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(54) **Electrostatic recording sheet and electrostatic recording method.**

(57) The surface of an electrostatic recording sheet, which has a recording (2) layer of a liquid crystal polymer directly or indirectly on a substrate (1), is selectively charged by a head before or after heating the liquid crystal polymer to a temperature higher than the temperature of forming the liquid crystal phase of the polymer, thus enlarging the domain size of the liquid crystal phase and recording information. Information is deleted by heating the liquid crystal polymer to a temperature higher than that of forming an isotropic phase of the polymer and then cooling the polymer uniformly with no application of voltage to the head, thus reducing the domain size and deleting recorded information.

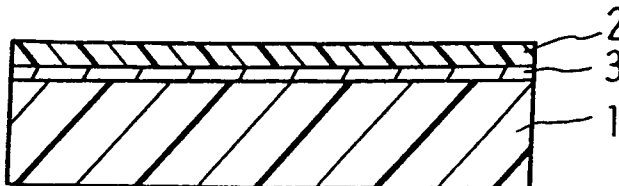


FIG. 2

The invention relates to a reversible electrostatic recording sheet which is capable of recording, saving and having information deleted from it and can be used repeatedly, and an electrostatic recording method.

The electrostatic recording method of adhering toner to a charged section of a nonrecording material has been applied as a conventional recording method for facsimiles and the like. Electrostatic recording sheets colored by heating, heat transfer recording techniques transferring ink by heating, and the like have also been used as methods of recording documents and pictures.

Published Unexamined Japanese Patent Application No. Hei 1-184640 discloses an optical recording medium capable of recording information and being erased by a photon to heat mode recording.

Recursive thermal recording materials for recording and deleting observable information have also been disclosed in Published Unexamined Japanese Patent Application Nos. Hei 2-175280, Hei 2-236518 and Hei 3-159785.

However, since conventional electrostatic recording and thermal recording methods cannot remove transferred toner or ink and colored sections, it has been difficult to repeatedly use recording paper with information recorded on it.

Because conventional thermal recording media and recursive thermal recording materials employ optical heads using a laser light source and thermal heads or the like as recording means, they have the problems of low energy efficiency and slow recording speed.

An objective of the invention is to provide an electrostatic recording sheet, which has high recording sensitivity and can provide direct thermally reversible recording and deletion of information, and an electrostatic recording method which achieves high speed recording by using the electrostatic recording sheet of the invention.

In order to accomplish these objectives, the electrostatic recording sheet of the invention comprises a recording layer formed directly on a substrate or indirectly on at least one other layer on the substrate, which comprises a liquid crystal polymer used for reversible electrostatic recording.

It is preferable in this composition that the liquid crystal polymer is a thermotropic liquid crystal polymer.

It is also preferable in this composition that a conductive layer is formed between the substrate and the recording layer.

It is further preferable in this composition that the conductive layer is colored.

It is preferable in this composition that the conductive layer is made from a transparent conductive material.

It is preferable in this composition that the value of resistance of the conductive layer is 10^6 - $10^9 \Omega/\square$.

It is also preferable in this composition that a heat-resistant layer is formed on the surface of the recording layer.

It is further preferable in this composition that the center line average height of the heat-resistant layer is 1-15 μm .

It is preferable in this composition that the heat-resistant layer comprises particles of 3-20 μm in size.

It is also preferable in this composition that the heat-resistant layer is selected from the group consisting of curable resins and thermoplastic resins having a heat deformation temperature greater than 100°C.

It is further preferable in this composition that the electrostatic recording layer comprises an oriented film disposed between the substrate and the conductive layer or the recording layer.

It is preferable in this composition that the substrate is selected from the group consisting of curable resins and thermoplastic resins having a heat deformation temperature greater than 100°C.

The electrostatic recording method of the invention comprises the steps of:

applying voltage to a stylus (or recording electrode) set up over one surface of the recording layer containing a liquid crystal polymer of an electrostatic recording sheet, and to a counter electrode provided on the opposite surface of the electrostatic recording sheet or to the conductive layer of the recording sheet, thereby discharging electricity; and

heating the liquid crystal polymer higher than the temperature of forming the liquid crystal phase of the polymer before or after the electrification of the recording layer, thus enlarging the domain size of the liquid crystal phase in the recording layer.

It is preferable in this method that the domain size of the liquid crystal phase is reduced uniformly by cooling the liquid crystal polymer, which had been heated beforehand to a temperature higher than that which forms an isotropic phase of the polymer, while voltage is not applied to the stylus and the electrode, thereby deleting any previously recorded information.

It is also preferable in this method that the stylus is a monostylus or a multistylus.

Since the recording layer comprises the liquid crystal polymer, the electrostatic recording sheet of the invention has a high recording sensitivity and can provide direct thermally reversible recording and deletion of information. The invention, at the same time, presents an electrostatic recording method of recording information at high speed by employing the electrostatic recording sheet of the invention. More specifically, the

recording layer comprising the liquid crystal polymer can control the level of light scattering by changing the size of domains formed in the liquid crystal phase.

When an electrostatic recording sheet comprises no colored substrate, conductive layer and light absorbing layer, an incident light shone on one surface of the electrostatic recording sheet can pass through it and the opposite surface of the sheet and can be observed from the latter surface (transmitted light observation). On the other hand, when the incident light is only observed from the same surface as the surface where the light is shone, the observation is called a reflected light observation.

For instance, if the domain size is less than about 10 μm , light is scattered by the existence of optical anisotropy among domains in the recording layer. An incident light shone on the surface of the recording layer is mostly scattered at the layer before reaching and being absorbed by other layers or a substrate, and becomes a diffuse reflection light. Therefore, the incident light is observed as reflected light from the surface of the recording layer, presenting bright opaque areas in the electrostatic recording sheet. From the opposite side, however, the light can barely be observed since it is hardly transmitted, thus a dark, black sheet is observed.

In addition, if the domain size is larger than the thickness of the recording layer, incident light shone on the surface of the recording layer is transmitted through and hardly diffused in the layer. Thus, in a reflected light observation from the surface of the recording layer, the electrostatic recording sheet shows dark black or colored areas. When the electrostatic recording sheet comprises no colored substrate, conductive layer or light absorbing layer, the incident light is transmitted through the recording layer and observed from the surface opposite to the surface where the light is shone, thus presenting bright opaque areas in the sheet.

Since the recording layer comprises the liquid crystal polymer, the domain size can be partially increased by applying an external electric field to the recording layer at a temperature higher than that of forming the liquid crystal phase, thus recording information in the electrostatic recording sheet. Recorded information can also be deleted due to the decrease in the domain size by cooling the liquid crystal polymer after heating the polymer higher than the temperature of forming an isotropic phase, while the external electric field is not applied to the recording layer. The external electric field can be applied to the recording layer by electrification with a multistylus head or the like provided at the surface of the electrostatic recording sheet. The use of the multistylus head instead of a monostylus head can improve the recording speed. The electrostatic recording sheet of the invention, therefore, can repeatedly delete recorded information and record information at high speed.

When the liquid crystal polymer is a thermotropic liquid crystal polymer, the thermotropic liquid crystal polymer can have a liquid crystal phase appearing above the glass-transition temperature and an isotropic phase appearing above the temperature of forming the liquid crystal phase. The liquid crystal phase has two uniformly composed conditions including a monodomain condition and a polydomain condition composed of multiple domains. When the thermotropic liquid crystal polymer has the polydomain condition in the liquid phase, light scatters intensely. However, if the thermotropic liquid crystal polymer has the monodomain condition in the liquid crystal phase or the isotropic phase, light hardly scatters.

The electrostatic recording sheet comprising the conductive layer between the substrate and the recording layer can preferably record information faster than the sheet comprising no conductive layer when electrification is directed to these sheets at the same surface potential. This is because a larger electric field can be applied to the recording layer of the sheet comprising the conductive layer than to the layer of the sheet having no conductive layer.

When the conductive layer is made from a transparent conductive material, the electrostatic recording sheet can be observed with transmitted light. The conductivity of the conductive layer becomes preferable if the resistance value of the layer is 10^6 - $10^9 \Omega/\square$.

The electrostatic recording sheet can be heated from the surface of the recording layer by contacting the layer with a heated roller or the like when the recording layer has a heat-resistant layer on the surface.

