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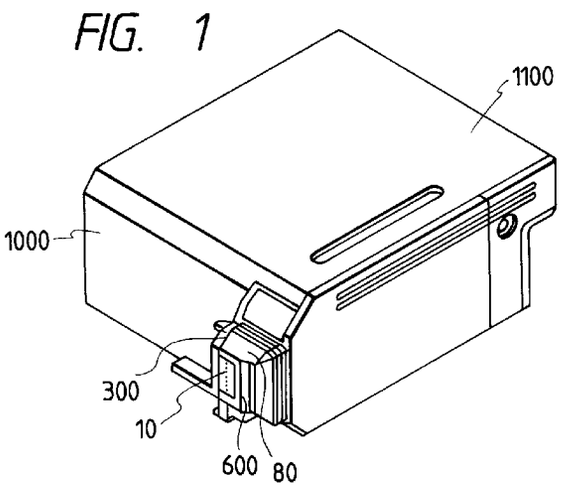
(54) Method for manufacturing an ink jet recording head and a recording head manufactured thereby.

(57) A method for manufacturing an ink jet head, which is provided with discharging ports, ink passes conductively connected to the discharging ports, and energy generating elements for generating energy to be utilized for discharging . ink, comprises the processes of giving hydrophilic property to the side of the discharging port formation plane of a work piece for constructing the discharging ports, forming an intermediate layer having a coupling agent containing Si on the plane to which the hydrophilic property is given, and forming a water repellence layer on the upper layer of the intermediate layer. Then, after machining the discharging ports by irradiating a pulse laser onto the plane of the discharging port formation member having the water repellence layer, the hydrophilic by-product generated in the vicinity of the discharging ports when the discharging ports are machined is removed to recover the water repellency around the discharging ports, thereby to enable the prevention of the adhesion of ink thereto. Hence preventing the degradation of the printing quality.

FIG. 1



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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an ink jet recording head and a method for manufacturing the recording head. More particularly, the invention relates to a recording head having a discharging port formation member (herein-after also referred to as "orifice plate") with discharging ports formed therein.

Related Background Art

As an example of the ink jet apparatus which discharges ink from its recording head to perform a desired recording, there is an ink jet recording apparatus which utilizes thermal energy to cause the state of ink to be changed and discharges ink by the pressure which is exerted at that time.

The head used for this apparatus has many numbers of discharging ports for discharging ink, ink passes connected to be respective discharging ports, and a common ink chamber which reservoirs ink to be supplied to the ink passes.

The recording head is formed by coupling a plate member called a discharging port plate with the discharging ports formed therein and the head main body in which the ink passes are arranged by positioning each of the ink passes and each of the discharging ports.

The discharging ports are formed in the discharging port plate by a perforative press or perforative etching or by utilizing a photosensitive resin.

However, it is quite difficult to enhance the precision with which the discharging ports and ink passes are positioned, and as they are coupled for the mounting, it is also difficult to improve the system reliability.

Accordingly, by integrating a grooved ceiling plate which constitutes the ink passes and the discharging port plate, an integrated member of the grooved ceiling plate and charging port plate is proposed to eliminate the complicated positioning of the ink passes and discharging ports.

Because of this integration of the discharging port plate and the grooved ceiling plate, the discharging port formation method hitherto adopted can no longer be employed. Therefore, a method for forming the discharging ports by utilizing a laser light is proposed by the applicant hereof. With such a method proposed anew, it is possible to produce all the discharging ports uniformly just by a one-time laser irradiation. Moreover, there is no need of the complicated positioning. Thus, with this method, the manufacturing process becomes easier and more suitable for a large scale production.

On the other hand, the surface of the discharging port plate should desirably be provided with ink repellency against the discharging ink. In , other words, the discharged ink adheres to the circumference of the discharging ports and remains solidified thereon or the discharging orientation of the discharged ink is deviated due to the aggregated ink around the discharging ports. A problem of the kind must be solved for an improved operation, thus necessitating the design of the ink repellency on the plate surface.

Therefore, the surface of the discharging port plate is formed with a water repellent material so that on the discharging port formation plane or at least around the discharging ports, the water repellency is provided. In other words, a water repellent resin is coated over the orifice plate. Then, the resin coating is hardend by a photo or thermal treatment to form a water repellent layer on the discharging port formation plane. Also, depending on the material to be used, a material layer is formed by evaporating by a thermal treatment the solvent which dissolves the particular material or the dispersion medium which disperses it to produce the water repellent layer on the face plane. In such a case of thermal treatment, heating is given at temperatures higher than the glass transition point Tg or fusion point Tmp. In some cases, the structure is arranged so that the discharging port formation member itself is produced by a material having a water repellency.

This water repellence treatment is performed as a preperatory process before the laser perforation to be given because there is a possibility that if the perforation process is given after this water repellence treatment, the water repellent agent used for the treatment is allowed to get into the discharging ports thus formed and clog them or change the diameter of the discharging ports.

Now, in this respect, there have been many proposals made more than ever, for example, in Japanese Patent Application Laid-Open No. 56-89569, Japanese Patent Application Laid-Open No. 62-55154, Japanese Patent Application Laid-Open No. 2-153744, and others to solve the above-mentioned problem by forming an ink repellent layer 20 at least along the circumferential portion of the orifice 14 by giving the so-called water repellence treatment. For the water repellent agents used for this water repellence treatment, silicon polymer or oligomer, or further, fluorine polymer or oligomer or many others can be named.

The water repellence treatment layer 20 to be formed for the ink jet recording head should be not only effective enough in the water repellency, but also good enough in the durability of the water repellence treatment

layer itself when a usual ink jet recording is performed. Otherwise, it cannot be employed in practice. Hereunder, the description will be made of its durability.

When the ink jet recording method is applied, the circumferential portion of the orifice is always in contact with the recording liquid even if the water repellence treatment is given to the circumferential portion of the orifice. Accordingly, the orifice surface is generally wiped by an abosobent such as polyurethane foam to absorb the ink which has adhered thereto as a normal recovery operation. Therefore, the water repellence treatment layer is required to have an abrasion resistance and other properties good enough to maintain its adhesiveness even if rubbed by the abosobent or not allow the layer to be damaged thereby. If this resistivity is not sufficient, the water repellence treatment layer is gradually ripped or dropped off to loose its water repelling effect while the head is in use although it works properly in the initial stage. As a result, a stable discharging printing can no longer be expected.

Meanwhile, however, if the rigidity of the water repellence treatment layer is extremely high and the adhesiveness to the circumferential portion of the orifice is low, the ripping is caused to occur at the interface of the water repellence treatment layer and the orifice circumferential portion.

For the durability thus required for the ink jet recording head, the water repellence treatment layers formed by the conventional water repellent agents have not been effective enough in some cases.

Moreover, in such a case where the members surrounding the orificies are made of different materials, it is necessary to prepare a water repellence treatment layer which has an excellent adhesiveness to any one of such different materials. In this particular point, the water repellence treatment layers formed by the conventional water repellent agents are found to be unsatisfactory in some cases.

For example, there has been proposed a water repellence treatment layer which is provided by a surface O_3(Ozone) treatment process as disclosed in Japanese Patent Application Laid-Open No. 61-141565. However, there is still a room for improvement with respect to its durability against wiping because the coupling between the O_3 treatment layer and the water repellence treatment layer can hardly be good enough.

Also, in Japanese Patent Application Laid-Open No. 61-291148, there is disclosed a water repellence treatment layer for which a fluorine coating is given after the treatment by a silane coupling agent. With this, however, the silane coupling agent is not strongly coupled to the surface of the processed component and the durability against wiping is still insufficient.

It is an object of the present invention to provide a manufacturing method for an ink jet recording head capable of maintaining a desirable ink discharging condition for an excellent printing quality by attaining a water repellency having an excellent durability against wiping as well as sufficient water repellent maintainability over a long period of time, and a head manufactured by such a method.

Now, the machining of the discharging ports by laser is performed in such a way that a laser beam is irradiated onto the orifice plate having the water repellency over its discharging port plane by the above-mentioned treatment, and then the discharging ports are formed. However, it is found in reviewing the manufacturing method for the ink jet recording head that when the discharging ports are formed on the orifice surface by the application of the laser beam, there occurs a phenomenon that a by-product due to the orifice machining adheres to the vicinity of the discharging ports.

In other words, when the laser beam is irradiated to remove the portion of the material where the discharging ports are formed, the material is dissolved and a part thereof becomes carbon, for example, and is deposited on the circumference of the irradiated portion. Using the ceiling plate thus prepared, the recording heads are fabricated. Then, various printing durability tests are conducted with the results that in some cases, the aforesaid carbon layer is striped off the ceiling plate to fly, and eventually, the discharging ports are clogged by the carbon particles to cause the defective discharging or disabled discharging, leading to defective printings.

Further, a part of carbon is also deposited on the circumferential portion which should become the discharging ports, and it is observed that when printings are performed under such circumstances, the following problem is encountered.

If a deposited substance such as mentioned above is present on the surface of the discharging port plate, the physical property of the portion where such substance is deposited and where it is not deposited, particularly the wetting condition with respect to ink, is caused to change. Generally, the surface of the discharging port plate should desirably be even so that unnecessary ink puddles are not present thereon. Despite this consideration, the ink puddles exist in the circumference of the discharging ports where the deposit substance ispresent in the recording head processed by the laser machining. Because of an ink puddle of the kind, the flying orientation is not stable liquidly, which makes it impossible to perform a desirable printing. Also, if the ink puddles become great, the droplet discharging becomes disabled to cause the recording to be discontinued eventually.

SUMMARY OF THE INVENTION

It is an object of the present invention to solve the above-mentioned problems and obtain a highly reliable recording head having no ink puddles on the surface of the discharging port plate by removing the carbon layer completely in order to avoid any clogging up of the discharging ports by the carbon particles.

It is another object of the present invention to provide means to contribute to a further improvement of the recording quality of a recording head.

In a manufacturing method for an ink jet head having discharging ports, ink passes connected to the discharging ports, and energy generating members arranged in the ink passes to generate the energy which is utilized for discharging ink, it is still another object of the present invention to solve the above-mentioned problem and provide a manufacturing method for a head including the steps of processes to give a hydrophilic property to the discharging port formation surface side of the workpiece which constitures the discharging ports and to produce a water repellence layer which gives a water repellency to the upper layer of the intermediate layer.

Also, in a manufacturing method for an ink jet head having discharging ports, ink passes connected to the discharging ports, and energy generating members arranged in the ink passes to generate the energy which is utilized for discharging ink, it is still another object of the present invention to provide a manufacturing method for a head including the steps of processes to give an oxidation treatment to the surface of the discharging port formation side of the workpiece which constitutes the discharging ports, to provide an intermediate layer having a coupling agent containing Si on the oxidized surface of the discharging port formation side, and to provide a layer having a polymer containing a fluorine-containing heterocyclic structure in its principal chain on the upper layer of the aforesaid intermediate layer for giving a water repellency.

Further, in a manufacturing method for an ink jet head having discharging ports, ink passes connected to the discharging ports, and energy generating members arranged in the ink passes to generate the energy which is utilized for discharging ink, it is a further object of the present invention to provide a manufacturing method for a head including the steps of processes to give an oxidation treatment to the surface of the discharging port formation side of the workpiece which constitutes the discharging ports, to provide an intermediate layer containing an organometallic compound on the oxidized surface of the discharging port formation side, and to provide a layer having a polymer containing a fluorine-containing heterocyclic structure in its principal chain on the upper layer of the aforesaid intermediate layer for giving a water repellency.

