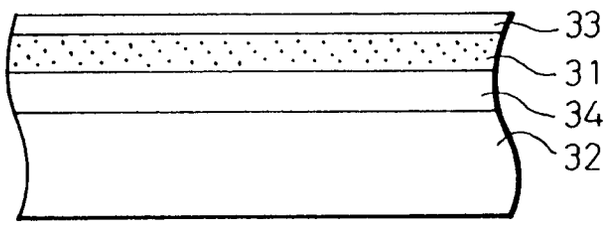


Fig.10

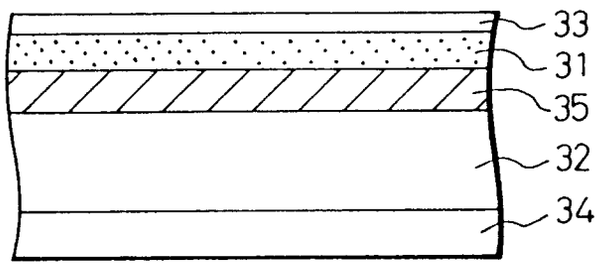


Fig.11

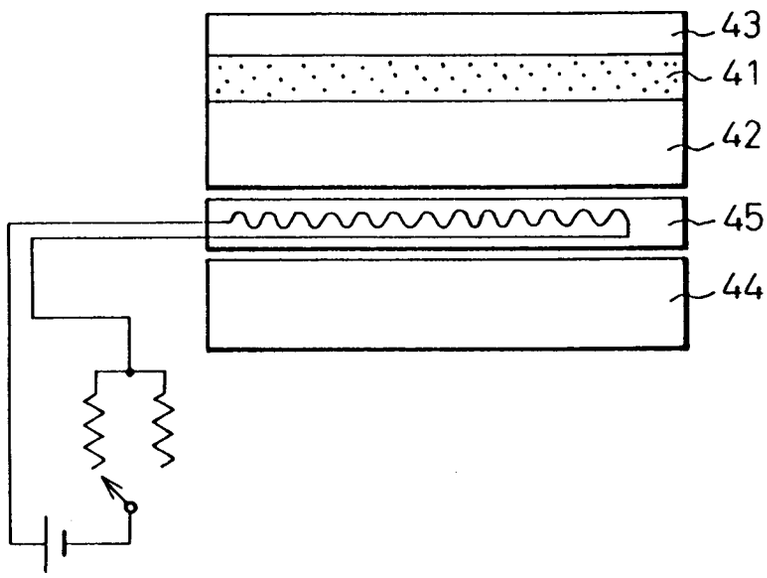


Fig.12

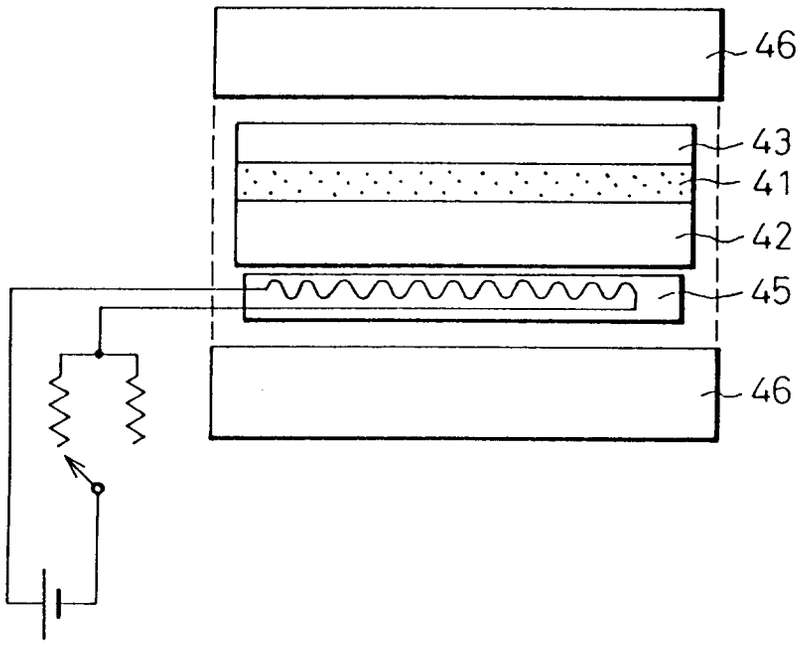