If the center line average height of the heat-resistant layer is 1-15 μm , the distance between a recording electrode (or stylus) and the recording layer (or heat-resistant layer) can be set at about 5-15 μm . At this distance, the break-down voltage is lowered, thus recording information stably. The repulsion among charges at the charged section also hardly occurs, thereby charging uniformly and recording information at high contrast.

The center line average height of the heat-resistant layer can be easily controlled to be about 1-15 μm if the layer comprises particles of 3-20 μm in size.

The heat-resistant layer is preferably a curable resin or a thermoplastic resin having a heat deformation temperature greater than 100°C. This is because the deformation of the recording layer and the adhesion of the layer to a heating device, due to the recording and deletion of information by heating, can be prevented. The curable resin includes thermo-setting resins, photo-setting resins and the like.

The liquid crystal polymer can be efficiently used if the oriented film is formed between the substrate and the conductive layer or the recording layer. The oriented film can be formed by treating a polymer film with a

rubbing or a drawing method. A deposited film with oblique incident angle of an inorganic compound can also be used as the oriented film.

When the substrate is a curable resin or a thermoplastic resin having a heat deformation temperature greater than 100°C, the electrostatic recording sheet of the invention becomes excellent in heat resistance and is suitable for mass production. The curable resin includes thermo-setting resins, photo-setting resins and the like.

In the electrostatic recording method of the invention, it is not necessary to heat recorded areas selectively. Thus, the method can provide direct reversible recording at higher speed.

In the method of the invention, moreover, recorded information can be easily deleted due to uniform reduction in the domain size of the liquid crystal polymer by cooling the polymer after heating it to a temperature higher than the temperature of forming an isotropic phase, while the external electric field is not applied to the recording layer.

Fig. 1 shows a cross-sectional view of an electrostatic recording sheet of one embodiment of the invention having a recording layer 2 on the surface of a substrate 1.

Fig. 2 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having a conductive layer 3 on a substrate 1 and a recording layer 2 on conductive layer 3.

Fig. 3 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having a recording layer 2 on a substrate 4, the latter also acting as a conductive layer.

Fig. 4 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having a sequentially laminated conductive layer 3, recording layer 2 and heat-resistant layer 5 on a substrate 1.

Fig. 5 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having a sequentially laminated light absorbing layer 7, transparent conductive layer 6 and recording layer 2 on a substrate 1.

Fig. 6 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having a sequentially laminated conductive layer 3, higher refractive layer 9 and recording layer 2 on a substrate 1.

Fig. 7 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention having an oriented film 8 on a substrate 1 and a recording layer 2 on oriented film 8.

Fig. 8 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention composed of a metal layer 10 having periodic concave and convex surfaces on a substrate 1 and a recording layer 2 on metal layer 10.

Fig. 9 shows a cross-sectional view of an electrostatic recording sheet of another embodiment of the invention composed of a metal layer 10 having periodic concave and convex surfaces on a cured resin layer 11 which is formed on a substrate 1, and a recording layer 2 on metal layer 10.

Fig. 10 shows a schematic side view of an electrostatic recording method and apparatus of one embodiment of the invention.

Fig. 11 shows a schematic side view of an electrostatic recording method and apparatus of another embodiment of the invention.

Fig. 12 shows a cross-sectional view of an electrostatic recording head of one embodiment of the invention.

Fig. 13 shows a schematic side view of an electrostatic recording method and apparatus of one embodiment of the invention.

Fig. 14 shows an equivalent circuit diagram of one embodiment of the invention.

The invention will now be explained specifically in the following examples.

The electrostatic recording sheet of the invention comprises a recording layer containing a liquid crystal polymer on a substrate surface. Examples of an electrostatic recording sheet of the invention are shown in Figs. 1, 2, 3, 4, 5, 6 and 7. In Figs. 1-7, 1 indicates a substrate; 2 is a recording layer; 3 shows a conductive layer; 4 is a substrate which is also a conductive layer; 5 indicates a heat-resistant layer; 6 shows a transparent conductive layer; 7 is a light absorbing layer; and 8 indicates an oriented film. When an electrode opposite the stylus head is to be provided on the underside of a substrate of electrostatic recording sheet, a recording layer 2 is formed directly on a substrate 1 as shown in Fig. 1. In this case, it is not necessary to form a conductive layer on the substrate surface.

As shown in Fig. 2, both recording layer 2 and conductive layer 3 may be formed on the surface of substrate 1. In this case, the conductive layer becomes a counter electrode to the head. Substrate 1 may be also used as a conductive layer 4 as shown in Fig. 3. In Fig. 4, moreover, heat-resistant layer 5 is formed on recording layer 2 while conductive layer 3 is formed below the recording layer on substrate 1.

The most preferable structure of the electrostatic recording sheet of the invention is shown in Fig. 5. In this figure, the recording sheet has both transparent conductive layer 6 and light absorbing layer 7 between

recording layer 2 and substrate 1. Since transparent conductive layer 6 normally has a higher refractive index than the recording layer in this structure, Fresnel reflection from the back of the recording layer becomes large, thus increasing the contrast.

The electrostatic recording sheet shown in Fig. 6 also has the same effect as the recording sheet shown in Fig. 5. In Fig. 6, the electrostatic recording sheet has both higher refractive layer 9 and conductive layer 3 between recording layer 2 and substrate 1.

When an oriented film 8 is formed between a recording layer 2 and substrate 1 as shown in Fig. 7, the formation of domains in the liquid crystal polymer is promoted. The domain size is also enlarged. Therefore, the recording speed is improved.

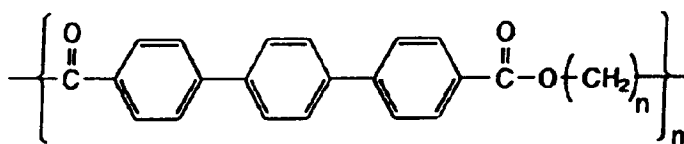
Films made of thermoplastic resins such as polyethylene terephthalate, polyethylene naphthalate, polycarbonate, polysulfone, acrylic resin, polyethylene, polypropylene and the like, or synthetic papers can be used as substrate 1.

Recording layer 2 comprises a liquid crystal polymer. The domain size of the liquid crystal polymer can be controlled by the external electric field. The liquid crystal polymer has a particular temperature range to form a liquid crystal phase. It is possible to produce an electrostatic recording since the domain size can be fixed at the temperature lower than the glass-transition temperature of the liquid crystal polymer.

Compared with a phase-separative polymer generating light scattering by the formation of amorphous domains due to the crystallization of low molecular weight molecules and the phase separation among polymers, a liquid crystal polymer is the aggregate only of domains in its liquid crystal phase. In addition, since each domain in the liquid crystal phase exhibits double refraction, the light scattering effect is significant. Therefore, a liquid crystal polymer has a higher light scattering effect than does a phase-separative polymer.

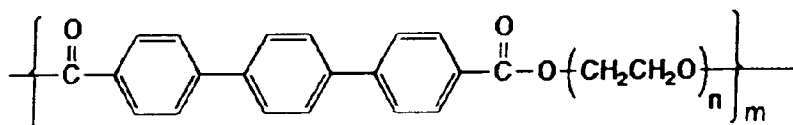
Liquid crystal polymers disclosed in Published Unexamined Japanese Patent Application Nos. Hei 1-184640, Hei 2-236518, Hei 3 -122623 and Hei 3-138687 can be used as the liquid crystal polymer of the invention. These liquid crystal polymers are shown in the following Formulas A-K.