Furthermore, in a manufacturing method for an ink jet head having discharging ports, ink passes connected to the discharging ports, and energy generating members arranged in the ink passes to generate the energy which is utilized for discharging ink, it is also another object of the present invention to provide a manufacturing method for a head including the steps of processes to give an oxidation treatment to the surface of the discharging port formation side of the workpiece which constitutes the discharging ports, to provide an intermediate layer having an aluminum resin on the oxidized surface of the discharging port formation side, and to provide a layer having a polymer containing a fluorine-containing thermal plastic resin in its principal chain on the upper layer of the aforesaid intermediate layer for giving a water repellency.

Also, in a manufacturing method for an ink jet head having discharging ports, ink passes connected to the discharging ports, and energy generating members arranged in the ink passes to generate the energy which is utilized for discharging ink, it is still another object of the present invention to provide a manufacturing method for a head including the steps of processes to give an oxidation treatment to the surface of the discharging port formation side of the workpiece which constitutes the discharging ports, to provide an intermediate layer having an aluminum hardening resin on the oxidized surface of the discharging port formation side, and to provide a layer having a polymer containing a fluorine-containing thermal plastic resin in its principal chain on the upper layer of the aforesaid intermediate layer for giving a water repellency.

With a preparatory process given to a water repellent material with respect to the basic member, the adhesiveness is enhanced to secure a long-time stability of the water repellency, thereby to attain a better durability against the cleaning performed by a blade or the like for the improvement of the discharging characteristics.

The present invention is designed to solve the above-mentioned problems present in the conventional art, and it is an object thereof to provide a recording head capable of preventing the degradation of the printing quality and a manufacturing method therefor in such a manner that subsequent to having performed an orifice machining by irradiating a pulse laser onto the orifice plate which has a water repellence layer on its discharging port surface or which is itself composed of a water repellent agent, the by-product having strong hydrophilic property, which has deposited adhesively on the vicinity of the orifice, are removed or a predetermined process is given thereto in order to recover the water repellency around the orifice, thus preventing the ink adhesion to the vicinity of the orifice.

To achieve this in an ink jet recording head having an orifice plate, it is an object of the present invention to provide a head having a recovered water repellency in the vicinity of the orifice by giving the following treat-

ments to the orifice plate which has a water repellence layer on its discharging port surface or the orifice plate which is composed itself of a water repellent material after having removed the by-product adhesively deposited on the vicinity of the discharging ports when they are machined by irradiating a pulse laser or for an orifice plate having the by-product part adhesively deposited on the circumference of the discharging ports when the discharging ports are machined:

1) heating process treatment
2) cleaning process by ultrasonic
3) cleaning by ultrasonic water flow
4) cleaning by high pressure water flow
5) repeated application and removal of tapes having adhesive layer
6) plural combinations of the above treatments, and others

With the structure mentioned above, it is possible to obtain a recording head capable of preventing the degradation of the printing quality by the ink wetting around the discharging ports as well as of performing a stable printing despite a change with the passage of time by removing or changing the state of the hydrophilic part produced in the vicinity of the discharging ports as a result of the laser machining.

Particularly, when the heating treatment is given to the by-product generated at the time of the laser machining, there will result the enhancement of adhesiveness of the water repellence layer which is the base of the water repellent by-product, thus making it possible to obtain an ink jet recording head capable of performing stable printings notwithstanding a change with the passage of time.

In the manufacturing method for an ink jet recording head which can be obtained by machining perforation to an orifice plate portion of a ceiling plate formed integrally with a liquid chamber, flow passes, orifice surface (hereinafter referred to as orifice plate) so that the flow passes and the head are conductively connected, the present invention is designed on the basis of the knowledge that the prevention of the adhesion of the adhesives is possible in machining the orifice by the use of an assist gas blowing together with the irradiation of laser light when the discharging ports are machined.

The present invention is designed on the basis of the above-mentioned knowledge, and in the manufacturing method for an ink jet recording head provided with a substrate having energy generating elements for generating energy used for discharging ink, a ceiling plate having concavities for the formation of the ink passes in the locations where the aforesaid energy generating elements are arranged by coupling it to the aforesaid substrate, and a discharging port formation member formed discharging ports thereon for discharging ink by connecting them conductively with the aforesaid ink passes, it is an object of the present invention to provide a manufacturing method for a head which forms the aforesaid discharging ports by providing processes to irradiate an excimer laser light and blow a helium gas for the aforesaid discharging port formation member.

Also in the manufacturing method for an ink jet re-recording head provided with a substrate having energy generating elements for generating energy used for discharging ink, a ceiling plate having concavities for the formation of the ink passes in the locations where the aforesaid energy generating elements are arranged by coupling it to the aforesaid substrate, and a discharging port formation member formed discharging ports thereon for discharging ink by connecting them conductively with the aforesaid ink passes, it is an object of the present invention to provide a manufacturing method for a head for which the aforesaid discharging ports are formed by providing the proccesses to irradiate an excimer laser light and blow an ionized air.

On the surface of the orifice of the orifice plate of the ceiling plate thus obtained by the above-mentioned means, no removals at the time of machining remain adhesively and there exist no ink puddles on the orifice plate, hence enabling a desired discharging of droplets.

In the manufacturing method for an ink jet recording head provided with a substrate having energy generating elements for generating energy used for discharging ink, a ceiling plate having concavities for the formation of the ink passes in the locations where the aforesaid energy generating elements are arranged by coupling it to the aforesaid substrate, and a discharging port formation member formed discharging ports thereon for discharging ink by connecting them conductively with the aforesaid ink passes, it is an object of the present invention to provide a manufacturing method for a head including the steps of processes to form a film at least on a part of the integral member produced by the aforesaid ceiling member and discharging port formation member, to form the aforesaid discharging ports by irradiating a laser light, and to remove the aforesaid film.

Here, the aforesaid ceiling plate has concavities for the formation of the aforesaid liquid passes, and it is possible to form the aforesaid discharging ports by irradiating an excimer laser light from the aforesaid concavity side.

Then, it is possible for the aforesaid part to include the location where the carbon adheres by the aforesaid discharging port formation process by the laser light.

Also, aforesaid film is made of a material having a liquid repellency, and the film made of such a material should be formed at least in the aforesaid location and in the circumference of the surface where the aforesaid

discharging ports are arranged. Then, in the aforesaid removal process, only the film in the aforesaid locations can be removed selectively.

According to the present invention, the deposition layer of the carbon generated by the irradiation of the excimer laser, for example, can be removed completely by providing the film removal process. Therefore, there is no dropping off of the carbon particles in using the recording head, thereby to make it possible to provide an ink jet head which satisfies a long-term reliability because there are no ink discharge and others affected by such a clogging caused thereby.

Also, it is possible to perform a liquid repellence treatment process in the circumference of the discharging ports simultaneously.

Also, in the manufacturing method for an ink jet recording head provided with discharging ports, ink passes connected conductively to the aforesaid discharging ports, energy generating elements arranged in the aforesaid ink passes for generating energy used for discharging ink, it is an object of the present invention to provide a manufacturing method for a head, comprising:

a process to give a hydrophilic property to the discharging port formation side of the workpiece which constitutes the aforesaid discharging ports;

a process to provide an intermediate layer having a coupling agent containg Si on the plane to which the aforesaid hydrophilic property is given;

a process to provide a water repellence layer for givining a water repellency to the upper layer of the aforesaid intermediate layer;

a process to form discharging ports by irradiating a pulse laser beam; and

a process to give a heat treatment to the by-product deposited adhesively on the circumference of the discharging ports at the time of the orifice machining or the orifice plate with the by-product which adhered to the circumference of the discharging ports thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view illustrating the external appearance of an ink jet recording head;

Fig. 2 is a schematic view illustrating the external appearance of a grooved ceiling plate integrally formed with a discharging port plate according to the present invention;

Fig. 3 is a view showing the state that the discharging ports are being formed on the ceiling plate by a laser beam machining;

Figs. 4A and 4B are a perspective view and a plan view schematically showing the durability tests performed for ink jet recording heads of the present embodimet and a comparison example, respectively;

Fig. 5 is a partial enlargement showing a state of the by-product adhesion immediately after a discharging port has been formed on the discharging port plate by the laser beam machining;

Fig. 6 is a partial enlargement showing a part of the discharging port plate subsequent to having completed the by-product removal process;

Fig. 7 is a diagram showing the characteristics of heating temperatures and times with respect to a heat treatment apparatus according to the present invention;

Fig. 8 is a schematic view showing an the gas discharging means provided at the time of laser beam machining;

Figs. 9A and 9B are cross-sectional side views showing the states of the coating layer of the grooved ceiling plate integrally formed with the discharging plate before and after a cleaning process, respectively;

Fig. 10 is a schematic view showing an example of the ceiling plate after machining when its coating layer is formed with a water repellent agent; and

Fig. 11 is a view schematically showing an ink jet recording apparatus in which a recording head of the present invention can be mounted.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, with conjunction to the accompanying drawings, the present invention will be described.

At first, the description will be made of the schematic structure of an ink jet head to which the present invention is applicable.

An ink jet recording head shown in Fig. 1 is provided with a recording head main body (not shown) which is structured by combining a ceiling plate having concavities (hereinafter referred to as grooves) constituting ink passes and a common liquid chamber, which is further formed integrally with an orifice plate 10, with a substrate (hereinafter referred to as heater board) on which electro-thermal converting elements (hereinafter referred to as discharging heater) and Al wirings for supplying electric signals to the discharging heaters are , formed

on an Si substrate.

Also, in Fig. 1, a reference numeral 600 designates a sub-ink tank which is arranged adjacent to the recording head main body. This sub-ink tank 600 and the aforesaid main body are supported by a cover 300. Further, reference numeral 1,000 designates a cartridge main body and 1,100, a covering member of the cartridge main body. In the inside of the cartridge main body, an ink tank is incorporated to supply ink to the sub-ink tank 600 appropriately.

Fig. 2 is a view schematically showing a structural example of the grooved ceiling plate integrally formed with a discharging plate (hereinafter referred simply to as ceiling plate in some cases) 7 which constitutes the aforesaid head.

The ceiling plate 7 according to the present example has ink pass grooves 14 and ink discharging ports 11 formed on an orifice plate 10 corresponding to the ink pass grooves in a number as desired (in Fig. 2, two pieces being shown for simplification), and is structured with a discharging port plate 10 which is integrally arranged with the ceiling plate.

Then, in the structural example shown in Fig. 2, the ceiling plate 7 is molded integrally with the orifice plate 10 simultaneously in a metallic mold using a resin having an excellent ink resistivity such as polysulfone, polyether sulfone, polyphenylene oxide, and polypropylene.

Now, the description will be made of a method for forming the ink pass grooves 14 and orifice 11. For the ink pass grooves, it is possible to form the liquid pass grooves 14 by a resin which is formed by a method using a technique to cut the fine grooves having a pattern opposite to the ink pass grooves or the like, thus enabling the formation of the liquid pass grooves 14 on the ceiling plate 7.

The discharging ports on the orifice plate of the ceiling plate 7 can be formed as given below.

Fig. 3 illustrates a state where the orifice is being machined by irradiating an excimer laser light from the ink pass side to the orifice plate which is formed integrally with the ceiling plate, in which the same reference signs are given to the same elements appearing in Fig. 1. In Fig. 3, a reference numeral 1 designates a laser oscillator for oscillating KrF excimer laser light; 2, a pulse laser beam having a wavelength of 248 nm or 365 nm with a pulse width of approximately 15 nsec emitted from the laser oscillator 1; 3, a synthesized quarts lens for converging the laser beam 2; and 4, a projection mask which shields the laser beam 2 with a deposition of aluminum and constructs an orifice pattern with a plurality of holes of 133 μm diameter arranged at pitches of 212 μm.

