⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 632 344 A2**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **94108189.5**

⑸① Int. Cl.⁶: **G03G 15/20**, H05B 3/26

㉒ Date of filing: **27.05.94**

㉚ Priority: **28.05.93 JP 127102/93**
03.06.93 JP 133536/93
07.06.93 JP 136171/93
03.08.93 JP 192177/93
28.10.93 JP 270891/93

㊸ Date of publication of application:
04.01.95 Bulletin 95/01

(84) Designated Contracting States:
DE FR GB IT

(71) Applicant: **CANON KABUSHIKI KAISHA**
30-2, 3-chome, Shimomaruko,
Ohta-ku
Tokyo (JP)

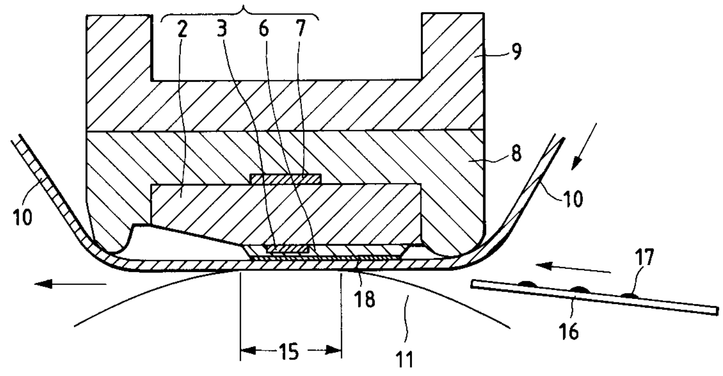
(72) Inventor: **Taniguchi, Yasushi, c/o Canon**
Kabushiki Kaisha
30-2, 3-chome, Shimomaruko
Ohta-ku,
Tokyo 146 (JP)

(74) Representative: **Pellmann, Hans-Bernd,**
Dipl.-Ing.
Patentanwaltsbüro
Tiedtke-Bühling-Kinne & Partner
Bavariaring 4
D-80336 München (DE)

㊹ Heater and image heating device utilizing the same.

㊼ An image heating device having a heater and a plastic film contacting the heater on a face and contacting the unfixed toner image on the recording sheet on the other face, thus transmitting heat from the heater to the toner image through the plastic film, is provided with a hard carbon film, a hydrogenated amorphous carbon film or a diamond-like carbon film at the interface between the heater and the plastic film in order to improve the sliding performance and durability.

FIG. 3



EP 0 632 344 A2

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an image forming apparatus such as a copying machine, a laser beam printer or the like, and more particularly to a heater and an image heating device, adapted for heating an unfixed image.

Related Background Art

An image heating device utilizing a fixed heater and a thin film sliding on the heater, as shown in Fig. 51, is proposed for example in U.S. Patent No. 5,149,941. In Fig. 51 there are shown a heater 500, a film 505 sliding on the heater 500, a driving roller 506 for driving the film 505, driven roller 507, and a pressure roller 508 in contact with the heater 500 across the film 505. The heater 500 is provided with a substrate 501, a resistance layer 502 provided on the substrate 501 and generating heat by electric current supply, an insulating protective layer 503 for protecting the resistance layer 502, and a supporting frame 504 for supporting the foregoing elements.

Thermal fixation of an unfixed image is achieved by transmitting heat of the heater through the insulating protective layer thereon and a sliding contact face of the film. However, because of sliding contact between the insulating protective layer and the film, there generally occurs significant abrasion of the film when the total distance of sliding movement reaches about 60 km. The resulting abraded powder is unevenly deposited on the roller for driving the film. As a result, the film driving speed becomes irregular, so that the fixation of the unfixed image also becomes ununiform.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a heater provided with a protective layer excellent in sliding performance to a film, and an image heating device.

Another object of the present invention is to provide an image heating device provided with a film excellent in sliding performance to a heater.

Still another object of the present invention is to provide a heater and an image heating device, provided with a protective layer excellent in sliding performance and thermal conductivity.

Still another object of the present invention is to provide a heater of which protective layer is provided, at least on the surface thereof, with a hard carbon film, a hydrogenated amorphous carbon film or a diamond-like layer.

Still another object of the present invention is to provide an image heating device provided, at the sliding portion between a heating member and a film, with a hard carbon film, a hydrogenated amorphous carbon film or a diamond-like layer.

Still other objects of the present invention will become fully apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plan view of a heater of the present invention, at the side of a heat-generating resistance thereof;

Fig. 2 is a plan view of a heater of the present invention, at the rear side thereof;

Fig. 3 is a cross-sectional view of a fixing device, utilizing the heater embodying the present invention;

Figs. 4A to 4E are partial cross-sectional views of a heater embodying the present invention;

Fig. 5 is a view of an apparatus, used in the formation of a hard carbon film in an embodiment of the present invention;

Fig. 6 is a cross-sectional view of a fixing device, utilizing the heater of the present invention of another embodiment;

Fig. 7 is a view of an apparatus, used in the formation of a hard carbon film in another embodiment of the present invention;

Fig. 8 is a view of an apparatus, used in the formation of a hard carbon film in still another embodiment of the present invention;

Figs. 9 and 10 are cross-sectional views of a fixing device utilizing the heaters of still other embodiments of the present invention;

Figs. 11A to 11E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 12 is a view of an apparatus, used in the formation of a DLC film in another embodiment of the present invention;

Fig. 13 is a view of an apparatus, used in the formation of an a-C:H film in another embodiment of the present invention;

Fig. 14 is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Figs. 15A to 15E are partial cross-sectional views of the heater of another embodiment of the present invention;

Figs. 16 to 18 are cross-sectional views of a fixing device, utilizing the heater of still other embodiments of the present invention;

Figs. 19A to 19E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 20 is a view of an apparatus, used in the formation of a DLC film in another embodiment of the present invention;

Fig. 21 is a view of an apparatus, used in the formation of an a-C:H film in another embodiment of the present invention;

Figs. 22 and 23 are cross-sectional views of a fixing device utilizing the heater of still other embodiments of the present invention;

Figs. 24A to 24E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 25 is a view of an apparatus, used in the formation of a DLC film in another embodiment of the present invention;

Fig. 26 is a view of an apparatus, used in the formation of an a-H:C film in another embodiment of the present invention;

Fig. 27A is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Fig. 27B is a chart showing the relationship between the content of added metal of the present invention and the friction coefficient;

Figs. 28A to 28E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 29 is a view of an apparatus, used in the formation of a DLC film in another embodiment of the present invention;

Fig. 30 is a cross-sectional view of a fixing device utilizing the heater of still another embodiment of the present invention;

Figs. 31 and 32 are views showing an apparatus used in the formation of an a-C:H film in other embodiments of the present invention;

Fig. 33 is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Figs. 34A to 34E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 35 is a view of an apparatus used in the formation of a DLC film in another embodiment of the present invention;

Fig. 36 is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Fig. 37 is a view of an apparatus used in the formation of an a-C:H film in another embodiment of the present invention;

Fig. 38 is a view of an apparatus used in fluorination of an a-C:H film in another embodiment of the present invention;

Fig. 39 is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Fig. 40 is a chart showing the Raman spectrum of diamond crystals of the present invention;

Fig. 41 is a cross-sectional view of a fixing device utilizing the heater of still another embodiment of the present invention;

Figs. 42A to 42F are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 43 is a view of an apparatus, used in the formation of diamonds in another embodiment of the present invention;

Fig. 44 is a view of an apparatus, used in the formation of diamonds in another embodiment of the present invention;

Fig. 45 is a cross-sectional view of a fixing device, utilizing the heater of still another embodiment of the present invention;

Figs. 46A to 46E are partial cross-sectional views of the heater of another embodiment of the present invention;

Fig. 47 is a view of an apparatus used in the formation of a DLC film in another embodiment of the present invention;

Fig. 48 is a view of an apparatus used in the formation of an a-C:H film in another embodiment of the present invention;

Fig. 49 is a view of an apparatus used in the formation of a hard carbon film in another embodiment of the present invention;

Fig. 50 is a view of an apparatus used in ashing of a hard carbon film in another embodiment of the present invention; and

Fig. 51 is a view of a conventional fixing device.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be described by preferred embodiments shown in attached drawings.

A heater of the present invention is shown in Figs. 1 and 2, seen respectively from the side of the heat-generating resistor and the rear (substrate) side.

Referring to Figs. 1 and 2, the heater 1 is provided with an electrical insulating slender substrate 2 of a high heat resistance and low heat capacity, an electrically heat-generating member 3 formed as a narrow straight stripe on a face (surface side) of the substrate 2 along the longitudinal direction thereof at the center of the width thereof, electrode terminals (connecting terminals) 4, 5 formed on the surface of the substrate at both ends of the heat-generating resistor, an electrical insulating protective layer 6 composed for example of glass and covering the surface, bearing the heat-generating resistor, of the substrate 2, and a temperature detecting element 7, such as a thermistor, formed on the other face (rear side) of the substrate 2. The substrate 2 is composed for example of a ceramic plate, such as of Al_2O_3, AlN or SiC, of a width of 10 mm, a thickness of 1 mm and a length of 240 mm. The heat-generating resistor 3 is a patterned layer of Ag/Pd (silver-palladium alloy), RuO_2 or Ta_2N coated by screen printing, followed by sintering in air, for example of a thickness of 10 μm and a width of 1 mm. The electrode terminals 4, 5 are patterned layers for example of Ag, coated with a thickness of 10 μm by screen printing, followed by sintering in air. The electrodes 4, 5 are connected by a connector (not shown) to wires for electric power supply.

For maintaining and controlling the temperature on the fixing face of the heater 1, the heat-generating resistor 3 is positioned, in the cross section, at the approximate center of the width of a fixing nip 15. The heater 1 is in contact, at the side of the electrical insulating protective layer 6 thereof, with a sliding film. A voltage is applied between the electrode terminals 4, 5 of the heat-generating resistor 3 from an AC power source 12 to heat the heat-generating resistor 3, whereby temperature of the heater 1 rises.

The temperature of the heater 1 is detected by the temperature detecting element 7 at the rear side of the substrate, and the detected information is fed back to a power supply control circuit to control the power supply from the AC power source 12 to the heat-generating resistor 3, thereby maintaining the heater at a predetermined temperature. The temperature detecting element 7 of the heater 1 is provided at a position on the rear side of the substrate corresponding to the position of best heat response on the fixing face, namely the position of the heat-generating resistor 3 on the surface side of the substrate.

At first there will be explained the formation of a hard carbon film, according to the present invention, on the insulating protective film or the heat-generating resistor of the heater.

The hard carbon film of the present invention macroscopically has an amorphous structure, consisting of carbon atoms of sp^2, sp^3 bondings, and is almost free from hydrogen, less than 1 atom % even when it is present. The density of the hard carbon film is within a range larger than that of graphite (2.26 g/cm^3) and smaller than that of diamond (3.51 g/cm^3). Also the physical properties of the hard carbon film are represented, for example, by a hardness of 2000 - 5000 kg/mm^2, a friction coefficient $\mu < 0.2$ and an electrical resistance (volume resistivity) of 10^5 - 10^{11} Ωcm.

The hard carbon film to be employed in the present invention can be formed, for example, by plasma sputtering, ion beam sputtering, ion beam evaporation, ion beam mixing, ion plating, cluster ion beam, ion implantation, arc discharge or laser evaporation. The solid carbon source to be used in these methods can be graphite or glass-like carbon of a high purity. When carbon-containing gas, for example a hydrocarbon such as methane, ethane, propane, ethylene, benzene or acetylene; a halogenated hydrocarbon such as methylene chloride, carbon tetrachloride, chloroform or trichloroethane; an alcohol such as methyl alcohol or ethyl alcohol; a ketone such as $(CH_3)_2CO$ or $(C_6H_5)_2CO$; or CO or CO_2 is used as a gaseous carbon source, it is used as a carbon ion beam after mass separation. Also a raw material gas for the assisting ion beam can be He, N_2, H_2, O_2, H_2O, Ar, Ne, Kr or Xe.

The thickness of the hard carbon film to be formed on the insulating protective film or the heat-generating resistor of the heater can be within a range from several nanometer to several tens of microns, preferably from several tens of nanometer to several microns, because a film thinner than several nanometers cannot provide sufficient lubricating or insulating ability, while a film thickner than several tens of micron can be easily peeled off from the substrate by the stress of the film. In case of direct film formation on the heat-generating resistor, a film of a high electrical resistance is required in order to secure sufficient insulating ability. In case of formation on the film, a thickness of several to several hundred nanometers is preferable, because a thickness smaller than several nanometers cannot provide sufficient lubricating ability while a thickness larger than several hundred nanometer may lead to the peeling-off of the carbon film from the plastic film or the curling of the plastic film due to the stress in the carbon film. If the plastic film still curls within the above-mentioned preferred thickness range of the carbon film, the hard carbon film may be formed on both sides of the plastic film.

The density of the hard carbon film is located, as explained before, between those of graphite and diamond, but practically needs to be equal to or higher than 2.0 g/cm^3. A film whose density is less than 2.0 g/cm^3 is of low hardness, low electrical resistance and low adhesion strength because of an increased content of the sp^2-bonded (graphite) component, and is not suitable as the lubricating protective film of the present invention.

The lubricating protective film of the present invention may be formed not only on the insulating protective film or the heat-generating resistor of the heater or on the plastic film, but also on a heater holder portion coming into contact with the plastic film, thereby further improving the sliding performance between the heater and the film.

The present invention is to improve the abrasion resistance and the sliding performance between the heater and the film by forming a hard carbon film as a lubricating protective layer by gaseous synthesis on the insulating protective film or the heat-generating resistor of the heater coming into contact with the plastic film, or on the plastic film, thereby extending service life of the heater.

In the following there will be explained specific embodiments of the present invention with reference to the attached drawings.

[Embodiment 1]

Fig. 3 is a magnified partial cross-sectional view of a thermal fixing device utilizing a heater embodying the present invention, wherein a heater 1 is supported by a heater support portion 9 across a heat-insulating heater holder 8. In the heater 1 there are provided a ceramic substrate 2; a heat-generating resistor 3 consisting of Ag/Pd; a glass-liked insulating protective layer 6; a hard carbon film 18 formed on said insulating protective layer 6; and a temperature detecting element 7. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 μm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow, in contact with the edges of the heater holder 8 while sliding on a face of the heater 1 in close contact with the face of the heater, by driving member (not shown) or by rotating force of the pressure roller 11. The heat generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus, the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion 15 together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 4A to 4E are schematic cross-sectional views of the heater of first embodiment, wherein shown are electrode terminals 4, 5 composed of Cu; a heater holder 8; an electrode tab 12; AuSi solder 13; and a wire 14.

The heater of the present embodiment was prepared at first by applying Ag/Pd paste by screen printing on an Al_2O_3 substrate 2, followed by burning in air. The heat-generating resistor 3, was trimmed to a desired resistance after the resistance was measured. Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under controlled oxygen partial pressure (Fig. 4A). Then the insulating protective film 6 was formed by applying low-softening lead silicate glass by screen printing, followed by burning in air (Fig. 4B). Subsequently a hard carbon film 18 was formed with a thickness of 500 nm by DC sputtering (Fig. 4C). Fig. 5 is a schematic view of a DC magnetron sputtering apparatus employed for the formation of the hard carbon film, wherein shown are a vacuum chamber 40; a substrate 41; a graphite target 42 of a purity of 99.99%; a gas introduction system 43; a DC power source 44; and an evacuating system 45. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, Ar was introduced from the gas introducing system to a pressure of 0.9 Pa. The substrate was maintained at the room temperature, and there were employed a discharge power of 50 W and a substrate-target distance of 40 mm. Prior to the film formation, pre-sputtering of target was conducted at 300 W for 20 minutes. When a film prepared under the same conditions was analyzed by HFS (hydrogen forward scattering spectrometry), a hydrogen concentration was 0 atom %. The film hardness, measured with a thin film hardness meter, was 2200 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.10 in a measurement conducted in air with a relative humidity of 45%, employing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 2.2 N and a sliding velocity of 0.04 m/s. The density, measured by RBS (Rutherform backscattering spectrometry) was 2.8 g/cm^3.

Then the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 4C). Subsequently the wire 14 was connected by pressure to the electrode tab 12, and the heater 1 was adhered to the heater holder 8 (Figs. 4D and 4E). At the preparation of the heater 1, the surfaces of the electrode terminals 4, 5 were Au flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 ° C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The thermal fixing device thus prepared was free from formation of abraded powder by the friction between the heater and the plastic film, thus being capable of maintaining stable sliding performance for a long period.

[Embodiment 2]

Fig. 6 is a magnified partial cross-sectional view of a thermal fixing device employing a heater embodying the present invention, wherein same components as those in Fig. 3 are represented by the same reference numerals and will not be explained further in the following. In Fig. 6 there are shown a groove G, and a hard carbon film 18.

A groove G of a dimension of 350 mm x 2 mm x 12 µm for forming the heat-generating resistor was mechanically formed on an Al_2O_3 substrate same as in the embodiment 1. In the groove, Ag/Pd paste was applied with a thickness of 11 µm by screen printing, followed by burning in air. The heat-generating resistor 3 was then trimmed to a desired resistance after the resistance was measured. Then the substrate was set in a sputtering apparatus (not shown), and a W (tungsten) layer 3a was formed with a thickness of 1 µm on the resistor layer in order to prevent mutually diffusion of Ag/Pd and C. Subsequently a hard carbon film of a thickness of 600 nm was formed with a dual ion beam sputtering apparatus shown in Fig. 7, in which shown are a vacuum chamber 20; a sputtering ion source 21; an assistant ion source 22; a graphite target 23; a substrate 24; a gas introducing system 25; and a vacuum system 26. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, and Ar was introduced at 20 sccm from the gas introducing system to the sputtering ion source and the assistant ion source to a pressure of 4 x 10^{-4} Torr. The graphite target was sputtered by the sputtering ion source with an Ar ion beam of an ion energy of 1 keV and an ion current density of 4 mA/cm^2, and simultaneously the substrate was irradiated by the assistant ion source with an Ar ion beam of an ion energy of 200 eV and an ion current density of 0.1 mA/cm^2. The film hardness, measured with the thin film hardness meter as in the embodiment 1, was 2500 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.08 in a measurement conducted in air of a relative humidity of 50%, employing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 1.0 N and a sliding velocity of 0.04 m/s. The density, measured by RBS (Rutherford backscattering spectrometry) was 2.6 g/cm^3, and the hydrogen concentration in the film, measured by HFS (hydrogen forward scattering spectrometry) was less than 1 atom %. Subsequently the heater was completed by connecting the electrode tabs and wires to the electrode terminals and adhering to the heater holder as in the embodiment 1.

The thermal fixation of the recording material was conducted in the same manner as in the embodiment 1 using a thermal fixing device equipped with thus obtained heater. As a result, stable fixing ability and durability were obtained as in the embodiment 1.

[Embodiment 3]

A hard carbon film was formed, as a lubricating protective film, on the insulating protective layer, in a manner similar to the embodiment 1. Fig. 8 is a schematic view of a DC magnetron sputtering apparatus employed in the embodiment 1, in which an assistant ion source was added. There are shown a vacuum chamber 30, an assistant ion beam source 31; an ionizing chamber 32; a gas introducing system 33; an ion beam extracting electrode 34; a substrate 35; a graphite target 36; a vacuum system 37; and a DC power source 38. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, Ar was introduced from the gas introducing system to the vacuum chamber and the assistant ion source at 100 sccm and 35 sccm, respectively, to a pressure of 6 x 10^{-2} Pa. Graphite was sputtered with a discharge power of 1 kW, and the substrate was simultaneously irradiated with an Ar ion beam of an ion energy of 300 eV and an ion current density of 0.2 mA/cm^2 from the assistant ion source, thereby forming a hard carbon film of a thickness of 500 nm.

The film hardness, measured with the thin film hardness meter as in the embodiment 1, was 2700 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.07, in a measurement conducted in air of relative humidity of 45%, employing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 1.0 N and a sliding velocity of 0.04 m/s. The density evaluated by RBS (Rutherford backscattering spectrometry) was 2.8 g/cm^3, and the hydrogen concentration in the film, measured by HFS (hydrogen forward scattering spectrometry) was less than 1 atom %. A heater was then completed by connecting the electrode tabs and wires to the electrode terminals and adhering to the heater holder.

The thermal fixation of the recording material was conducted in the same manner as in the embodiment 1 using a thermal fixing device equipped with thus obtained heater. As a result, stable fixing ability and durability were obtained as in the embodiment 1.

[Embodiment 4]

A hard carbon film of a thickness of 450 nm was formed on the insulating protective film of the heater under the same conditions as in the embodiment 3, except that the ion current density of the Ar ion beam from the assistant ion source was fixed at 0.2 mA/cm^2 and the ion energy was varied within a range of 0 - 500 eV. Samples 1 - 4 of thus prepared heaters were subjected to the evaluation of hydrogen concentration, film density, film hardness, electrical resistance (volume resistivity) and friction coefficient. The obtained results are summarized in Table 1. The hydrogen concentration was measured by HFS, density by RBS, hardness by the thin film hardness meter, electrical resistance by the four probe method and friction coefficient under the same conditions as in the embodiment 3.

Table 1

Sample	Ion energy (ev)	Hydrogen concentration (atom %)	Density (g/cm^3)	Hardness (kg/mm^2)	Electrical resistance (Ωcm)	Friction coefficient (μ)
1	10	< 1	2.1	2100	2 x 10^6	0.12
2	100	< 1	2.8	2700	1 x 10^8	0.07
3	200	< 1	2.0	1800	6 x 10^5	0.13
4	400	< 1	1.5	1300	1 x 10^0	0.15

A thermal fixing device equipped with thus obtained heater was used for the thermal fixation of the recording material as in the embodiment 1. The samples 1 to 3 indicate stable fixing performance and durability as in the embodiment 1, but the sample 4 indicates slight local film peeling off with the increase in the number of fixing operations.

[Embodiment 5]

A hard carbon film of a thickness of 50 nm was formed on both faces 10a of a polyimide film as shown in Fig. 9, under the same conditions as in the embodiment 1. Also a hard carbon film of a thickness of 200 nm was similarly formed on a portion 8a, coming into contact with the plastic film, of the heater holder.

A thermal fixing device employing thus obtained heater and film, was subjected to thermal fixation of the recording material as in the embodiment 1, and indicated stable fixing performance and durability as in the embodiment 1.

In the following there will be explained formation, according to the present invention, by gaseous synthesis of a hydrogenated amorphous carbon film (hereinafter written as a-C:H film) or a diamond-like carbon film (hereinafter written as DLC film), which is of a high electrical insulation, a high thermal conductivity, a high hardness and a low friction coefficient, on the heater or on the insulating protective layer thereof.

The a-C:H film or DLC film of the present invention is featured by a thermal conductivity of 200 - 600 W/m•K, an electrical resistance (volume resistivity) of 10^8 - 10^{11} Ωcm and a hardness of 2000 - 5000 kg/mm^2.

The a-C:H film or DLC film to be employed in the present invention may be formed, for example, by microwave plasma CVD, DC plasma CVD, high frequency plasma CVD, magnetic field microwave plasma CVD, ion beam sputtering, ion beam evaporation, or reactive plasma sputtering. Examples of the carbon-containing raw material gas to be employed in these method include hydrocarbons such as methane, ethane, propane, ethylene, benzene and acetylene; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform and trichloroethane; alcohols such as methyl alcohol and ethyl alcohol; ketones such as $(CH_3)_2CO$ and $(C_6H_5)_2CO$; and gasses such as CO and CO_2; and mixtures thereof with other gasses such as N_2, H_2, O_2, H_2O and Ar.

The a-C:H film or the DLC film contains hydrogen in several tens of atom % in the film. The properties of the film vary significantly with the hydrogen content. For example, an a-C:H film containing hydrogen in 50 atom % or higher is a transparent polymer-like film having a large optical band gap, a high electrical resistance but a low hardness and a high thermal conductivity. On the other hand, an a-C:H film containing hydrogen in 10 - 40 atom % is featured by a high thermal conductivity, a high insulating property and a high hardness, having a Vickers hardness as high as 2000 - 5000 kg/mm^2, an electrical resistance exceeding 10^8 Ωcm, a thermal conductivity exceeding 200 W/m•K and a friction coefficient less than 0.2. These properties are considered attributable to the sp^3 bonds, present in a proportion of 40 - 70% in the film. Consequently, for the protective film of the present invention, there should be employed the a-C:H film or DLC film with a hydrogen content of 10 40 atom %. Also it is difficult to clearly distinguish the a-C:H film from the DLC film. Both films are macroscopically amorphous, contain hydrogen in the film, consist of sp^2- and sp^3-bonded carbon and have similar physical properties as explained above. The DLC film in the present invention microscopically has the crystalline structure of diamond, for example a diffraction pattern specified as diamond in electron beam diffraction analysis.

On the aforementioned insulating ceramic substrate such as of Al_2O_3, AlN or SiC, the heat-generating resistor is formed for example by sputtering, and it is trimmed, if necessary, to a desired resistance after the resistance is measured. Then electrode terminals are formed similarly by the sputtering of Au, Ag or Cu. Then the insulating protective layer, consisting for example of low-softening lead silicate glass, is formed on the heat-generating resistor and the electrode terminals by screen printing, followed by burning. The heater is prepared by forming on the insulating protective layer, a protective layer consisting of an a-C:H film or a DLC film. The thickness of the a-C:H film or DLC film should be in a range capable of ensuring a mechanical strength and a friction coefficient for protecting the heater from the fixing pressure at the use of the heater, and can be in a range of several nanometers to several ten microns, preferably from several ten nanometers to several microns. The formation of the heat-generating resistor and the electrode terminals is not limited to a PVD method such as sputtering, vacuum evaporation or ion plating, but may also be achieved by a CVD method, plating or screen printing. Thereafter the heater is completed by mounting the electrode tabs to the electrode terminals for example by soldering, then connecting the wires to the electrode tabs and adhering the heater to the heater holder.

The present invention utilizes an a-C:H film or a DLC film formed by gaseous synthesis as the protective layer for the heater in order to improve the abrasion resistance and the sliding performance of the heater protective layer, thereby extending the service life of the heater.

[Embodiment 6]

Fig. 10 is a magnified partial cross-sectional view of a thermal fixing device utilizing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8.

The heater 1 is provided with a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; an insulating protective glass layer 6; a protective layer 18a consisting of a DLC film; and a temperature detecting element 7. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 µm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus, the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 11A to 11E are schematic cross-sectional views of the heater of the embodiment 6, wherein shown are electrode terminals 4, 5 composed of Cu; a heater holder 8; an electrode tab 12; AuSi solder 13; and a wire 14.