Formula A



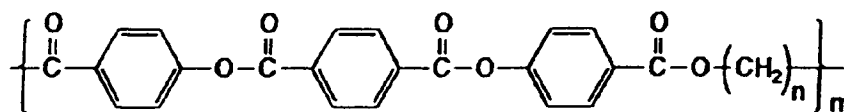
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula B

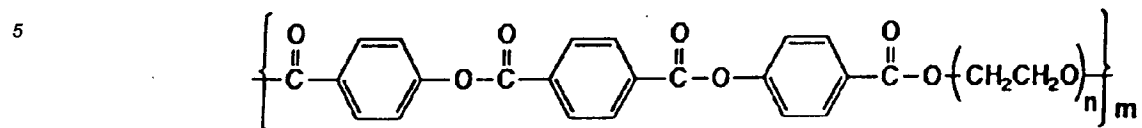


wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

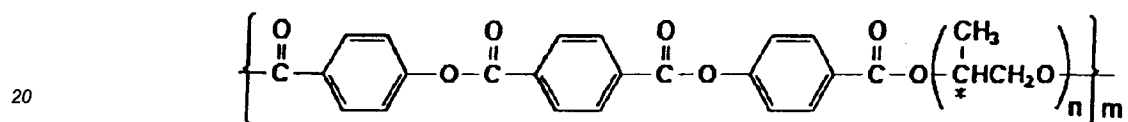
Formula C



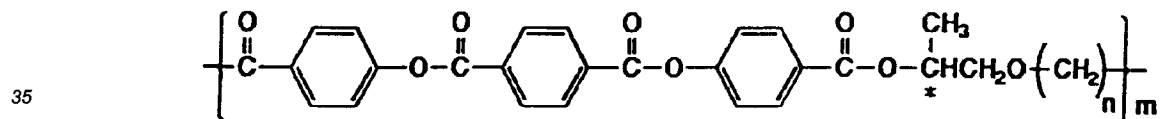
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula D

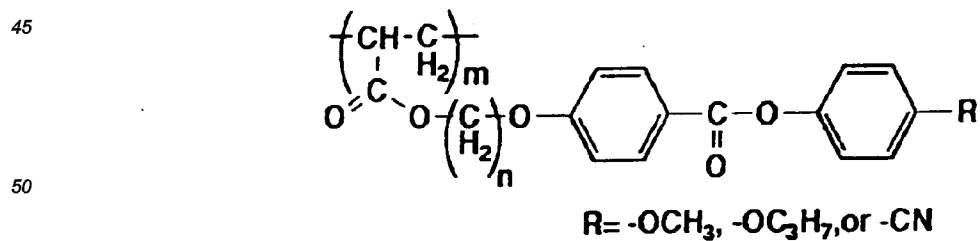
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula E

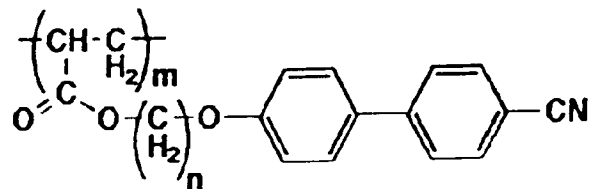
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula F

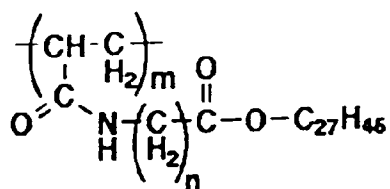
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula G

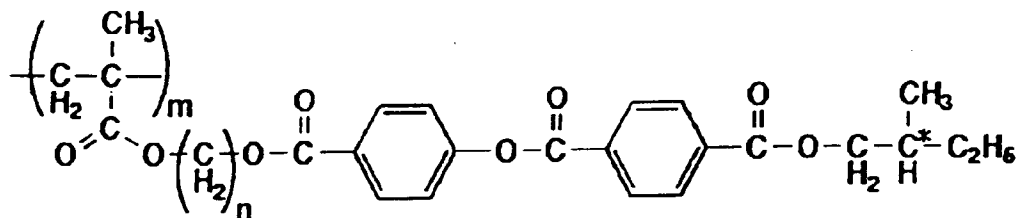
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula H

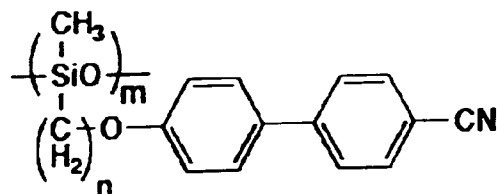
wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula I

wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula J

wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

Formula K

wherein n represents an integer from 2 to 12, and m represents an integer from 2 to 100.

However, other liquid crystal polymers such as ferroelectric liquid crystal polymers or antiferroelectric liquid crystal polymers can also be used in the invention.

It is preferable to use a thermotropic liquid crystal for the liquid crystal polymer of the invention. The in-

intermediate phase of the thermotropic liquid crystal can be any of the nematic, smectic and cholesteric states. As this thermotropic liquid crystal polymer, a main-chain type liquid crystal polymer comprising mesogen groups or rigid atomic groups bonded with flexuous molecular chains as well as a side-chain type liquid crystal polymer comprising mesogen groups or rigid atomic groups at the side chains are included. However, the liquid crystal polymer of the invention is not limited to these liquid crystal polymers. Mixed polymers or a mixture of liquid crystal polymers can also be used as the liquid crystal polymer of the invention.

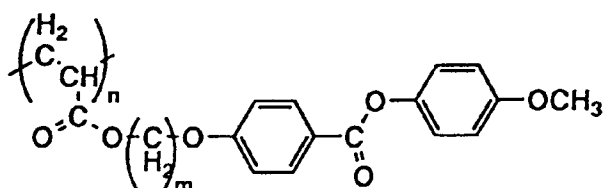
When the liquid crystal polymer is a thermotropic liquid crystal polymer, the liquid crystal polymer has a liquid crystal phase at a temperature higher than the glass-transition temperature and an isotropic phase at a temperature higher than the temperature of forming the liquid crystal phase. In addition, the liquid crystal phase has a monodomain state and a polydomain state composed of multiple domains. When the thermotropic liquid crystal polymer is in the polydomain state, light scatters intensely. On the other hand, if the polymer is in the monodomain state or the isotropic phase, light hardly scatters.

The liquid crystal polymer normally is in a polydomain state when the external electric field is not applied to the recording layer. However, if the external electric field is applied to the recording layer, the liquid crystal polymer is in a monodomain state. Therefore, with or without the application of the external electric field to the recording layer at the temperature of forming the liquid crystal phase, light can be either scattered very little or scattered very much.

The glass-transition temperature of the liquid crystal polymer is preferably from 60°C to 120°C in order to save recorded information stably and to provide appropriate heating conditions for recording.

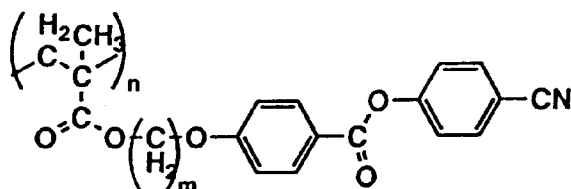
As liquid crystal polymers, the ones shown in the following Formulas 1-8 can be used. However, the liquid crystal polymer of the invention is not limited to these examples.

Formula 1

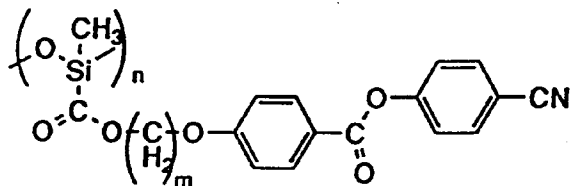


wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

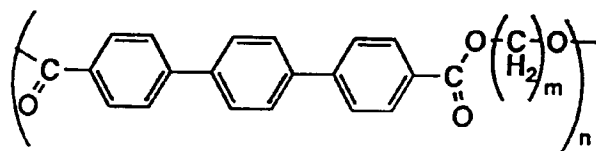
Formula 2



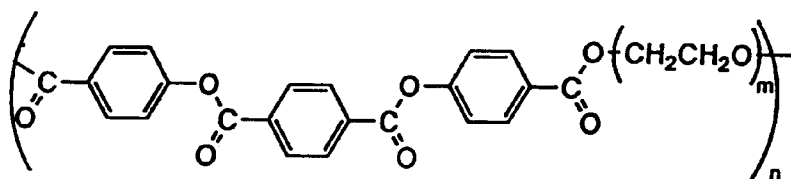
wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