Embodiment 1

Using the laser beam having a wavelength of 248 nm, a hydrophilic oxidation treatment layer is produced at least on the circumference of a portion where the orifice is expected to be formed on the ceiling plate having the aforesaid orifice plate by the oxidation using an oxidizing agent or by cleaning with UV/O_3 or the like.

Subsequently, this ceiling plate is dipped in an amino silane coupling agent (for example, AIII0γ - aminopropyl trimetoxylen: Nippon Unika -). Then, excessive silane coupling agent is removed in a pure water to form a single molecular layer of silane coupling agent on the orifice circumference uniformly.

Then, after an air drying, a water repellence treatment is given. For the water repellence treatment agent, there is used a dilution prepared by diluting the solution (5 weight %) of CTX-805A (Asahi Glass Inc.) and CTX-105A (Asahi Glass Inc.) by CT-Solve 100:CT-Solve 180 (boiling point being 100°C and 180°C respectively: this ceiling plate is dipped by Asahi Glass Inc.) in a ratio of 4 : 1. As to the density, while it is possible to adopt a range of 0.01 weight % to 5.0 weight %, particularly, the range of 0.1 to 0.7 weight % is best suited. As a method for coating the agent to the head, a brush coating, casting method, or the like can be adopted. Then, a thermal drying treatment is given for an hour at 150°C. Subsequently, a laser perforation is performed to form the discharging orifice, and a substrate having discharging pressure generating elements is bonded thereto adhesively. The head thus fabricated is prepared as sample 1.

As an example of the water repellent agent used for the present invention, a fluorine-containing heterocyclic agent can be named. The fluorine-containing heterocyclic structure means an organic substance of five to eight rings containing one to two heteroatoms in a chemical constitution formula. The heteroatoms are the atoms other than carbon (C). More specifically, oxygen (O), nitrogen (N), sulfur (S), phosphorus (P), and others are used. Particularly, oxygen (O) is suitably used from the viewpoint of its chemical stability and safety.

In the present invention, the fluorine-containing polymer having the heterocyclic structure should have a fluorine content ratio of 10 weight % or more from the viewpoint of the ink repellency (contact angle), and it should preferably be 25 weight % or more and further preferably be 50 weight % or more.

Also, the ratio of the cyclic structure in the principal chain should be 10% or more in consideration of the strength of an object film or its solvency to the solvent or from the viewpoint of its adhesiveness to the substrate or the like, and it should preferably be 20% or more and further preferably be 30% or more.

In the present invention, it is preferably to use particularly a noncrystalline polymer among the fluorine-containing polymers having the heterocyclic structure. The noncrystalline polymer is excellent in its film strength, adhesiveness to the substrate, film uniformity, and the like. Therefore, with this polymer, the effects of the present invention can be more prominently displayed.

As the fluorine-containing polymer having the heterocyclic structure in the principle chain in the present invention, it is preferable to use those disclosed in the specification of the U.S. Patent No. 3,418,302, the specification of the U.S. Patent No. 3,978,030, Japanese Patent LaidOpen Application No. 63-238111, Japanese Patent Laid-Open Application No. 63-238115, Japanese Patent Laid-Open Application No. 1-131214, Japanese Patent Laid-Open Application No. 1-131215, and others, for example.

Among the polymers having the heterocyclic structures mentioned above, those given below are typical ones. It is to be understood, however, that the contents of the present invention are not confined only to those mentioned here.

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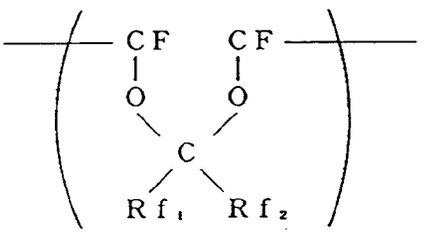

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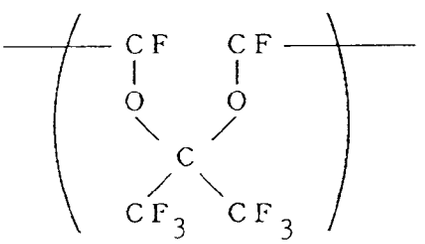

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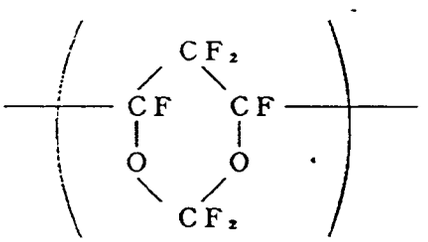

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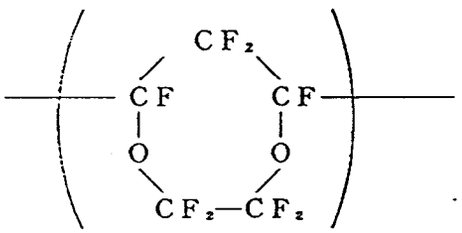

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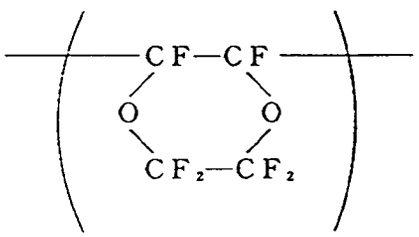
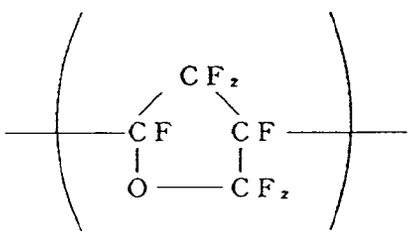
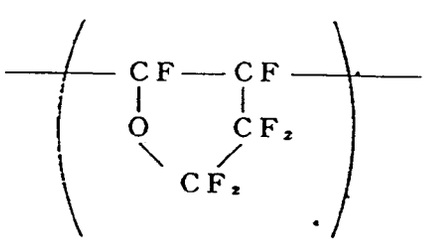


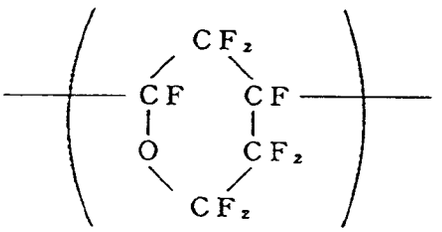
⑥



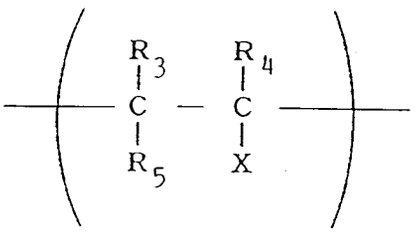
⑦



⑧



Futhermore, in order to enhance the adhesiveness to the substrate or to control the solubility to Tg and solution, it may be possible to introduce the following structure into the principal chain:



(where R_3, R_4, and R_5 are H, F, Cl, and Rf (fluorine-containing alkyl), and X is H, F, Cl, Rf_3, and Rf_4. However, Rf_3 is a fluorine-containing organic substituent having acid, ester, alcohol, amine, amide, and other functional group at its terminal Rf_4 is a fluorine-containing alkyl and fluorint-containing ether.) These constructions can be obtained by copolymerizing the comonomers given below.

$CF_2 = CF\text{-}O\text{-}CF_2CF(CF_3)\text{-}O\text{-}CF_2CF_2SO_2F$,

$CF_2 = CF\text{-}O\text{-}CF_2CF_2CF_2COOCH_3$,

$CF_2 = CF\text{-}CF_2CF(CF_3)\text{-}O\text{-}CF_2CF_2SO_2F$

Embodiment 2

In the embodiment 1, a head fabricated without cleaning in a pure water is prepared as sample 2.

Embodiment 3

In the embodiment 1, a head fabricated with the wavelength of laser being 365 nm is prepared as sample 3 .

Comparison example 1

An ink jet recording head is fabricated in the same manner as the first embodiment except that no treatment with silane coupling agent is performed. A head of the kind is prepared as sample 4.

Evaluation of durability

Friction durability tests are conducted as given below on the samples 1 through 4 of the ink jet recording heads fabricated in the embodiments 1, 2, and 3, and the comparison example 1.

Figs. 4A and 4B are a perspective view and a plan view to illustrate respectively such a friction durability testing briefly.

As shown in Figs. 4A and 4B, when a silicone rubber plate 21 structured in the same manner as a cleaning blade is caused to rotate by the rotation of a member 22, the surface treatment layer 20 of the ink jet recording head 1 is slidably rubbed by the silicone rubber plate 21 under a pressure of approximately $10g/cm^2$. Also, in order to condition the slidable rubbing as close as to the actual state in use, the ink droplets 25 of a water color ink are sprayed from an ink spraying device 24 over the portion slidably rubbed.

Using this apparatus, the durability test is conducted for 1,000 to 20,000 times with the frequency of the ink spraying being once in ten seconds. During this test, the head is removed each at 1,000, 5,000, 10,000, and 20,000 times of the slidable rubbings, and used for printing for the observation. The results are stated in Table 1. In this respect, each of the marks appearing in the Table 1 indicates the printing condition which has

been obtained, and a mark ○ shows desirable printing condition, △, ordinary printing condition, and X, inferior printing condition, respectively. The desirable or inferior printing condition is determined both by measuring the amount of the deviated dots from the impact points and an organoleptic test by eye-sight. The averaged evaluation for each of the samples tested is stated in Table 1.

Table 1

	Sample 1	Sample 2	Sample 3	Sample 4
1,000	○	○	○	○
5,000	○	○	○	X
10,000	○	△	○	—
20,000	○	△	○	—

○... desirable △ ... ordinary X ... inferior

As clear from the results shown in the Table 1, the recording head (Sample 4) fabricated by the comparison example 1 shows an inferior printing condition at 5,000 slidable rubbings. This is caused by the separation of the surface treatment layer. As compared with the sample 4, the heads (Samples 1, 2, and 3) fabricated by the embodiments 1, 2, and 3 show the desirable or ordinary printing conditions until 20,000 slidable rubbings. Particularly, as a result of the comparison among them, it is observed that the quality of the samples 1 and 3 is stable after 20,000 slidable rubbings because of the water treatment given to each of them.

In the present invention, it may be possible to attain a strong bonding state between the substrate and water repellent agent by providing a layer containing not only Si coupling agent as an intermediate layer but an organometallic compound, amine resin, amine hardening resin also as the intermediate layer.

On the grooved ceiling plate 7 formed integrally with the discharging port plate thus fabricated, the by-product generated by the laser perforation adheres to the circumference of the discharging ports. Now, hereunder, various methods for removing this by-product or removing any adverse effects produced thereby will be disclosed.

Embodiment 4 - Heating treatment method -

The grooved ceiling plate integrally formed with the discharging port plate, for which a water repellence treatment has been processed by the method shown in the embodiment 3, is mounted on a laser perforation apparatus shown in Fig. 3 (manufactured by L'Monix) to from discharging ports by irradiating a laser light of 365 nm (for two seconds) with 200 pulses per second.