The heater of the present embodiment was prepared at first by applying Ag/Pd paste by screen printing on an Al_2O_3 substrate 2, followed by burning in air. The heat-generating resistor 3 was trimmed to a desired resistance after the resistance was measured. Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under a controlled oxygen partial pressure (Fig. 11A). Then the insulating protective film 6 was formed by applying low-softening lead silicate glass by screen printing, followed by burning in air (Fig. 11B). Subsequently a DLC film 6 was formed with a thickness of 200 nm by ECR plasma CVD (Fig. 11C). Fig. 12 is a schematic view of an ECR plasma CVD apparatus employed for the formation of the DLC film, wherein shown are a plasma chamber 50 of cavity resonator type; a gas introducing system 51; a microwave introducing window 52; a microwave guide tube 53; a magnet 54; a microwave oscillator 55; a substrate and a holder therefor 56; a vacuum chamber 57; and a vacuum system 58. The substrate after electrode formation was placed on the substrate holder, and the vacuum chamber was evacuated to 1×10^{-7} Torr. Then C_6H_6 at 31 sccm and H_2 at 14 sccm were introduced from the gas introducing system to a pressure of 3.3×10^{-4} Torr, and plasma was generated in the plasma chamber by introduction of microwave of 2.45 GHz at 1.2 kW. In this state an external magnetic field was formed by the magnet so as to provide ECR conditions of 1600 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator, and 700 Gauss at the position of the substrate. The DLC film was formed under the application of a voltage of -500 V to the substrate by an unrepresented DC power source. The hardness of the DLC film, measured with the thin film hardness meter, was 3000 kg/mm^2 in Vickers hardness. The friction properties were evaluated by the pin-on-disk method. The friction coefficient was 0.08 - 0.09 in a measurement conducted in air of relative humidity of 45%, utilizing a ball (5 mm in diameter) of bearing steel as the pin, with a load of 2.2N and a sliding velocity of 0.04 m/s.

Then the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 11C). Subsequently the wire 14 was maintained in contact with the electrode tab 12 (Fig. 11D), and the heater 1 was adhered to the heater holder 8 (Fig. 11E). At the preparation of the heater 1, the surfaces of the electrode terminals 4, 5 were Au flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 °C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The heater thus prepared was capable of efficiently supplying the recording material with heat generated by electric power, and realizing stable heater performance without thermal or electrical deterioration of the components of the heater. Particularly the improvement in the abrasion resistance and the sliding performance of the heater protective layer provided a service life more than twice of the conventional service life.

[Embodiment 7]

On a ceramic substrate, Au was sputtered with a thickness of 10 µm as the heat-generating resistor 3, as in the embodiment 6. After the resistance was measured, the resistor was trimmed to a desired resistance. Subsequently Cu was sputtered to form the electrode terminals 4, 5. Then the insulating protective glass layer 6 was formed, and an a-C:H film 18b was formed thereon. Fig. 13 is a schematic view of an ion beam evaporation apparatus, used in the formation of the a-C:H film, wherein shown are a vacuum chamber 60; an ion beam source 61; an ionizing chamber 62; a gas introducing system 63; an ion beam extracting electrode 64; a substrate 65; a substrate holder 66; and a vacuum system 67. The substrate after the electrode formation was placed on the substrate holder, and the vacuum chamber was evacuated to 1×10^{-7} Torr. Then CH_4 at 16 sccm and H_2 at 31 sccm were introduced from the gas introducing system, and the gas pressure was regulated at 3.2×10^{-4} Torr to generate plasma in the plasma chamber. The substrate was irradiated with an ion beam extracted with a voltage of 1 kV applied to the extracting electrode, whereby an a-C:H film of a thickness of 1 µm was formed in a predetermined position on the insulating protective glass layer. A similarly prepared a-C:H film showed, in HFS (hydrogen forward scattering spectrometry) a hydrogen content of 30 atom %. The film hardness and the friction coefficient, measured in the same manner as in the embodiment 6, were respectively 2500 kg/mm^2 and 0.07. Subsequently the heater was completed in the same manner as in the embodiment 6, by connection of the electrode tabs and the wires and adhesion to the heater holder.

In the thermal fixation of the recording material as in the embodiment 6, this heater could achieve stable fixation as in the embodiment 6.

In the foregoing embodiments, the a-C:H film or DLC film may be formed directly on the resistor 3, without the insulating protective layer 6.

In the following there will be explained an embodiment of the present invention in which a groove for forming the heat-generating resistor, is formed in advance on a ceramic substrate, then the heat-generating resistor is formed so as not to protrude from the surface of the ceramic substrate, and an a-C:H film or a DLC film of a high electrical insulation, a high thermal conductivity, a high hardness and a low friction coefficient is formed thereon by gaseous synthesis, as the insulating protective layer.

A groove for forming the heat-generating resistor is mechanically formed on the aforementioned ceramic substrate such as of Al_2O_3, AlN or SiC. More specifically, a peelable film or a resist material is formed on the entire surface of a ceramic substrate of a size of 350 mm x 350 mm, and a groove corresponding to the heat-generating resistor layer, for example of a dimension of 2 mm x 350 mm x 10 µm is formed in a predetermined position. The heat-generating resistor is formed in the groove by a PVD method such as sputtering, and is trimmed, if necessary to a desired resistance after the resistance is measured. The formation is so conducted that the heat-generating resistor layer does not protrude by more than 2 µm from the surface of the ceramic substrate. If it protrudes in excess of 2 µm, the a-C:H film or the DLC film becomes inevitably thicker for obtaining sufficient step coverage and causes peeling off. After the film or resist material formed on the ceramic substrate is removed, the electrode terminals are formed by sputtering of Au, Ag or Cu. Then an a-C:H film or a DLC film is formed on the heat-generating resistor to complete the heater substrate. The thickness of the a-C:H film or DLC film should be in a range capable of ensuring a mechanical strength and a friction coefficient for protecting the heater from the fixing pressure at the use of the heater, and can be in a range of several nanometers to several ten microns, preferably from several ten nanometers to several microns. The formation of the heat-generating resistor and the electrode terminals is not limited to a PVD method such as sputtering, vacuum evaporation or ion plating, but may also be achieved by a CVD method, plating or screen printing. Thereafter the heater of the present invention is completed by mounting the electrode tabs to the electrode terminals of each heater, cut into a desired size, for example soldering, then connecting by pressure the wires to the electrode tabs and adhering the heater to the heater holder. It is also possible to further improve the sliding performance of the heater and the film, by similarly forming an a-C:H film or a DLC film on a portion, coming into contact with the film, of the heater holder.

Thus the present invention utilizes an a-C:H film or a DLC film formed by gaseous synthesis as the protective layer for the heater, thereby improving the abrasion resistance and the sliding performance between the heater and the film and extending the service life of the heater.

[Embodiment 8]

Fig. 14 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. A heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 µm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the edges of the heater holder 8 and with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus, the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 15A to 15E are schematic cross-sectional views of the embodiment 8, wherein shown are a heater 1; a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; Cu electrode terminals 4, 5; a protective layer 18a consisting of a DLC film; a heater holder 8; an electrode tab 12; an AuSi solder 13; and a wire 14.

In this embodiment, a groove of a dimension of 350 mm x 2 mm x 12 µm, for forming the heat-generator resistor, was at first mechanically formed on an Al_2O_3 substrate, and in the groove, the heat-generating resistor 3 was formed by applying Ag/Pd paste by screen printing, followed by burning in air, and was trimmed to a desired resistance after the resistance was measured. In this state the surface of the heat-generating resistor layer coincides with the surface of the ceramic substrate. Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under controlled oxygen partial pressure (Fig. 15A). Then the DLC film 18a, serving as the insulating protective film, was formed (Fig. 15B). The DLC film was formed with the apparatus shown in Fig. 12.

Then the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 15C). Subsequently the wire 14 was maintained in contact with the electrode tab 12 (Fig. 15D), and the heater 1 was adhered to the heater holder 8 (Fig. 15E). At the preparation of the heater 1, the surfaces of the electrode terminals 4, 5 were Au flash-plated in order to improve wettability with the solder, thereby achieving stable reliability connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 °C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The heater thus prepared was capable of efficiently supplying the recording material with heat generated by electric power, and realizing stable heater performance without thermal or electrical deterioration of the components of the heater. Particularly it was free from the generation of abraded powder caused by the friction between the heater and the film, and could maintain stable sliding performance.

[Embodiment 9]

Fig. 16 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. The structures of the components are same as those in Fig. 14.

A groove for forming the heat-generating resistor was formed mechanically on a ceramic substrate, as in the embodiment 8. In the groove, the heat-generating resistor 3 was formed by sputtering Au with a thickness of 10 µm and a W (tungsten) layer 3a with a thickness of 50 nm. The groove for forming the heat-generating resistor was shaped same as in the embodiment 8, and the W layer was formed for preventing mutual diffusion of Au and C. The heat-generating resistor was trimmed to a desired resistance, after the resistance measurement. Subsequently the electrode terminal 4 was formed by Cu sputtering, and then an a-C:H film 18b, serving as the insulating protective film, was formed.

The a-C:H film 18b was formed with the apparatus shown in Fig. 13. The substrate after the electrode formation was placed on the substrate holder, and the vacuum chamber was evacuated to 1×10^{-7} Torr. Then CH_4 at 12 sccm and H_2 at 25 sccm were introduced from the gas introducing system, and the gas pressure was regulated to 2.8×10^{-4} Torr to generate plasma in the plasma chamber. The substrate was irradiated with an ion beam, extracted by a voltage of 0.75 kV applied to the extracting electrode, thereby forming an a-C:H film of a thickness of 400 nm in a predetermined position on the heat-generating resistor. A similarly prepared a-C:H film indicated, in HFS (hydrogen forward scattering spectrometry), a hydrogen content of 27 atom %. Also the film hardness and the friction coefficient, measured in the same manner as in the embodiment 6, were respectively 2500 kg/mm^2 and 0.07. The heater was subsequently completed by connecting the electrode tabs and the wires to the electrode terminals, and adhering the heater to the heater holder.

In thermal fixation of the recording material as in the embodiment 8, the heater thus prepared indicated stable fixing ability and durability as in the embodiment 6.

[Embodiment 10]

Fig. 17 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. The structures of the components are same as those shown in Fig. 14.

The heat-generating resistor layer was formed with a thickness of about 10 μm, in a similar manner as in the embodiment 8. The depth of the groove for forming the heat-generating resistor was made as 12 μm. After the formation of the electrode terminal 4 as in the embodiment 8, low-softening lead silicate glass was coated by screen printing on the groove containing the heat-generating resistor and was burnt in air to form an insulating protective layer 6' of a thickness of about 2 μm. Thereafter a DLC film 18a of a thickness of 200 nm was formed on the entire surface of the heater, with same method and conditions as in the embodiment 8. Subsequently, the electrode tabs and the wires were connected to the electrode terminals as in the embodiment 8, and the substrate was adhered to the heater holder, bearing a DLC film of a thickness of 60 nm in the contacting portion with the film as in the embodiment 9, to complete the heater.

In the thermal fixation of the recording material as in the embodiment 8, thus obtained heater indicates stable fixing ability and durability as in the embodiment 8.

In the following there will be explained an embodiment of the present invention, in which a hydrogenated amorphous carbon film (a-C:H film) or a DLC film of a high hardness and a low friction coefficient is formed, by gaseous synthesis, on the surface of the film in sliding contact with the heater.

An a-C:H film or a DLC film is formed by the above-explained method on a face, coming into contact with the heater, of a heat-resistant film, such as of polyimide, formed as an endless belt or an elongated web. The thickness of the a-C:H film or DLC film is preferably within a range from several nanometers to several hundred nanometers, because a thickness less than several nanometers cannot provide sufficient lubricating performance, while a thickness larger than several hundred nanometers results in peeling off the the film from the plastic film or the curling thereof, due to the stress in the film. The plastic film may also be curled even when the film is formed within the above-mentioned preferred thickness range. In such case the a-C:H film or the DLC film may be formed on both sides of the plastic film. The sliding performance between the heater and the plastic film may be further improved by formation of the a-C:H film or the DLC film also on the insulating protective layer of the heater or on the heater holder, coming into contact with the plastic film.

Thus the present invention is to form, as a lubricating protective layer, an a-C:H film or a DLC film by gaseous synthesis on the surface of the plastic film in sliding contact with the heater, thereby improving the abrasion resistance and the sliding performance between the heater and the plastic film, and extending the service life of the heater.

[Embodiment 11]

Fig. 18 is a magnified partial cross-sectional view of a thermal fixing device, employing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 μm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves a predetermined speed in a direction indicated by an arrow in contact with the edges of the heater holder 8 and with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 19A to 19E are schematic cross-sectional views of the heater of the embodiment 11, wherein shown are a heater 1; an insulating substrate 2 for example of ceramics; an Ag/Pd heat-generating resistor 3; a Cu electrode terminal 4; an insulating protective glass layer 6; a heater holder 8; an electrode tab 12;

an AuSi solder 13; and a wire 14.

In the heater of the present embodiment, Ag/Pd paste was at first applied by screen printing on an Al_2O_3 substrate and was burnt in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance after the resistance was measured. Then Cu paste was applied by screen printing, and the electrode terminal 4 was formed by burning under a controlled oxygen partial pressure. Subsequently low-softening lead silicate glass was applied by screen printing and burnt in air to form the insulating protective film.

Then the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13. Subsequently the wire 14 was maintained in contact with the electrode tab 12, and the heater was adhered to the heater holder 8. At the preparation of the heater 1, the surface of the electrode terminal 4 was Au flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 ° C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

Fig. 20 is a schematic view of an ECR plasma CVD apparatus, employed in the formation of the DLC film 118 on the polyimide film 10, wherein shown are a plasma chamber 70 of cavity resonator type; a gas introducing system 71; a microwave introducing window 72; a microwave guide tube 73; a magnet 74; a microwave oscillator 75; a mechanism 76 for feeding and taking up a film under a constant tension and a constant speed; a vacuum chamber 77; a vacuum system 78; and a cover 79 for limiting the film forming area. After the vacuum chamber was evacuated to 1×10^{-7} Torr, C_6H_6 at 40 sccm and H_2 at 25 sccm were introduced from the gas introducing system to a pressure of 4.0×10^{-4} Torr, and plasma was generated in the plasma chamber by introducing microwave of 2.45 GHz at 1.0 kW. In this state, an external magnetic field was provided by the magnet to realize the ECR conditions of 1200 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator and 700 Gauss at the position of the substrate. The DLC film 118, shown in Fig. 18, was formed with a thickness of 70 nm, under the application of a voltage of 500 V to the substrate by DC power source (not shown). The hardness of the DLC film, measured with the thin film hardness meter, was 2500 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.10 in a measurement conducted in air with relative humidity of 50%, utilizing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 2.2N and a sliding velocity of 0.04 m/s. In the above-mentioned operation, the moving speed of the film was 1 m/min., and the film forming speed was 0.5 nm/sec.

Thus prepared thermal fixing device was free from generation of the abraded powder resulting from the friction between the heater and the plastic film, and was capable of maintaining stable sliding performance over a prolonged period.

[Embodiment 12]

An a-C:H film was formed, as in the embodiment 11, as a lubricating protective film on the plastic film. Fig. 21 is a schematic view of an ion beam deposition (IBD) apparatus employed in the formation of the a-C:H film, wherein shown are a vacuum chamber 80; ion beam sources 81; ionizing chambers 82; gas introducing systems 83; ion beam extracting electrodes 84; a substrate 85; a mechanism 86 for feeding and taking up a film under a constant tension and a constant speed; a vacuum system 87; and covers 88 for limiting the film forming area. There are provided a pair of the ion sources 81 in mutually opposed positions across the plastic film. After the vacuum chamber was evacuated to 1×10^{-7} Torr, CH_4 at 12 sccm and H_2 at 25 sccm were introduced from the gas introducing system to a pressure of 2.5×10^{-4} Torr to generate plasma in the plasma chamber. The plastic film was irradiated on both sides thereof with ion beams extracted with a voltage of 0.8 kW applied to the extracting electrodes, whereby a-C:H films of a thickness of 60 nm were formed on both faces of the plastic film. In HFS analysis, the a-C:H film showed a hydrogen content of 27 atom %. Also the film hardness and the friction coefficient, measured as in the embodiment 6, were respectively 3000 kg/mm^2 and 0.12.

A thermal fixing device equipped with the plastic film prepared as explained above, indicated stable fixing performance and durability as in the embodiment 11, in thermal fixation of the recording material as in the embodiment 6.

[Embodiment 13]

Fig. 22 is a magnified partial cross-sectional view of a thermal fixing device employing the heater embodying the present invention, wherein shown is a DLC film 119. Other components are same as those in Fig. 18.

A DLC film was formed with a thickness of 65 nm on a polyimide film, in a similar manner as in the embodiment 11. Also a DLC film of a thickness of 200 nm was formed on the insulating protective layer 6 provided on the heat-generating resistor layer of the heater in the embodiment 11 and on a portion, coming into contact with the plastic film, of the heater holder.

A thermal fixing device utilizing thus prepared plastic film and heater, provided stable fixing performance and durability as in the embodiment 11, in the thermal fixation of the recording material in the same manner as in the embodiment 11.

The a-C:H film or the DLC film may also be provided only on the heater or the heater holder.

In the following there will be explained an embodiment of the present invention in which a hydrogenated amorphous carbon film (a-C:H film) or a diamond-like carbon (DLC) film of a high electrical insulation, a high thermal conductivity, a high hardness and a low friction coefficient, formed by gaseous synthesis, is utilized as a protective layer of the heater.

The a-C:H film or DLC film of the present invention is featured by a thermal conductivity of 200 - 600 W/m•K, an electrical resistance (volume resistivity) of 10^8 - 10^{11} Ωcm and a hardness of 2000 - 5000 kg/mm^2.

The a-C:H film or DLC film to be employed in the present invention may be formed, for example, by microwave plasma CVD, DC plasma CVD, RF plasma CVD, magnetic field microwave plasma CVD, ion beam sputtering, ion beam evaporation, or reactive plasma sputtering. Examples of the carbon-containing raw material gas to be employed in these methods include hydrocarbons such as methane, ethane, propane, ethylene, benzene and acetylene; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform and trichloroethane; alcohols such as methyl alcohol and ethyl alcohol; ketones such as $(CH_3)_2CO$ and $(C_6H_5)_2CO$; and gasses such as CO and CO_2; and mixtures thereof with other gasses such as N_2, H_2, O_2, H_2O and Ar.

The a-C:H film or the DLC film contains hydrogen in several ten atom % in the film, and the properties of the film vary significantly with the hydrogen content. For example an a-C:H film containing hydrogen in 50 atom % or higher is a transparent polymer-like film having a large optical band gap, a high electrical resistance but a low hardness and a high thermal conductivity. On the other hand, an a-C:H film containing hydrogen in 15 - 35 atom % is featured by a high thermal conductivity, a high insulating property and a high hardness, having a Vickers hardness as high as 2000 - 5000 kg/mm^2, an electrical resistance exceeding 10^8 Ωcm, a thermal conductivity exceeding 200 W/m•K and a friction coefficient less than 0.2. These properties are considered attributable to the sp^3 bonds, present in a proportion of 40 - 70% in the film. Consequently, for the protective film of the present invention, there should be employed the a-C:H film or DLC film with a hydrogen content of 15 - 35 atom %.

On the aforementioned insulating ceramic substrate such as of Al_2O_3, AlN or SiC, the heat-generating resistor is formed by a PVD method such as sputtering, and it is trimmed, if necessary, to a desired resistance after the resistance measurement. Then the electrode terminals are formed similarly by the sputtering of Au, Ag or Cu. The heater substrate is prepared by then forming the protective layer consisting of an a-C:H film or a DLC film. The thickness of the a-C:H film or DLC film should be in a range capable of ensuring a sufficient insulation at the use of the heater and a mechanical strength for protecting the heater from the fixing pressure, and can be within a range from several microns to several hundred microns, preferably from several microns to several ten microns. The formation of the heat-generating resistor and the electrode terminals is not limited to a PVD method such as sputtering, vacuum evaporation or ion plating, but may also be achieved by a CVD method, plating or screen printing. Thereafter the heater is completed by mounting the electrode tabs for example by soldering, then connecting the wires to the electrode tabs and adhering the heater substrate to the heater holder.

Thus the present invention utilizes an a-C:H film or a DLC film, formed by gaseous synthesis, for the protective layer of the heater, thereby improving the thermal efficiency of the heater, reducing the power consumption thereof and realizing a heater excellent in the abrasion resistance and the sliding performance.

[Embodiment 14]

Fig. 23 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. A heater 1 is supported by a heater supporting member 9, across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 μm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 24A to 24E are schematic cross-sectional views of the embodiment 14, wherein shown are a heater 1; a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; Cu electrode terminals 4, 5; a protective layer 6 consisting of a DLC film; a heater holder 8; an electrode tab 12; an AuSi solder 13; and a wire 14.

In this embodiment, Ag/Pd paste was at first applied by screen printing in a predetermined position on an Al_2O_3 substrate and sintered in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. Then Cu paste was applied by screen printing, and the electrode terminal 4 was formed by sintering under a controlled oxygen partial pressure (Fig. 24A). Then there was formed a DLC film 6 as the insulating protective film (Fig. 24B). Fig. 25 is a schematic view of an ECR plasma CVD apparatus employed in the formation of the DLC film, wherein shown are a plasma chamber 90 of cavity resonator type; a gas introducing system 91; a microwave introducing window 92; a microwave guide tube 93; a magnet 94; a microwave oscillator 95; a substrate holder 96 with a substrate; a vacuum chamber 97; and a vacuum system 98. The substrate after the electrode formation was placed on the substrate holder, and the vacuum chamber was evacuated to 1×10^{-7} Torr. Then C_6H_6 at 30 sccm and H_2 at 15 sccm were introduced from the gas introducing system to a pressure of 3.4×10^{-4} Torr, and plasma was generated in the plasma chamber by introduction of microwave of 2.45 GHz at 1 kW. In this state an external magnetic field was generated by the magnet to establish ECR conditions of 1500 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator and 700 Gauss at the position of the substrate. Furthermore a voltage of -500 V was applied to the substrate by DC power source (not shown), and the DLC film was formed with a thickness of 10 μm. The thermal conductivity of the DLC film, measured with a photo AC thermal constant measuring apparatus, was 400 W/m•K. Also the electrical resistance was 2×10^{11} Ωcm.

Subsequently the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 24C). Then the wire 14 was maintained in contact with the electrode tab 12 (Fig. 24D), and the heater substrate was adhered to the heater holder 8 (Fig. 24E). At the preparation of the heater 1, the surface of the electrode terminal 4 was Au-flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250°C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The heater thus prepared is capable of efficiently supplying the recording material with the heat generated by electric power, and can realize stable performance without thermal deterioration of the heater components.

[Embodiment 15]

In a similar manner as in the embodiment 14, the heat-generating resistor 3 was formed on a ceramic substrate by successive sputterings of Ti of 20 nm and Au of 10 μm, and was then trimmed to a desired resistance according to the resistance measurement. Then the electrode terminals 4, 5 were prepared by Cu sputtering. Subsequently an a-C:H film 6 was formed as the insulating protective layer. Fig. 26 is a schematic view of an ion beam deposition (IBD) apparatus employed in the formation of the a-C:H film, wherein shown are a vacuum chamber 200; an ion beam source 201; an ionizing chamber 202; a gas introducing system 203; an ion beam extracting electrode 204; a substrate 205; a substrate holder 206; and a vacuum system 207. The substrate after the electrode formation was placed on the substrate holder, and the vacuum chamber was evacuated to 1×10^{-7} Torr. Then CH_4 at 15 sccm and H_2 at 30 sccm were introduced from the gas introducing system to a pressure of 3.1 x 10^{-4} Torr to generate plasma in the plasma chamber. The substrate was irradiated with an ion beam extracted by a voltage of 0.7 kV applied to the extracting electrode, whereby an a-C:H film of a thickness of 15 µm was formed in a predetermined position on the heat-generating resistor. A similarly prepared film showed, in HFS analysis, a hydrogen content of 25 atom %. Also the thermal conductivity and the electrical resistance, measured as in the embodiment 14, were respectively 250 W/m•K and 2 x 10^{11} Ωcm. The heater was subsequently completed by the connection of the electrode tabs and the wires to the electrode terminals and the adhesion to the heater holder as in the embodiment 14.

In the thermal fixation of the recording material as in the 14th embodiment, thus prepared heater indicated stable fixing ability as in the embodiment 14.

In the following there will be explained an embodiment of the present invention, in which an a-C:H film or a DLC film, containing a metallic element, is formed by gaseous synthesis on the insulating protective film or the heat-generating resistor of the heater.

The a-C:H film or DLC of the present invention is featured by a thermal conductivity of 200 - 600 W/m•K, an electrical resistance (volume resistivity) of 10^8 - 10^{11} Ωcm and a hardness of 2000 - 5000 kg/mm^2.

The a-C:H film or DLC film to be employed in the present invention may be formed, for example, by microwave plasma CVD, DC plasma CVD, high frequency plasma CVD, magnetic field microwave plasma CVD, ion beam sputtering, ion beam evaporation or reactive plasma sputtering. Examples of the carbon-containing raw material gas to be employed in these methods include hydrocarbons such as methane, ethane, propane, ethylene, benzene and acetylene; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform and trichloroethane; alcohols such as methyl alcohol and ethyl alcohol; ketones such as $(CH_3)_2CO$ and $(C_6H_5)_2CO$; and gasses such as CO and CO_2; and mixtures thereof with other gasses such as N_2, H_2, O_2, H_2O and Ar. Also there may be employed a solid carbon source such as graphite or glass-like carbon of a high purity. An element, such as Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si to be added to the a-C:H film or the DLC film can be supplied from a solid metal, a semiconductor, or from organometallic gas, silane gas, higher silane gas, diborane gas or higher borane gas containing such metal.

The a-C:H film or the DLC film contains hydrogen in veral ten atom % in the film, and the properties of the film vary significantly with the hydrogen content. For example an a-C:H film containing hydrogen in 50 atom % or higher is a transparent polymer-like film having a large optical band gap, a high electrical resistance but a low hardness and a high thermal conductivity. On the other hand, an a-C:H film containing hydrogen in 10 - 45 atom % is featured by a high thermal conductivity, a high insulating property and a high hardness, having a Vickers hardness as high as 2000 - 5000 kg/mm^2, an electrical resistance exceeding 10^8 Ωcm, a thermal conductivity exceeding 200 W/m•K and a friction coefficient less than 0.2. These properties are considered attributable to the sp^3 bonds, present in a proportion of 40 - 70 % in the film. Consequently, for the protective film of the present invention, there should be employed the a-C:H film or DLC film with a hydrogen content of 10 - 45 atom %. Also it is difficult to clearly distinguish the a-C:H film from the DLC film. Both films are macroscopically amorphous, contain hydrogen in the film, consist of sp^2- and sp^3-bonded carbon and have similar physical properties as explained above. The DLC film in the present invention microscopically has the crystalline structure of diamond, for example a diffraction pattern specified as diamond in the electron beam diffraction analysis.

The friction coefficient of the a-C:H film or the DLC film is as low as 0.02 in vacuum or in dry nitrogen atmosphere, but tends to become larger as the relative humidity increases. In the ordinary state the friction coefficient is less than 0.2, but it becomes worse under a higher relative humidity or with an increase in the distance of sliding movement. On the other hand, the friction coefficient of the a-C:H film or the DLC film containing Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si according to the present invention remains constant, regardless of the humidity or the distance of sliding movement. The concentration of such element in the film should not exceed 30 atom %, because a content exceeding 30 atom % not only increases the friction coefficient in comparison with the case without the addition of such element but also deteriorates the film hardness. Particularly preferred is an element concentration of 10 - 20 atom % which minimizes the friction coefficient. Fig. 27B shows the relationship between the element concentration and the friction coefficient. Also the addition of the above-mentioned element can increase the adhesion strength to the substrate.

The a-C:H film or the DLC film, containing metal, is formed by the aforementioned methods on the insulating protective film or the heat-generating resistor of the heater. The thickness of such a-C:H film or DLC film should be in a range from several nanometers to several ten microns, preferably several ten nanometers to several microns, because a thickness smaller than several nanometers cannot provide sufficient lubricating or insulting ability, while a thickness exceeding several ten microns may result in peeling of the film from the substrate due to the film stress. In case of direct film formation on the heat-generating resistor, the element to be added and the amount thereof should be so selected as to ensure sufficient insulation (to obtain a desired electrical resistance).