Formula 3

wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

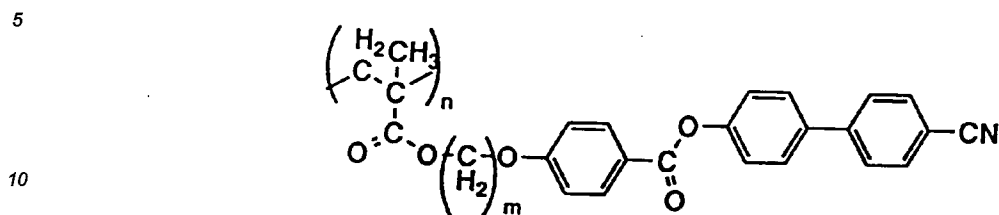
Formula 4

wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

Formula 5

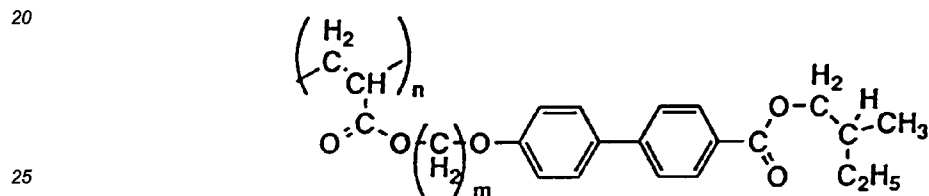
wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

Formula 6



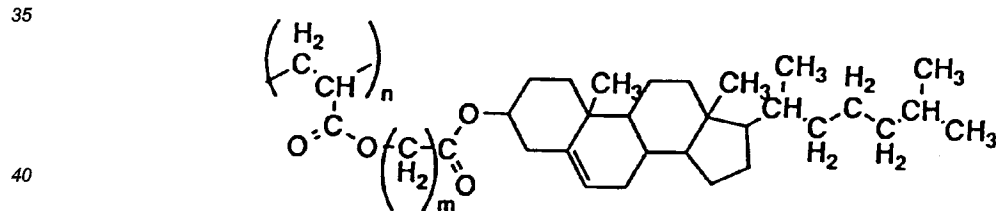
wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

Formula 7



wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

Formula 8



wherein m represents an integer from 2 to 12, and n represents a degree of polymerization.

In addition to the liquid crystal polymer, the recording layer may contain additional agents such as an ultraviolet ray absorbent, an antioxidant, or the like. The recording layer can also comprise a polymer which is not compatible with the liquid crystal polymer. In order to provide improved contrast, the polymer added to the recording layer preferably has the same refractive index as the principal refractive index of the liquid crystal polymer.

In consideration of the conductive characteristics of the electrostatic recording sheet of the invention, the value of resistance of the conductive layer is preferably 10^6 - $10^9\Omega/\square$. The conductive layer can be made from resins containing electron-conductive compounds or ion-conductive compounds. More specifically, the material of the conductive layer is prepared by dissolving or dispersing electron-conductive compounds such as metals, or ion-conductive compounds including alkali metal salts, quaternary ammonium salts, high molecular electrolytes such as polystyrene sulfonate, etc. into gelatin, (modified or unmodified) cellulose, (completely or partially saponified) polyvinyl alcohol, polyvinyl acetal, polyvinyl formal, polyvinyl butyral, acrylic resins, epoxy resins, urethane resins, or the like.

The conductive layer can also be used as a light absorbing layer if it comprises colored conductive com-

pounds such as carbon black, nonconductive dyes or nonconductive pigments.

A thin layer of zinc oxide, stannic oxide, indium tin oxide, or the like can be used as a transparent conductive layer. These materials have electric conduction properties as well as high refractive indices. Therefore, scattering reflectance is intensified at the conductive layer when light is scattered at the recording layer, thus improving the contrast.

For the higher refractive layer, materials such as WO_3 , Fe_2O_3 , PbO , ZnSc , Bi_2O_3 , TiO_2 , SiO and the like disclosed in Published Unexamined Japanese Patent Application No. Hei 2-175280 can be used.

The light absorbing layer comprises a material which absorbs visible light. Suitable materials are dyes and pigments. Among these materials, carbon black is relatively cheap and useful. By dispersing the materials in resins, the materials for the light absorbing layer can be easily prepared.

The light absorbing layer itself can also be used as a substrate. A material absorbing visible light should be dissolved or dispersed in the material of the substrate, thus preparing the material of the light absorbing layer.

The metal layer having periodic convex and concave surfaces can also be used as the light absorbing layer. When the wavelength of the visible light is longer than the period of concave and convex surfaces of the metal layer, the layer can efficiently absorb light. The metal layer can also be used as a conductive layer.

An example of an electrostatic recording layer comprising a metal layer, which is also used as a light absorbing layer and a conductive layer, is shown in Fig. 8. As shown in Fig. 8, a metal layer 10 having periodic convex and concave surfaces is formed on substrate 1, and a recording layer 2 is laminated on metal layer 10.

The period of convex and concave surfaces is preferably below the wavelength of the light which is to be absorbed. For example, in order to color the electrostatic recording sheet black, the period is preferably less than 400nm since visible light has to be absorbed. The absorption efficiency improves as the amplitude of convex and concave surfaces increases. However, the amplitude is preferably larger than one third of a period.

A simple way of forming a metal layer having periodic concave and convex surfaces is to apply metals on a substrate having periodic concave and convex surfaces.

For a substrate having periodic convex and concave surfaces, thermoplastic resins such as polyethylene terephthalate, polyethylene naphthalate, polycarbonate, polysulfone, acrylic resin, polyvinyl alcohol, and the like, or curable resins including urethane resin, phenol resin, urea resin, epoxy resin, and the like can be used. In order to prevent the deformation of the periodic convex and concave surfaces during the deletion of recorded information, the substrate is preferably made from curable resins or thermoplastic resins having a thermal deformation temperature greater than 100°C.

Periodic convex and concave surfaces are formed on a substrate surface by the following methods:

(1) methods using injection molding, compression molding or embossing by using a stamper with periodic convex and concave surfaces; and

(2) a method of curing a thermo-setting resin or a photo-setting resin between a stamper having periodic convex and concave surfaces and a substrate, thus transferring and forming periodic convex and concave surfaces on both resin and substrate (2P method).

Fig. 9 shows an example of an electrostatic recording sheet manufactured by method (2). In Fig. 9, a cured resin layer 11 having periodic convex and concave surfaces, a metal layer 10 with periodic convex and concave surfaces and a recording layer 2 are sequentially laminated on a substrate 1.

Method (1), especially the embossing method with the use of a rolled stamper, is excellent for mass-production. However, when periodic convex and concave surfaces are formed on thermoplastic resins by method (1), the convex and concave surfaces of the resins are likely to return to a flat state due to stress relaxation. Therefore, the residual stress of convex and concave surfaces of the resin has to be kept small in this method. In method (2), on the other hand, periodic convex and concave surfaces formed on thermo-setting or photo-setting resins cannot be easily deformed even by heating the recording layer, since these resins are used in this method. However, in method (2), the adhesiveness of the cured resin layer having periodic convex and concave surfaces to a substrate is required to be strong. If not, it is necessary to form an adhesive layer on the substrate surface.

The stamper having periodic convex and concave surfaces can be formed by applying an optical lithography technique to a photoresist.

In other words, interference fringes are recorded on a photoresist by an interference exposure method by using two or more luminous fluxes, and the interference fringes are then developed, thus providing a developed photoresist having periodic convex and concave surfaces. The period of interference fringes is determined by the angle of incidence of each luminous flux on the photoresist and by the crossed axes angles between the luminous fluxes. However, the depth or shape of convex and concave surfaces can be arranged by light exposure and developing conditions.

In forming periodic convex and concave surfaces on a photoresist by interference fringes, it is preferable that the photoresist exposed to luminous fluxes is again exposed to luminous fluxes from the direction of a lattice vector different from the direction of fluxes previously irradiated onto the photoresist, thus reducing the dependency of light absorbance on polarized light. For instance, a photoresist which was previously exposed to two luminous fluxes can again be exposed to two luminous fluxes after being rotated by 180°. If more than three luminous fluxes, whose vectors of incidence are not the same, are directed onto a photoresist, the formation of convex and concave surfaces can be done at once.

A metal stamper having periodic convex and concave surfaces is provided by depositing a metal such as chromium on the surface of a developed photoresist to add conductivity, electroforming nickel or the like, and removing the remaining photoresist.

Instead of electroforming metals, periodic convex and concave surfaces are reproduced by a curable resin, thus forming a plastic stamper. However, since the plastic stamper does not have sufficient heat-resistant properties, it is not applicable for method (1). If silicone-based or fluorine-based resins are used as curable resins, the plastic stamper which can be easily separated from these resins can be made in method (2).