Fig.13

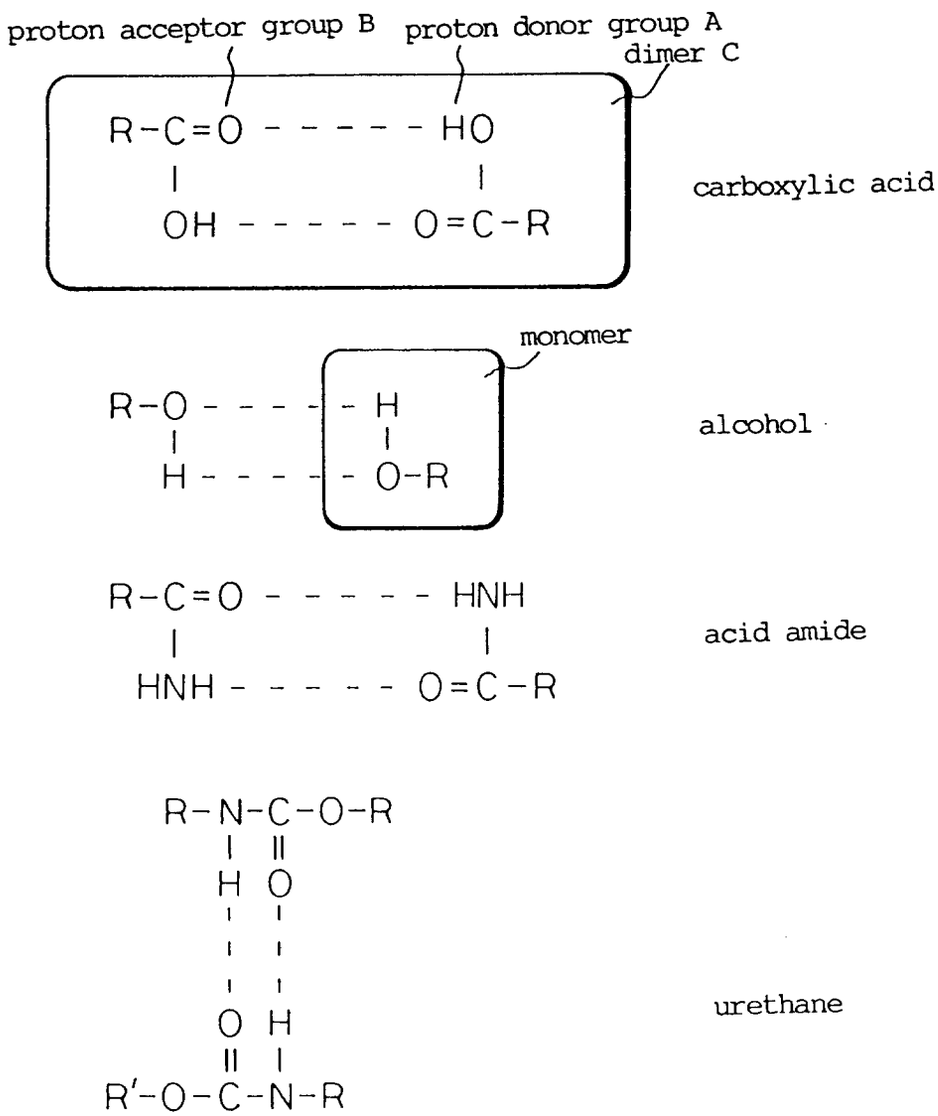
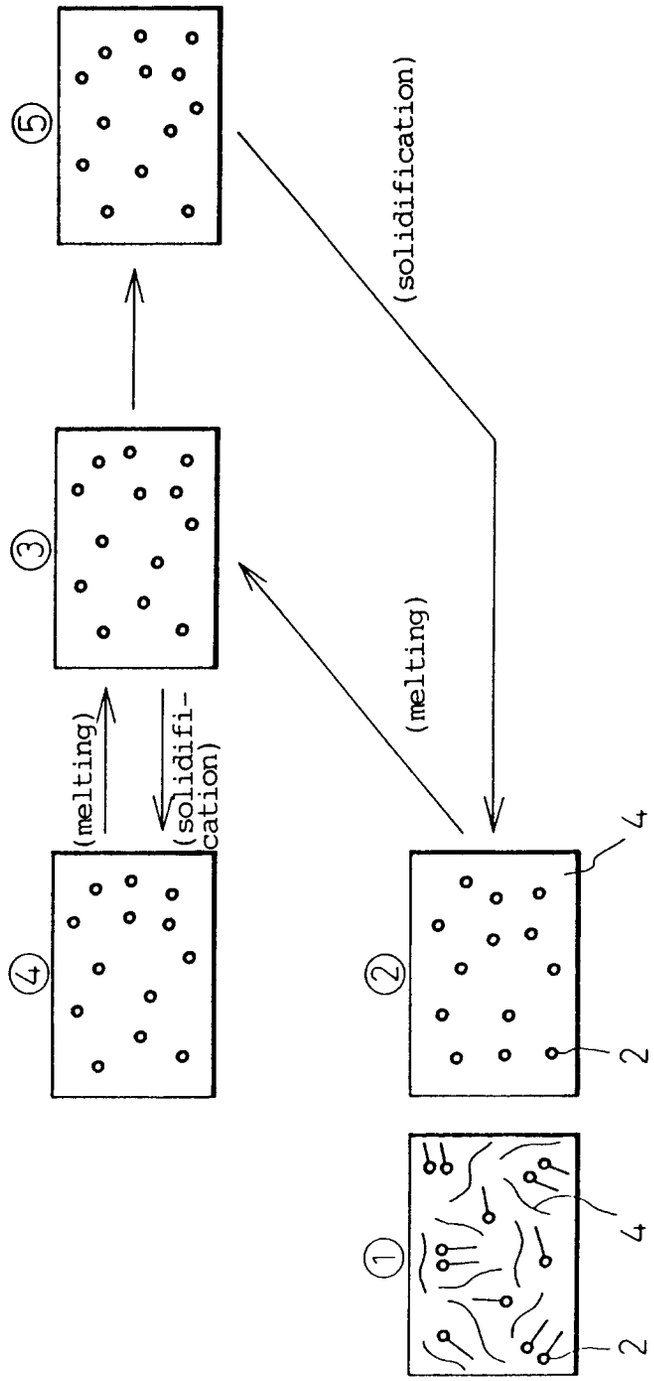