In the following there will be explained the method of adding a metal element to the a-C:H film or DLC film, for example, in case of the DC magnetron sputtering. Reactive sputtering is conducted utilizing a target of a metal element to be added (for example Ta), and mixing carbon-containing gas (for example C_2H_2) and sputtering inert gas (rare gas such as Ar or nitrogen) in a suitable ratio. In this operation DC plasma is generated by introducing a power of several hundred W to several kW from a DC power source and applying a suitable bias voltage to the substrate. The concentration of the added element is controlled by the flow rate ratio of the reaction gas and the sputtering gas. The concentration can be made higher by increasing the flow rate of the sputtering gas.

The sliding performance between the heater and the palstic film can be further improved by forming the lubricating protective film of the present invention not only on the insulating protective film or the heat-generating resistor of the heater but also on the plastic film coming into contact with the heater and/or on the heater holder.

Thus the present invention is to form an a-C:H film or a DLC film, containing a metal element, by gaseous synthesis as the lubricating protective layer on the insulating protective film or the heat-generating resistor of the heater, which is in sliding contact with the plastic film, thereby improving the abrasion resistance and the sliding performance between the heater and the plastic film and extending the service life of the heater.

[Embodiment 16]

Fig. 27A is a magnified partial cross-sectional view of a thermal fixing device, employing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 µm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing the film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the edges of the heater holder 8 and with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined a temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 28A to 28E are schematic cross-sectional views of the embodiment 16, wherein shown are a heater 1; a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; Cu electrode terminals 4, 5; an insulating protective glass layer 6; a DLC film 120 containing metal element; a heater holder 8; an electrode tab 12; AuSi solder 13; and a wire 14.

In this embodiment, Ag/Pd paste was at first applied by screen printing on an Al_2O_3 substrate and burnt in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under a controlled oxygen partial pressure (Fig. 28A). Then the insulating protective film was prepared by application of low-softening lead silicate glass by screen printing, followed by burning in air. Subsequently a DLC film of a thickness of 400 nm, containing Ta was formed by ECR plasma CVD (Fig. 28C). Fig. 29 is a schematic view of an ECR plasma CVD apparatus employed in the formation of the DLC film, wherein shown are a plasma chamber 210 of cavity resonator type; a glass introducing system 211; a microwave introducing window 212; a microwave guide tube 213; a magnet 214; a microwave oscillator 215; a substrate 216; a vacuum chamber 217; a vacuum system 218; and a Ta target 219 of a purity of 99.99 %. After the vacuum chamber was evacuated to 1×10^{-7} Torr, C_2H_2 at 40 sccm, H_2 at 20 sccm and Ar at 120 sccm were introduced from the gas introducing system to a pressure of 2.0×10^{-3} Torr, and plasma was generated in the plasma chamber by introducing microwave of 2.45 GHz at 1.0 kW. In this state an external magnetic field was formed with the magnet to establish the ECR conditions of 1200 Gauss at the introducing window, 875 Gauss at the Ta target 219 at the exit of the cavity resonator, and 600 Gauss at the position of the substrate. Also a voltage of -500 V was applied to the substrate by an unrepresented DC power source, and the DLC film 120 shown in Fig. 28C was formed. A similarly prepared film showed, in the HFS (hydrogen forward scattering) analysis, a hydrogen content of 20 atom %. Also the

Ta concentration in the film, analyzed by EPMA, was 10 atom %. The hardness of the film, measured by the thin film hardness meter, was 2000 kg/mm^2 in Vickers hardness. The friction properties of the film was evaluated by pin-on-disk method. The friction coefficient was 0.06 in a measurement conducted in air of relative humidity of 60 %, utilizing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 2.2N and a sliding velocity of 0.04 m/s.

Subsequently the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 28D). Then the wire 14 was maintained in contact with the electrode tab 12 and the heater substrate was adhered to the heater holder 8 (Fig. 28E). At the preparation of the heater 1, the surface of the electrode terminals 4, 5 were Au-flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 °C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The thermal fixing device thus prepared was free from generation of abraded power resulting from the friction between the heater and the plastic film, and could maintain stable sliding performance over a long period.

[Embodiment 17]

A groove of a dimension of 350 mm x 2 mm x 12 µm, for forming the heat-generating resistor layer, was mechanically formed on an Al_2O_3 substrate same as in the embodiment 16. Ag/Pd paste was applied in said groove by screen printing with a thickness of 11 µm and was sintered in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. The substrate was then placed in sputtering apparatus (not shown) and a W (tungusten) layer 3a of a thickness of 1 µm on the resistor layer in order to prevent mutual diffusion of Ag/Pd and C. Then, in the ECR plasma CVD apparatus, as shown in Fig. 29, employed in the embodiment 16 but without the target 219, there was formed an a-C:H film containing Si. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, C_6H_6 at 25 sccm, H_2 at 15 sccm and SiH_4 at 10 sccm were introduced from the gas introducing system to a pressure of 3.6 x 10^{-4} Torr, and plasma was generated in the plasma chamber by introduction of microwave of 2.45 GHz at 1.2 kW. In this state an external magnetic field was formed with the magnet to establish the ECR conditions of 1500 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator and 650 Gauss at the position of the substrate. Also a voltage of -700 V was applied to extracting electrode (not shown) provided at the exit of the cavity resonator, and there was formed an a-$C_{1-x}Si_x$:H film with a thickness of 400 nm. The range of x was $0 \leqq x \leqq 0.4$ as an x value exceeding 0.4 increases the SiC component in the film, thus increasing the friction coefficient in excess of 0.2. Fig. 30 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. The hardness of the film, measured with the thin film hardness meter, was 2500 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.05 in a measurement conducted in air of relative humidity of 50 %, utilizing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 2.2N and a sliding velocity of 0.04 m/s. The hydrogen content in the film, measured by HFS (hydrogen forward scattering) analysis, was 25 atom %.

A thermal fixing device equipped with thus prepared heater, provided stable fixing performance and durability as in the embodiment 16, in the thermal fixation of the recording material conducted in the same manner as in the embodiment 16.

[Embodiment 18]

An a-C:H film was formed as the lubricating protective layer on the insulating protective layer, in a similar manner as in the embodiment 17. Fig. 13 is a schematic view of an ion beam deposition (IBD) apparatus employed in the formation of the a-C:H film, wherein shown are a vacuum chamber 220; an ion beam source 221; an ionizing chamber 222; a gas introducing system 223; an ion beam extracting electrode 224; a substrate 225; an electron gun 226; and a vacuum system 227. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, CH_4 at 15 sccm and H_2 at 35 sccm were introduced from the gas introducing system to a pressure of 3.8 x 10^{-4} Torr, thus generating plasma in the plasma chamber. The substrate was irradiated with an ion beam, extracted by a voltage of 0.8 kV applied to the extracting electrode. At the same time the metal to be added was evaporated by the electron gun 226. The added metal was Ta, W, Mo, Nb, Cr, Fe, B or Si, and the total film thickness was made 450 nm. Samples 1 - 9 of thus prepared heaters, and a sample 10 utilizing a non-doped a-C:H film, were subjected to the measurements of the hydrogen content, metal content, film hardness and friction coefficient. The obtained results are summarized in Table 2. The hydrogen content was measured by HFS analysis, metal concentration by EPMA, film hardness by the thin film hardness meter and friction coefficient under the same conditions as in the embodiment 17.

Table 2

Sample	Added element	Hydrogen concentration (atom %)	Added element concentration (atom %)	Hardness (kg/mm^2)	Friction coefficient (μ)
1	Ta	25	16	2200	0.07
2	W	24	20	2000	0.08
3	Mo	24	29	1800	0.09
4	Nb	26	10	2300	0.10
5	Ti	25	18	2000	0.09
6	Cr	25	12	2100	0.08
7	Fe	27	8	2000	0.12
8	B	23	15	2200	0.08
9	Si	22	23	2300	0.07
10	-	25	-	2700	0.27

Thermal fixing devices equipped with thus prepared heaters, were used in the thermal fixation of the recording material as in the embodiment 16. The samples 1 to 9 indicate stable fixing performance and durability as in the embodiment 16, but the sample 10 indicates some generation of film abraded powder with the increase in the number of fixing operations.

[Embodiment 19]

A heater provided with the insulating protective film as in the embodiment 16, was placed in a DC magnetron sputtering apparatus shown in Fig. 32, in which shown are a vacuum chamber 230; a substrate 231; a target 232; a gas introducing system 233; a DC power source 234; and a vacuum system 235. The target was composed of Ta of a purity of 99.9 %. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, C_2H_2 and Ar were introduced from the gas introducing system, and a Ta-containing a-C:H film was formed with a thickness of 400 nm, with the C_2H_2/Ar flow rate ratio varied within a range of 0 - 60 %. In this operation there were employed a gas pressure of 0.4 Pa, a substrate temperature equal to the room temperature, a discharge power of 2 kW, and a substrate-target distance 70 mm. Samples 11 - 15 of thus prepared heaters were subjected to the measurement of hydrogen content, content of the added element, film hardness and friction coefficient, and the obtained results are summarized in Table 3. The hydrogen content was measured by the HFS analysis, added element content by EPMA, film hardness by the thin film hardness meter, and friction coefficient under the same conditions as in the embodiment 17.

Table 3

Sample	C_2H_2/Ar (%)	Hydrogen concentration (atom %)	Added element concentration (atom %)	Hardness (kg/mm^2)	Friction coefficient (μ)
11	0.05	26	6	2500	0.08
12	0.34	24	15	2300	0.07
13	0.10	15	29	2000	0.13
14	0.05	6	32	1800	0.18
15	Ar = 0	27	0	2800	0.21

Thermal fixing devices equipped with thus prepared heaters were used in the thermal fixation of the recording material as in the embodiment 16. Samples 11 to 13 indicate stable fixing performance and durability as in the embodiment 16, but samples 14 and 15 indicate some generation of the abraded powder from the plastic film, with an increase in the number of fixing operations.

In the following there will be explained an embodiment of the present invention, in which an a-C:H film or a DLC film, containing fluorine, by gaseous synthesis on the insulating protective film or the heat-generating resistor of the heater, or on the plastic film.

The forming method and the raw materials for the a-C:H film or DLC film employed in the presnet embodiment are same as those in the foregoing embodiments, but the addition of an element such as Ta or W by an organometallic gas may be dispensed with if necessary.

The friction coefficient of the a-C:H film or DLC film is as low as 0.02 in vacuum or in dry nitrogen atmosphere, but tends to increase as the relative humidity becomes higher. The friction coefficient is less than 0.2 in the normal state, but becomes higher as the relative humidity becomes higher or the distance of sliding movement becomes longer.

On the other hand, the a-C:H film or DLC film, containing fluorine according to the present invention shows a constant friction coefficient, regardless of the humidity or the length of sliding movement. The concentration of fluorine in the film should not exceed 30 atom %, since a content exceeding 30 atom % deteriorates the properties inherent to the a-C:H or DLC film. There will particularly result a loss in the film hardness, and the adhesion to the substrate will also be deteriorated.

The reason for the constant friction coefficient of the fluorine-containing a-C:H or DLC film regardless of the ambient conditions (particularly humidity) or the state of use (length of sliding movement) is still unclear, but it is presumed that the dangling bonds present in the a-C:H or DLC film are reduced by termination with fluorine atoms, whereby the film is stabilized to the ambient conditions or the state of use.

The fluorine-containing a-C:H or DLC film is formed by the aforementioned methods, on the insulating protective film or the heat-generating resistor of the heater, or on the plastic film. The thickness of such a-C:H or DLC film should be, in case formation on the insulating protective film or on the heat-generating resistor, within a range from several nanometers to several ten microns, preferably from several ten nanometers to several microns, since a thickness less than several nanometers cannot provide sufficient lubricating or insulating ability, while a thickness larger than several ten microns tends to result in the film peeling from the substrate because of the stress in the film. In case of direct formation on the heat-generating resistor, it is necessary to ensure sufficient insulation (to achieve a desired electrical resistance). On the other hand, in case of film formation on the plastic film, there is preferred a range from several to several hundred nanometers, since a thickness less than several nanometers cannot provide sufficient lubricating ability, while a thickness larger than several hundred nanometers results in the film peeling from the plastic film or curling of the plastic film because of the stress in the film. If the plastic film curling takes place even within the above-mentioned preferred thickness range, the film may be formed on both faces of the plastic film.

Fluorine can be added to the a-C:H or DLC film, in the aforementioned film forming methods, for example by employing a fluorine-containing gas such as CF_4 or $C_6H_{6-m}F_m$ (m = 0 to 6) as the raw material gas, or by exposing the a-C:H or DLC film to plasma of fluorine-containing gas such as CF_4 thereby fluorinating the surface of such film, or implantation of fluorine ions.

The sliding performance between the heater and the palstic film may be further improved by forming the lubricating protective film of the present invention not only on the heater or the heater holder coming into contact with the plastic film but also on said plastic film in sliding contact with the heater.

Thus the present invention forms, as the lubricating protective layer, an a-C:H film or a DLC film, containing fluorine, by gaseous synthesis on the insulating protective film or the heat-generating resistor, coming into sliding contact with the plastic film, of the heater, thereby improving the abrasion resistance and the sliding performance between the heater and the plastic film and extending the service life of the heater.

[Embodiment 20]

Fig. 33 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 μm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing said film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow, in contact with the edges of the heater holder 8 and with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and, a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 34A to 34E are schematic cross-sectional views of the heater of the embodiment 20, wherein shown are a heater 1; a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; a Cu electrode terminal 4; an insulating protective glass layer 6; a DLC film 121 containing fluorine; a heater holder 8; an electrode tab 12; an AuSi solder 13; and a wire 14.

In the heater of this embodiment, Ag/Pd paste was at first applied by screen printing on an Al_2O_3 substrate and burnt in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement.

Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under a controlled oxygen partial pressure. Then the insulating protective film was prepared by application of low-softening lead silicate glass by screen printing, followed by sintering in air. Subsequently a DLC film 121 containing fluorine was formed with a thickness of 800 nm, by ECR plasma CVD. Fig. 35 is a schematic view of an ECR plasma CVD apparatus employed in the formation of the DLC film, wherein shown are a plasma chamber 250 of cavity resonator type; a gas introducing system 251; a microwave introducing window 252; a microwave guide tube 253; a magnet 254; a microwave oscillator 255; a substrate 256; a vacuum chamber 257; and a vacuum system 258. After the vacuum chamber was evacuated to 1×10^{-7} Torr, C_2H_2 at 30 sccm, CF_4 at 10 sccm and H_2 at 20 sccm were introduced from the gas introducing system to a pressure of 2.0×10^{-3} Torr, and plasma was generated in the plasma chamber by introduction of microwave of 2.45 GHz at 1.0 kW. In this state an external magnetic field was formed with the magnet to establish the ECR conditions of 1200 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator and 600 Gauss at the position of the substrate. Furthermore a voltage of -500 V was applied to the substrate from DC power source (not shown), and the fluorine-containing DLC film 121 shown in Fig. 34C was formed. A similarly prepared film showed, in HFS (hydrogen forward scattering) analysis, a hydrogen content of 20 atom %. Also the fluorine concentration, measured by RBS (Rutherford backscattering spectroscopy), was 10 atom %. The hardness of the film, measured with the thin film hardness meter, was 2500 kg/mm^2 in Vickers hardness. The friction properties were evaluated by pin-on-disk method. The friction coefficient was 0.05 in a measurement conducted in air of relative humidity of 50 %, utilizing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 1.5N and a sliding velocity of 0.04 m/s.

Subsequently the electorde tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13. Then the wire 14 was maintained in contact with the electrode tab 12 and the heater substrate was adhered to the heater holder 8. At the preparation of the heater 1, the surface of the electrode terminals 4, 5 were Au flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250°C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni, or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The thermal fixing device thus prepared was free from generation of abraded powder resulting from the friction between the heater and the plastic film, and could maintain stable sliding performance over a prolonged period.

[Embodiment 21]

A groove of a dimension of 350 mm x 2 mm x 12 μm, for forming the heat-generating resistor layer, was mechanically formed on an Al_2O_3 substrate same as in the embodiment 20. Ag/Pd paste was applied in said grove by screen printing with a thickness of 11 μm and was burnt in air to form a heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. The substrate was then placed in an unrepresented sputtering apparatus and a W (tungsten) layer 3a of a thickness of 1 μm on the resistor layer in order to prevent mutual diffusion of Ag/Pd and C. Then, in the ECR plasma CVD apparatus, shown in Fig. 35, a fluorine-containing a-C:H film was formed as in the embodiment 20. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, C_6H_5F at 25 sccm and H_2 at 15 sccm were introduced from the gas introducing system to a pressure of 3.6 x 10^{4} Torr, and plasma was generated in the plasma chamber by the introduction of microwave of 2.45 GHz at 1.2 kW. In this state an external magnetic field was formed by the magnet to establish the ECR conditions of 1500 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator and 650 Gauss at the position of the substrate. Also a voltage of -700 V was applied to an unrepresented extracting electrode (grid) provided at the exit of the cavity resonator, and the a-C:H, F film was formed with a thickness of 1000 nm. Subsequently a sample 1 of the heater was completed by the connection of the electrode tabs and the wires to the electrode terminals and the adhesion to the heater holder in the same manner as in the embodiment 20. Fig. 36 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention. Samples 2 and 3 were prepared under the same conditions, except that the raw material gas was respectively replaced by $C_6H_3F_3$ or C_6F_6. These samples were subjected to the measurement of hydrogen content, fluorine content, film hardness and friction coefficient, and the obtained results are summarized in Table 4. The hydrogen content was measured by HFS analysis, fluorine content by RBS analysis, film hardness by the thin film hardness meter, and friction coefficient under the same conditions as in the embodiment 20.

Table 4

Sample	Raw material gas	Hydrogen concentration (atom %)	Fluorine concentration (atom %)	Hardness (kg/mm^2)	Friction coefficient (μ)
1	C_6H_5F	25	16	2200	0.07
2	$C_6H_3F_3$	24	30	1800	0.05
3	C_6F_6	15	32	1100	0.06

Thermal fixing devices equipped with thus prepared heaters were subjected to the thermal fixation of the recording material as in the embodiment 20. Samples 1 and 2 provided stable fixing performance and durability as in the embodiment 20, but sample 3 developed slight film peeling with the increase in the number of fixing operations.

[Embodiment 22]

An a-C:H film was formed, as the lubricating protective film, on the insulating protective layer as in the embodiment 20. Fig. 37 is a schematic view of an ion beam deposition (IBD) apparatus employed in the formation of the a-C:H film, wherein shown are a vacuum chamber 260; an ion beam source 261; an ionizing chamber 262; a gas introducing system 263; an ion beam extracting electrode 264; a substrate 265; and a vacuum system 266. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, CH_4 at 15 sccm and H_2 at 35 sccm were introduced from the gas introducing system to a pressure of 3.0 x 10^{4} Torr to generate plasma in the plasma chamber. The substrate was irradiated with an ion beam extracted by the application of a voltage of 0.7 kV to the extracting electrode, and the a-C:H film was formed with a thickness of 400 nm. The substrate was then placed in an RF plasma CVD apparatus shown in Fig. 38, wherein shown are a vacuum chamber 270; a gas introducing system 271; an electrode 272; a substrate 273; a vacuum system 274; and an RF power source 275. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, CF_4 was introduced at 100 sccm from the gas introducing system to a pressure of 3.0 x 10^{-2} Torr, and RF plasma was generated by introduction of a power of 1.5 kW from the RF power source. The substrate bearing the a-C:H film was exposed to the RF plasma, whereby the surface of the film was fluorinated. The film indicated a hydrogen content of 30 atom %, a fluorine content of 5 atom %, a film hardness of 2500 kg/mm^2 and a friction coefficient of 0.05. The fluorine concentration in the film decreased from the surface toward the substrate. The methods and conditions of these measurements were same as in the embodiment 14. Subsequently the heater was completed by the connection of the electrode tabs and the wires to the electrode terminals and by the adhesion to the heater holder, in the same manner as in the embodiment 20.

A thermal fixing device equipped with thus prepared heater was used in the thermal fixation of the recording material in the same manner as in the embodiment 20, there were obtained stable fixing performance and durability as in the embodiment 20.

[Embodiment 23]

In a similar manner as in the embodiment 22, a-C:H films were formed with a thickness of 450 nm on the insulating protective film, with a thickness of 550 nm on the heater holder coming into contact with the plastic film, and with a thickness of 30 nm on the plastic film. Then the heater, heater holder and plastic film, bearing the a-C:H film thereon, were placed in the RF plasma CVD apparatus shown in Fig. 38 in the same manner as in the embodiment 22, and the surface of the a-C:H films was fluorinated. Fig. 39 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention.

A thermal fixing device equipped with thus prepared heater was used in the thermal fixation of the recording material as in the embodiment 20, and there were obtained stable fixing performance and durability as in the embodiment 20.

In the following there will be explained an embodiment utilizing, as the protective layer of the heater, a diamond film of a high electric insulation, a high thermal conductivity, a high hardness and a low friction coefficient, formed by gaseous synthesis.

The diamond crystals of the present invention is featured by a thermal conductivity of 600 - 2100 W/m•K, an electrical resistance (volume resistivity) of 10^{10} - 10^{16} Ωcm, and a hardness of 10000 kgf/mm^2.

The substrate for forming the diamond film of the present invention is preferably composed of a material suitable for the formation of diamond crystals and enabling mechanical grinding and etching. Examples of such material include Si, Ta, Mo, W, SiC, WC, SiO_2, Al_2O_3 and Si_3N_4.

The gaseous synthesis of diamond crystals to be employed in the present invention can be achieved, for example, by heated filament CVD, microwave plasma CVD, DC plasma CVD, RF plasma CVD, magnetic field microwave plasma CVD or combustion flame method. Examples of the carbon-containing raw material gas include hydrocarbons such as methane, ethane, propane, ethylene, benzene and acetylene; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform and trichloroethane; alcohols such as methyl alcohol and ethyl alcohol; ketones such as $(CH_3)_2CO$ and $(C_6H_5)_2CO$; gasses such as CO and CO_2; and mixtures thereof with other gas such as N_2, H_2, O_2, H_2O or Ar.

Synthesis of diamond crystals is conducted, for example in case of microwave plasma CVD utilizing hydrogen and methane as the raw material gas, with a methane gas concentration of 0.1 - 1.0 %; a substrate temperature of 600 - 900 ° C; a gas pressure of 1.33 - 26.6 kPa and a total gas flow rate of 100 - 1000 ml/min. The forming conditions of the diamond crystals are variable according to the synthesizing method.

The diamond crystals mentioned in this invention are those identifiable as the diamond crystals for example by X-ray diffraction, electron beam diffraction or Raman spectroscopy. For example the Raman spectroscopy shows, as shown in Fig. 40, a sharp peak of diamond at about 1333 cm^{-1}, and weak broad peaks, resulting from non-diamond carbon component, at about 1360 and 1550 cm^{-1}. The thermal conductivity of diamond crystals depends greatly on the crystallinity of diamond, and becomes higher as the crystallinity becomes higher and the impurity becomes less. Consequently there are preferred diamond crystal not showing the broad peaks around 1360 and 1550 cm^{-1} in Raman spectrum. By expressing the proportion of diamonds and amorphous carbon by the intensity ratio (I_{1550}/I_{1333}) of the peak of the amorphous carbon (broad peak around 1550 cm^{-1}) and the peak of diamonds (1333 cm^{-1}) in the Raman spectrum, there is preferred a range $0 \leqq I_{1550}/I_{1333} \leqq 1$. Above the upper limit of this range, the crystallinity of diamonds becomes deteriorated, and the thermal conductivity becomes worse. Also the crystallinity of diamonds is significantly correlated with the species and concentration of the raw material gasses employed in the film formation. For example, in the methane-hydrogen system, a lowered methane concentration improves the crystallinity, with an increase in the thermal conductivity. In the methane-hydrogen-oxygen system, a diamond film with satisfactory crystallinity can be obtained by selecting the carbon-oxygen atom ratio as O/C = 0.8. Satisfactory crystallinity of diamond realizes the aforementioned physical properties of diamond, thus realizing high insulating property in addition the high thermal conductivity.

The thickness of the diamond layer should be so selected as to ensure a mechanical strength capable of protecting the heater from the fixing pressure and a sufficient insulation at the use of heater, and is generally within a range from several to several thousand microns, preferably from several ten to several hundred microns.

After a diamond film or layer is formed on the aforementioned substrate, the heat-generating resistor is formed by a PVD method such as sputtering, and is trimmed, if necessary, to a desired resistance based on the resistance measurement. The electrode terminals are similarly formed by sputtering of Au, Ag or Cu. Then ceramic paste (adhesive) is applied by screen printing on the diamond film, heat-generating resistor and electrode terminals, and a ceramic insulating substrate is applied thereon and adhered thereto by burning. The heat-generating resistor and the electrode terminals may be formed not only by a PVD method such as sputtering, vacuum evaporation or ion plating but also by CVD, plating or screen printing. Thereafter the substrate for diamond film formation is removed by mechanical grinding or chemical etching. The surface of the diamond film, reflecting the polycrystalline nature, has a larger surface roughness as the crystallinity increases, and is generally in a range from several thousand Angstroms to several microns in Rmax. However, the surface roughness of the diamond film after the substrate removal is equal to that of the substrate used for diamond film formation, so that the surface roughness of an overcoat layer can be made equal to or less than several hundres Angstroms in Rmax. Then the heater of the present invention is completed by mounting the electrode tabs to the electrode terminals for example by soldering, then pressing the wires to the electrode tabs and adhering the heater substrate to the heater holder.

Thus the present invention utilizes a diamond film obtained by gaseous synthesis as the protective layer of the heater, thereby improving the thermal efficiency of the heater, reducing the power consumption thereof and realizing a heater excellent in the abrasion resistance and sliding performance.

[Embodiment 24]

Fig. 41 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 µm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing said film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 42A to 42F are schematic cross-sectional views of the 24th embodiment, wherein shown are a heater 1; a ceramic substrate 2; a Ag/Pd heat-generating resistor 3; a Cu electrode terminal 4; a substrate 5 for example of Si for diamond film formation; a protective layer 6 consisting of a polycrystalline diamond film; a heater holder 8; an electrode tab 12; AuSi solder 13; and a wire 14.

In this embodiment, a polycrystalline diamond film 6 was at first formed on the Si substrate 5 for diamond film formation (Fig. 42A). On the Si substrate, areas not subjected to the diamond film formation were masked in advance with a resist material. This substrate was immersed in alcoholic dispersion of diamond grinding particles of 15 - 30 µm and subjected to scarring treatment with an ultrasonic oscillator, and the masking resist was then removed. This substrate was then subjected to the formation of the diamond film in a heated filament CVD apparatus shown in Fig. 43, wherein shown are a quartz reaction tube 270; an electric over 271; a tantalum filament 272; a substrate 273; a raw material gas inlet 274 connected to unrepresented gas containers, gas flow regulators and valves; and gas outlet 275 connected to a mechanical booster pump, a rotary pump and valve which are not illustrated. After the substrate was placed in the apparatus and the interior was evacuated with vacuum pump (not shown), methane at 1 ml/min. and hydrogen at 999 ml/min. were introduced from gas containers (not shown) into the quartz reaction tube, and the pressure therein was regulated at 6.00 Pa by regulator valve (not shown). The interior of the reaction tube was heated to 900 °C by the electric oven, and the filament was heated to 2100 °C, and the diamond film was formed in 20 hours, with a thickness of 40 µm. According to the observation under a scanning electron microscope (SEM), the obtained diamond film was a polycrystalline film with clear facets. The Raman spectroscopy showed a sharp peak of diamond around 1333 cm^{-1}, and the intensity ratio of the amorphous carbon peak to the diamond peak was $I_{1550}/I_{1333} \leqq 0.1$. Also a diamond film prepared under the same conditions showed a thermal conductivity, measured by the radiation cooling method, of 900 W/m•K.