Metals used for the stampers are not limited to any particular kinds. However, it is preferable to use metals whose optical characteristics cannot be changed by oxidization or the like. Such metals include gold, platinum, palladium, silver, nickel, aluminum, chromium and the like.

Metal layers having periodic convex and concave surfaces can be manufactured by depositing the metals on substrates with periodic concave and convex surfaces, or the like.

When a metal layer having periodic convex and concave surfaces is formed on a recording layer with periodic convex and concave surfaces, it is necessary to prevent the deformation of the convex and concave surfaces during recording and deletion of information by heating. This is done by introducing a bridge structure into the recording layer without disturbing the layer's light scattering properties.

A heat-resistant layer may be formed on the recording layer to prevent the deformation of the recording layer and the deposition of the recording layer onto the heating device during the processes of recording and deleting information by heating. Lubricants such as silicone oil, curable resins containing particles like silica, silicone resins, or fluorine-modified thermoplastic resins can be used for the heat-resistant layer.

The center line average height of the heat-resistant layer is preferably 1-15 μm . This surface roughness can keep the distance between the recording electrode and the surface of an electrostatic recording sheet at a preferable level for generating a gaseous discharge. The repulsion between charges can also be kept small, thus providing a uniformly charged condition and recorded images with high contrast.

In order to form a heat-resistant layer with this level of surface roughness, it is preferable that the layer comprise particles of 3-20 μm in size. The particles are not limited to any particular kinds of materials. However, in order to keep the light scattering in the heat-resistant layer small, the difference in refractive indices between the particles and other materials such as the curable resin is preferably small.

An electrostatic recording sheet of the invention comprising a metal layer with periodic concave and convex surfaces as a light absorbing layer is manufactured by the following methods.

The first method comprises the steps of:

- (1) pressing a stamper having periodic convex and concave surfaces on a substrate, thus transferring convex and concave shapes to the substrate surface;
- (2) forming a metal layer on the surface of the substrate having periodic convex and concave surfaces; and
- (3) forming a recording layer by coating a solution comprising a liquid crystal polymer on the metal layer and drying the solution.

In order to form a heat-resistant layer on the recording layer, a step (step (4)) of coating a solution containing the materials of the heat-resistant layer on the recording layer, drying the solution and then sometimes curing the solution can be added to this method.

When the substrate is made from a thermo-setting resin, the substrate can be cured by heating in step (1). Thus, convex and concave surfaces transferred to the substrate surface will not lose their shape and flatten out.

If the substrate is made of a photo-setting resin, irradiation of light to the substrate in step (1) can prevent its concave and convex surfaces from flattening out.

By heating the substrate made from a thermoplastic resin to a proper temperature in step (1), convex and concave surfaces can be transferred to the substrate surface. If the heat deformation temperature of the resin is close to the heating temperature during the processes of recording and deleting information, the probability of the resin surface flattening out increases. However, the resin is the best choice for mass-production.

Coating methods such as a blade coating method, a gravure coating method, or the like can be applied for coating high molecular compounds in steps (3) and (4).

By changing the drying temperature and drying gas volume in steps (3) and (4), the conditions of an electrostatic recording sheet including a transparent condition, a colored condition and an opaque condition can be selected.

The second method comprises the steps of:

- 5 (1) transferring periodic convex and concave surfaces to a substrate surface by adhering a photo-setting resin between a stamper with periodic convex and concave surfaces and the substrate, polymerizing the resin by light irradiation, and finally binding the resin having periodic convex and concave surfaces to the substrate surface after separating the stamper from the resin;
- (2) forming a metal layer on the substrate surface having periodic convex and concave surfaces; and
- 10 (3) coating a solution comprising a liquid crystal polymer on the surface of the metal layer and drying the solution, thus forming a recording layer.

Step (4) of the first method can also be added to this second method. In step (1), the time for curing the photo-setting resin can be shortened since the quantity of the resin required to be cured is small.

Steps (1) and (2) of these methods can be replaced with a step of coating a solution comprising a light absorbing material on a substrate surface to form a light absorbing layer. In this way, an electrostatic recording sheet composed of a light absorbing layer and a recording layer comprising a liquid crystal polymer is formed.

The oriented film of the invention can be the same as an oriented film used for general liquid crystal elements. More specifically, the oriented film is a deposited film with oblique incident angle of an inorganic compound, a high molecular compound film treated with rubbing or the like. As examples of the inorganic compound, SiO and SiO_2 are included. The high molecular compounds used for the oriented film include polyimide, polyamide, polyester, polyvinyl alcohol, or fluororesins such as poly(vinylidene fluoride).

The rubbing treatment is a treatment of rubbing a high molecular compound film with a cloth or the like in one direction. The exact cause of the orientation of the mesogen groups of the oriented film has not been found. However, it is thought that the surface of the high molecular compound film receives a shearing stress from the treatment and is then oriented, thus providing the effect of the orientation of the mesogen groups.

Even if a conductive layer and a light absorbing layer are not formed between a recording layer and a substrate, the same effects can be provided as long as the substrate itself is a drawn film composed of oriented high molecular compounds.

The electrostatic recording method of the invention is now explained in detail.

30 Figs. 10-11 show side views of recording information by heating before or after electrification. In Figs. 10-11, 12 shows an electric recording sheet; 13 is a heated roller; 14 indicates a recording electrode (stylus); 15 is a counter electrode; and 16 is a high voltage power supply. Before or after electrification, electrostatic recording sheet 12 is passed through between recording electrode 14 and counter electrode 15, while the recording layer of the electrostatic recording sheet is faced to recording electrode 14 with a gap of several μm in between and electrostatic recording sheet 12 keeps in contact with counter electrode 15. Voltage higher than a predetermined level is applied to recording electrode 14 and counter electrode 15 while the electrostatic recording sheet is running, thus discharging from recording electrode 14 and charging at the surface of the recording layer.

40 If the temperature of the charged recording layer is at the temperature of forming the liquid crystal layer or above, the domain size of the liquid crystal is enlarged and a section having no light scattering is formed at the charged section of the recording layer.

The domain size is then fixed by cooling the recording layer to a temperature lower than the glass-transition temperature.

45 The recording electrode is shaped like a needle, and a multi-stylus type electrode head is prepared by lining up multiple recording electrodes.

The counter electrode does not necessarily have to be located on the opposite side of the recording electrode with the electrostatic recording sheet in between. More specifically, as shown in Fig. 12, when the cross section of the counter electrode is significantly larger than that of the recording electrode, the conductive layer can be set at a similar potential to the counter electrode even without being in contact with the counter electrode. Therefore, the discharge from the recording electrode to the conductive layer as well as recording information become possible. Fig. 13 shows an example of recording device using an electrostatic recording head (composed of a recording electrode and a counter electrode) as shown in Fig. 12. In Figs. 12-13, 1 indicates a substrate; 2 is a recording layer; 3 shows a conductive layer; 12 is an electrostatic recording sheet; 13 indicates heated rollers; 14 indicates a recording electrode; 16 and 16' indicate high voltage power supplies; 50 17 is an electrostatic recording head; 18 shows a counter electrode; and 19 is a platen to maintain contact between the electrostatic recording head and the electrostatic recording sheet.

55 Fig. 14 is an equivalent circuit diagram. VR is the voltage applied to the recording electrode; VC is the voltage applied to the counter electrode; C1 indicates the capacitance of a gap between the recording electrode

and the recording layer; C2 shows the capacitance of the recording layer under the electrostatic electrode; C3 is the capacitance between the counter electrode and the conductive layer; C4 indicates the capacitance between the heated roller and the conductive layer; R1 shows the resistance of the conductive layer between the above recording electrode and counter electrode; and R2 indicates the resistance of the conductive layer between the above counter electrode and heated roller.

If the cross section of the counter electrode is significantly larger than that of the recording electrode, $C1 < C2 < C3$. The capacitance of applied voltage ($VR + VC$) is divided at C1, C2 and C3. As a result, most of the voltage is applied to C1, generating a gaseous discharge.

The invention will be explained specifically with reference to the following illustrative embodiments.

Example 1

A liquid crystal polymer solution 1 was prepared by dissolving 30 weight parts of poly(5-(4-4'-cyanobiphenoxy)pentylmethacrylate) into 70 weight parts of dichloroethane.