proton acceptor group B
proton donor group A
dimer C
R-C=O - - - - - HO
OH - - - - - O=C-R
carboxylic acid
monomer
R-O - - - - - H
H - - - - - O-R
alcohol
R-C=O - - - - - HNH
HNH - - - - - O=C-R
acid amide
R-N-C-O-R
H O
O H
R'-O-C-N-R
urethane

Fig.14



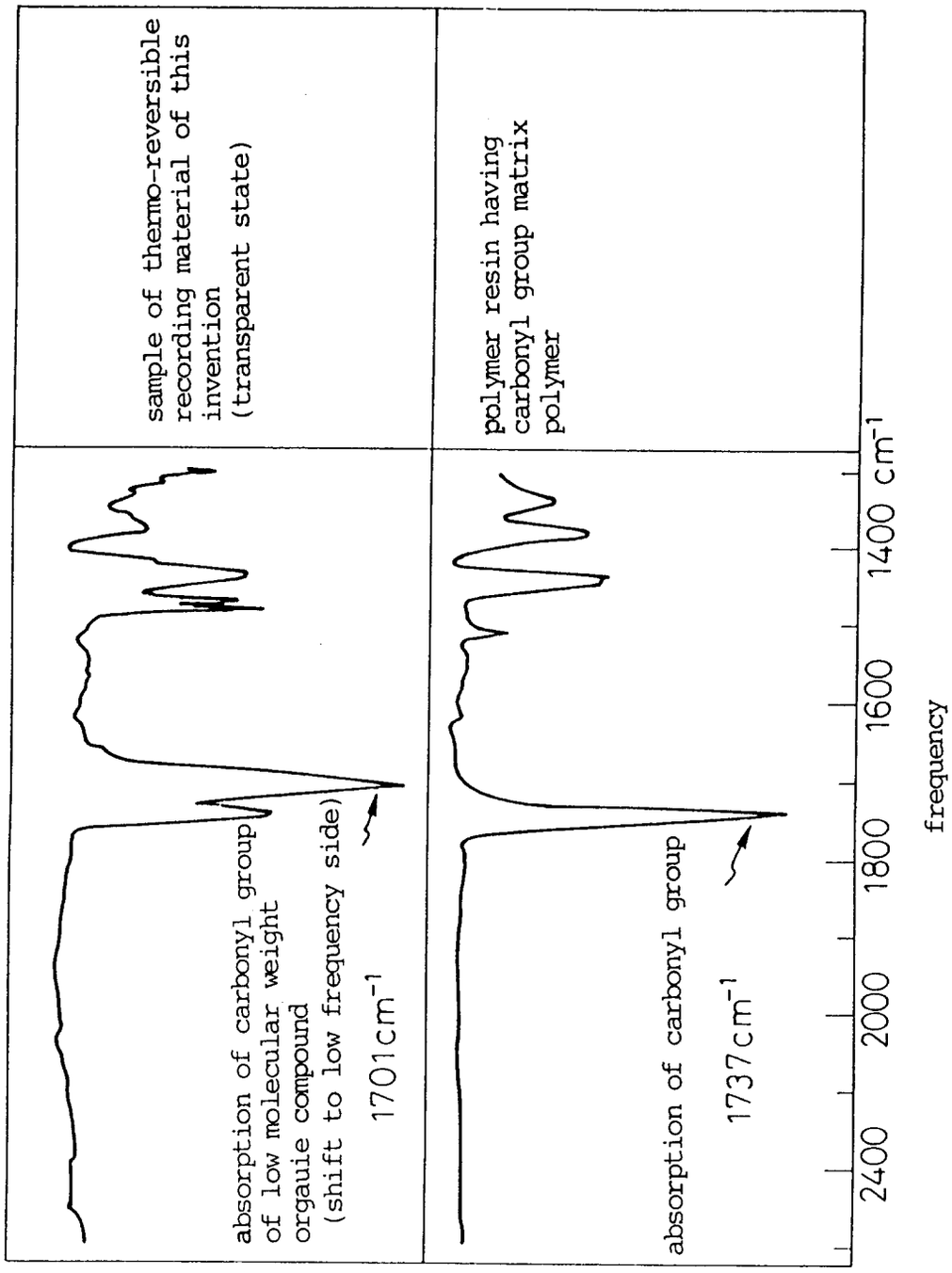


Fig.15A

Fig.15B

Fig.16