There is shown in Fig. 5 a partial enlargement of the discharging port plate immediately after the formation of the discharging ports by the irradiation of the laser light. In Fig. 5, a reference numeral 2 designates an excimer laser beam; 10, an orifice plate; 6, a water repellence layer; 11, the dischanging opening formed by the discharging port machining device shown in Fig. 2; and 8, the by-product generated by the orifice machining, which has adhered to the vicinity of the discharging port. In the present embodiment, the incidence of the laser beam 2 is given to form the discharging opening 11 from the plane of the discharging port plate 10 where no water repellence layer has been provided.

The discharging plate with the adhesive deposition of the by-product on the vicinity of its discharging openings due to a discharging port machining of the kind is processed by heating under the conditions given below in order to obtain an optimal value of the heating treatment process.

The heating device used is a clean oven (Model No. Yamato DE-42). The heating temperatures are set at 90°C ± 2°C, 120°C±2°C, 150°C±2°C, and 170°C±2°C. The heating times are set for 0.5 hour, 1.0 hour, 2.0 hours, and 4.0 hours. After the treatment processes given in these combinations, the grooved ceiling plates integrally formed with the discharging port plate, which have been treated by the heating process, are immersed

in an ink of 60°C (for an extremely short period of time or only dropping of ink droplets (represented as initial), 40 hours, and 100 hours) and then the ink wetting conditions around the , discharging ports are observed by a metallurgical microscope. Here, seven samples are observed for each. The results are stated in Table 2 given below.

Table 2

Heating time \ Heating temperature	90°C			120°C			150°C		
	60°C ink immersion			60°C ink immersion			60°C ink immersion		
	Initial	After 40 hr	After 100 hr	Initial	After 40 hr	After 100 hr	Initial	After 40 hr	After 100 hr
0.5 h	○ △ × 0 0 7	○ △ × —	○ △ × —	○ △ × 4 3 0	○ △ × 0 1 6	○ △ × 0 0 7	○ △ × 7 0 0	○ △ × 3 4 0	○ △ × 0 3 4
1.0 h	0 0 7	—	—	6 1 0	0 0 7	0 0 6	7 0 0	6 1 0	0 5 2
2.0 h	0 0 7	—	—	7 0 0	0 4 3	0 0 7	7 0 0	5 2 0	0 3 4
4.0 h	0 0 7	—	—	6 1 0	0 4 3	0 0 7	7 0 0	4 2 0	0 3 3

In this respect, the mark ○ in the Table 2 indicates that there are no wetting phenomenon around the discharging ports; Δ, slight wetting around the discharging ports; and X, conspicuous wetting around the discharging ports, respectively. The numeral under each mark indicates the number ofthe samples showing the wetting phenomenon of the corresponding mark.

Here, in the heating treatment process at 170°C±2°C, the ink wetting phenomenon is almost equal to or better than the results obtained in observing those processed at 150°C±2°C. However, there are some samples which have been deformed because the grooved ceiling plate integrally formed with the discharging plate is made of a polysulfone whose fusing point is 180°C.

Accordingly, an experiment to ascertain the upper limit of the heating temperature is conducted under the heating condition given to 170°C by raising the temperatures from 150°C by 5°C each. Then, until 165°C, the samples have been obtained without any essential problems.

It is therefore preferable to set the heating treatment temperature between 120°C or more and 165°C or less or more preferably between 140°C or more and 165°C or less.

In the present embodiment, 150°C can be selected as a most preferable temperature which produces no adverse effect on polysulfone. Here, this temperature depends on the material of the head and water repellent agent to be used. Hence, the heating temperature is arbitrarily selective by the materials to be used.

For the heating time, however, a sufficient effect is obtainable if only it is more than one hour. The upper limit of the heating hour in the present embodiment is four hours, which is considered long enough, but it may be possible to make it longer.

Here, in the actual manufacturing process, there are the rising time and falling time for the temperature of the heating oven. As a result, the grooved ceiling plate formed integrally with the discharging port plate should be left in the oven for eight hours to twelve hours. However, the temperature control must be carried out so that the ceiling plate is held for more than one hour at least at the optimal temperature of 150°C.

In other words, in the actual manufacturing process, the oven which presents a temperature curve as shown in Fig. 7 is adopted in condition that the heating temperature is set at 150°C±2°C for the heating time being one hour (at H in Fig. 7) with the oven temperature being at 153°C, and during the heating, the N_2 flow rate is set for 20 l/min. In this respect, the material should be removed from the oven after the temperature is lowered to 80°C or less.

In a heating treatment process such as the present embodiment, the water repellent agent is affected by the added heat to become fluid. Thus, it runs out to cover the by-product generated by the laser perforation, and eventually, the plate surface is entirely covered by the water repellent agent. In this way, it is possible to produce the grooved ceiling plate formed integrally with the discharging plate having a desirable water repellency.

Embodiment 5

Now, an example of a cleaning by ultrasonic in a water will be disclosed.

As described earlier, subsequent to the machining of the discharging ports by the discharging port machining device, a ultrasonic cleaning is given to the orifice plate having the adhesively adhering by-product on the circumference of the discharging ports. For the discharging port plate 10, a polyether sulfone film is used. Also, as the water repellent agent, KP801 (Product name: Shinetsu Kagaku Inc.) is used to coat the discharging port plate 10. Then, the heating treatment process is given at 150°C for one hour to form the water repellence layer 6. To the discharging port plate 10 with the water repellence layer 6 thus formed, a KrF excimer later beam is irradiated from the plane opposite to the plane where the water repellence layer 6 has been formed. Hence, the discharging ports 11 are formed. Then, the ultrasonic cleaning is given in a water to the discharging port plate 10 with the discharging ports 11 thus formed. In this way, the by-product 8 generated at the time of orifice machining is almost removed.

The orifice is machined as above. Then, the ink jet recording head is fabricated with the orifice plate, the by-product deposited on which has been removed, and is mounted on a printer for the observation of the discharging droplets as well as for the recording onto a recording sheet. As a result, it is found that the discharging orientation of the flying droplets is stable as compared with the ink jet recording head fabricated with an orifice plate which is not given any ultrasonic cleaning, and that the resultant printing is also desirable.

Embodiment 6

Subsequently, there will be disclosed an example of a recording head fabricated in the same manner as the embodiment 5 with the exception of the use of an XeCl excimer laser light as the laser light source of the discharging machining apparatus. After the discharging port plate has been machined as described earlier, the

discharging port plate having the by-product adhesively deposited on the circumference of the discharging ports is cleaned by a ultrasonic water flow. For the discharging port plate 10, a polyimide film is used. Also, for the water repellent agent, KP801 (Product name: Shinetsu Kagaku Inc.) is used to coat the discharging port plate 10. Then, the heating treatment process is given at 150°C for one hour to form the water repellence layer 6. To the discharging port plate 10 with the water repellence layer 6 thus formed, an XeCl excimer laser beam is irradiated from the plane opposite to the plane where the water repellence layer 6 has been formed. Hence, the discharging ports 11 are formed. Then, the cleaning by a ultrasonic water flow using a pure water is given to the discharging port plate 10 with the discharging ports 11 thus formed. In this way, the by-product 8 generated at the time of orifice machining is almost removed.

The discharging ports are machined as above Then, the ink jet recording head is fabricated with the orifice plate, the by-product deposited on which has been removed, and is mounted on a printer for the observation of the discharging droplets as well as for the recording onto a recording sheet. As a result, it is found that the discharging orientation of the flying droplets is stable as compared with the ink jet recording head fabricated with a discharging port plate which is not given any cleaning by the ultrasonic water flow, and that the resultant printing is also desirable.

Embodiment 7

Now, hereunder, another embodiment will be described.

After the aforesaid machining by the discharging port machining device, the discharging port plate having the by-product adhesively deposited on the circumference of the discharging ports is cleaned by a high pressure water flow. For the discharging port plate 10, a polyether sulfone film is used. Also, for the water repellent agent, Si-top (Product name: Asahi Glass Inc.) is used to coat the discharging port plate 10. Then, the heating treatment process is given at 120°C for one hour to form the water repellence layer 6. To the discharging port plate 10 with the water repellence layer 6 thus formed, a KrF excimer laser beam is irradiated from the plane opposite to the plane where the water repellence layer 6 has been formed. Hence, the discharging ports 11 are formed. Then, to the discharging ports 11 thus formed on the discharging port plate 10, a high pressure water flow produced by discharging a pure water continuously under a pressure of 200 kgf/cm^2 from a sapphier nozzle of 50 microns is applied in the direction of the discharging ports. Then, as shown in Fig. 6, although the by-product 8 generated at the time of orifice machining in a location where the high pressure water flow has not reached cannot be removed sufficiently, the by-produce due to the laser machining which has adhered to the circumference of the discharging ports of the discharging port plate is removed.

The discharging ports are machined as above. Then, the ink jet recording head is fabricated with the orifice plate, the by-product deposited on which has been removed, and is mounted on a printer for the observation of the discharging droplets as well as for the recording onto a recording sheet. As a result, it is found that the discharging orientation of the flying droplets is stable as compared with the ink jet recording head fabricated with a discharging port plate which is not given any cleaning by the high pressure water flow, and that the resultant printing is also desirable.

Embodiment 8

Now, hereunder, still another embodiment will be described.

After the aforesaid machining by the discharging port machining device, the application and removal of cellophane tapes are repeated five times against the discharging port plate having the by-product adhesively deposited on the circumference of the discharging ports. For the discharging port plate 10, a polyimide film is used. Also, for the water repellent agent, KP801 (Product name: Shinetsu Kagaku Inc.) is used to coat the discharging port plate 10. Then, the heating treatment process is given at 150°C for one hour to form the water repellence layer 6. To the discharging port plate 10 with the water repellence layer 6 thus formed, an XeCl excimer laser beam is irradiated from the plane opposite to the plane where the water repellence layer 6 has been formed. Hence, the discharging ports 11 are formed. Then, the application and removal of the cellophane tapes repeated five times each against both planes of the discharging port plate 10 having the office 11 thus formed. In this way, the by-product generated at the time of discharging port machining is removed.

The discharging ports are machined as above. Then, the ink jet recording head is fabricated with the orifice plate, the by-product deposited on which has been removed, and is mounted on a printer for the observation of the discharging droplets as well as for the recording onto a recording sheet. As a result, it is found that the discharging orientation of the flying droplets is stable as compared with the ink jet recording head fabricated with a discharging port plate for which no application and removal of the cellophane tapes are conducted, and that the resultant printing is also desirable.

Embodiment 9

As shown in Fig. 8, an excimer laser light is irradiated from a laser device to the position where the orifice should be formed from the ink pass side of the orifice plate. The resin is thus removed and evaporated so that the orifice 11 is produced. When this excimer laser light is irradiated, helium is blown as an assist gas for machining. In the present implementation, a helium gas 50 of 99.9999% purity is continuously blown from a helium blowing nozzle 51 as shown in Fig. 8 during the machining by the laser irradiation.

To the ceiling plate which is being machined with the blowing helium gas in such a manner as this, no removals by the laser light adhere to the surface of the orifice plate.

Embodiment 10

Subsequently, the description will be made of a second embodiment according to the present invention.

In the present embodiment, too, the structure of the head and the devices to be used for forming the discharging ports are the same.

In the present embodiment, the blowing of the helium gas is conducted in the direction toward the laser light with the ceiling and orifice plates being sandwiched therebetween. When the helium gas is blown in this direction, the helium gas is allowed to reach the surface of the orifice plate more efficiently. As a result, it becomes more difficult for the removals of the machining toadhere to the surface thereof. Also, in this method, the effect of the helium gas blowing is the same if it is blown just before the portion of the discharging ports to be formed is penetrated on the way of the machining by the laser light irradiation.

Embodiment 11

Now, as an embodiment according to the present invention, the description will be made of a method using an ionized air.