On the diamond film, the heat-generating resistor 3 was formed by sputtering Ti for a thickness of 200 Å and Au for a thickness of 10 µm in succession, and trimmed to a desired resistance based on the resistance measurement. Subsequently the electrode terminal 4 was formed by Cu sputtering (Fig. 42A). Then alumina paste (adhesive) was coated, and an alumina substrate 2 was applied and integrated by burning (Fig. 42B). Thereafter the Si substrate was removed with mechanical lapping and with Si etchant (for example $HF/HNO_3/CH_3COOH$) (Fig. 42C).

In the heater substrate or insulating substrate in which the Si substrate is removed, the electrode terminal 4, the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered and alloyed with the solder 13 of AuSi by heating above the melting point (370 °C) of the solder (Fig. 42D). Then the wire 14 was pressed to thus mounted electrode tab 12 (Fig. 42E), and the heater 1 was adhered to the heater holder 8 (Fig. 42F). At the preparation of the heater 1, the surface of the electrode terminal 4 was Au-flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze The solder preferably has a melting point of at least 250 °C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminal with Au, Ni or Au/Ni in order to prevent surface oxidation of the Cu electrode terminal until the soldering operation and to provide the terminal with chemical resistance at the removal of the Si substrate. The Ni layer is to prevent excessive diffusion of Cu into the solder.

The heater thus prepared was capable of efficiently supplyig the recording material with the heat generated by electric power supply, and could realize stable heater performance without thermal deterioration of the heater components.

[Embodiment 25]

A polycrystalline diamond film was formed on an Si substrate in a similar manner as in the embodiment 24. Fig. 44 is a schematic view of a microwave plasma CVD apparatus employed in the formation of the diamond film, wherein shown are a quartz reaction tube 286; an Si substrate 287; a raw material gas introducing system 288; a microwave source 289; a microwave guide tube 280; and a vacuum system 281.

After an Si substrate subjected to scarring treatment with diamond grinding particles was placed in the apparatus shown in Fig. 44, the interior was evacuated by the vacuum system 281, and carbon monoxide at a rate of 25 ml/min. and hydrogen at a rate of 375 ml/min. were introduced from the gas introducing system to the quartz reaction tube. The pressure in the reaction tube was regulated to 5.3 kPa with the regulating valve, and the diamond film was synthesized in 10 hours with a thickness of 150 µm, with a microwave output of 4 kW supplied from the microwave source 289 and a substrate temperature of 900 °C. A similarly synthesized diamond film was a polycrystalline film with clear facets in the SEM observation, and showed a thermal conductivity of 1500 W/m•K in the radiation cooling method.

On the diamond film, the heat-generating resistor 3 was formed in a predetermined position by applying Ag/Pd paste with screen printing, and was then trimmed to a desired resistance, if necessary, based on the resistance measurement. Then the electrode terminal 4 was prepared by applying Cu paste by screen printing. Subsequently alumina paste (adhesive) was applied, then an alumina ceramic substrate 2 was applied and adhered by sintering. Then the heater substrate was prepared by removing the Si substrate in the same manner as in the embodiment 24. The heater was completed by connection of the electrode tabs and wires to the electrode terminals and by adhesion to the heater holder. Thus obtained heater, in the thermal fixation of the recording material as in the embodiment 24, could achieve stable fixing operation as in the embodiment 24.

In the foregoing embodiments, there has been explained the formation of a carbon film on the protective layer, the resistor layer or the plastic film, but, in certain circumstances or conditions of use, thus formed carbon film may be locally peeled off or damaged, so that the thermal fixing device may become no longer usable for the fixing operations.

The present invention is to resolve also the above-mentioned drawback, by regenerating the lubricating protective carbon film, locally peeled or damaged, on the heater or on the plastic film, thereby providing a thermal fixing device of a high durability (long service life) and a low cost.

More specifically, the above-mentioned drawback can be resolved, according to the present invention, by removing the carbon film of a high hardness and a low friction coefficient, formed as a lubricating protective film on the insulating protective film or the heat-generating resistor of the heater, or on the plastic film, by means of ashing (oxidation treatment) and forming a carbon film again.

The carbon film of the present invention is a hydrogenated amorphous carbon film (a-C:H film), a diamond-like carbon film (DLC film) or a hard carbon film. There is also included an a-C:H film or a DLC film containing at least one of the following elements Ta, W, Mo, Nb, Ti, Cr, Fe, B, Si and fluorine. The a-C:H film and the DLC film are featured by certain physical properties represented for example by a thermal conductivity of 200 - 600 W/m•K, an electrical resistance (volume resistivity) of 10^8 - 10^{11} Ωcm, a hardness of 2000 - 5000 kg/mm^2 and a friction coefficient smaller than 0.2. Also the hard carbon film is featured by certain physical properties represented for example by a hardness of 2000 - 5000 kg/mm^2, a friction coefficient $\mu < 0.2$, and an electrical resistance (volume resistivity of 10^5 -10^{11} Ωcm.

The oxidation can be achieved, for example, by microwave plasma CVD, DC plasma CVD, RF plasma CVD, magnetic field microwave plasma CVD, ion beam sputtering, ion beam evaporation or ion plating, which is used in the preparation of the above-mentioned a-C:H film, DLC film or hard carbon film. In these method, oxygen is employed as the reaction gas to generate oxygen plasma or an oxygen ion beam to which the carbon film is exposed, whereby the carbon film is ashed (eoxidized and removed). The reaction gas can be a mixture of oxygen with H_2, N_2, air, Ar or CF_4. Also after the oxidation, the substrate may be etched with plasma or an ion beam of H_2, N_2, air or CF_4. The state of ashing can be known by monitoring the plasma in the ashing operation, by spectroscopic method, and the end point of the ashing operation can thus be determined.

Thereafter the lubricating protective film of the heater or the plastic film is regenerated by again forming the carbon film by the film forming method explained above. The ashing and the regeneration may be conducted in continuation in a same apparatus, or there may be added a washing step with organic solvent after the ashing.

[Embodiment 26]

Fig. 45 is a magnified partial cross-sectional view of a thermal fixing device, utilizing the heater embodying the present invention, wherein a heater 1 is supported by a heater supporting member 9 across a heat-insulating heater holder 8. A heat-resistant film 10 is composed for example of polyimide of a thickness of about 40 µm, formed as an endless belt or an elongated web. A rotary pressure roller 11 serves as the pressing member for pressing said film toward the heater 1. The film 10 rotates or moves at a predetermined speed in a direction indicated by an arrow in contact with the edges of the heater holder 8 and with the face of the heater 1, thus sliding thereon by driving member (not shown) or by the rotating force of the pressure roller 11. The heat-generating resistor 3 is electrically powered to heat the heater to a predetermined temperature, and a recording material 16 bearing an unfixed toner image thereon at the side of the film 10 is inserted into a fixing nip portion 15 which is in the condition that the film 10 is being moved. Thus the recording material 16 is maintained in contact with the film 10 and passes the fixing nip portion together with the film 10. In the course of the passing, thermal energy is given from the heater 1 to the recording material 16 across the film 10 to fix by fusion the unfixed toner image 17 on the recording material 16.

Figs. 46A to 46E are schematic cross-sectional views of the heater of the embodiment 26, wherein shown are a heater 1; a ceramic substrate 2; an Ag/Pd heat-generating resistor 3; Cu electrode terminals 4, 5; an insulating protective glass layer 6; a DLC film 122 containing a metal element; a heater holder 8; an electrode tab 12; AuSi solder 13; and a wire 14.

In the heater of this embodiment, Ag/Pd paste was at first applied by screen printing on an Al_2O_3 substrate and burnt in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. Then Cu paste was applied by screen printing, and the electrode terminals 4, 5 were formed by burning under a controlled oxygen partial pressure (Fig. 46A). Then the insulating protective film was prepared by application of low-softening lead silicate glass by screen printing, followed by burning in air (Fig. 46B). Subsequently a DLC film 122 was formed with a thickness of 400 nm, by ECR plasma CVD (Fig. 46C). Fig. 47 is a schematic view of an ECR plasma CVD apparatus employed in the preparation of the DLC film, wherein shown are a plasma chamber 290 of cavity resonator type; a gas introducing system 291; a microwave intorducing window 292; a microwave guide tube 293; a magnet 294; a microwave oscillator 295; a substrate 296; a vacuum chamber 297; and a vacuum system 298. Similarly there were formed a DLC film containing Si at 10 atom % and a DLC film containing fluorine at 10 atom %, with a thickness of 400 nm. The hydrogen content, Si content, fluorine content, film hardness and friction coefficient of these DLC films were evaluated respectively by HFS (hydrogen forward scattering spectrometry), EPMA, RBS (Rutherford backscattering spectrometry), thin film hardness meter, and pin-on disk method. The friction coefficient was measured in air of relative humidity of 45 %, employing a ball (5 mm in diameter) of bearing steel (SUJ2) as the pin, with a load of 1.2N and a sliding velocity of 0.04 m/s. The obtained results are summarized in Table 5.

Table 5

Sample	Hydrogen concentration (atom %)	Si concentration (atom %)	Fluorine concentration (atom %)	Hardness (kg/mm^2)	Friction coefficient (μ)
1	25	-	-	2500	0.08
2	24	10	-	2400	0.05
3	23	-	10	2300	0.07

Subsequently the electrode tab 12 of a copper alloy and the ceramic substrate 2 were soldered with AuSi solder 13 (Fig. 46C). Then the wire 14 was maintained in contact with the electrode tab 12 and the heater substrate was adhered to the heater hodler 8 (Figs. 46D and 46E). At the preparation of the heater 1, the surfaces of the electrode terminals 4, 5 were Au-flash-plated in order to improve wettability with the solder, thereby achieving stable reliability for connection. The electrode tab may also be formed, instead of copper alloy, of covar, 42 alloy or phosphor-bronze. The solder preferably has a melting point of at least 250 °C, and can also be composed of AuGe or AuSn instead of AuSi. Furthermore, soldering could be achieved in more stable manner by flash-plating the Cu electrode terminals with Au, Ni or Au/Ni in order to prevent oxidation and contamination until the soldering operation. The Ni layer is to prevent excessive diffusion of Cu into the solder.

A thermal fixing device equipped with thus prepared heater was used in continuous fixation of 300,000 unfixed images, and local peeling could be observed in any of the above-mentioned heaters. Thus the regeneration of the heater was conducted in the following manner.

After the heater was placed in the ECR plasma CVD apparatus used in the formation of the carbon film, the vacuum chamber was evacuated to 1 x 10^{-7} Torr, and O_2 was introduced at a rate of 100 sccm from the gas introducing system to a pressure of 3 x 10^{-3} Torr. Subsequently oxygen plasma was generated in the plasma chamber by the introduction of microwave of 2.45 GHz at 1.0 kW. In this state an external magnetic field was formed with the magnet to establish the ECR conditions of 1500 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator, and 650 Gauss at the position of the substrate. The ashing of the carbon film on the insulating protective layer was conducted under these conditions. The end point of the ashing was determined by monitoring, by plasma emission spectroscopy, the variation in time of the intensity of the ultraviolet light at 297.7 nm, emitted from electronically excited CO in plasma. In the ashing operation, the electrodes were masked in order to prevent oxidation.

After the completion of ashing, the heater was taken out and subjected to the DLC film formation with the same method and conditions as explained above. The hydrogen content, Si content, fluorine content, film hardness and friction coefficient in the regenerated DLC film were same as those in the film before regeneration. The thermal fixing device, equipped with thus regenerated heater, showed stable fixing performance and durability same as those before regeneration. Similar investigations on the DLC film containing Ta, W, Mo, Nb, Ti, Cr, Fe or B provided similar results as in the case of the DLC film containing Si.

[Embodiment 27]

A groove of a dimension of 350 mm x 2 mm x 12 µm, for forming the heat-generating resistor layer, was mechanically formed on an Al_2O_3 substrate same as in the embodiment 26. Ag/Pd paste was applied in the groove by screen printing with a thickness of 11 µm and was burnt in air to form the heat-generating resistor 3, which was then trimmed to a desired resistance based on the resistance measurement. The substrate was then placed in an unrepresented sputtering apparatus and W (tungsten) layer 3a of a thickness of 1 µm on the resistor layer, in order to prevent mutual diffusion of Ag/Pd and C. Then, in an ion beam deposition (IBD) apparatus shown in Fig. 48, an a-C:H film was formed with a thickness of 500 nm. In Fig. 48 there are shown a vacuum chamber 300; an ion beam source 301; an ionizing chamber 302; a gas introducing system 303; an ion beam extracting electrode 304; a substrate 305; and a vacuum system 306. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, CH_4 at 15 sccm and H_2 at 30 sccm were introduced from the gas introducing system to a pressure of 3.0 x 10^{-4} Torr to generate plasma in the plasma chamber. An a-C:H film was formed by the irradiation of the substrate with an ion beam, extracted under the application of 0.8 kV to the extracting electrode. The hydrogen content in the a-C:H film, measured by HFS analysis, was 30 atom %. Also the film hardness and the friction coefficient, measured as in the embodiment 26, were respectively 3000 kg/mm^2 and 0.11.

A thermal fixing device, equipped with thus obtained heater developed local peeling off in the thermal fixation of the recording material in the same manner as in the embodiment 26, and the heater was regenerated in the following manner. After the heater was placed in the IBD apparatus shown in Fig. 48, the vacuum chamber was evacuated to 1 x 10^{-7} Torr, and O_2 at 30 sccm was introduced from the gas introducing system to a pressure of 3 x 10^{-4} Torr, thereby generating oxygen plasma in the plasma chamber. The carbon film on the heater was ashed by irradiation with an oxygen ion beam, extracted by the application of a voltage of 0.5 kV to the extracting electrode. Subsequent to the ashing, Ar at 30 sccm was introduced from the gas introducing system to a pressure of 3 x 10^{-4} Torr, and the heat-generating resistor layer and the ceramic substrate were etched by 5 nm with an Ar ion beam extracted with a voltage of 0.5 kV. After the etching operation, the a-C:H film was reformed in the same manner as explained above. The regenerated a-C:H film was of same quality as that before regeneration. The thermal fixing device, equipped with the regenerated heater, showed stable fixing performance and durability same as those prior to the regeneration, in thermal fixation of the recording material.

[Embodiment 28]

An a-C:H film containing Si was formed with a thickness of 25 nm on a polyimide film, employing an ECR plasma CVD apparatus shown in Fig. 47, additionally provided with an extracting electrode (grid) at the exit of the cavity resonator. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, C_6H_6 at 30 sccm, H_2 at 15 sccm and SiH_4 at 10 sccm were introduced from the gas introducing system to a pressure of 4.1 x 10^{-4} Torr, and plasma was generated in the plasma chamber by the introduction of microwave of 2.45 GHz at 1.5 kW. In this state an external magnetic field was formed with the magnet to establish the ECR conditions of 1200 Gauss at the introducing window, 875 Gauss at the exit of the cavity resonator, and 650 Gauss at the position of the substrate. Also a voltage of -500 V was applied to extracting electrode (not shown) provided at the exit of the cavity resonator to extract an ion beam, thereby forming a film of the composition a-$C_{1-x}Si_x$:H, wherein x was within a range $0 \leqq x \leqq 0.4$. In evaluations same as in the embodiment 26, the obtained film showed a film hardness of 2500 kg/mm^2, a friction coefficient of 0.05, a hydrogen content of 20 atom %, and a Si content of 15 atom %.

In the thermal fixation of the recording material as in the embodiment 26, the thermal fixing device equipped with thus obtained film developed local peeling, and the film was therefore regenerated in the folowing manner. After the polyimide film was placed in the ECR plasma CVD apparatus, the vacuum chamber was evacuated to 1 x 10^{-7} Torr, and O_2 was introduced at 10 sccm from the gas introducing system to a pressure of 3.0 x 10^{-3} Torr to generate oxygen plasma in the plasma chamber, and the ashing was conducted by irradiation of the film with oxygen plasma without voltage application to the extracting electrode. After the ashing, CF_4 was introduced at 30 sccm from the gas introducing system to a pressure of 3 x 10^{-4} Torr, and the film was etched by 5 nm by the CF_4 plasma irradiation. In succession, the a-$C_{1-x}Si_x$:H film was formed again with the method and conditions same as those explained before. The regenerated film was same in quality as the film before regeneration. The thermal fixing device equipped with thus regenerated film showed stable fixing performance and durability, in thermal fixation of the recording material, same as those prior to the regeneration.

[Embodiment 29]

A hard carbon film of a thickness of 300 nm was formed, as a lubricating protective film, in the same manner as in the embodiment 26 on the insulating protective layer. Fig. 49 is a schematic view of a DC magnetron sputtering apparatus employed in the formation of the hard carbon film, wherein shown are a vacuum chamber 310; a substrate 311; a graphite target 312 of a purity of 99.99 %; a gas introducing system 313; a DC power source 314; and a vacuum system 315. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, Ar was introduced from the gas introducing system to a pressure of 0.9 Pa. In this operation there were employed conditions of a substrate temperature at the room temperature, a discharge power of 50 W, and a substrate-target distance of 40 mm. Prior to the film formation, the target was pre-sputtered for 20 minutes at 300 W. In the evaluations as in the embodiment 26, the obtained film showed a film hardness of 2100 kg/mm^2, a friction coefficient of 0.12 and a density of 2.8 g/cm^3.

In the thermal fixation of the recording material as in the embodiment 26, the thermal fixing device equipped with thus obtained heater develop local peeling, and the heater was therefore regenerated in the following manner. The heater was placed in an RF plasma CVD apparatus shown in Fig. 50, wherein shown are a vacuum chamber 320; a gas introducing system 321; an electrode 322; a substrate 323; a vacuum system 324; and an RF power source 325. After the vacuum chamber was evacuated to 1 x 10^{-7} Torr, O_2 at 80 sccm and CF_4 at 20 sccm were introduced from the gas introducing system to a pressure of 3.0 x 10^{-2} Torr, and RF plasma was generated by the introduction of an electric power of 1 kW from the RF power source. The ashing was conducted by exposing the heater, bearing the hard carbon film, to said RF plasma. Subsequently the hard carbon film was formed again with the same method and conditions as those explained before. The regenerated film was same in quality as that prior to regeneration. The thermal fixing device equipped with thus regenerated heater, indicates stable fixing performance and durability same as those prior to regeneration in the thermal fixation of the recording material.

Though the present invention has been explained by the preferred embodiments thereof, the present invention is by no means limited to such embodiments and is subject to various modifications within the scope and spirit of the appended claims.

An image heating device having a heater and a plastic film contacting the heater on a face and contacting the unfixed toner image on the recording sheet on the other face, thus transmitting heat from the heater to the toner image through the plastic film, is provided with a hard carbon film, a hydrogenated amorphous carbon film or a diamond-like carbon film at the interface between the heater and the plastic film in order to improve the sliding performance and durability.

Claims

1. A heater comprising:

an insulating substrate;

a resistor layer provided on said insulating substrate and adapted to generate heat by electric current supply; and

a protective layer for protecting said resistor layer;

wherein said protective layer includes, at least on the surface thereof, a hard carbon film, a hydrogenated amorphous carbon film or a diamond-structure layer.

2. A heater according to claim 1, wherein said hard carbon film has a hydrogen concentration in the film less than 1 atom %, and a density not less than 2.0 g/cm^3.

3. A heater according to claim 1, wherein said diamond-structure layer is diamond-like carbon film.

4. A heater according to claim 1, wherein said hydrogenated amorphous carbon film contains a metal.

5. A heater according to claim 4, wherein said metal is Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si, of which concentration in the film is less than 30 atom %.

6. A heater according to claim 1, wherein said hydrogenated amorphous carbon film contains fluorine.

7. A heater according to claim 6, wherein the concentration of said fluorine in the film is less than 30 atom %.

8. A heater according to claim 3, wherein said diamond-like carbon film contains a metal.

9. A heater according to claim 8, wherein said metal is Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si, of which concentration in the film is less than 30 atom %.

10. A heater according to claim 3, wherein said diamond-like carbon film contains fluorine.

11. A heater according to claim 10, wherein the concentration of said fluorine in the film is less than 30 atom %.

12. A heater according to claim 1, wherein said diamond-structure layer is formed by gaseous synthesis.

13. A heater according to claim 1, wherein said protective layer is composed entirely of a hard carbon film, a hydrogenated amorphous carbon film or a diamond-structure layer.

14. A heater according to claim 1, wherein said insulating substrate is provided with a groove, and said resistor layer is formed in said groove.

15. A heater according to claim 1, wherein said hard carbon film or said hydrogenated amorphous carbon film is removable by an oxidation treatment.

16. A heater according to claim 3, wherein said diamond-like carbon film is removable by an oxidation treatment.

17. An image heating device comprising:

a heating member; and

a film whose one face slides with said heating member and the other face contacts with an image on a recording material;

wherein the image on the recording material is heated by the heat supplied from said heating member through said film, and a hard carbon film, a hydrogenated amorphous carbon film or a diamond-structure layer is present at a sliding portion between said heating member and said film.

18. An image heating device according to claim 17, wherein said heating member includes an insulating substrate; and a resistor layer provided on said insulating substrate and adapted to generate heat by electric current supply, and said hard carbon film, hydrogenated amorphous carbon film or diamond-structure layer is provided on said resistor layer.

19. An image heating device according to claim 17, wherein said heating member includes an insulating substrate; a resistor layer provided on said insulating substrate and adapted to generate heat by electric current supply; and a protective layer for protecting said resistor layer, and said hard carbon film, hydrogenated amorphous carbon film or diamond-structure layer is provided on said protective layer.

20. An image heating device according to claim 17, wherein said hard carbon film, hydrogenated amorphous carbon film or diamond-structure layer is provided on said film.

21. An image heating device according to claim 17, wherein said hard carbon film has a hydrogen concentration in the film less than 1 atom %, and a density not less than 2.0 g/cm^3.

22. An image heating device according to claim 17, wherein said diamond-structure layer is a diamond-like carbon film.

23. An image heating device according to claim 17, wherein said hydrogenated amorphous carbon film contains a metal.

24. An image heating device according to claim 23, wherein said metal is Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si, of which concentration in the film is less than 30 atom %.

25. An image heating device according to claim 17, wherein said hydrogenated amorphous carbon film contains fluorine.

26. An image heating device according to claim 25, wherein the concentration of said fluorine in the film is less than 30 atom %.

27. An image heating device according to claim 22, wherein said diamond-like carbon film contains a metal.

28. An image heating device according to claim 27, wherein said metal is Ta, W, Mo, Nb, Ti, Cr, Fe, B or Si, of which concentration in the film is less than 30 atom %.

29. An image heating device according to claim 22, wherein said diamond-like carbon film contains fluorine.

30. An image heating device according to claim 29, wherein the concentration of said fluorine in the film is less than 30 atom %.

31. An image heating device according to claim 17, wherein said diamond-structure layer is formed by gaseous synthesis.

32. An image heating device according to claim 18, wherein said insulating substrate is provided with a groove and said resistor layer is formed in said groove.

33. An image heating device according to claim 19, wherein said insulating substrate is provided with a groove and said resistor layer is formed in said groove.

34. An image heating device according to claim 17, wherein said hard carbon film or said hydrogenated amorphous carbon film is removable by an oxidation treatment.

35. An image heating device according to claim 22, wherein said diamond-like carbon film is removable by an oxidation treatment.