A coating material was prepared by dissolving and dispersing a mixture of carbon black, butyral resin (S-leck BX-1: manufactured by Sekisui Chemical Co., Ltd.) and multifunctional isocyanate solution (Coronate L: manufactured by Nippon Polyurethane Industrial Co., Ltd.) at a ratio of 7:2.5:0.5 into a mixed solvent of toluene and methylethylketone at a ratio of 2:1. The coating material was coated on a 100 μm thick poly(ethylene terephthalate) (PET) film by a gravure coater and then dried, thus forming an approximately 2 μm thick conductive layer which was also used as a light absorbing layer. The PET film formed with the conductive layer was then cured in a constant-temperature drier at 70°C for 24 hours.

Liquid crystal polymer solution 1 was coated on the conductive layer by a gravure coater and then dried, thereby forming about a 10 μm thick recording layer on the conductive layer. As a result, an electrostatic recording sheet A was manufactured.

Example 2

On electrostatic recording sheet A manufactured as in Example 1, a 2-propanol solution containing a photosetting resin (Ripoxy SP-1509: manufactured by Showa Highpolymer Co., Inc.) was coated and then dried. As a result, about a 0.5 μm thick heat-resistant layer was formed on the recording layer of electrostatic recording sheet A, and was then irradiated with a mercury lamp, thus curing the layer and manufacturing an electrostatic recording sheet B.

Example 3

A 2-propanol solution containing 7 weight parts of a photosetting resin (Ripoxy SP-1509: manufactured by Showa Highpolymer Co., Ltd.) and 3 weight parts of silica particles of about 10 μm in particle size was coated on the recording layer of electrostatic recording sheet A, and then dried. As a result, about a 2.3g/m² heat-resistant layer was formed and then cured by irradiation with a mercury lamp, thereby manufacturing an electrostatic recording sheet C.

Example 4

A liquid crystal polymer solution 2 was prepared by dissolving 30 weight parts of 2-[4-(4-cyanophenylcarbonyloxy)phenoxy]ethylacrylate into 70 weight parts of dichloroethane.

A coating material was prepared by dissolving and dispersing a mixture of carbon black, butyral resin (S-leck BX-1: manufactured by Sekisui Chemical Co., Ltd.) and multifunctional isocyanate solution (Coronate L: manufactured by Nippon Polyurethane Industrial Co., Ltd.) at a ratio of 7:2.5:0.5 into a mixed solvent of toluene and methylethylketone at a ratio of 2:1. The coating material was coated on a 100 μm thick PET film and then dried, thus forming about a 4 μm thick conductive layer on the PET film. The PET film formed with the conductive layer was cured in a constant-temperature drier at 70°C for 24 hours.

WO₃ was then deposited on the conductive layer to a thickness of about 20nm (200 angstroms), thus forming a higher refractive layer. A 10 μm thick recording layer was formed on the higher refractive layer by coating and then drying liquid crystal polymer solution 2. As a result, an electrostatic recording sheet D was manufactured.

Example 5

A 100 μm thick PET film containing carbon black was used as a substrate as well as a light absorbing layer in this example. A transparent conductive layer was formed on the PET film by sputtering ZnO.

5 Liquid crystal polymer solution 1 was then coated and dried on the conductive layer, thus forming a 10 μm thick recording layer. As a result, an electrostatic recording sheet E was manufactured in this example.

Example 6

10 A transparent conductive layer was formed on a 75 μm thick PET film by depositing ITO (indium titanium oxide). Polyvinyl alcohol solution was coated on the conductive layer with a wire bar, and then dried. The surface of the polyvinyl alcohol film was rubbed with a rayon cloth to make it oriented.

Liquid crystal polymer solution 1 was coated on the oriented film and dried, thus forming a 10 μm thick recording layer. A 2-propanol solution containing 8 weight parts of photosetting resin (Ripox SP-1509: manufactured by Showa Highpolymer Co., Ltd.) and 2 weight parts of benzo guanamine particles of about 10 μm in particle size was then coated on the recording layer and dried, thus forming about a 2.3g/m² heat-resistant layer. The heat-resistant layer was irradiated with a mercury lamp and cured, thus manufacturing an electrostatic recording sheet F.

Example 7

A photoresist was coated on a 40cm-diameter glass substrate at a thickness of 300nm, and then dried. A 488nm argon ion laser was divided into two luminous fluxes, and the fluxes were irradiated onto the photoresist in a parallel condition with 54.4° and -54.4° angles of incidence, thus directing an interference exposure onto the photoresist. The glass substrate coated with the photoresist was rotated by 90°, and the interference exposure was again directed onto the photoresist. After the second exposure, the photoresist was developed.

Chromium was deposited on the surface of the developed photoresist, thus forming a chromium layer. As an electrode, the chromium layer was plated in a nickel bath, thus providing a 500 μm -thick nickel plate. The nickel plate was separated from the glass substrate, and the photoresist left on the separated side of the nickel plate was removed, thereby preparing a mother stamper. Similarly, the mother stamper was plated in a nickel bath as an electrode, thus providing a daughter stamper (stamper 1). On each surface of stamper 1, as a result, crossed concave and convex surfaces with a pitch of about 300nm and a depth of about 150nm were formed.

35 Stamper 1 was cut into a rectangular shape, and was wrapped around a steel cylinder 10cm in diameter, thus preparing an embossing roll. The embossing roll was fixed to a calender, and a 30 μm -thick polycarbonate film was supplied to the device. While the film on the supply side was heated with hot air, it was continuously embossed. Thus, a substrate 1 having periodic convex and concave surfaces was manufactured.

A metal layer was then formed on substrate 1 after sputtering aluminum on the substrate to a thickness of 7nm (70 angstroms) with an inline type sputtering machine.

40 Liquid crystal polymer solution 1 was then coated on substrate 1 by an inline type micro-gravure coater and dried, thus forming about a 10 μm thick recording layer on substrate 1. As a result, an electrostatic recording sheet G was manufactured.

Example 8

45 Electrostatic recording sheets A-G manufactured in Examples 1-7 were opaque. Each electrostatic recording sheet was set in a recording device comprising a heated roller with its copper roller covered with a silicone resin, a 6 dot/mm multi-stylus type electrode head and a 1kV high voltage power supply. The positive electrode of the high voltage power supply was connected to the conductive layer of the electrostatic recording sheet while the sheet surface facing the multi-stylus type electrode head became a negative electrode. Stripes were then recorded on the electrostatic recording sheet at 1cm intervals per line recording cycle of 500 microseconds. The recorded sections of the recording layer became transparent and black.

Example 9

55 The optical densities of the recorded and unrecorded sections of electrostatic recording sheets A-G of Example 8 were measured with light of 550nm wavelength by an integrating sphere spectrophotometer. Only for electrostatic recording sheet F, a black paper was placed at the back of the substrate. The results of the measurement are shown in the following Table 1.

Table 1

Electrostatic Recording Sheet	O.D.* of the R.S.**	O.D of the U.S.***	Difference in O.D.
A	1.34	0.55	0.79
B	1.31	0.56	0.75
C	1.28	0.51	0.76
D	1.27	0.25	1.02
E	1.28	0.23	1.05
F	1.35	0.30	1.05
G	1.04	0.45	0.59

* Optical Density

** Recorded Section

*** Unrecorded Section

Example 10

In this example, the same method as of Example 8 was again directed to the electrostatic recording sheets recorded in Example 8 except that the electrode needles of Example 8 were replaced with other electrode needles.

As a result, the section of the recording layer recorded in Example 8 was in a light scattering condition and deleted. The section recorded in this example, on the other hand, was colored as in Example 8.

Therefore, in the electrostatic recording method of the invention, recording as well as deletion of information can be carried out at the same time.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Claims

1. An electrostatic recording sheet comprising a recording layer formed directly on a substrate or indirectly on at least one other layer on said substrate, said recording layer comprising a liquid crystal polymer for reversible electrostatic recording.
2. An electrostatic recording sheet according to claim 1, wherein the liquid crystal polymer is a thermotropic liquid crystal polymer.
3. An electrostatic recording sheet according to claim 1 or 2, wherein a conductive layer is formed between

the substrate and the recording layer.