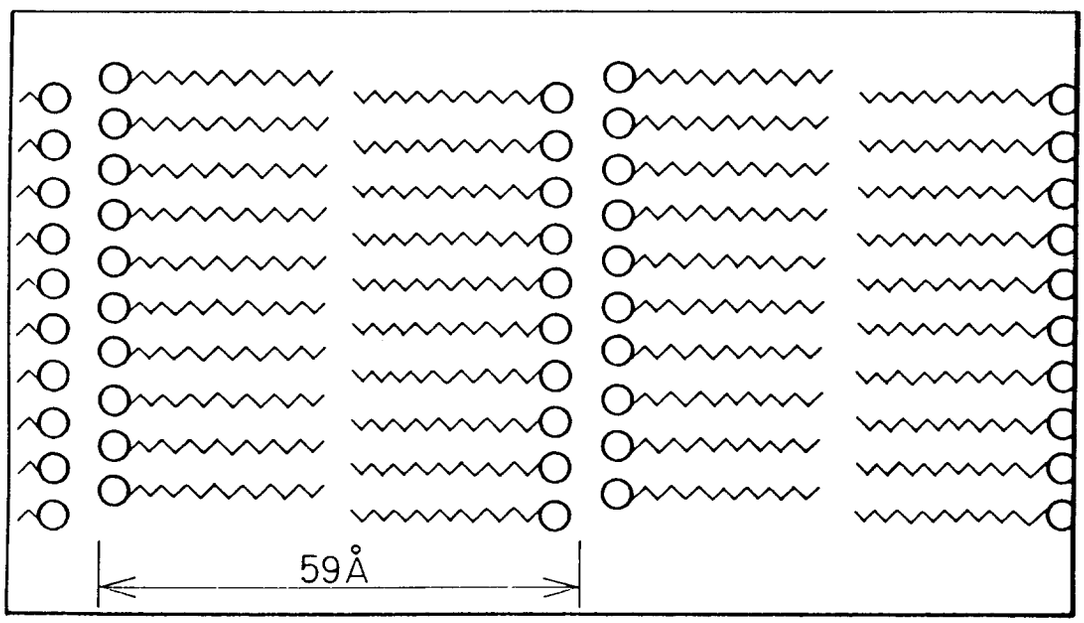


Fig.17

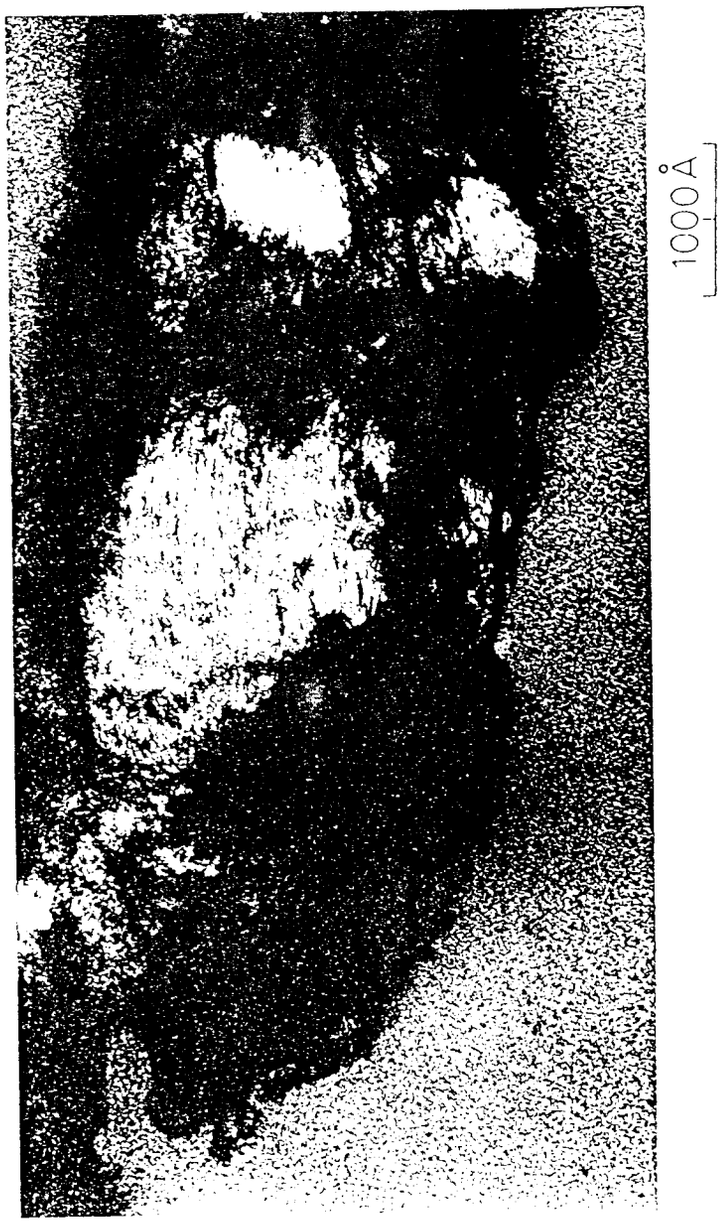
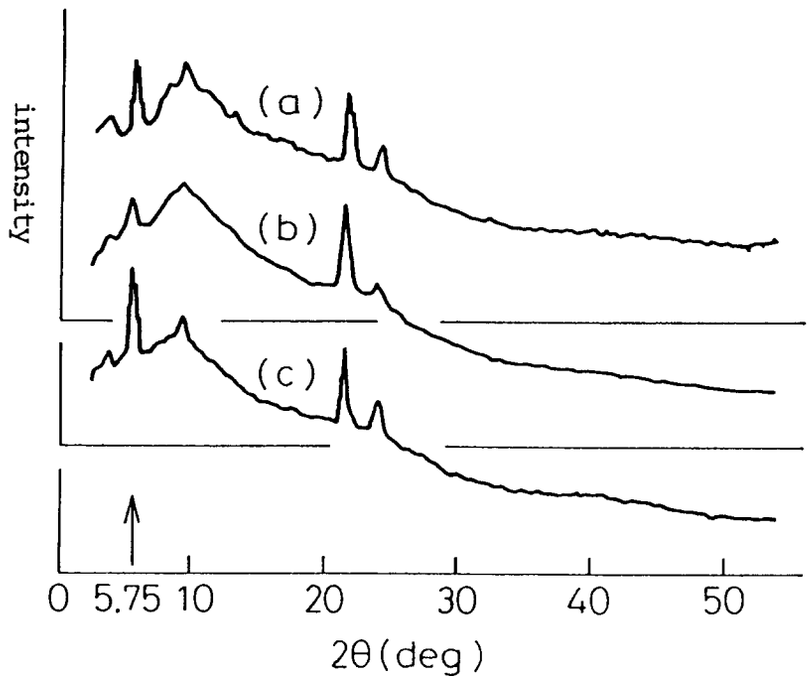
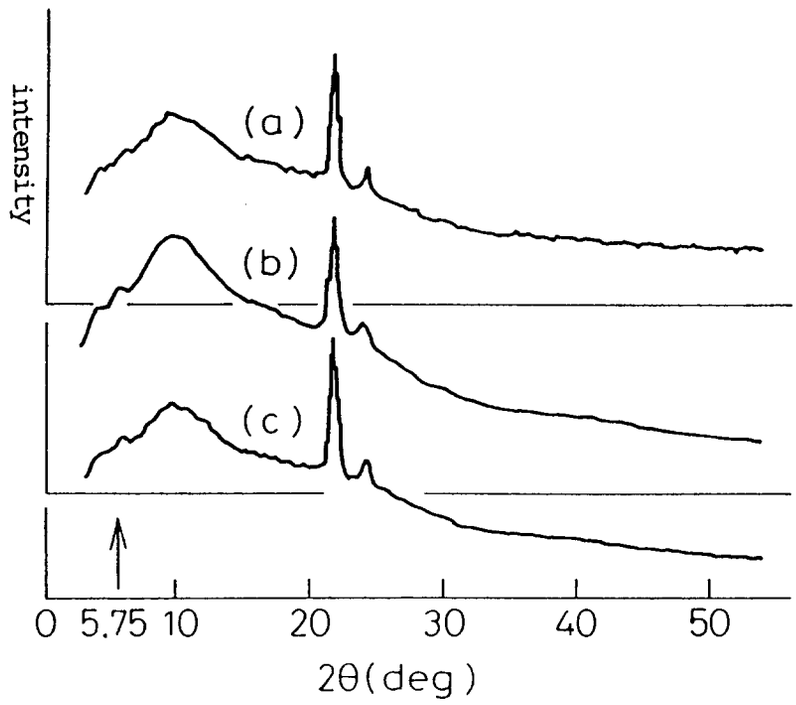