FIG. 1

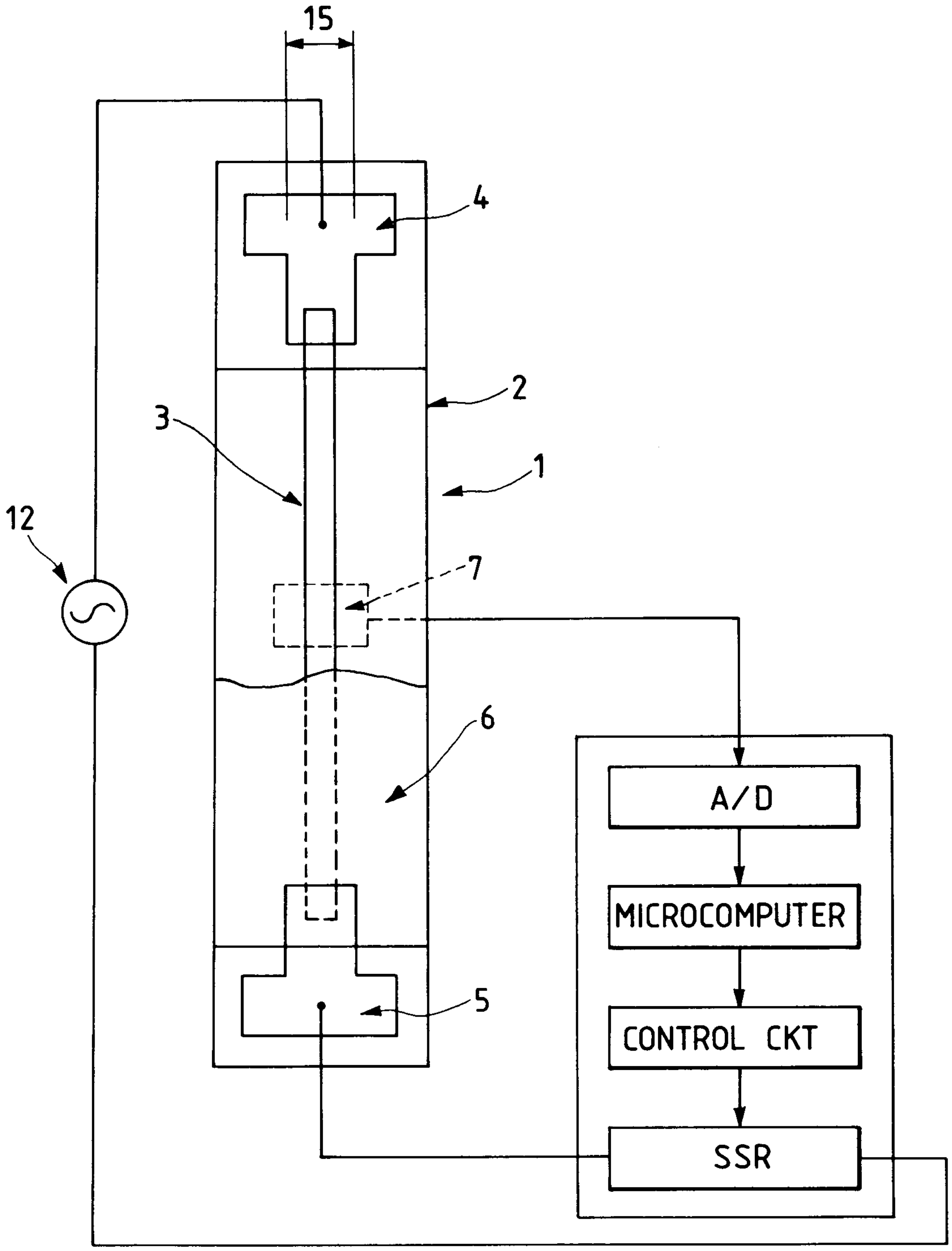


FIG. 2

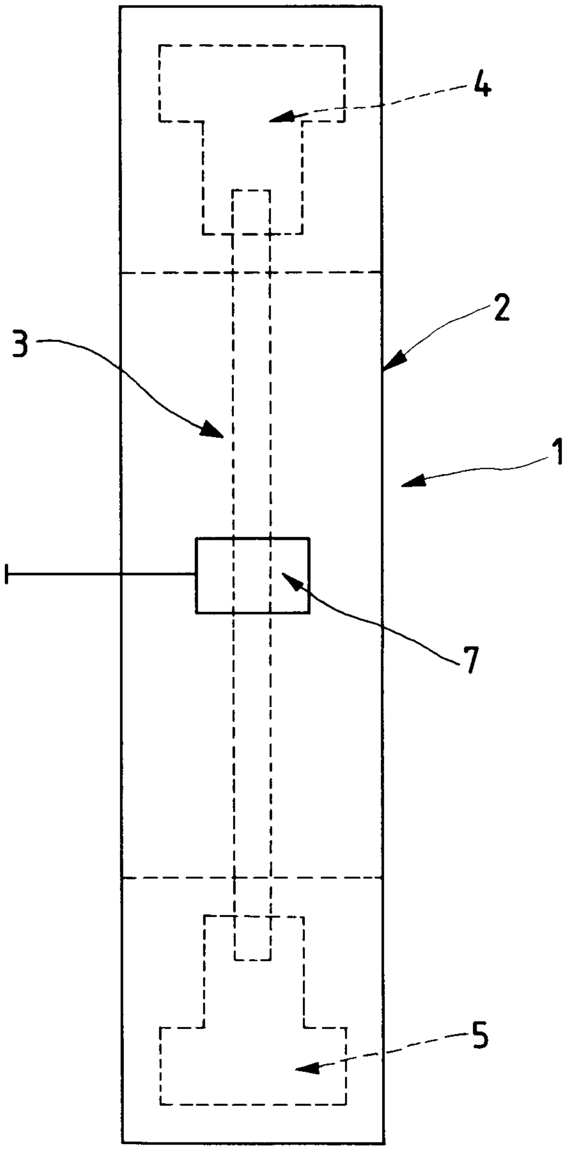


FIG. 3

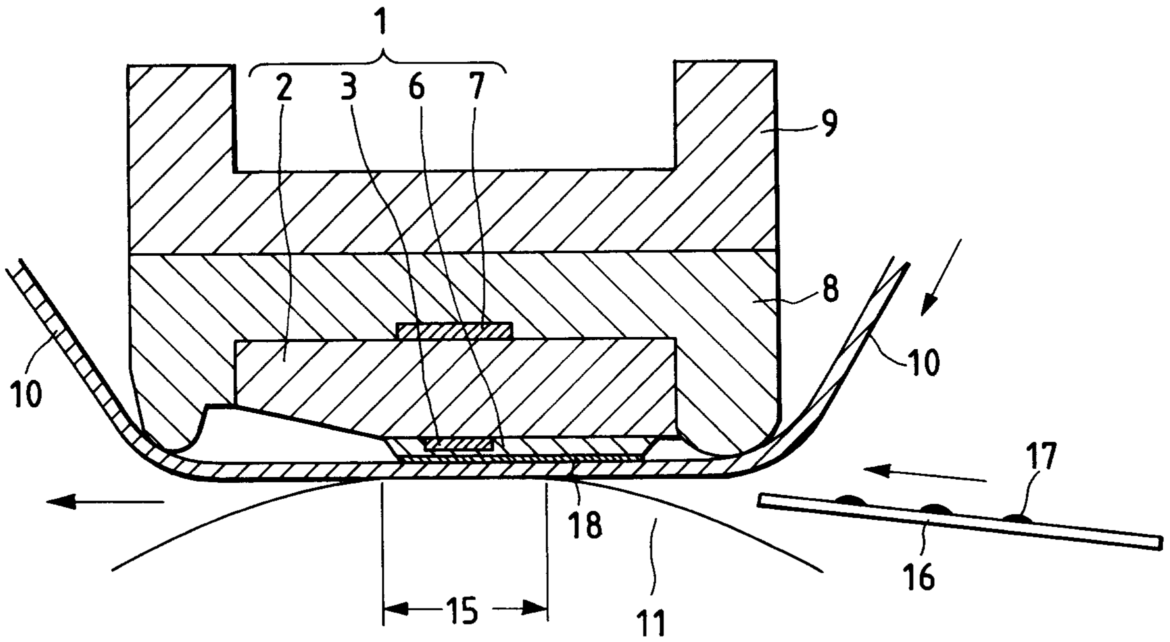


FIG. 4A

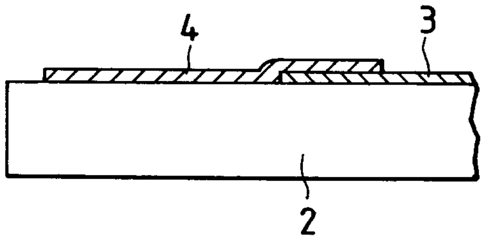


FIG. 4B

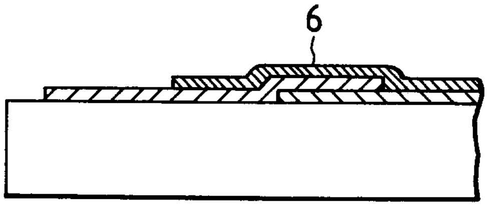


FIG. 4C

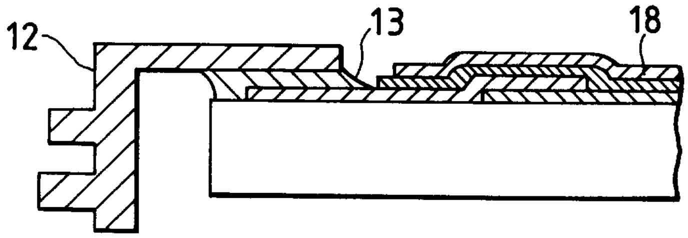


FIG. 4D

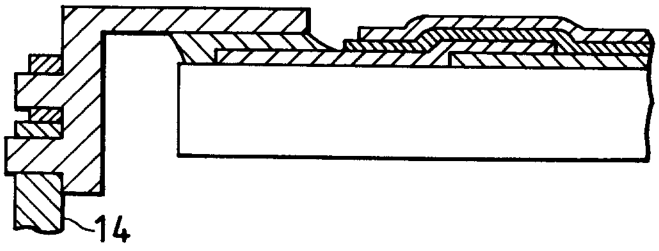


FIG. 4E

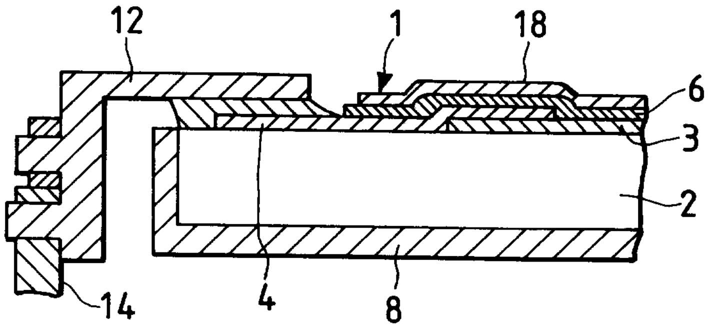


FIG. 5

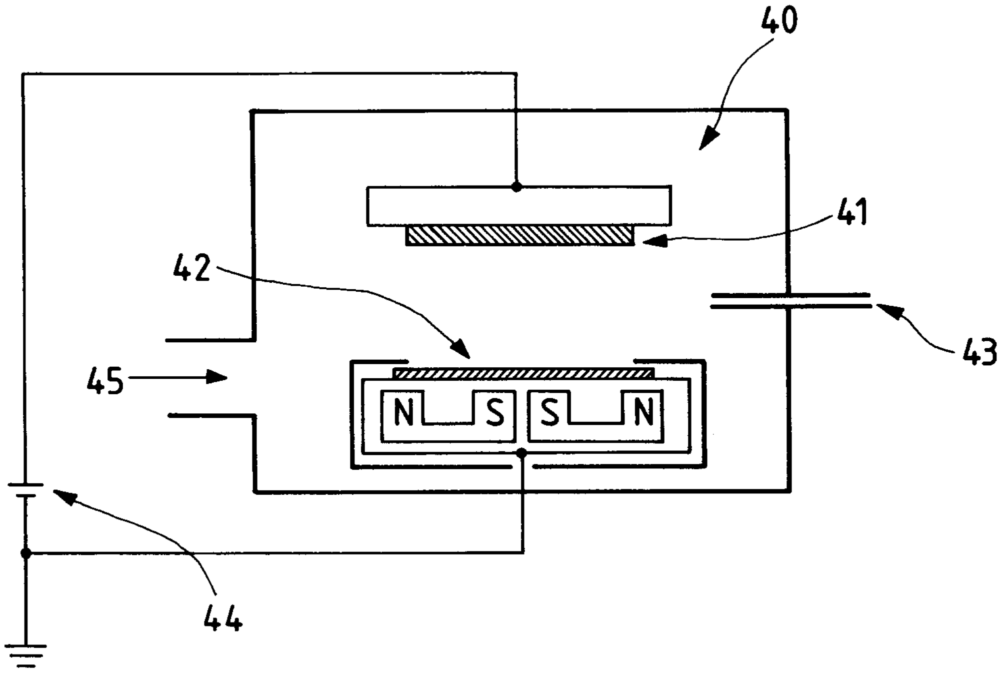


FIG. 6

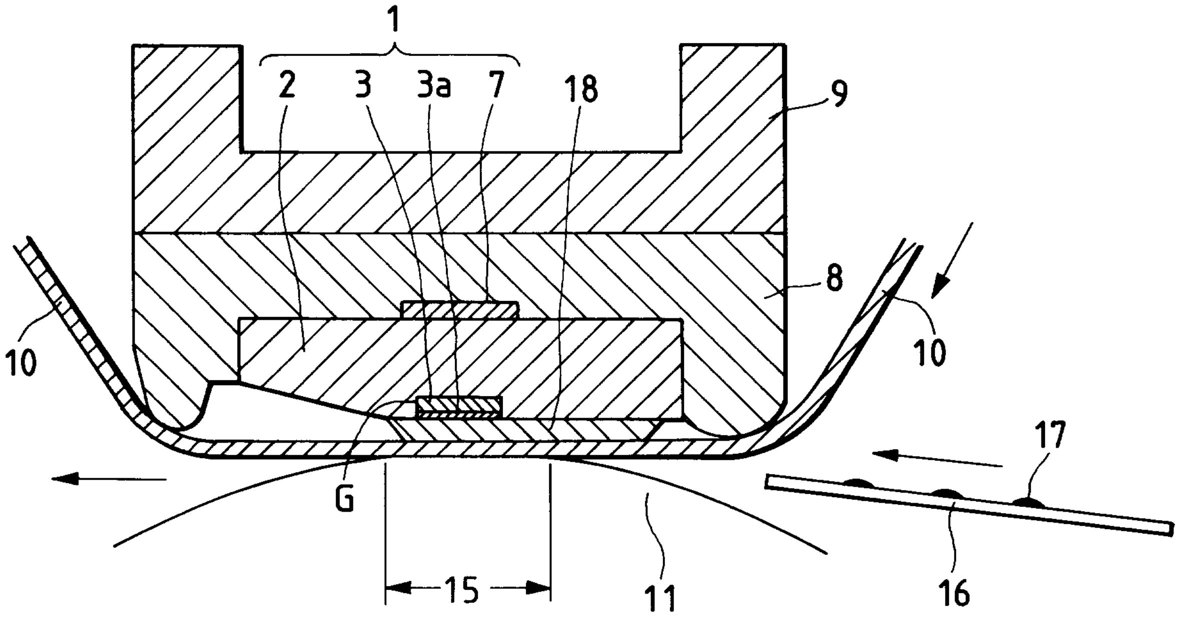


FIG. 7

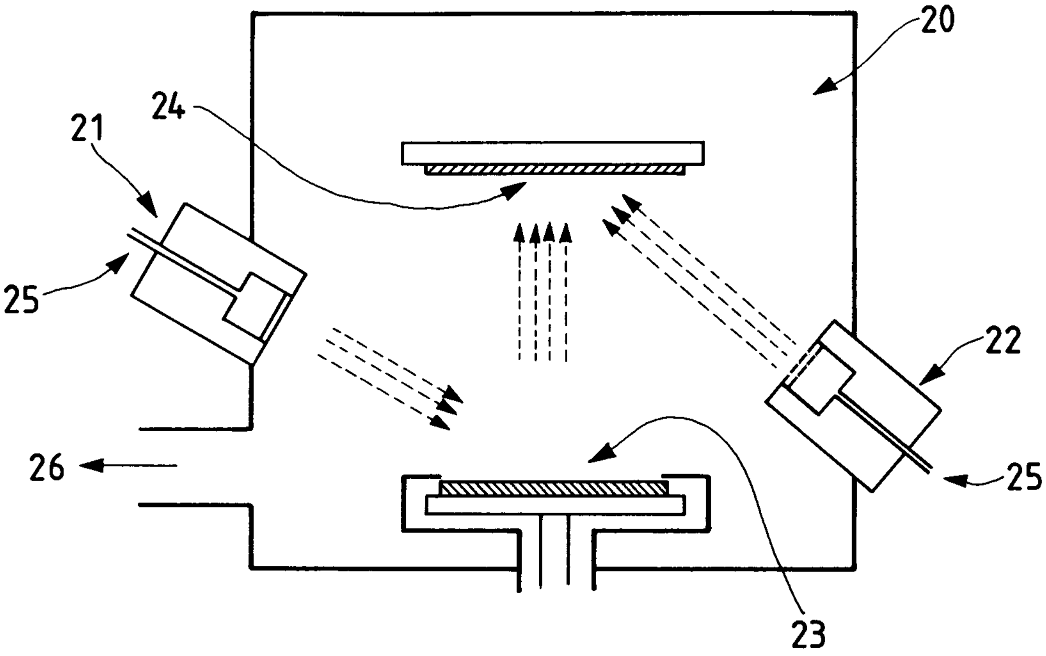


FIG. 8

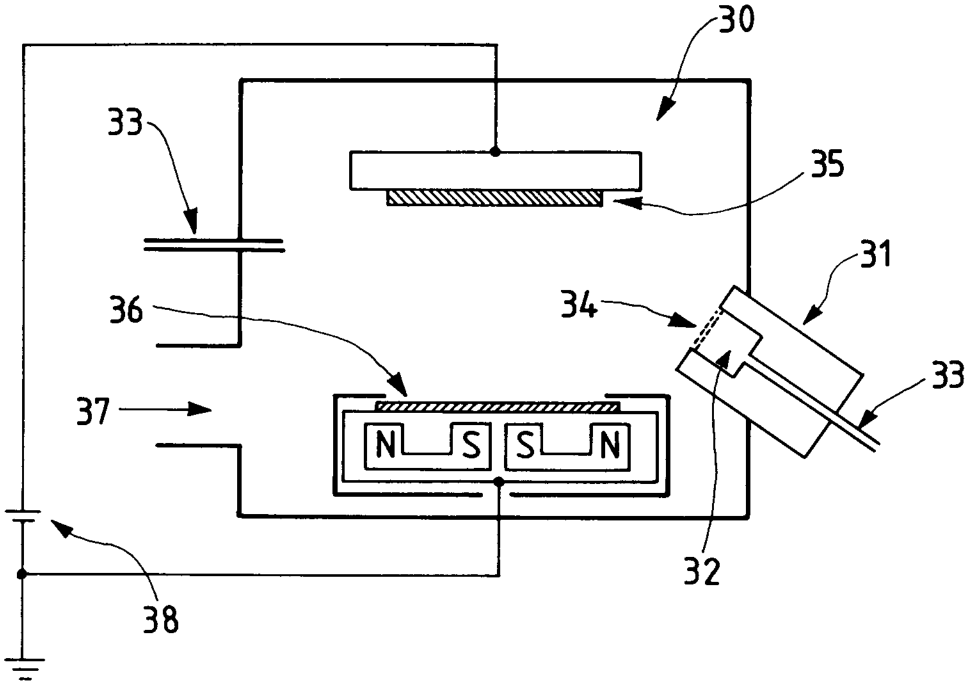


FIG. 9

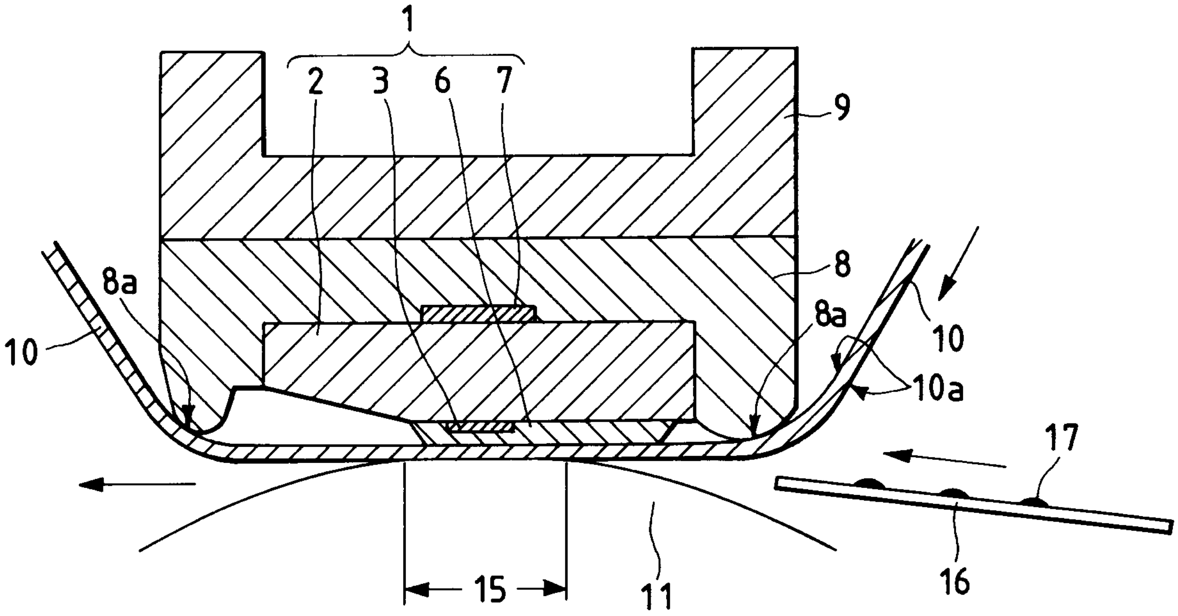

1
2
3
6
7
9
8
8a
10
8a
10
10a
17
16
15
11

FIG. 10

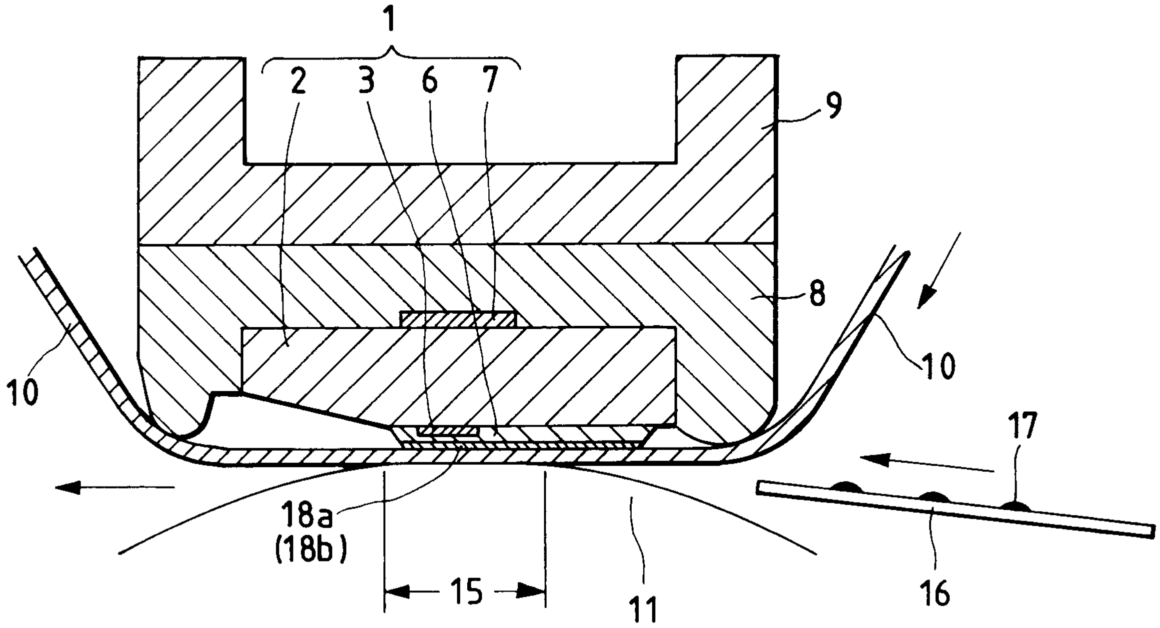

1
2
3
6
7
9
8
10
10
17
18a
(18b)
15
11
16

FIG. 11A

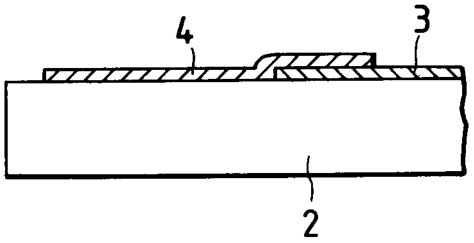


FIG. 11B

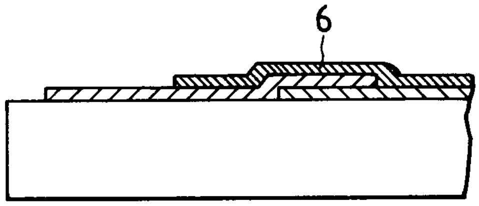


FIG. 11C

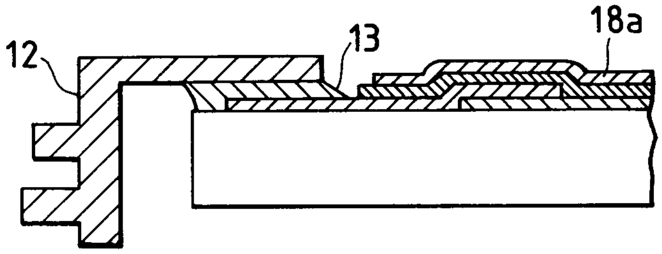


FIG. 11D

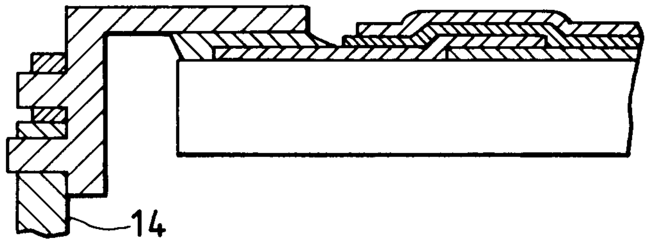


FIG. 11E

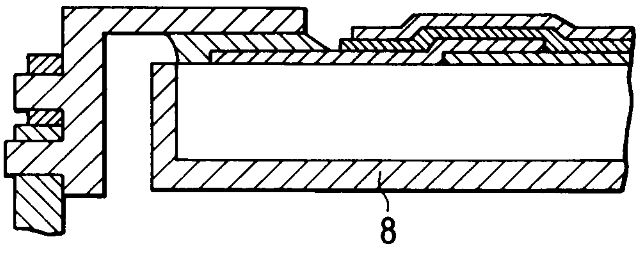


FIG. 12

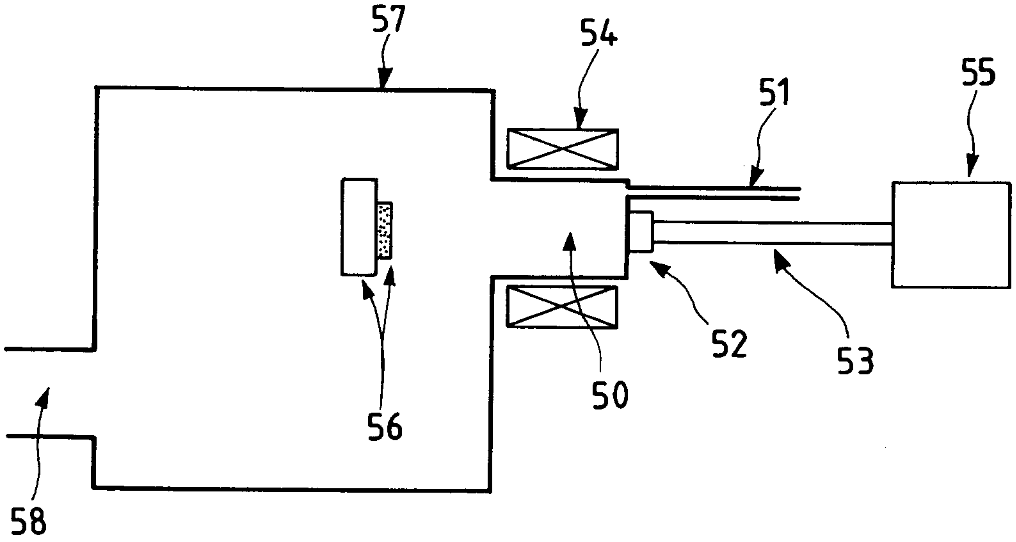


FIG. 13

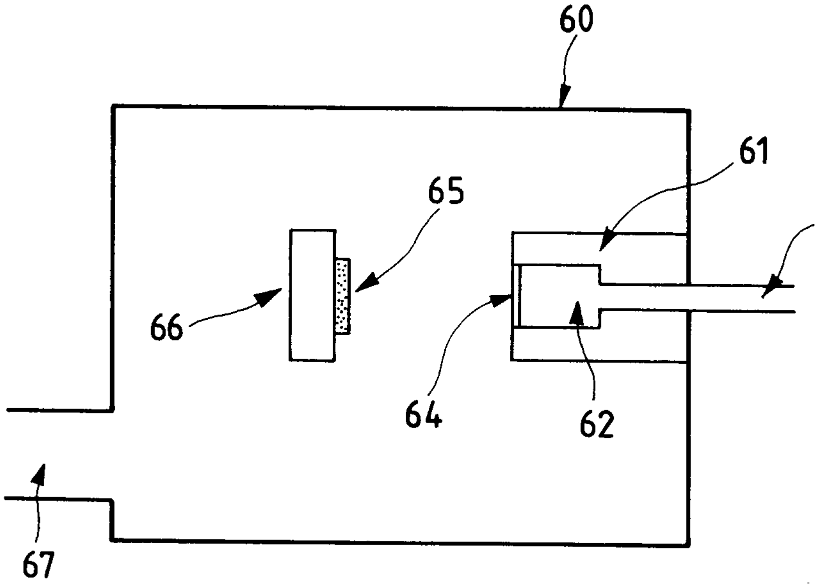


FIG. 14

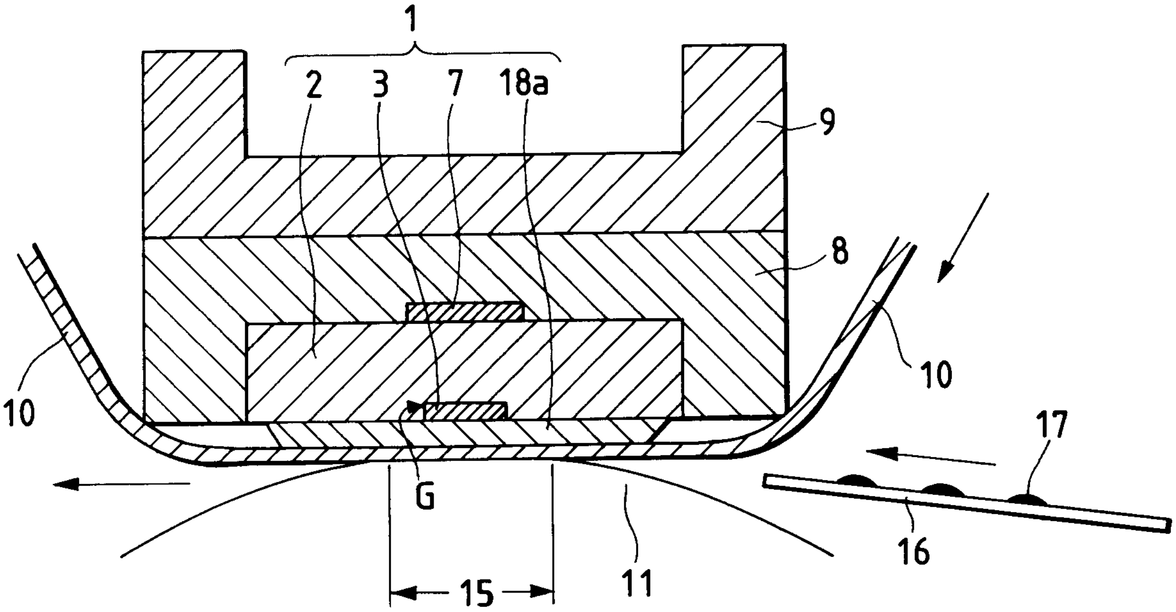
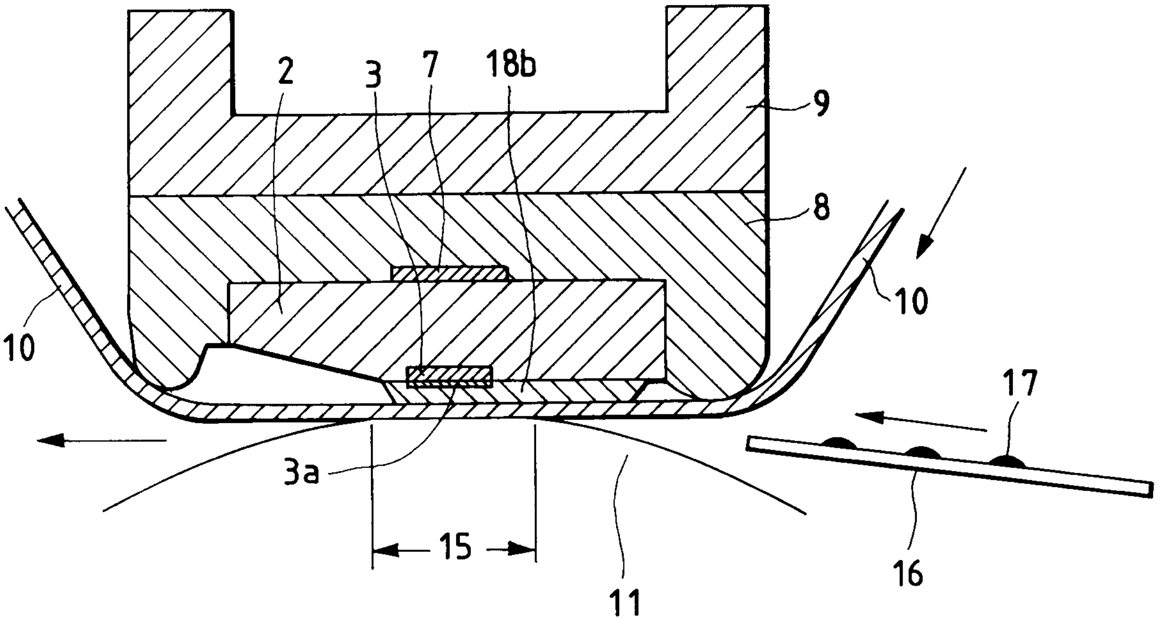