4. An electrostatic recording sheet according to claim 3, wherein the conductive layer is colored.
- 5 5. An electrostatic recording sheet according to claim 3 or 4, wherein the conductive layer is made from a transparent conductive material.
6. An electrostatic recording sheet according to any of claims 3 to 5, wherein the conductive layer has a resistance of from 10^6 to $10^9 \Omega/\square$.
- 10 7. An electrostatic recording sheet according to any of claims 1 to 6, wherein a heat-resistant layer is formed on the recording layer.
8. An electrostatic recording sheet according to claim 7, wherein the center line average height of the heat-resistant layer is from 1 to 15 μm .
- 15 9. An electrostatic recording sheet according to claim 7 or 8, wherein the heat-resistant layer comprises particles having sizes from 3 to 20 μm .
10. An electrostatic recording sheet according to any of claims 7 to 9, wherein the heat-resistant layer is made from a curable resin or a thermoplastic resin having a heat deformation temperature greater than 100°C.
- 20 11. An electrostatic recording sheet according to any of claims 1 to 10, wherein an oriented film is formed between the substrate and the conductive layer or the recording layer.
- 25 12. An electrostatic recording sheet according to any of claims 1 to 11, wherein the substrate is made from a curable resin or a thermoplastic resin having a heat deformation temperature greater than 100°C.
13. An electrostatic recording method comprising the steps of:
 applying voltage to a stylus placed above one surface of a recording layer of an electrostatic recording sheet comprising a liquid crystal polymer, and to a counter electrode fixed to the opposite surface of the electrostatic recording sheet or to the conductive layer of the electrostatic recording sheet, thus producing a discharge; and
 heating the recording layer to a temperature higher than a temperature of forming a liquid crystal phase of liquid crystal polymer before or after the electrification of the recording layer, thereby enlarging the domain size of the liquid crystal phase in the recording layer.
- 35 14. An electrostatic recording method according to claim 13, wherein the recording layer is heated to a temperature higher than a temperature at which an isotropic phase of the liquid crystal polymer is formed with no application of external electric field to the recording layer and then cooled, thereby reducing the domain size uniformly and deleting recorded information.
- 40 15. An electrostatic recording method according to claim 13 or 14, wherein the stylus is a monostylus or a multistylus.