Fig.18



(a), (c) ... transparent state sample
(b) ... opaque state sample

Fig.19



(a), (c) ... transparent state sample
(b) ...opaque state sample

Fig.20

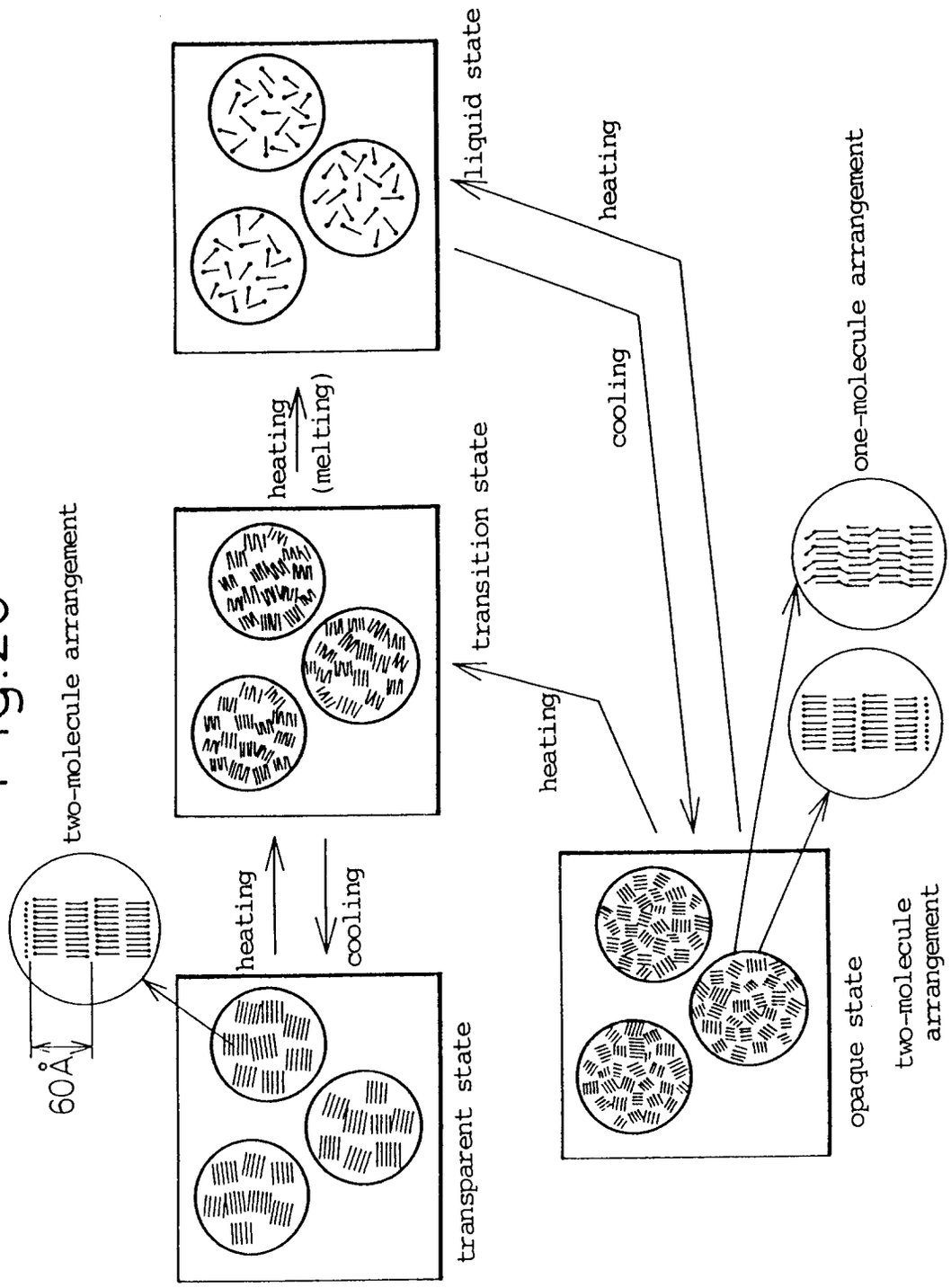
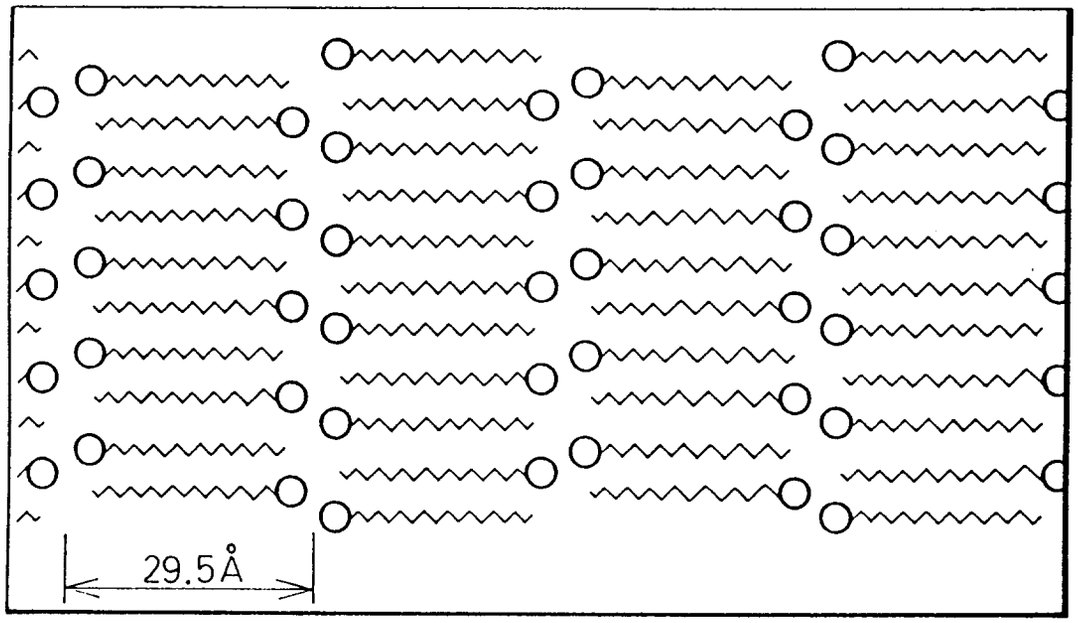

two-molecule arrangement
60Å
heating
cooling
transparent state
heating
(melting)
transition state
liquid state
heating
cooling
heating
one-molecule arrangement
opaque state
two-molecule
arrangement

Fig.21



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/01246

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[5] B41M5/26

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	B41M5/26

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 55-154198 (Chip Ex Technikvolfugangu Dabich), December 1, 1980 (01. 12. 80), & EP, A, 14826 & DE, A, 2907352 & CA, A, 1142357	1-11
Y	JP, A, 63-45085 (Ricoh Co., Ltd.), February 26, 1988 (26. 02. 88), (Family: none)	1-11
Y	JP, A, 63-84978 (Ricoh Co., Ltd.), April 15, 1988 (15. 04. 88), (Family: none)	1-11

* Special categories of cited documents: [10]

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
November 19, 1992 (19. 11. 92)	December 8, 1992 (08. 12. 92)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	