FIG. 16



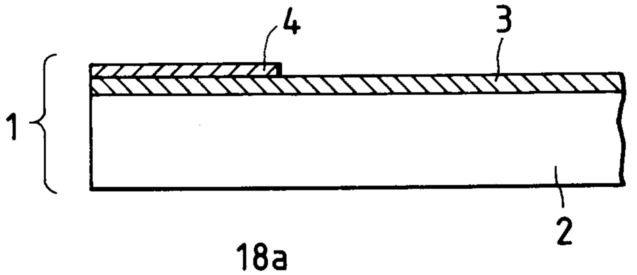


FIG. 15A

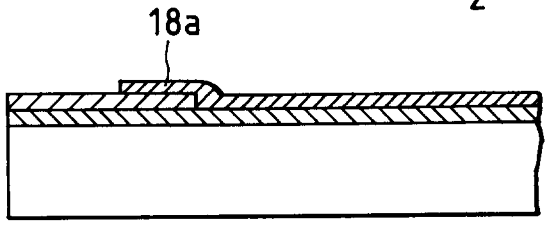


FIG. 15B

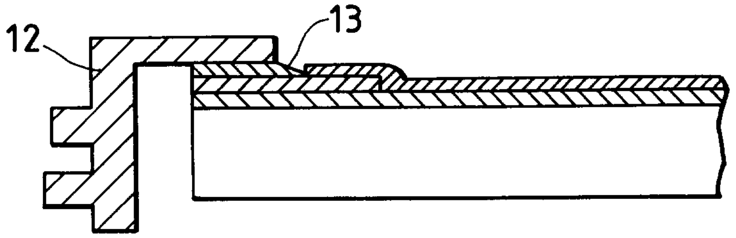


FIG. 15C

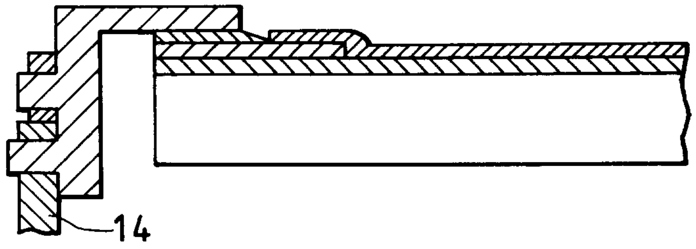


FIG. 15D

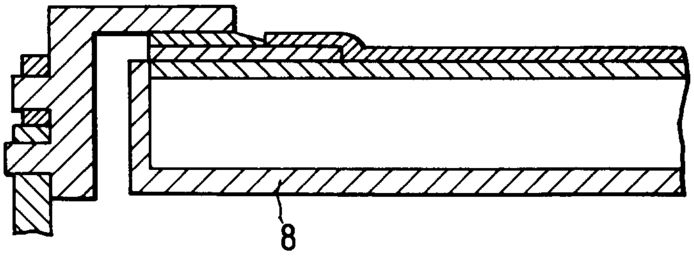


FIG. 15E

FIG. 17

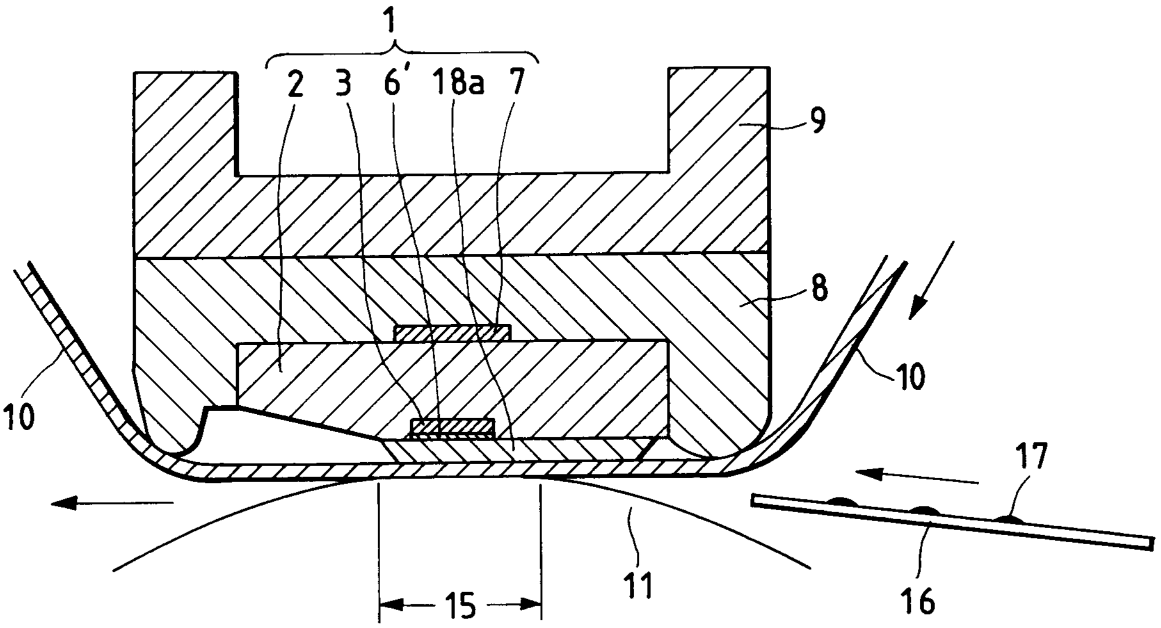


FIG. 18

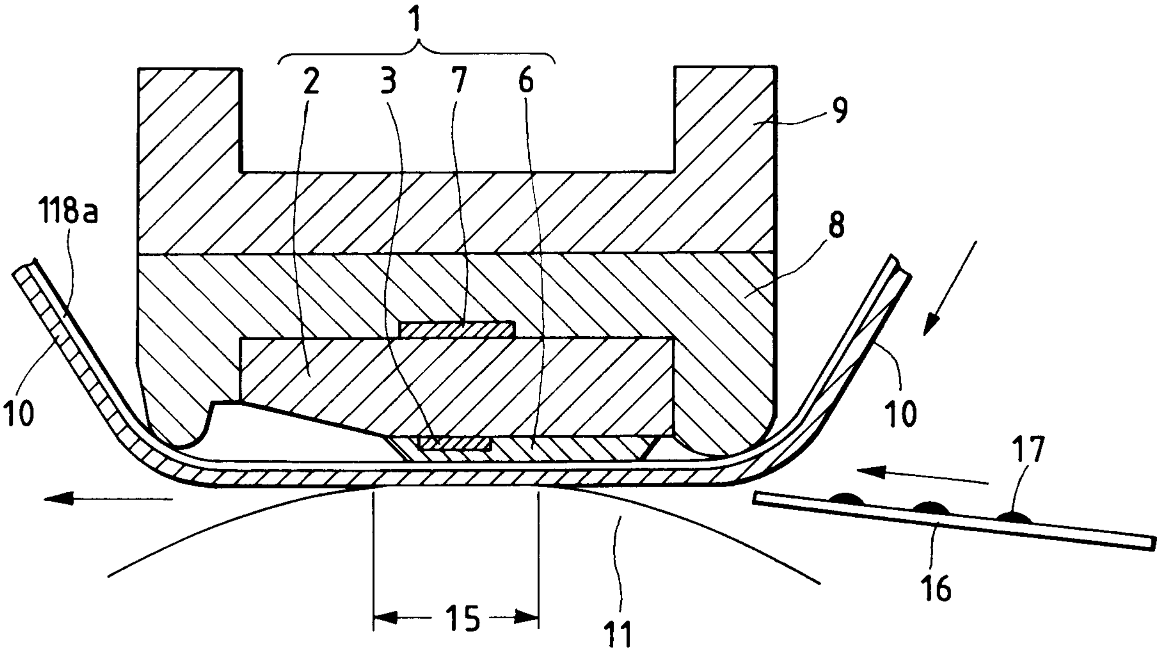


FIG. 19A

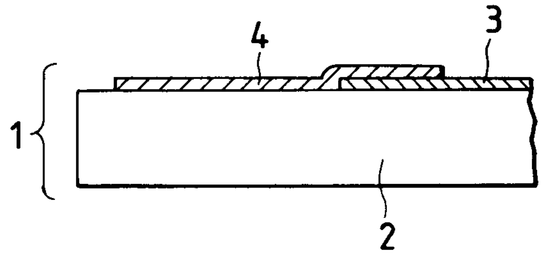


FIG. 19B

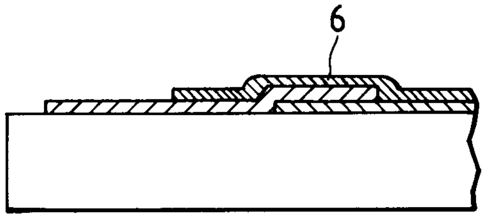


FIG. 19C

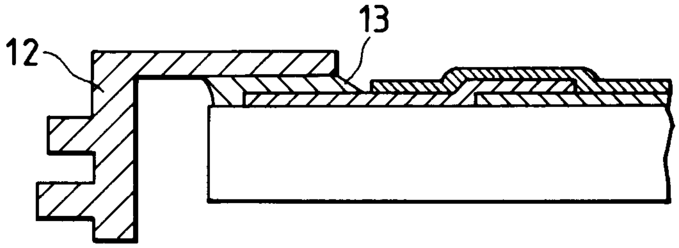


FIG. 19D

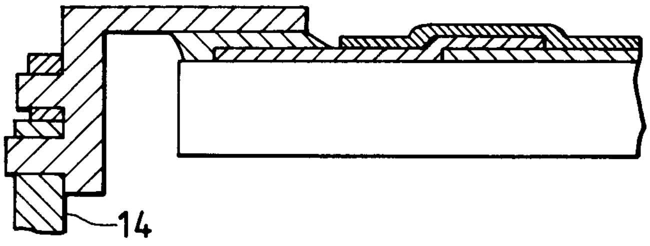


FIG. 19E

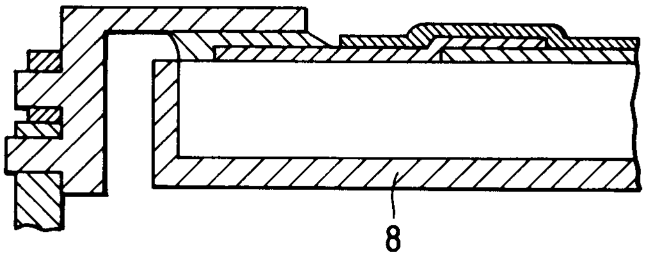


FIG. 20

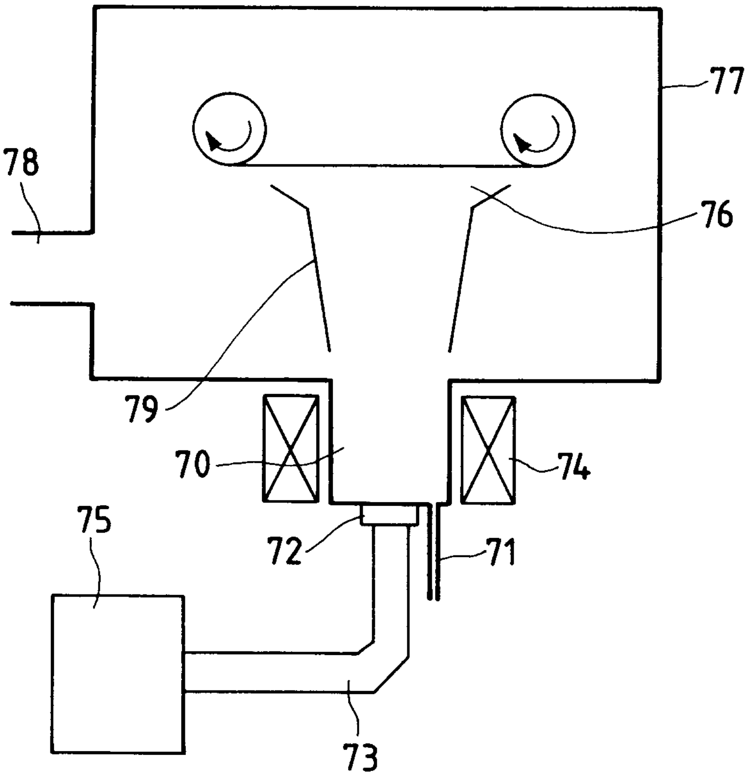


FIG. 21

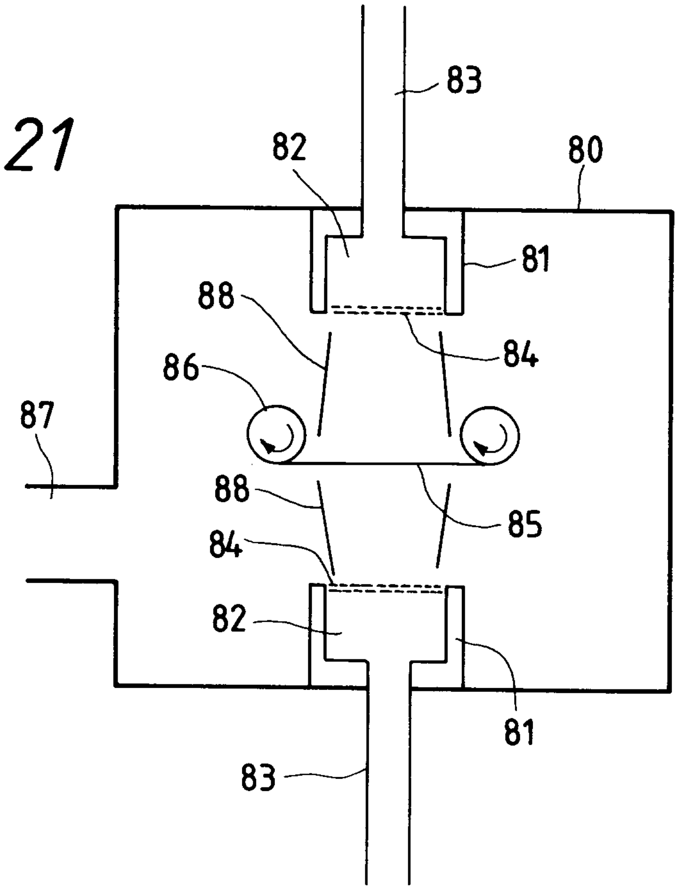


FIG. 22

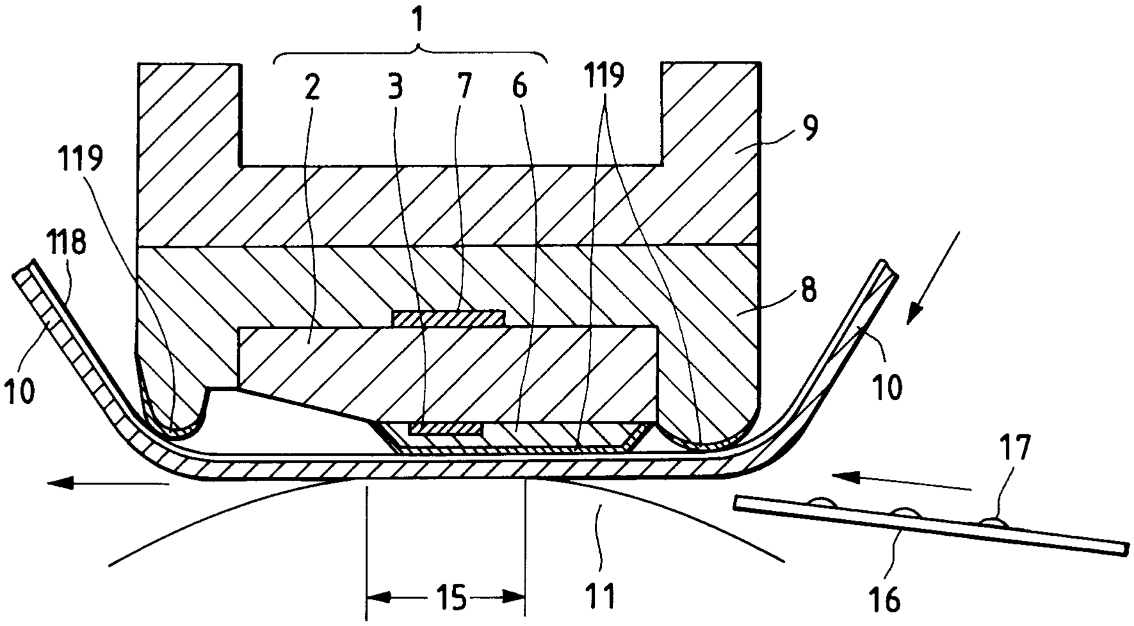


FIG. 23

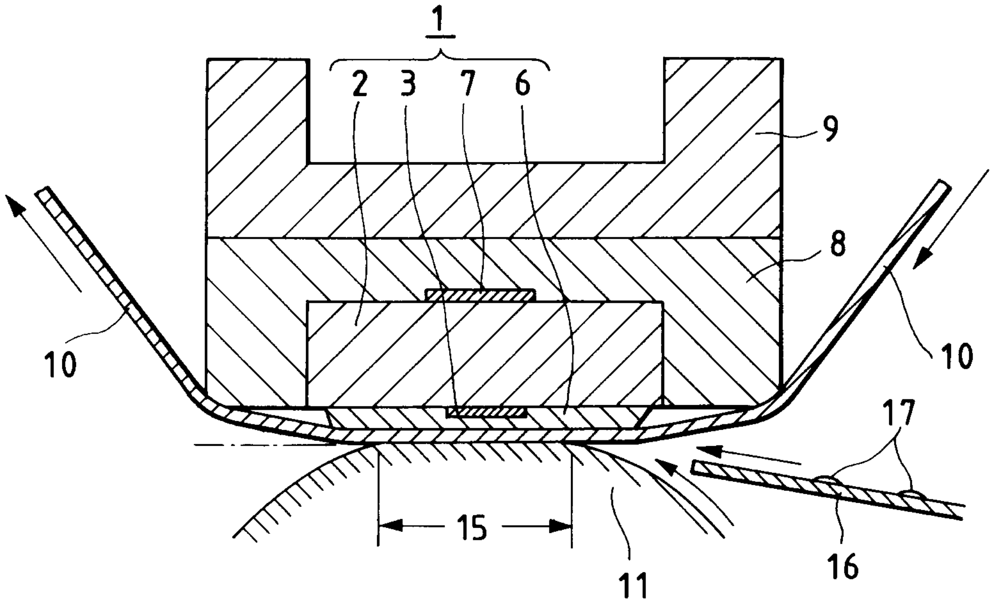


FIG. 24A

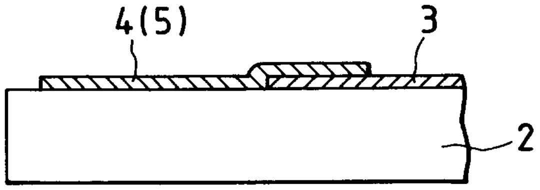


FIG. 24B

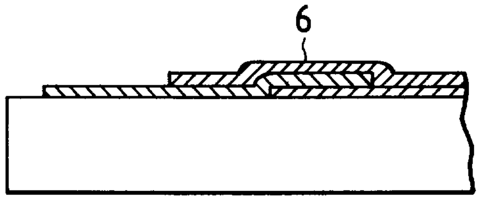


FIG. 24C

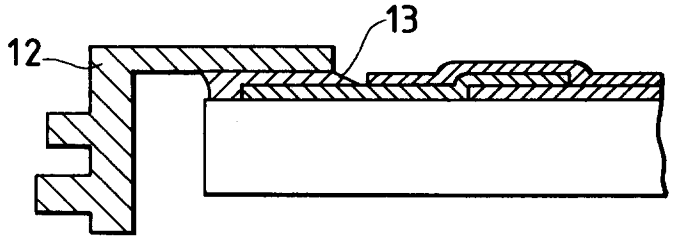


FIG. 24D

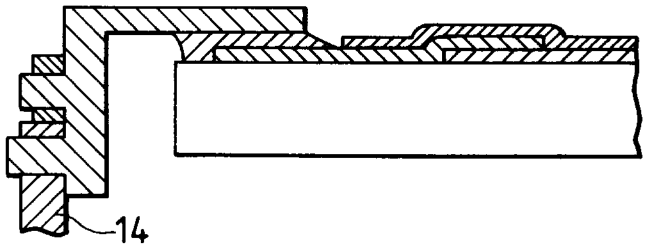


FIG. 24E

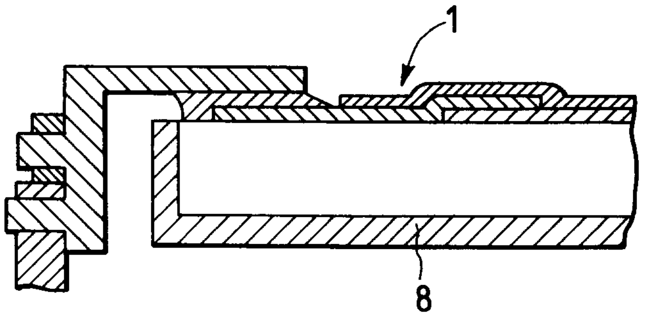


FIG. 25

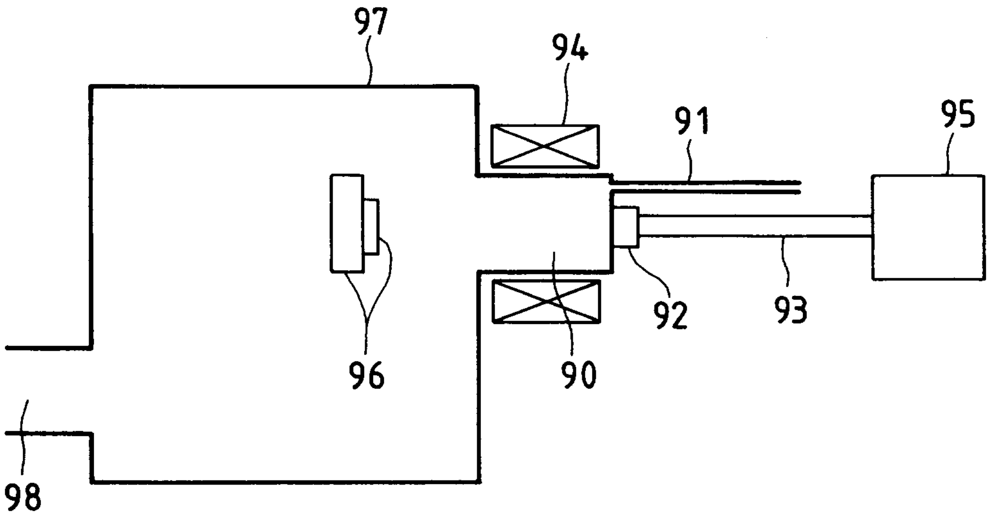


FIG. 26

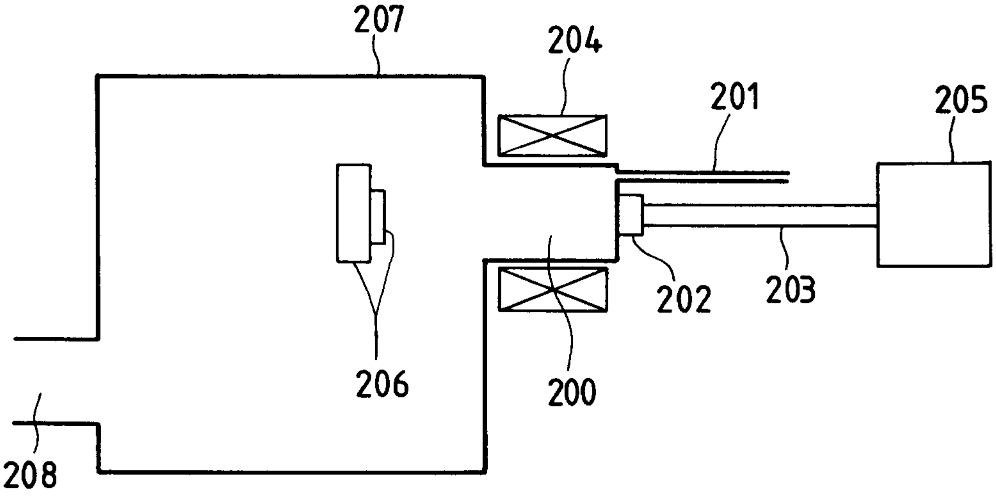


FIG. 27A

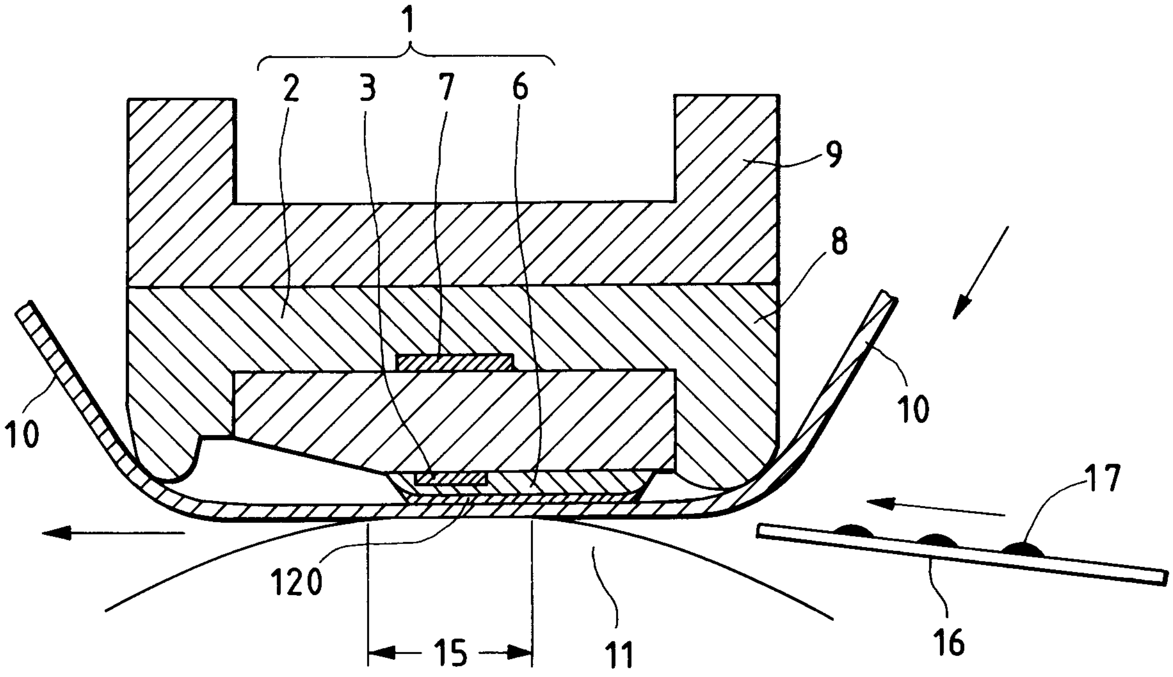
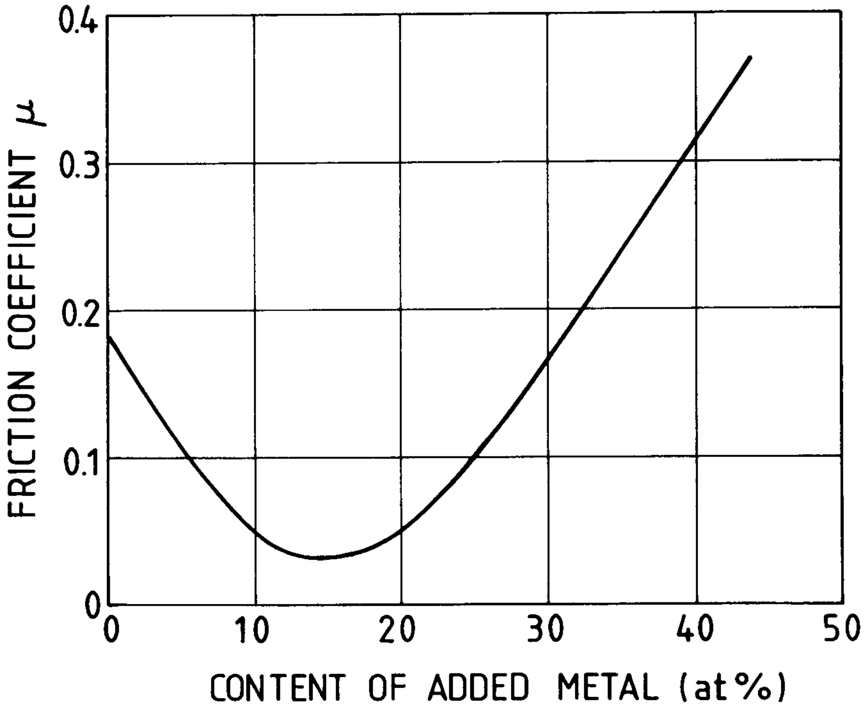