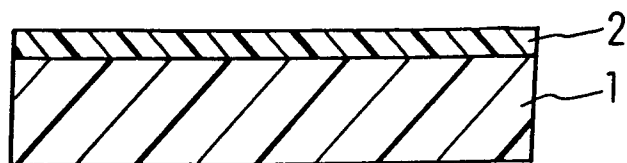


FIG. 1

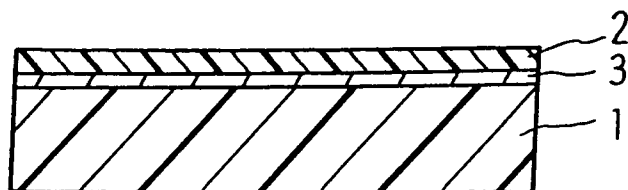


FIG. 2

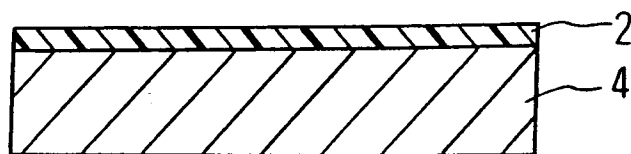


FIG. 3

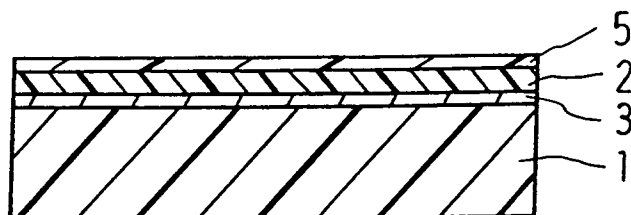


FIG. 4

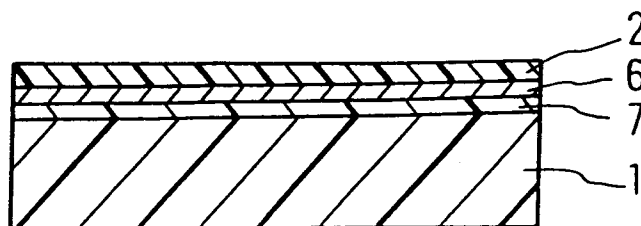


FIG. 5

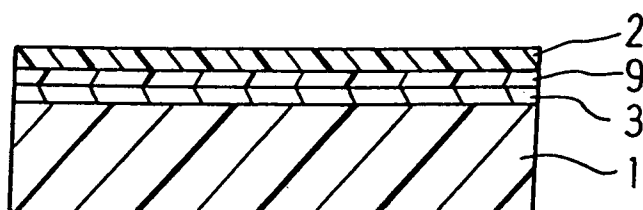


FIG. 6

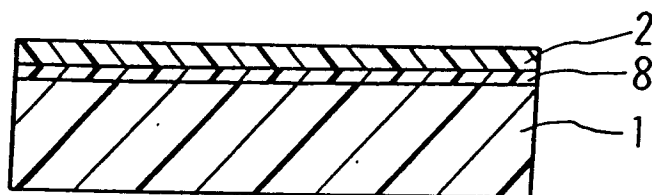


FIG. 7

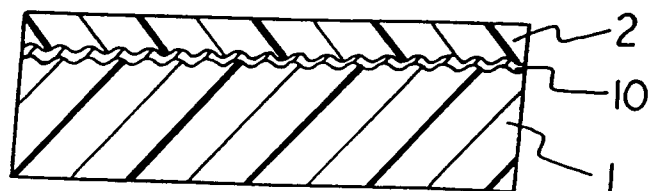


FIG. 8

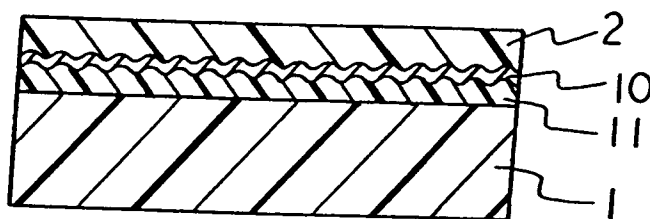


FIG. 9

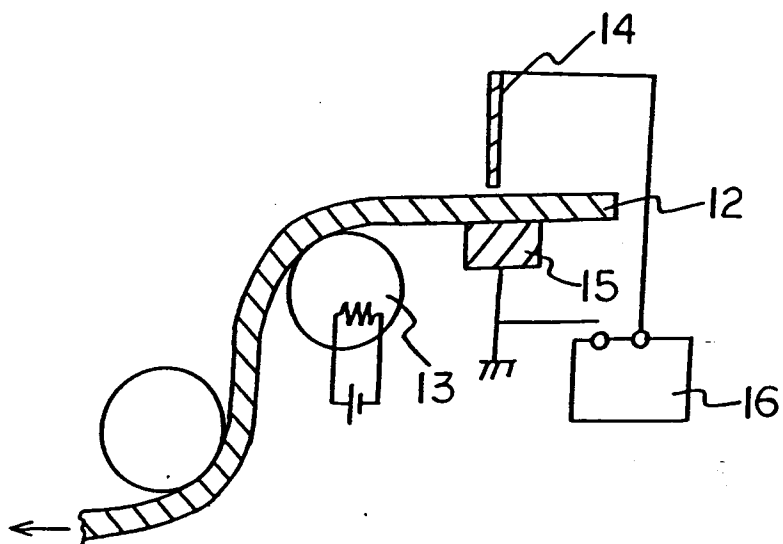


FIG. 10

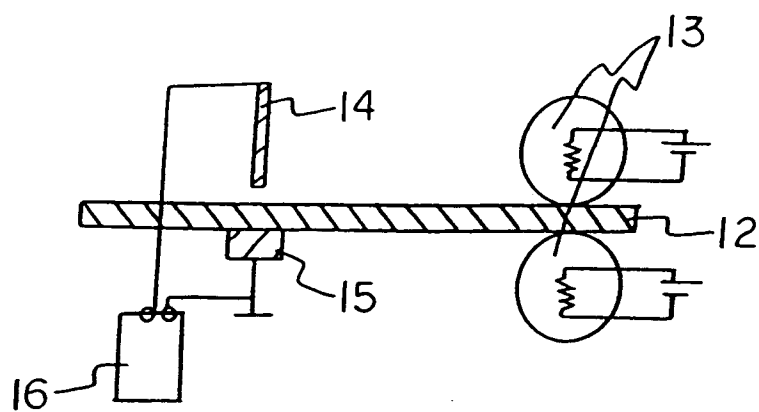


FIG. 11

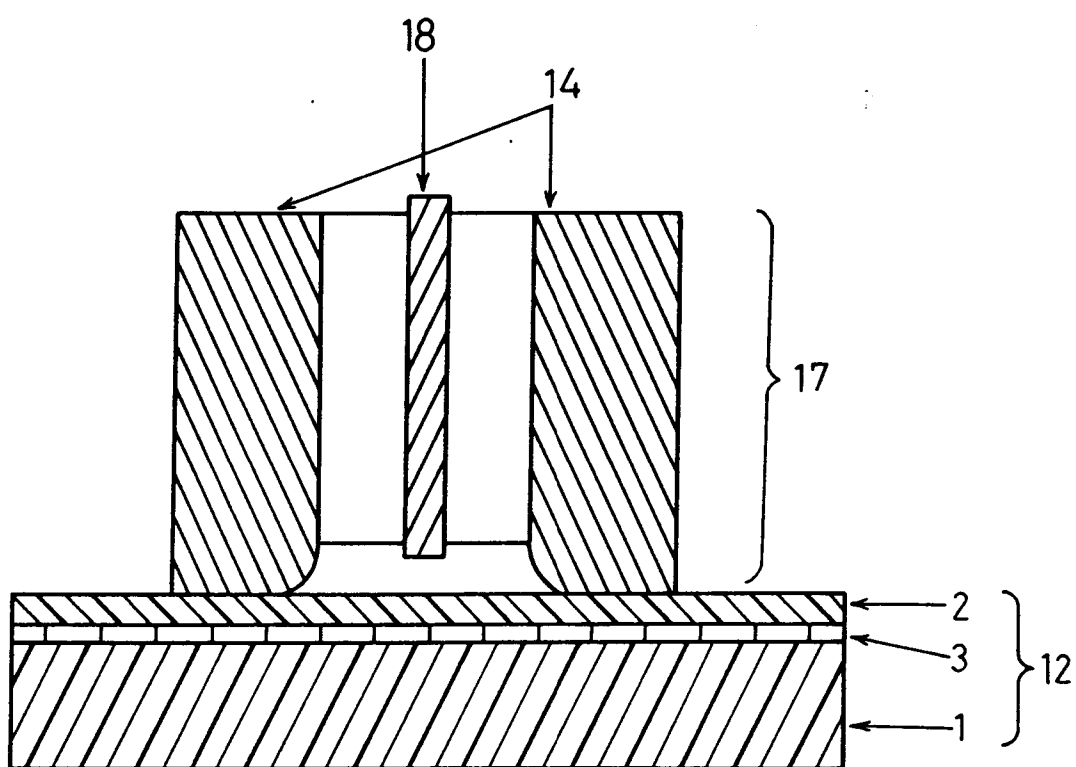


FIG. 12

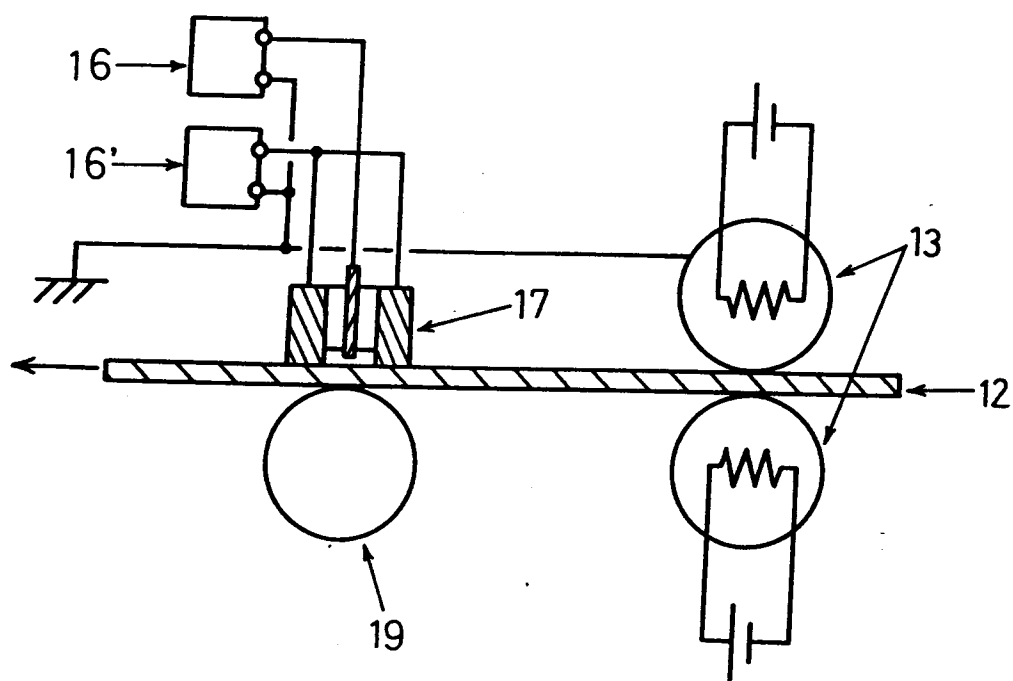


FIG. 13

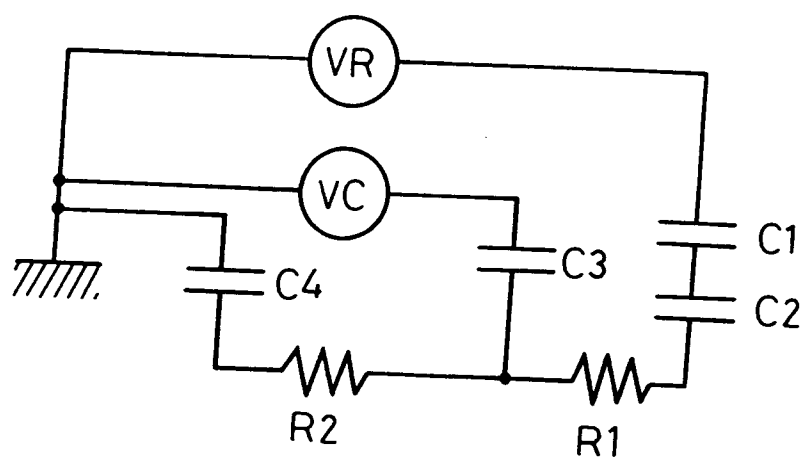


FIG. 14



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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 2581

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 471 (P-949)25 October 1989 & JP-A-01 184 640 (CANON INC.) 24 July 1989	1	G03G5/02
D,Y		3,6-10, 12	
D,A	* abstract *	13-15	
D,X	--- PATENT ABSTRACTS OF JAPAN vol. 14, no. 554 (P-1140)10 December 1990 & JP-A-02 236 518 (CANON INC.) 19 September 1990	1	
D,Y		3,6-10, 12	
D,X	--- DATABASE WPI Week 9130, Derwent Publications Ltd., London, GB; AN 91-218052 (30) & JP-A-3 138 687 (CANON K.K.) 13 June 1991	1	
D,Y		3,6-10, 12	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03G
Y	EP-A-0 454 869 (DAI NIPPON PRINTING CO., LTD.) * page 7, line 31 - page 9, line 37; example 1 *	3,6-10, 12	
A	--- PATENT ABSTRACTS OF JAPAN vol. 8, no. 159 (P-289)24 July 1984 & JP-A-59 057 243 (FUJITSU K.K.) 2 April 1984 * abstract *	3-6, 13-15	
	--- -/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 June 1994	Examiner Hindia, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1500 (12.92) (P/M/C/R)



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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 2581

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 464 784 (CANON KA) * page 4, line 6 - line 58; claim 1 * ---	1,13-15	
A	EP-A-0 404 575 (VICTOR COMPANY OF JAPAN, LTD.) * page 7, line 11 - line 23; claim 1 * -----	1,13,14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 June 1994	Examiner Hindia, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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