In the present embodiment, too, the structure of the head and the device used for forming the discharging ports are the same.

In the present embodiment, the ionized air is produced by a device which ionizes air. Such a device is installed in the same manner as in the first and second embodiments. When the device is actuated, the ionized air is blown from the blowing nozzle. While this air is being blown, the excimer later light is irradiated onto the orifice plate of the ceiling plate to perform the discharging port formation machining. In the present embodiment, the removals at the time of machining do not adhere to the surface of the orifice plate, either, as in the case of the previous embodiments.

Comparison example

The performance of the ink jet recording head obtained from the example embodying the present invention is examined and compared with those of the conventional head. The results are stated in Table 3 and Table 4.

Table 3

State of orifice plate at the time of recording	
Conventional head	large ink puddle observed
Embodiment 9	no ink puddle
Embodiment 10	no ink puddle
Embodiment 11	almost no ink puddle

Table 4

	Irregularity in flying direction	Recording result
Conventional head	±10°	fair
Embodiment 9	± 2°	good
Embodiment 10	± 1°	Particularly good
Embodiment 11	± 4°	good

Embodiment 12

The present embodiment is such that during the aforesaid fabricating process, a protection coating layer is produced before the performance of the laser perforation, and that the protection coating layer is removed after the laser perforation machining. Hereunder, the formation process of the ceiling plate formed integrally with the discharging port plate will be described sequentially.

I. At first, regarding the ink pass grooves, resin (polysulfone, polyether sulfone, polyphenylene oxide, polypropylene, or the like) is formed by a metallic mold prepared by a method of cutting or the like to produce a fine groove pattern opposite to the ink pass grooves, whereby to form the ink pass grooves 14 on the ceiling plate material.

II. Then, the ceiling plate material having the ink pass grooves 14 thus produced is immersed in an organic solvent, for example, to give a coating of the organic solvent thereon. For this organic solvent, it is fundamentally possible to use any type of organic solvents as desired if only it can be removed in the following fabrication process. In the present example, since the material of the ceiling plate is resin, there is a possibility that if an organic solvent is used in the removal process, a solvent cracking or the like occurs. Therefore, it is preferable to use a coating agent which can be removed by a removal agent, water or the like.

III. Subsequently, an excimer laser light is irradiated from the laser device to the position of the discharging ports to be formed from the ink pass side of the orifice plate 10 to remove locally and evaporate the resin of the ceiling plate for the formation of the discharging ports 11.

As clear from Fig. 8, and Fig. 9, the excimer laser light 2 is irradiated onto the orifice plate 10 from the ink pass side 14 through the aforesaid mask 4. Also, the excimer laser light 2 is converted in relation to the optical axis 13 at an angle of one side $\theta_1 = 2°$ and is irradiated in the direction perpendicular to the orifice plate 10 with an inclination of the optical axis 13 at an angle of $\theta_2 = 10°$.

By irradiating the laser light from the ink pass side in such a manner as this, the cross-sectional area of the orifice of a tapering shape presents a shape which is gradually reduced in the discharging direction.

Now, the description will be made of the excimer laser light to be used for this example embodying the present invention.

The excimer laser is a laser capable of oscillating ultraviolet light and has a high intensity, an excellent monochromaticity, directivity, capability of short pulse oscillation, capability of making energy density extremely great by converging a lens, and other advantages.

The excimer laser oscillator is a device capable of oscillating a short pulse (15 to 35 ns) ultraviolet light by the discharge excitation of a rare gas and halogen mixture, and Kr-F, Xe-Cl, Ar-F lasers are often employed therefor. The number of these oscillating energies is 100 mJ/pulse and the pulse repetition frequency is 30 to 1,000 Hz.

When a high luminance short pulse ultraviolet light such as this excimer laser light is irradiated onto the surface of a polymer resin, an ablative photodecomposition (APD) process is generated so that the irradiated portion is instantaneously dissolved and splashed with the accompanying plasma emission and impulsive sound. Hence, with this process, the polymer resin can be machined.

When comparing the machining precision by an excimer laser of the kind and the one by some other lasers in such a case that a laser as an excimer laser and other YAG laser and CO_2 laser are irradiated onto a polyimide (PI) film, it is found that a clear perforation is obtainable by a KrF laser because the light absorbing wavelength of PI is UV region whereas with the YAG laser which is not in the UV region, the edge of the perforation becomes rough although it is still obtainable, and with the CO_2 laser which is infrared, a crater is generated around the

perforation formed.

Also, an SUS and other metals, opaque ceramics, Si, and others are not affected by an irradiation of the excimer laser in the aerial atmosphere. Therefore, these can be used as a mask material for the excimer laser machining.

IV. Subsequently, the ceiling plate with the discharging ports thus provided is cleaned using an appropriate solvent and others in order to remove the carbon layer deposited on the coating layer. Both of the carbon layer and coating layer are removed together as if they are lifted off.

In Fig. 9A, there is schematically shown an adhesive state of the carbon layer at the time of the excimer laser machining subsequent to the coating of an organic solvent. In Fig. 9A, a reference numeral 16 designates the coating layer of an organic solvent and 17, the carbon layer deposited thereon. In this respect, there is a tendency that the carbon layer is most thickly deposited on the circumference of the discharging ports 11 of the orifice plate 10 where the excimer laser light is directly irradiated, and that the deposition becomes thinner as it is further away therefrom.

After this, an appropriate cleaning treatment is given. Then, although the details will be described later, it is possible to obtain a ceiling plate 5 without any carbon layer 17 as illustrated in Fig. 9B.

Using the grooved ceiling plate formed integrally with the discharging port plate fabricated as described above, it is possible to obtain a recording head main body in a cartridge mode as shown in Fig. 1, and further, using this, it is possible to construct an ink jet printer as shown in Fig. 11.

Here, in Fig. 11, a reference numeral 180 designates a cartridge shown in Fig. 1. This cartridge 180 is fixed on the carriage 151 by a pressure member 181 so as to be shuttled in the longitudinal direction along a shaft 121. Also, the positioning of the carriage 151 is performed by the nibs provided in a cover 1,300 and dowels or the like arranged on the carriage 1 side. Also, the electrical connection can be made by coupling a connector of the carriage 151 to a connecting pad provided on a wiring board.

The discharged ink from the recording head reaches a recording medium 118, the recording surface of which is controlled by a platen 119 with a fine space provided between the platen and recording head, to form an image on the recording medium 118.

To the recording head, discharging signals corresponding to image data are supplied from an appropriate data supply source through a cable 116 and terminal connected therewith. One or plural cartridges 180 (two in Fig. 11) can be provided in accordance with the color or colors of ink to be used and the like.

Now, hereunder, the description will be made of the embodiments in which the adhesive states of the carbon layer 17 of the ceiling plate 5 formed in accordance with various coating processes (the above-mentioned (II)) and removal processes (the above-mentioned (IV)) are observed and at the same time, the printing states of the recording head fabricated using such a ceiling plate are evaluated.

Embodiment 13

As a coating agent in the process (II), a positive type liquid resist used for the so-called photolithography (for example, a 5% solution of OFPR-800 manufactured by Tokyo Ohka Kogyo Inc.) is employed, and in such a solution, the ceiling plate material is immersed and dried naturally for 30 minutes after being lifted therefrom. Here, the ceiling plate member is formed in the aforesaid process (I) and polysulfone is used for its material.

Then, in the process (III), the discharging ports are machined and in the process (IV), the discharging port plate is immersed in a development (for example, NMD3: Tokyo Ohka Kogyo Inc.) for a five-minute ultrasonic cleaning.

Embodiment 14

As a coating agent in the process (II), a positive type liquid resist used for the so-called photolithography (for example, a 5% solution of OMR 83 manufactured by Tokyo Ohka Kogyo Inc.) is employed as in the case of the embodiment 13, and in such a solution, the ceiling plate material is immersed and dried naturally for 30 minutes after being lifted therefrom. In this respect, polypropylene is used for its material.

Then, in the process (III), the discharging ports are machined and in the process (IV), the discharging port plate is immersed in xylene-for a five-minute ultrasonic cleaning.

Embodiment 15

As a coating agent in the process (II), a polyvinyl alcohol (degree of polymerization 500 and saponification degree 80%) is employed to prepare a 0.5% water solution, and in such a solution, the ceiling plate material is immersed and dried naturally for 30 minutes after being lifted therefrom. Here, polysulfone is used for the

material.

Then, after the discharging ports are machined likewise, the discharging port plate is immersed in a water as the process (IV) for a five-minute ultrasonic cleaning.

Embodiment 16

Subsequently, the description will be made of the embodiment in which a metallic film is used for a film as a method for removing the carbon and others deposited particularly on the surface of the orifice plate.

For the ceiling plate material, polyether sulfone is used.

In the present embodiment, aluminum (Al) is provided on the surface of the orifice plate for a thickness of approximately 0.3 to 0.5 μm by sputtering. Then, after the discharging ports are machined in the process (III), the discharging port plate is immersed in a phosphoric solution for a three-minute ultrasonic cleaning. The polyether sulfone has a desirable chemical resistivity against phosphoric acid, and as there rarely occurs a crack in the ceiling plate, it is easier to remove the film.

Comparison example 2

In order to compare the above-mentioned embodiment, a ceiling plate is obtained by machining discharging ports on the ceiling plate material which has been prepared through the process (I) but not through the process (II), subsequent to which, the plate is immersed in a water for a five-minute ultrasonic cleaning. Here, polysulfone is used for the ceiling plate material.

As regards the above-mentioned embodiments 13 through 16 and the comparison example 2, the processes thereof, the evaluation of the carbon removal states of the ceiling plates, and the evaluation of the printing conditions are tabulated together and shown in Table 5.

Table 5

Coating agent	Coating agent Density/ Solvent	Coating method	Cleaning condition after excimer irradiation	Removal of carbon layer (Appearance Inspection)	Clogging in printing durability test	Ink puddles on orifice plate
Embodiment 13 OFPR-800 (Tokyo Ohka)	0.5%	Natural drying after immersion	NMD3 (Tokyo Ohka)	O	O	O
Embodiment 14 OMR-83 (Tokyo Ohka)	0.5%	-ditto-	Immersion in xylene	O	O	O
Embodiment 15 Polyvinyl alcohol Polymerization degree 500 Saponification degree 80%	0.5% water	Natural drying after immersion	Ultrasonic cleaning in water	O	O	O
Embodiment 16 AI	AI	Sputtering	Ultrasonic cleaning in phosphoric solution		O	O
None (Prior Art and comparison example 2)	——	——	Ultrasonic cleaning in water	△ - X	X	X

As clear from this table, there is no residual carbon recognized at all in each of the embodiments 13 through 15 when the removal conditions of the deposited carbon are observed by a metallurgical microscope. On the other hand, there are observed in the comparison example some cases where just a half of the carbon deposition has been removed or no carbon has been removed at all.

Also, actual printing durability tests are conducted on the recording heads completed with the ceiling plates thus obtained. Then, as shown in Table 5, while there are some cases where a disabled discharging occurs due to the clogging of carbon particles in the comparison example, no disabled discharging has taken place in each of the embodiments 13 through 15 during the durability test (up to 2,000 sheets of an A4-sized recording medium) and the printing conditions are desirable to the end. Also, there occur no ink puddles on the surface of the orifice plate and a desirable printing is performed with a stable flying orientation of the ink droplets.