FIG. 27B



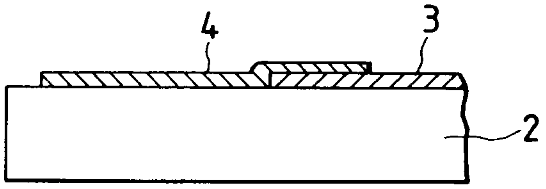


FIG. 28A

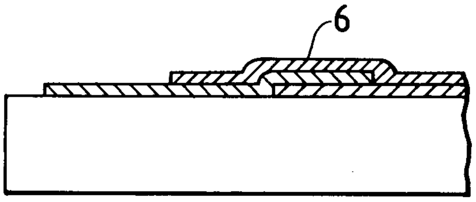


FIG. 28B

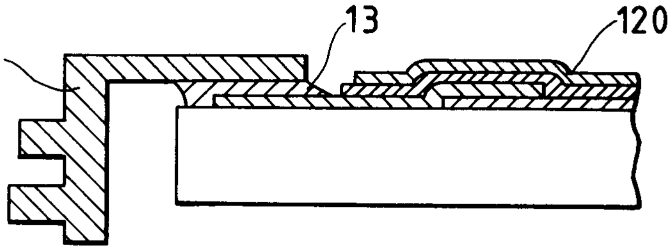


FIG. 28C

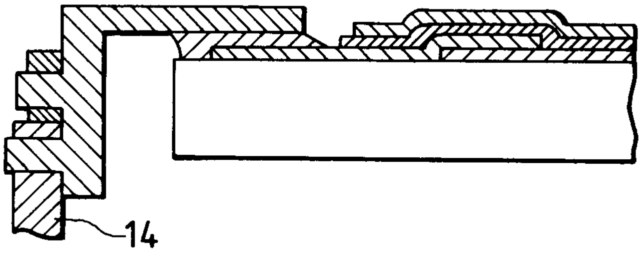


FIG. 28D

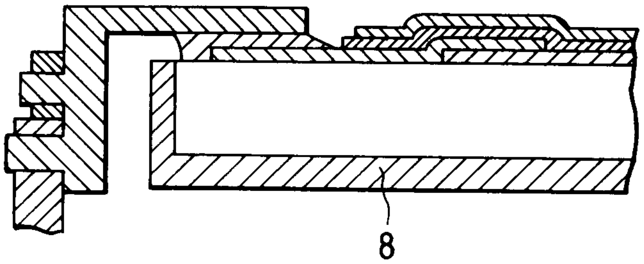


FIG. 28E

FIG. 29

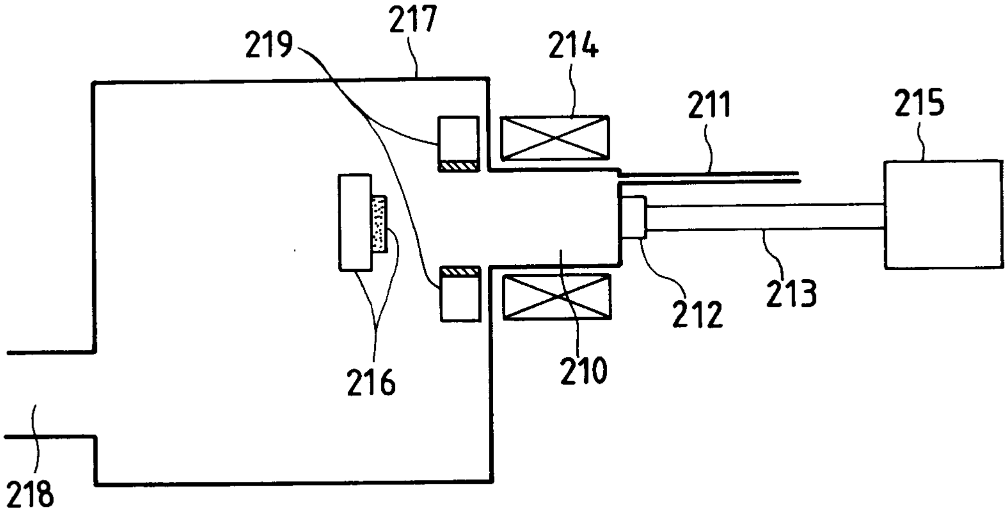

219
217
214
211
215
216
212
213
210
218

FIG. 30

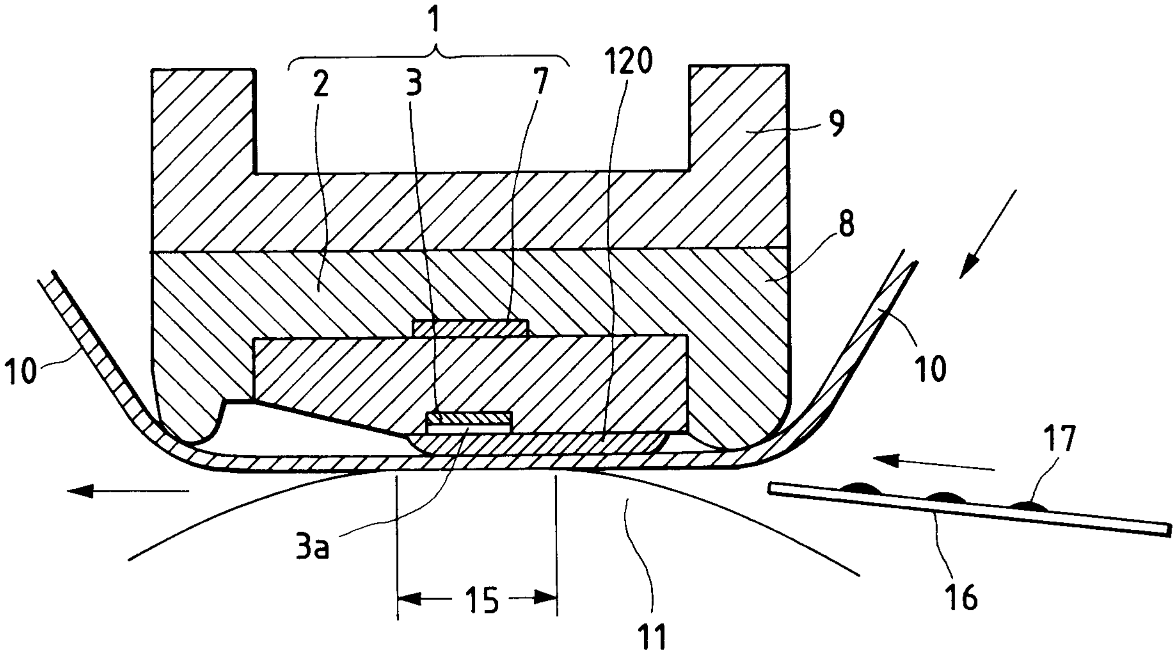

1
2
3
7
120
9
8
10
10
17
3a
15
11
16

FIG. 31

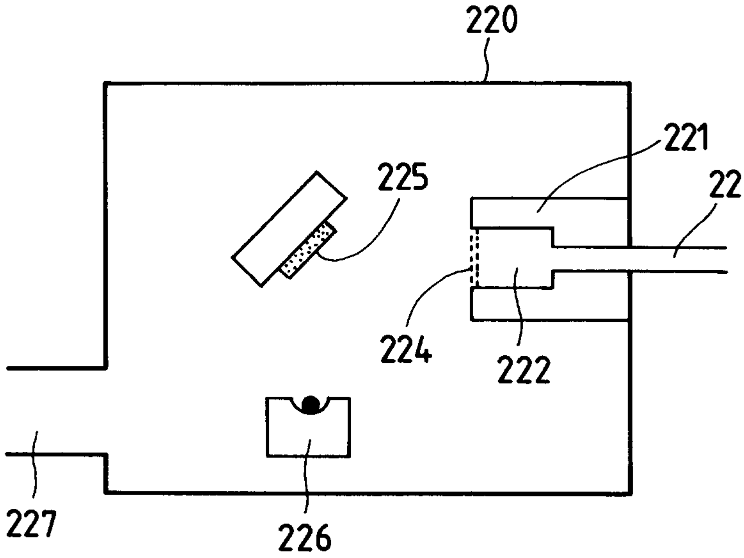


FIG. 32

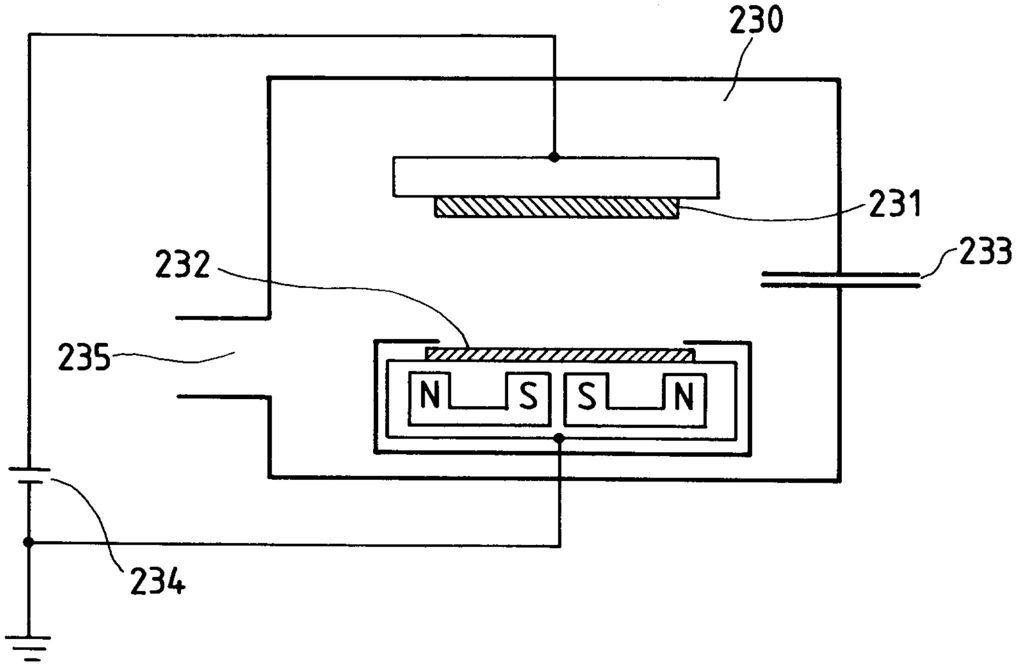


FIG. 33

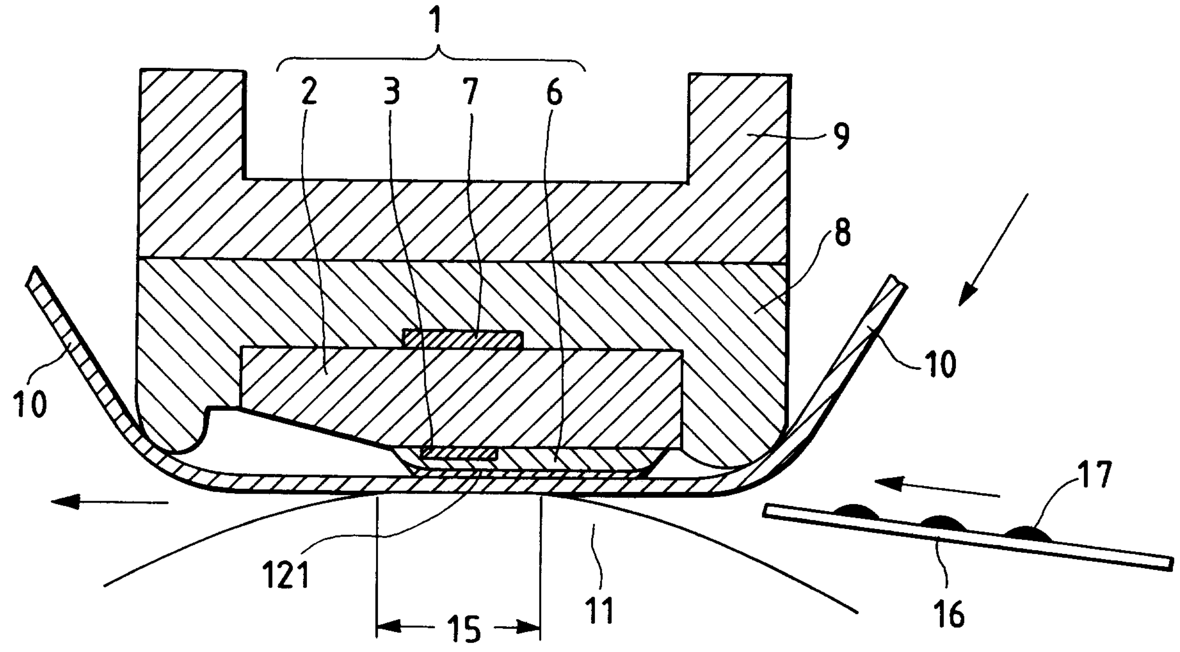


FIG. 35

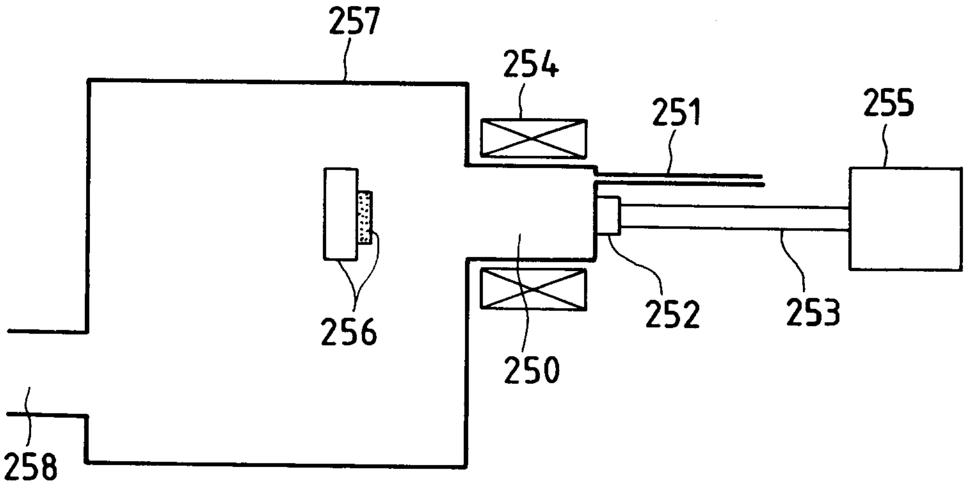


FIG. 34A

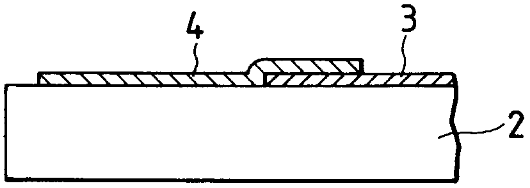


FIG. 34B

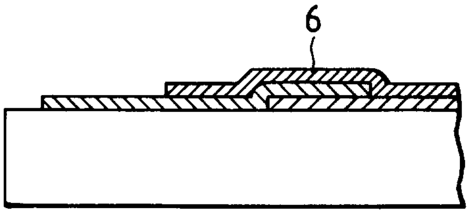


FIG. 34C

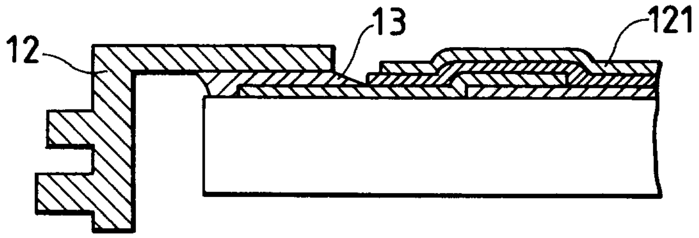


FIG. 34D

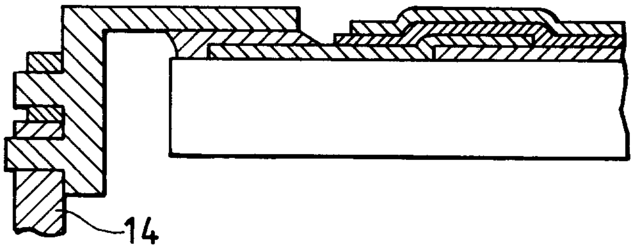


FIG. 34E

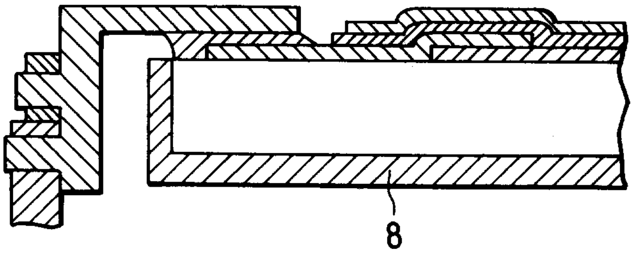


FIG. 36

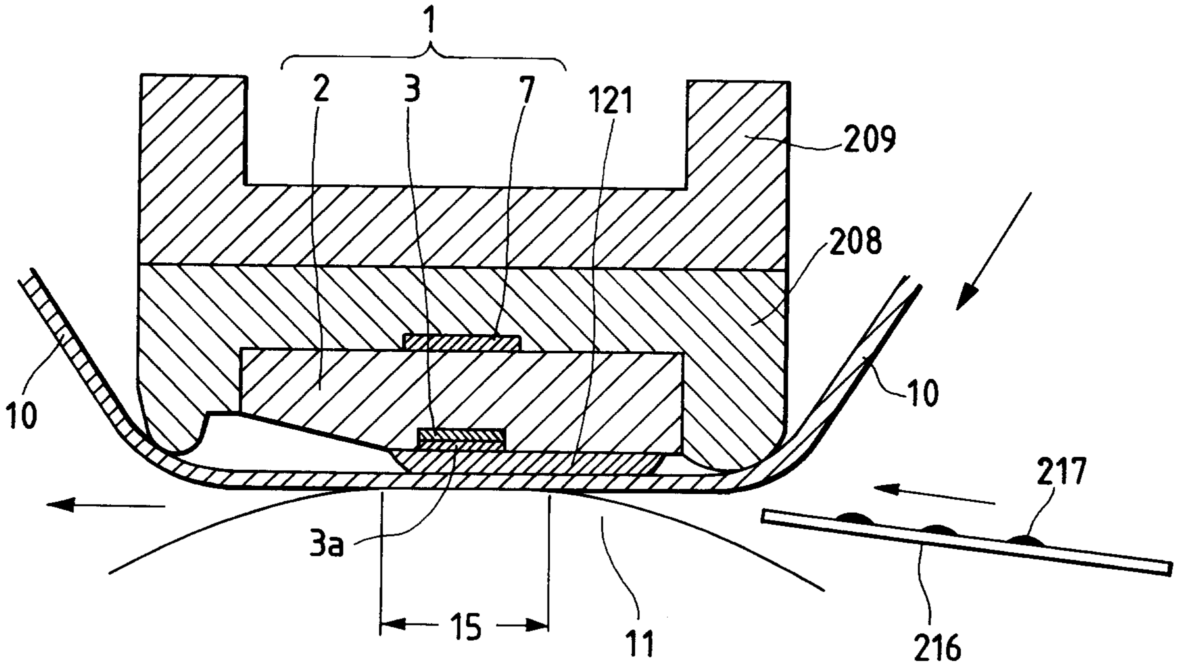

1
2
3
7
121
209
208
10
10
217
3a
15
11
216

FIG. 37

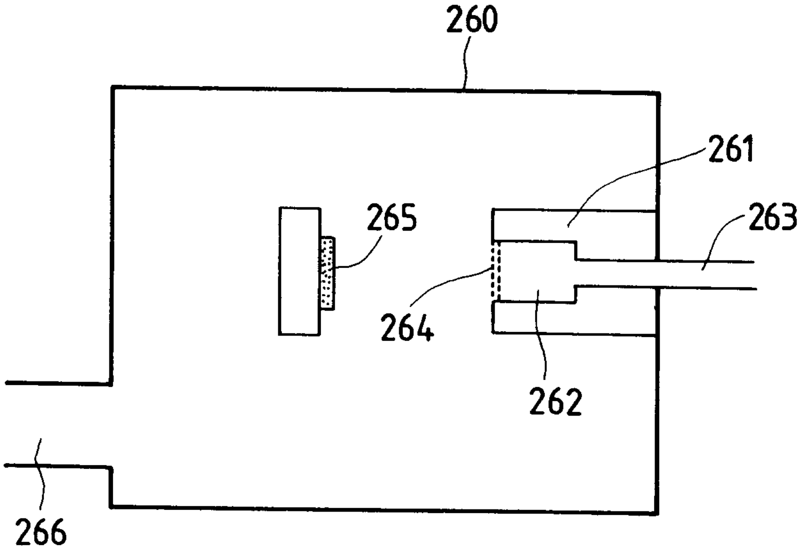

260
261
265
263
264
262
266

FIG. 38

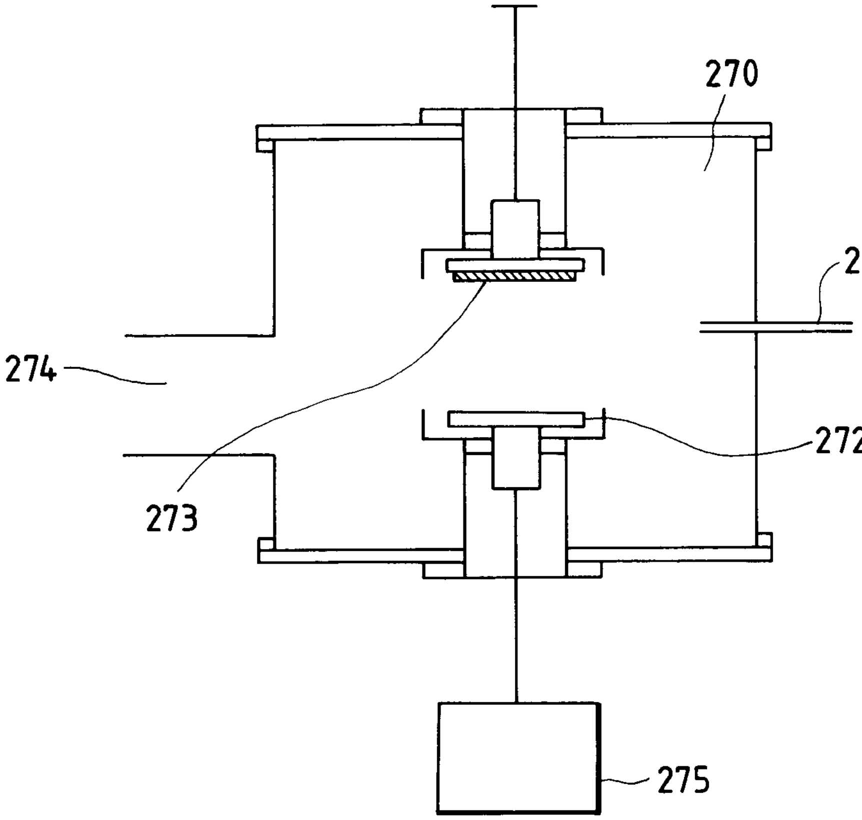


FIG. 39

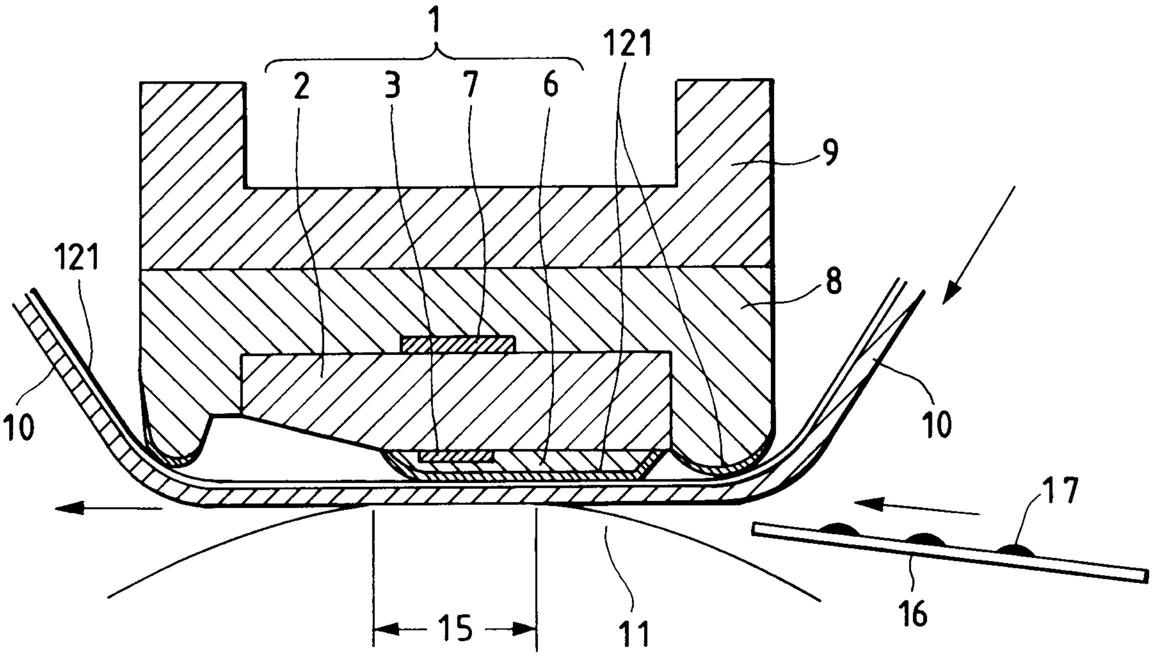


FIG. 40

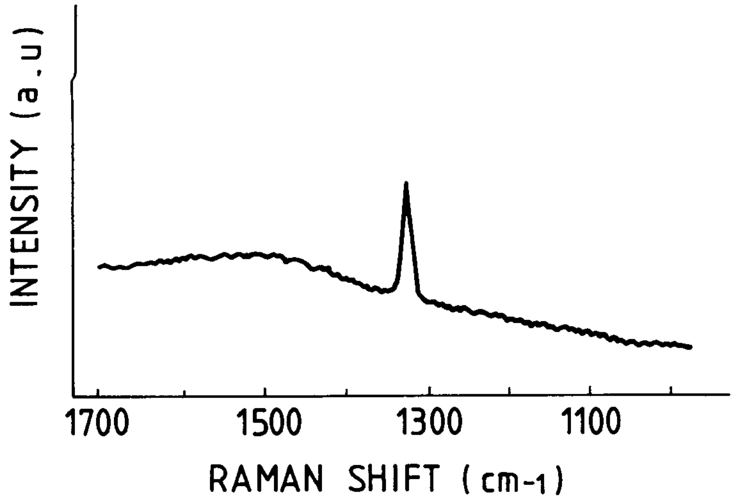
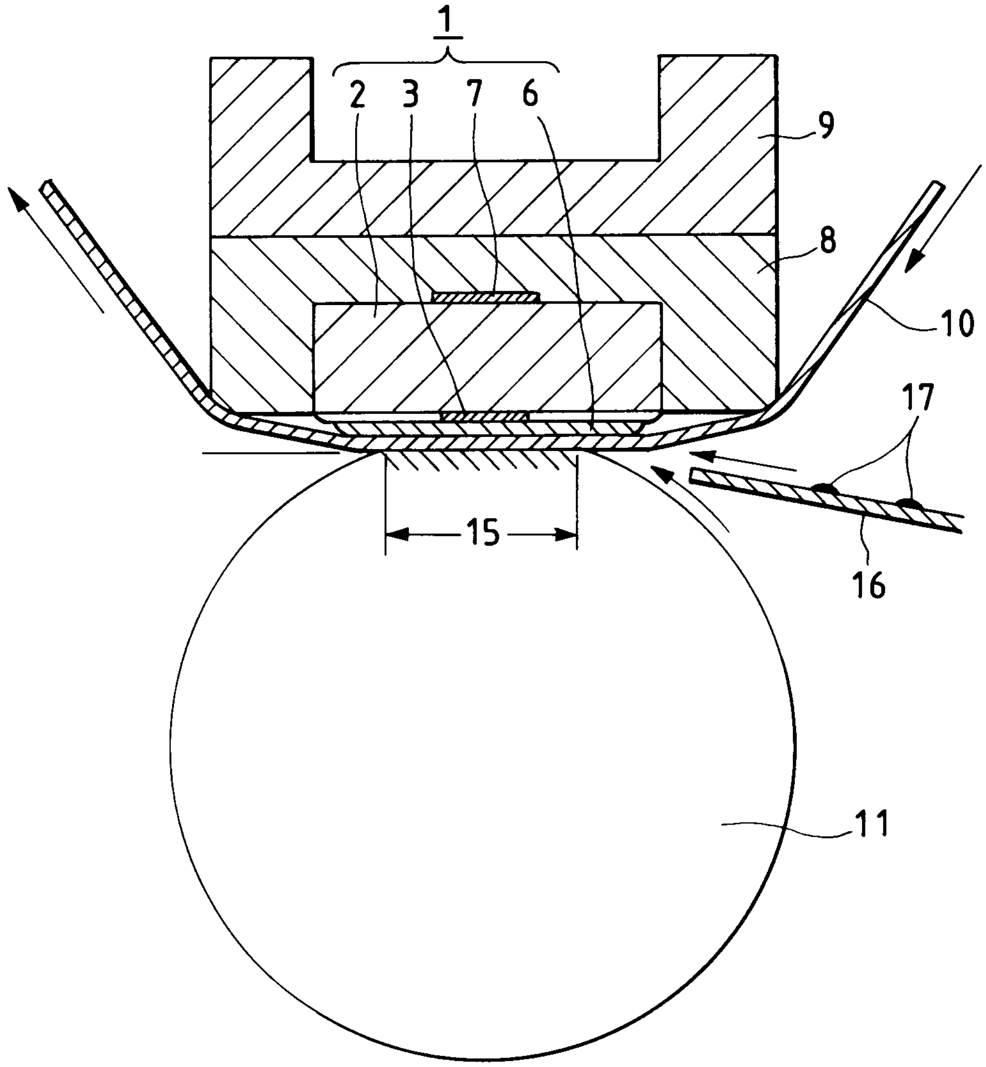

INTENSITY (a.u)
1700
1500
1300
1100
RAMAN SHIFT (cm-1)

FIG. 41


1
2
3
7
6
9
8
10
17
16
15
11

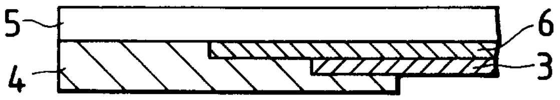


FIG. 42A

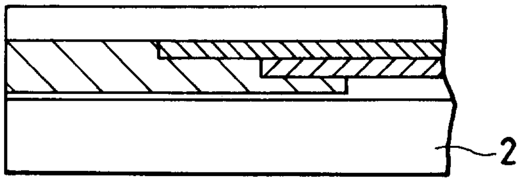


FIG. 42B

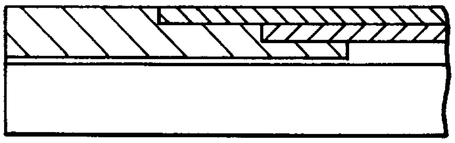


FIG. 42C

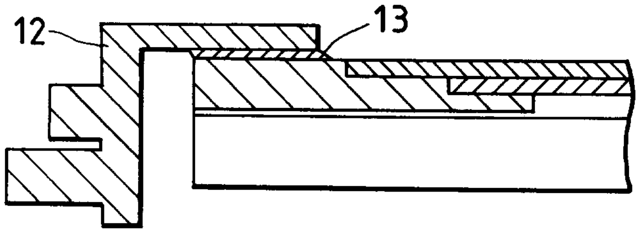


FIG. 42D

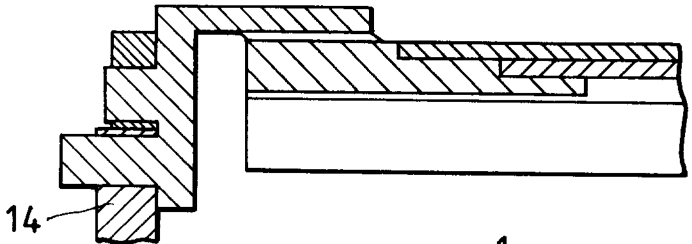


FIG. 42E

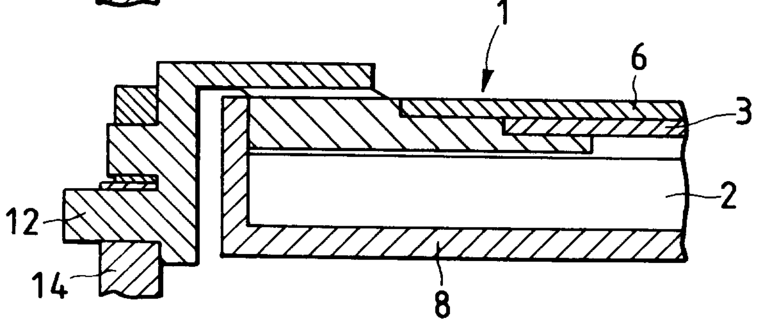


FIG. 42F

FIG. 43

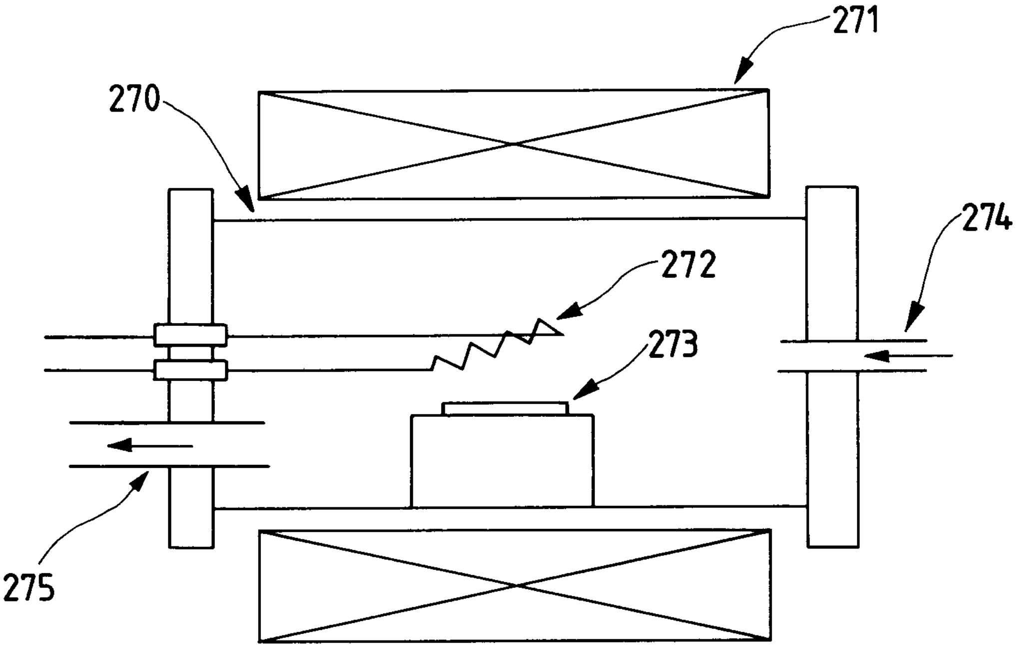


FIG. 44

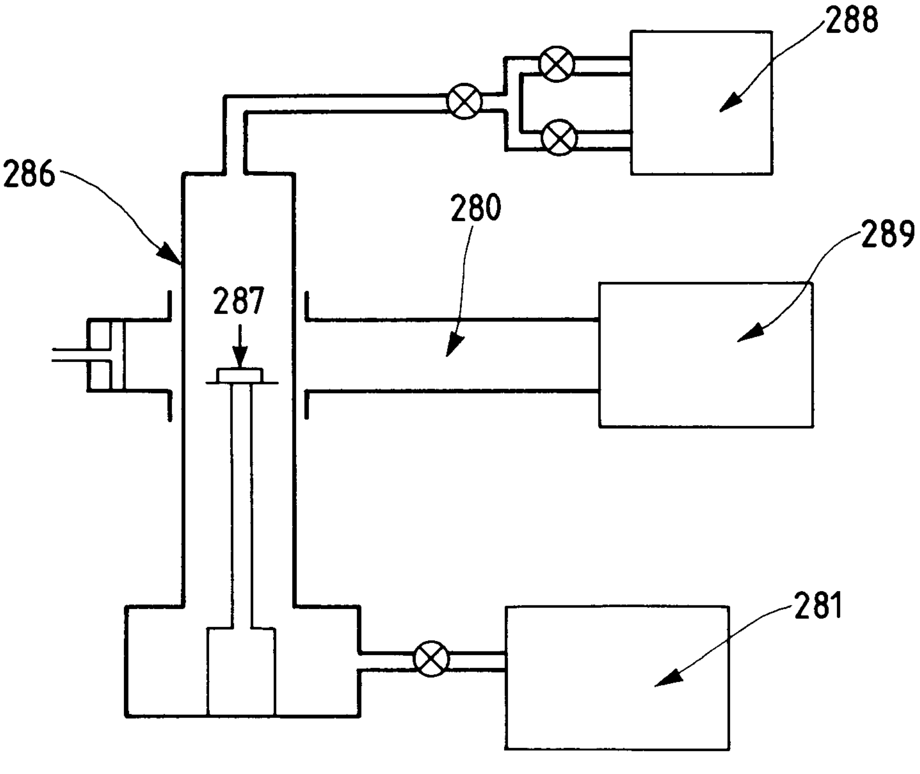


FIG. 45

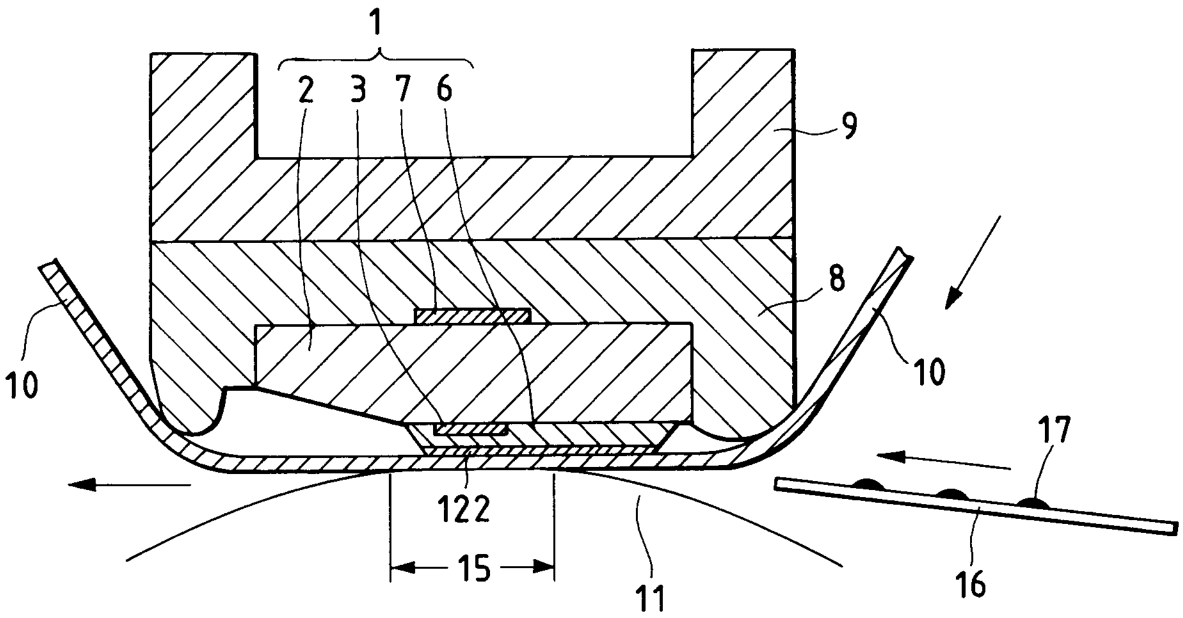


FIG. 47

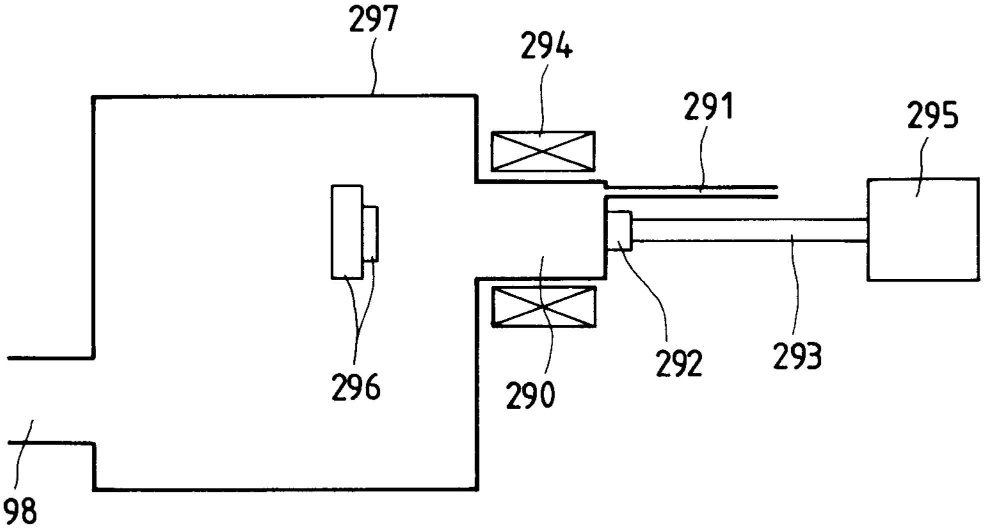


FIG. 46A

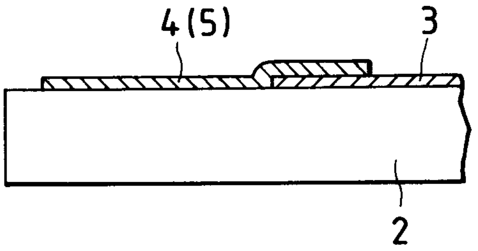


FIG. 46B

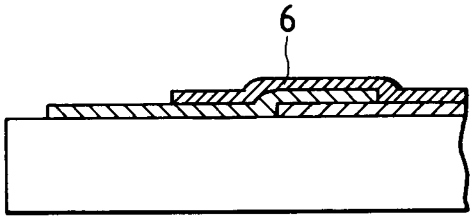


FIG. 46C

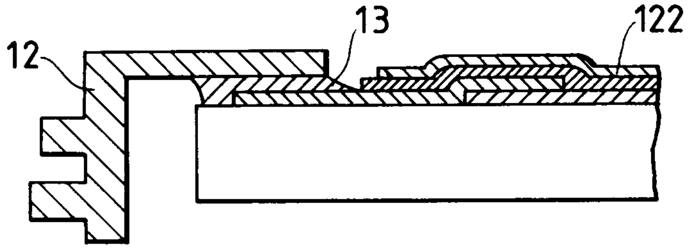


FIG. 46D

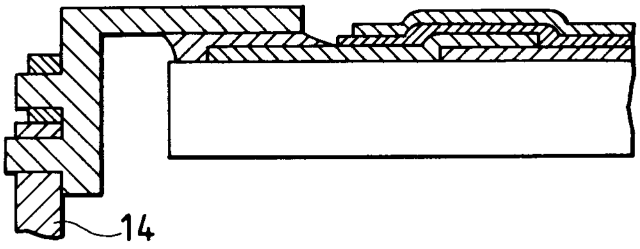


FIG. 46E

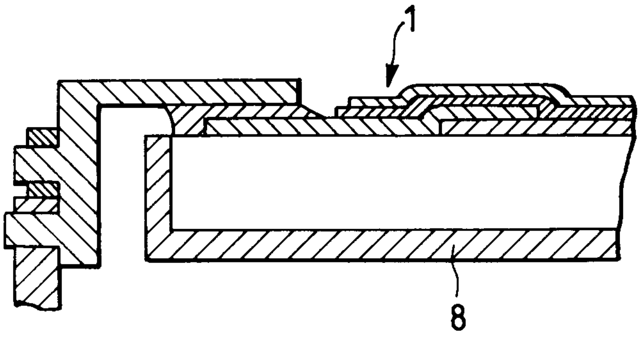


FIG. 48

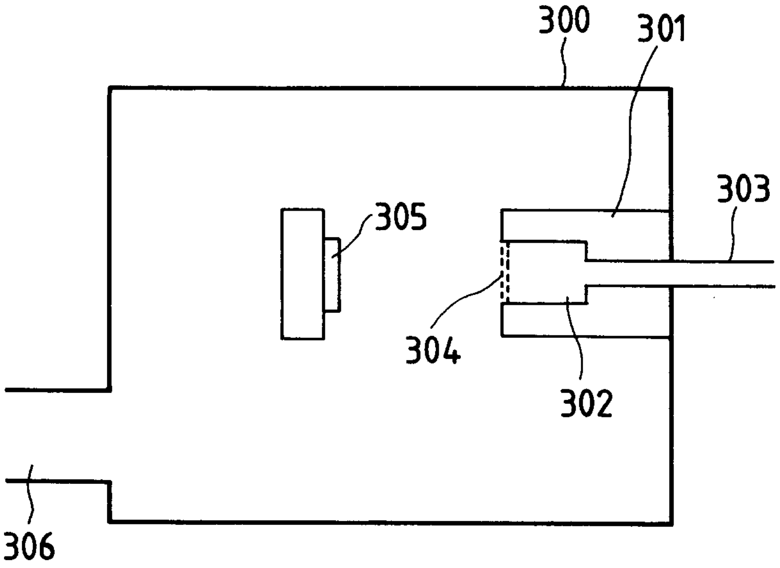


FIG. 49

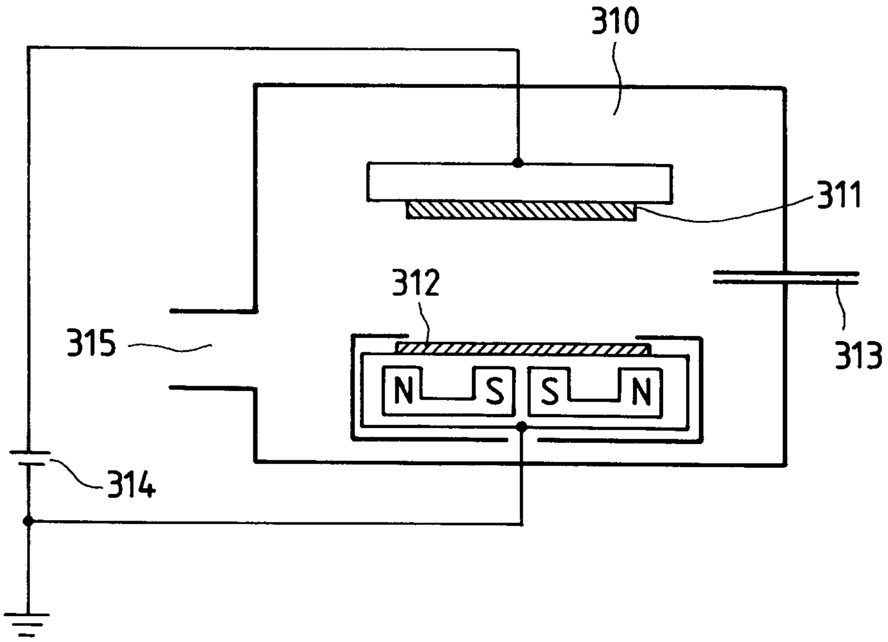


FIG. 50

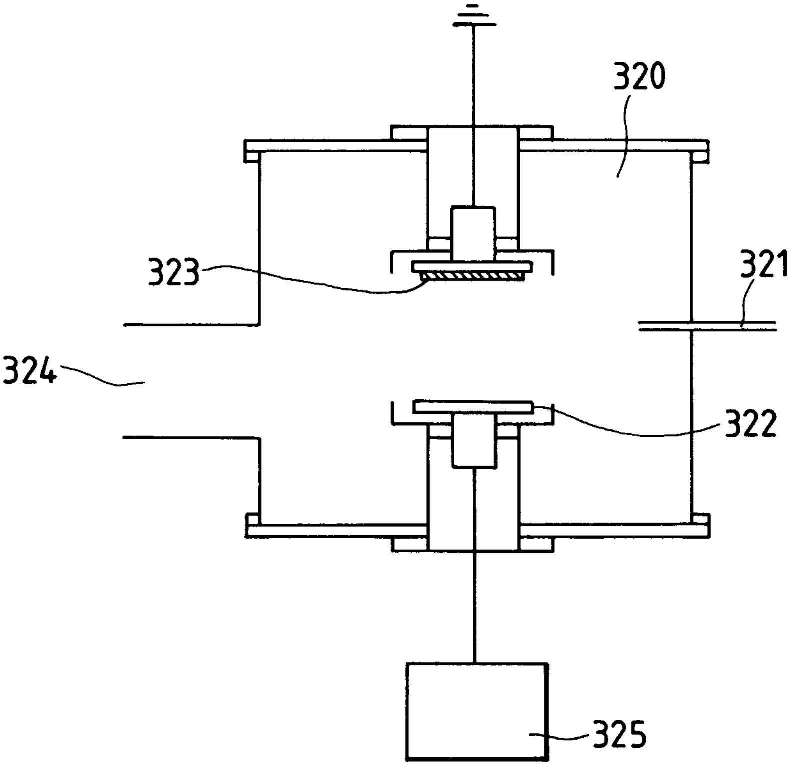


FIG. 51 PRIOR ART