Embodiment 17

In the above-mentioned embodiments, all the coating layer is removed in the cleaning process so that no residual carbon may remain at all. However, it may also be possible to allow the coating layer to remain unremoved from the location where no carbon is present or the location where the carbon is present but in a negligible quantity. For example, in a case where a photoresist coating is performed, it is possible to cause the coating layer to be removed or remain unremoved from a desired location selectively in the cleaning process by conducting a selective light irradiation before cleaning (for example, if a positive type resist is used, the cleaning should be given subsequent to the light irradiation locally to a portion where the removal is desired, or if a negative type resist is used, the cleaning should be given subsequent to the light irradiation locally to the portion where the coating is to remain unremoved).

This contributes not only to the reduction of the cleaning liquid and cleaning time, but also to the event given below in an ink jet recording head.

In other words, in the ink jet recording head, a liquid repellence treatment is given to the plane where the discharging ports are arranged (a discharging port arrangement plane or orifice plate surface in the above example) in some cases. This treatment is given in consideration of the fact that if the wettability of the discharging port arrangement plane is high, a part of ink tends to remain on the discharging port arrangement plane when the meniscus is returned after the ink discharging operation, which results in drawing the ink to be discharged next time thereby to twist its discharging direction.

In the present embodiment, a resin having liquid repellency is coated in the process (II) in order to cope with such a situation as this, and before the process (IV), there is performed a light irradiation to or shield from the discharging port arrangement plane which corresponds to the resist.

Fig. 10 is a view showing the ceiling plate 5A which is obtainable after cleaning subsequent to the above processes and on the front face of the orifice plate 10, a film 16A remains to serve as a liquid repellence layer. According to the present embodiment, there is no need of providing a liquid repellence layer separately or any process in a recording apparatus that may perform an automatic coating or the like.

Here, in such a liquid repellence layer as in the present embodiment, it may be possible to cause only the required portion in the circumference of the discharging ports to remain or if desired, it may be possible to cause such a layer to remain in some other portion (a predetermined portion in the reverse side of the orifice plate or in the ink pass). In either case, it is possible to obtain remaining portions as desired by controlling the irradiation of light or shielding thereof.

Furthermore, in the above-mentioned example, when the resin coating is given, the ceiling plate material is immersed in a resist solution. However, the present invention is capable of defining the kinds of the functionable layer, the layer deposition or the location thereof as a matter of course and is not limited to the example set forth above.

Others

In this respect, particularly among those available ink jet recording methods, the present invention is provided with means (for example, electrothermal converting element, laser light, or the like) for generating thermal energy as the energy which can be utilized for discharging ink because with the present invention not only it is possible to bring about an excellent effect in a recording head or a recording apparatus having such a method as generating a change of state for ink by the aforesaid thermal energy, but also it is possible to attain a higher density as well as a higher precision of recording by the use thereof.

For the typical structure and principle of such a method for the implementation thereof, it is preferable to adopt the fundamental principle disclosed in the specifications of U.S. Patent 4723129 and U.S. Patent 4740796, for example. This method is applicable both to the so-called on demand type and continuance type.

Particularly, in the case of the on demand type, there is applied at least one driving signal which gives a rapid temperature rise above the nuclear boiling to a recording liquid (ink) inresponse to the recording information provided for the electrothermal converter arranged with respect to a sheet or liquid pass in which a recording liquid (ink) is held. Thus the electrothermal converter is caused to generate thermal energy and a film boiling on the thermo-active plane of the recording head. In this way, the formation of bubble is made efficiently in the recording liquid (ink) one to one in response to such a driving signal. Then, the recording liquid (ink) is discharged into the atmosphere through the discharging ports by the active force generated in the course of the growth and contraction of this bubble to form at least one droplet. It is more preferable to produce this driving signal in the form of pulses. Then, the growth and contraction of the bubbles are appropriately effectuated instantaneously to implement the discharging of recording liquid particularly with an excellent responsibility. For this type of pulse driving signal, the one such as disclosed in the specifications of U.S. Patent 4463359 and U.S. Patent 4345262 is suitably adoptable. In this respect, it is possible to perform such an excellent recording still better if the conditions referred to in the invention on the temperature rise for the above-mentioned thermo-active plane disclosed in the specification of U.S. Patent 4313124.

As the structure of the recording head, the present invention includes a combination of the discharging port, liquid pass, electrothermal converter (linear liquid pass or rectangular liquid pass) such as disclosed in each of the above-mentioned specifications as well as the structure having the thermo-active portion arranged in the bending region using the configuration disclosed in the specifications of U.S. Patent 4558333 and U.S. Patent 4459600. In addition, the present invention is effective when its structure is arranged on the basis of the Japanese Patent Laid-Open Application No. 59-123670 which discloses a structure whereby to make a common slit to be the discharging ports of the electrothermal converters or of the Japanese Patent Laid-Open Application No. 59-138461 which discloses a structure whereby to arrange the discharging ports in relation to the opening holes which absorb the pressurized waves of thermal energy. In other words, this is possible because according to the present invention, a recording can be performed assuredly and efficiently irrespective of the modes of the recording heads.

Further, as to the full-line type recording head having a length corresponding to the maximum width of the recording medium on which the recorder can perform its recording, the present invention can also be adopted effectively. For such a recording head, there may be a structure made either by combining a plurality of recording heads or by an integrally constructed single recording head to attain such a recording length.

In addition, the present invention is effectively applicable either to the above-mentioned serial type recording head, the recording head fixed to the main body of the recording apparatus, a freely replaceable chip type recording head for which the electrical connection to the main body of the recording apparatus as well as the ink supply from the main body of the recording apparatus become possible when the chip is installed therein, or a cartridge type recording head having the ink tank integrally provided for the recording head itself.

Also, it is preferable to add a recovery means, preliminarily auxiliary means, and the like provided for the recording head as constituents of the recording apparatus according to the present invention because with these constituents, the effect of the present invention becomes more stable. To mention specifically, these constituents are a capping means for the recording head, cleaning means, compression or suction means, electrothermal converter or thermal element independent thereof or preliminary heating means provided by the combination thereof, and others. Also, it is effective to provide a preliminarydischarging mode which performs preliminary discharging besides the recording.

Also, as to the kinds and numbers of the recording heads to be mounted, it may be possible to adopt those having a plurality of recording heads for plural kinds of ink which are different in recording colors or densities in addition to the one having only one head for a single color ink, for example. In other words, the present invention is extremely effective when applied to an recording apparatus provided with at least one of the respective recording modes for compound colors by different colors or full colors by color mixtures irrespective of whether the recording head is constructed integrally for a single head or by combination of plural heads for the recording mode of the apparatus which is not confined only to a major color such as black.

Furthermore, in the embodiments of the present invention set forth above, while the description has been made of the ink which is a liquid, it may be possible to use the ink which is solidified at room temperature or less if only such ink can be softened or liquefied at room temperature, or if only such ink can be liquefied when a signal to use for recording is given because in an ink jet method, it is generally practiced that ink itself is kept within a temperature range of 30°C or more and 70°C or less to maintain its viscosity in a range of stable discharging. In addition, the temperature rise to be caused by the thermal energy is positively prevented by using such energy for changing the state of ink from solid to liquid, or for the prevention of ink evaporation, it may be possible to use the ink which is solidified when it is left intact but can be liquefied by heating. In any event, the present invention is also applicable to the ink which is liquefied in response to the provision of the recording signals generated by the thermal energy for discharging such a liquefied ink, or the ink which has a property

to be liquefied only by the provision of thermal energy and which already begins to be solidified just before reaching a recording medium or the like. When an ink such as this is used, it may be possible to adopt a mode in which the ink is held in a state of liquid or solid in concavities of a porous sheet or through holes so that the ink is placed to face the electrothermal converter as disclosed in Japanese Patent Laid-Open Application No. 54-56847 or Japanese Patent Laid-Open Application No. 60-71260. In the present invention, the mode which enables the implementation of the above-mentioned film boiling method is the most effective for each of the above-mentioned kinds of ink.

Moreover, as to the mode of the ink jet recording apparatus to which the present invention is applicable, there may be those used for copying machines in combination with readers, and facsimile apparatuses having transmitter and receiver, or the like in addition to the image output terminals for a computer or other information processing apparatuses.

Now, as described above, in an ink jet recording head according to the present invention, there is formed in the circumference of the orifice a water repellence treatment portion which is excellent both in water repellency and durability. Hence, it is possible to perform the stable discharging printings at all times for obtaining desirable quality in printing.

Also, as described above, by irradiating a pulse laser onto the orifice plate having a water repellence layer on its face or being constructed itself with a water repellent agent for the orifice machining and then by restoring the water repellency in the vicinity of the orifice with the removal or a treatment given to the removal of the by-product having a great hydrophilic property adhesively deposited in the vicinity of the orifice, it is possible to provide an ink jet recording head and manufacturing method therefor capable of preventing the adhesion of ink to the vicinity of the orifice and the degradation of the printing quality as well.

In this respect, by using a water repellent film material for the utilization of the carbon removal and allowing such a film to remain selectively, it is also possible for the present invention to contribute to simplifying the manufacturing processes because there is then no need of performing any separate process for giving the liquid repellence treatment to the discharging port arrangement plane.

Claims

1. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the processes of:

   giving hydrophilic property to the side of the discharging port formation plane of a work piece for constructing said discharging ports;

   forming an intermediate layer having a coupling agent containing Si on the plane to which said hydrophilic property is given; and

   forming a water repellence layer on the upper layer of said intermediate layer.

2. A method for manufacturing an ink jet head according to Claim 1, wherein

   said work piece is an organic material and is structured with an oxidation treatment layer in the process of giving said hydrophilic property.

3. A method for manufacturing an ink jet head according to Claim 1, wherein

   said coupling agent containing Si has an end group to be selected either from methoxy group or ethoxy group at one end and at the same time, has an end group to be selected either from amino group, epoxy group, or mercaptor group at the other end.

4. A method for manufacturing an ink jet head according to Claim 1, wherein

   said water repellence layer is a fluorine-containing noncrystalline thermoplastic resin.

5. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the processes of:

   giving an oxidation treatment to the surface side of the discharging port formation plane of a work piece for constructing said discharging ports;

   forming an intermediate layer having a coupling agent containing Si on the oxidation plane of the surface side of said discharging port formation plane; and

   forming a layer including a polymer containing a fluorine-containing hetero cyclic structure in its prin-

cipal chain for giving water repellency to the upper layer of said intermediate layer.

6. A method for manufacturing an ink jet head according to Claim 5, wherein
said process for covering with the oxidation treatment layer is performed by a UV-irradiation ozone cleaning.

7. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the proceses of:
giving an oxidation treatment to the surface side of the discharging port formation plane of a work piece for constructing said discharging ports;
forming an intermediate layer containing an organometallic compound on the oxidation plane of the surface side of said discharging port formation plane; and
forming a layer including a polymer containing a fluorine-containing hetero cyclic structure in its principal chain for giving water repellency to the upper layer of said intermediate layer.

8. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the processes of:
giving an oxidation treatment to the surface side of the discharging port formation plane of a work piece for constructing said discharging ports;
forming an intermediate layer containing an amine resin on the oxidation plane of the surface side of said discharging port formation plane; and
forming a layer including a polymer containing a fluorine-containing noncrystalline thermoplastic resin for giving water repellency to the upper layer of said intermediate layer.

9. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the processes of:
giving an oxidation treatment to the surface side of the discharging port formation plane of a work piece for constructing said discharging ports;
forming an intermediate layer containing an amine hardening resin on the oxidation plane of the surface side of said discharging port formation plane; and
forming a layer including a polymer containing a fluorine-containing noncrystalline thermoplastic resin for giving water repellency to the upper layer of said intermediate layer.

10. A method for manufacturing a recording head used for an ink jet printer, wherein
discharging ports are formed by irradiating a pulse laser beam subsequent to processing the discharging port formation plane of a discharging port formation member with a water repellent material, and further, thereafter, a heater treatment is given to the by-product adhesively deposited on the circumference of the discharging ports generated at the time of the orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

11. A method for manufacturing a recording head used for an ink jet printer, wherein
the discharging port formation member is structured with a water repellent material, and the discharging ports are formed by irradiating a pulse laser beam thereto, and further, thereafter, a heating treatment is given to the by-product adhesively deposited on the circumference of the discharging ports generated at the time of theorifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

12. A method for manufacturing a recording head used for an ink jet printer, wherein
the heating treatment is performed by giving heat at a temperature of the glass transition point Tg or a temperature higher than a fusion point Tmp.

13. A method for manufacturing a recording head used for an ink jet printer, wherein
discharging ports are formed by irradiating a pulse laser beam subsequent to processing the discharging port formation plane of a discharging port formation member with a water repellent material, and further, thereafter, an ultrasonic cleaning is given to the by-product adhesively deposited on the circum-

ference of the discharging ports generated at the time of the orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

14. A method for manufacturing a recording head used for an ink jet printer, wherein
discharging ports are formed by irradiating a pulse laser beam subsequent to processing the discharging port formation plane of a discharging port formation member with a water repellent material, and further, thereafter, an ultrasonic water flow cleaning is given to the by-product adhesively deposited on the circumference of the discharging ports generated at the time of the orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

15. A method for manufacturing a recording head used for an ink jet printer, wherein
discharging ports are formed by irradiating a pulse laser beam subsequent to processing the discharging port formation plane of a discharging port formation member with a water repellent material, and further, thereafter, a high pressure water cleaning is given to the by-product adhesively deposited on the circumference of the discharging ports generated at the time of the orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

16. A method for manufacturing a recording head used for an ink jet printer, wherein
discharging ports are formed by irradiating a pulse laser beam subsequent to processing the discharging port formation plane of a discharging port formation member with a water repellent material, and further, thereafter, an operation is performed once or more times for applying a tape having an adhesive layer adhesively to the discharging port formation plane of the port formation member, particularly, to the circumference of the discharging ports where the by-product at the time of orifice machining is adhesively deposited and then to remove such tape therefrom.

17. A method for manufacturing a recording head according to Claim 1 through Claim 7, wherein
said discharging port formation member is integrally formed with a ceiling plate which constitutes ink passes for the location where said discharging energy generating elements are arranged by coupling it to a substrate on which the energy generating elements are provided for the utilization of the ink discharging.

18. A method for manufacturing a recording head according to Claim 1 through Claim 7, wherein
said irradiation of a pulse laser beam is performed from the plane side coupling to the ink passes in the direction opposite to the said face plane for the formation of the discharging ports.

19. A method for manufacturing a recording head according to Claim 1 through Claim 7, wherein
said pulse laser is a ultraviolet laser light and is particularly an excimer laser for the orifice formation.

20. A method for manufacturing an ink jet recording head provided with a substrate having energy generating elements for generating the energy which is utilized for discharging ink, a ceiling plate having the concavities for forming ink passes with respect to the portion where said energy generating elements are arranged by coupling it to said substrate, and a discharging port formation member with the discharging ports which are formed to be conductively connected to said ink passes for discharging ink, comprising the processes of:
irradiating an excimer laser light onto said discharging port formation member; and
blowing a helium gas.

21. A method for manufacturing an ink jet recording head according to Claim 20, wherein
an excimer laser light is irradiated from one side of said discharging port formation member and a helium gas is blown from the other side with said discharging port formation member being sandwiched therebetween.

22. A method for manufacturing an ink jet recording head according to Claim 20, wherein
said helium gas blowing process is performed just before the termination of the discharging port formation process by said irradiation of laser light.

23. A method for manufacturing an ink jet recording head according to Claim 20, wherein
said helium gas blowing process is performed at the same time of said laser light irradiation process.

24. A method for manufacturing an ink jet recording head provided with a substrate having energy generating elements for generating the energy which is utilized for discharging ink, a ceiling plate having the concavities for forming ink passes with'respect to the portion where said-energy generating elements are arranged by coupling it to said substrate, and a discharging port formation member with the discharging ports which are formed to be conductively connected to said ink passes for discharging ink, comprising the processes of:

irradiating an excimer laser light onto said discharging port formation member; and
blowing an ionized air.

25. A method for manufacturing an ink jet recording head according to Claim 24, wherein
said ionized air blowing process is performed just before the termination of the discharging port formation process by said irradiation of laser light.

26. A method for manufacturing an ink jet recording head according to Claim 24, wherein
said ionized air blowing process is performed at the same time of said laser light irradiation process.

27. A method for manufacturing an ink jet recording head provided with a substrate having energy generating elements for generating the energy which is utilized for discharging ink, a ceiling plate having the concavities for forming ink passes with respect to the portion where said energy generating elements are arranged by coupling it to said substrate, and a discharging port formation member with the discharging ports which are formed to be conductively connected to said ink passes for discharging ink, comprising the processes of:

forming a film at least on a part of the material with which said ceiling plate member and said discharging port member are integrally constructed;
forming said discharging ports by irradiating a laser light; and
removing said film.

28. A method for manufacturing an ink jet recording head according to Claim 27, wherein
said ceiling plate has concavities for forming said liquid passes, and an excimer laser light is irradiated from the side of said concavity portion to form said discharging ports.

29. A method for manufacturing an ink jet recording head according to Claim 27, wherein
said part includes a location where carbon adheres due to the process of said discharging port formation by the irradiation of said laser light.

30. A method for manufacturing an ink jet recording head according to Claim 27, wherein
said film is formed with a material having water repellency, and the film of said material is formed at least on said location and the circumference of the surface where said discharging ports are arranged, and in said removal process, the film formed on said location is selectively removed.

31. A method for manufacturing an ink jet recording head according to Claim 27, wherein
said ceiling plate and said discharging port formation member are integrally formed in advance.

32. An ink jet recording head manufactured by the method for manufacturing an ink jet recording head according to Claim 1 through Claim 31.

33. An ink jet recording head according to Claim 32, wherein
said element causes the thermal energy to be applied to said ink for enabling said ink to generate film boiling.

34. An ink jet recording head according to Claim 32, wherein
said element is an electrothermal converting element.

35. A method for manufacturing an ink jet head provided with discharging ports, ink passes conductively connected to said discharging ports, and energy generating elements for generating energy to be utilized for discharging ink, comprising the processes of:

giving hydrophilic property to the side of the discharging port formation plane of a work piece for constructing said discharging ports;

forming an intermediate layer having a coupling agent containing Si on the plane to which said hydrophilic property is given; and

forming a water repellence layer on the upper layer of said intermediate layer;

forming discharging ports by irradiating a pulse laser beam; and

giving a heating treatment to the by-product adhesively deposited on the circumference of the discharging ports at the time of orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

36. A method for manufacturing an ink jet head according to Claim 35, wherein

said work piece is an organic material and is structured with an oxidation treatment layer in the process of giving said hydrophilic property.

37. A method of manufacturing an ink jet head according to Claim 35, wherein

said coupling agent containing Si has an end group to be selected either from methoxy group or ethoxy group at one end and at the same time, has an end group to be selected either from,amino group, epoxy group, or mercaptor group at the other end.

38. A method for manufacturing an ink jet head according to Claim 35, wherein

said water repellence layer is a fluorine-containing noncrystalline thermoplastic resin.

39. A method for manufacturing a recording head used for an ink jet printer, wherein

the discharging port formation member is structured with a water repellent material, and the discharging ports are formed by irradiating a pulse laser beam thereto, and further, thereafter, a heating treatment is given to the by-product adhesively deposited on the circumference of the discharging ports generated at the time of the orifice machining or to the orifice plate with the by-product adhering to the circumference of its discharging ports.

40. A method for manufacturing a recording head used for an ink jet printer, wherein

said heating treatment is performed by giving heat at a temperature of the glass transition point Tg or a temperature higher,than a fusion point Tmp.

41. A method of manufacturing an ink jet head having discharge ports with water repelling surfaces, characterised in that an intermediate layer of material is formed on said ports and a water repellent layer is formed on said intermediate layer.

42. A method according to claim 41, wherein said intermediate layer has a coupling agent.

43. A method according to claim 42, wherein said coupling agent contains silicon.

FIG. 1

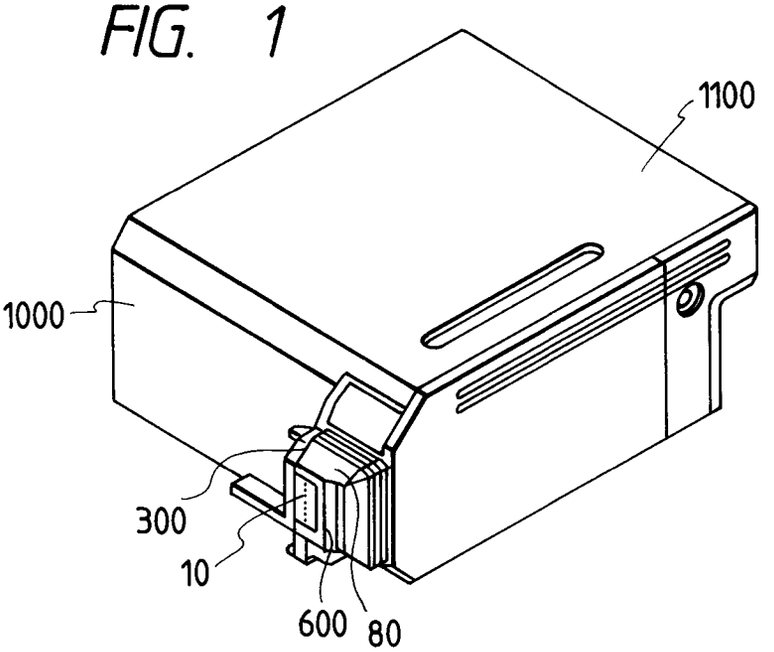


FIG. 2

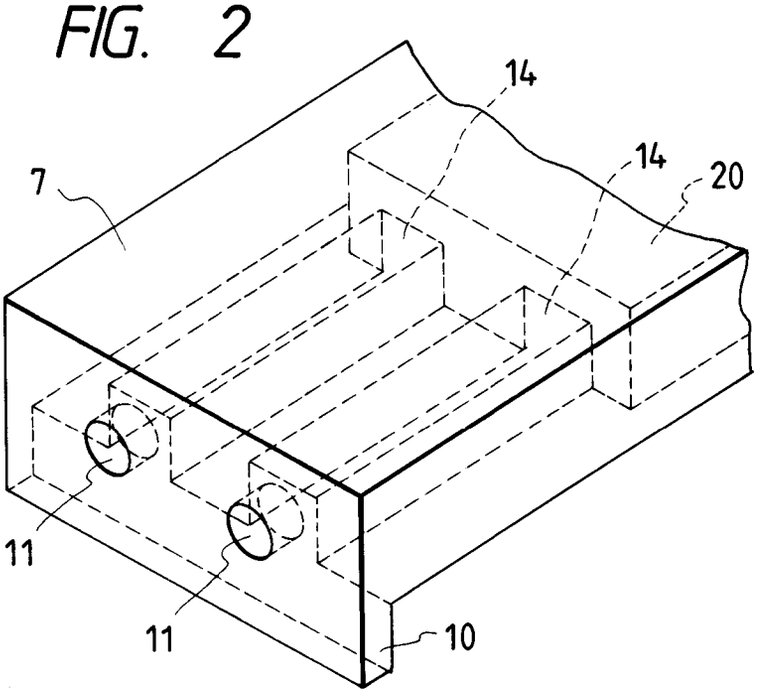


FIG. 3

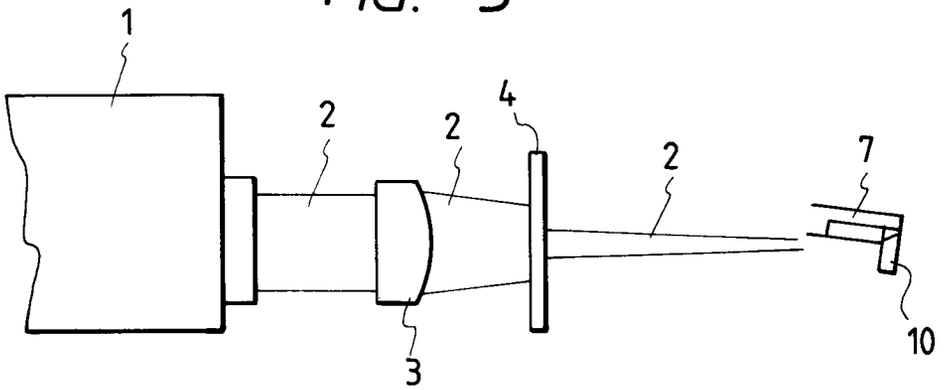


FIG. 4A

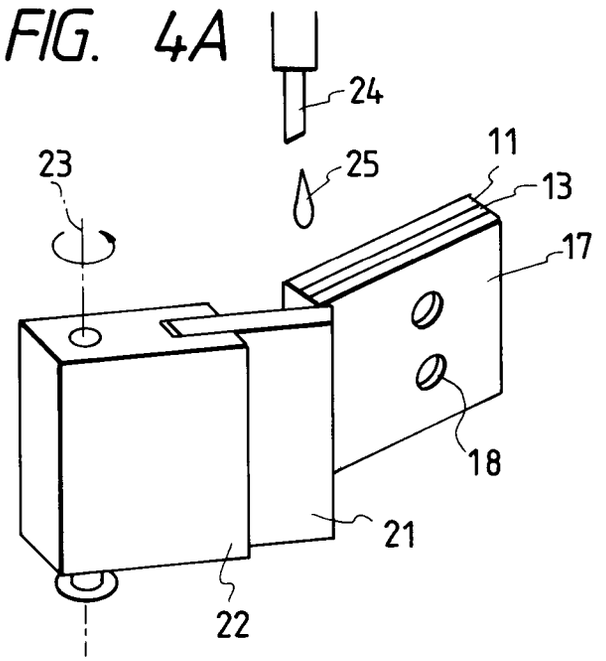


FIG. 4B

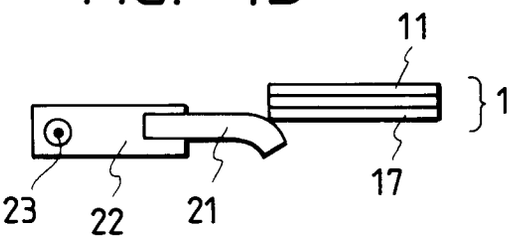


FIG. 6

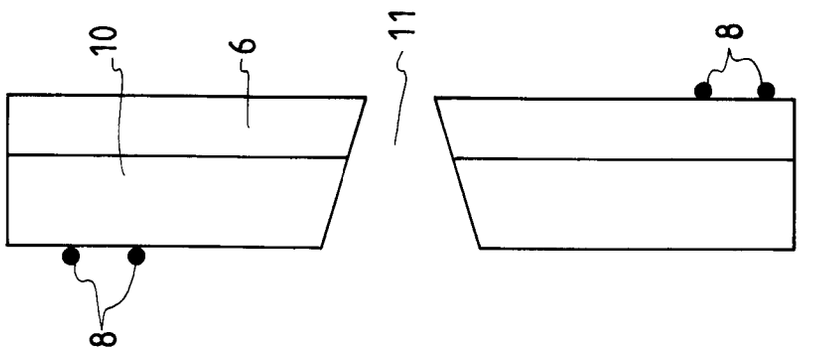


FIG. 5

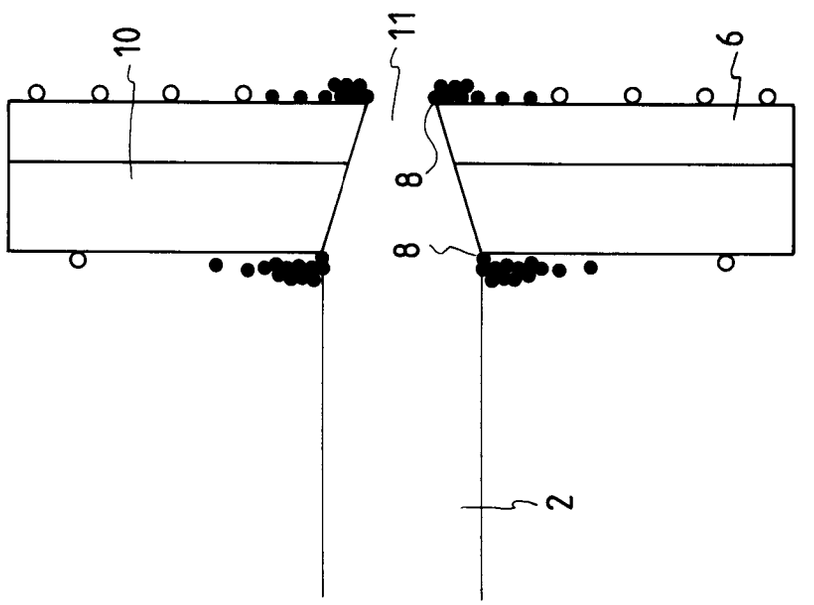


FIG. 7

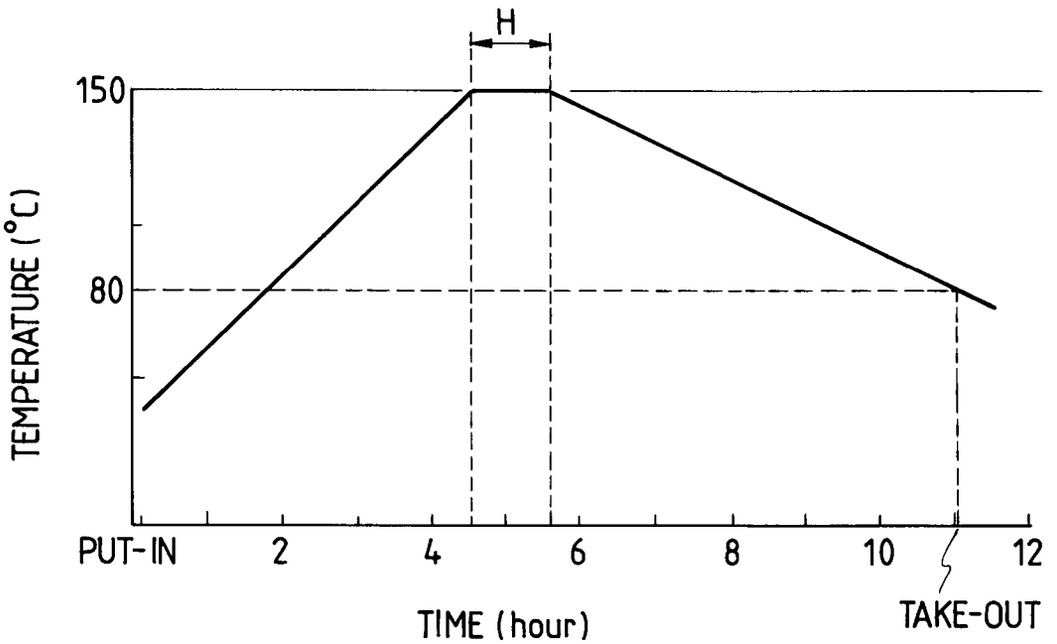
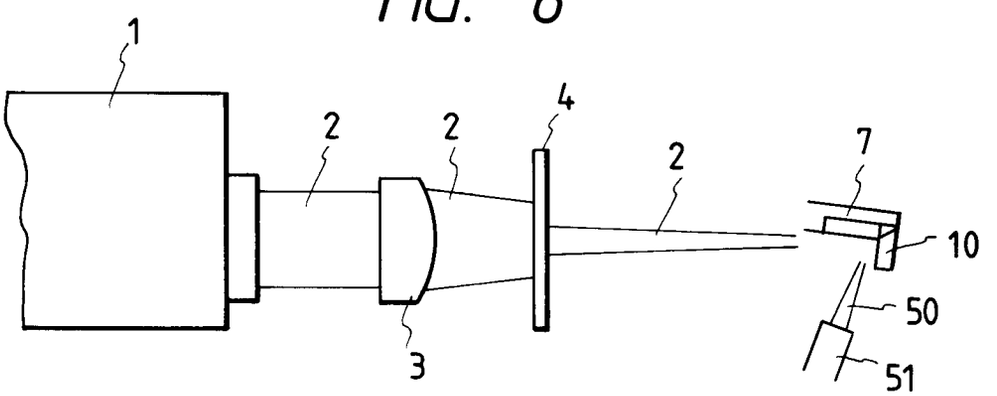

H
150
80
TEMPERATURE (°C)
PUT-IN
2
4
6
8
10
12
TIME (hour)
TAKE-OUT

FIG. 8


1
2
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4
2
7
10
50
51
3

FIG. 9A

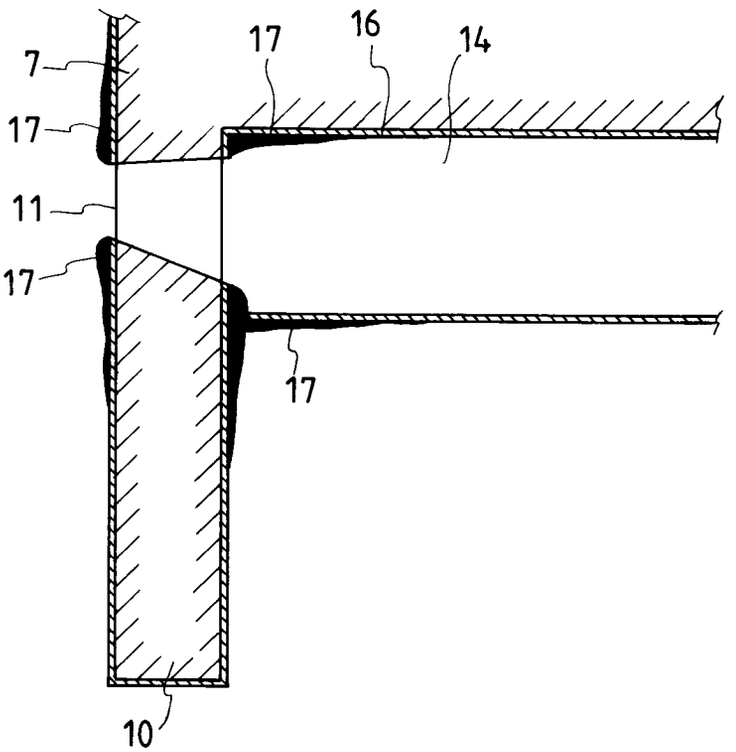


FIG. 9B

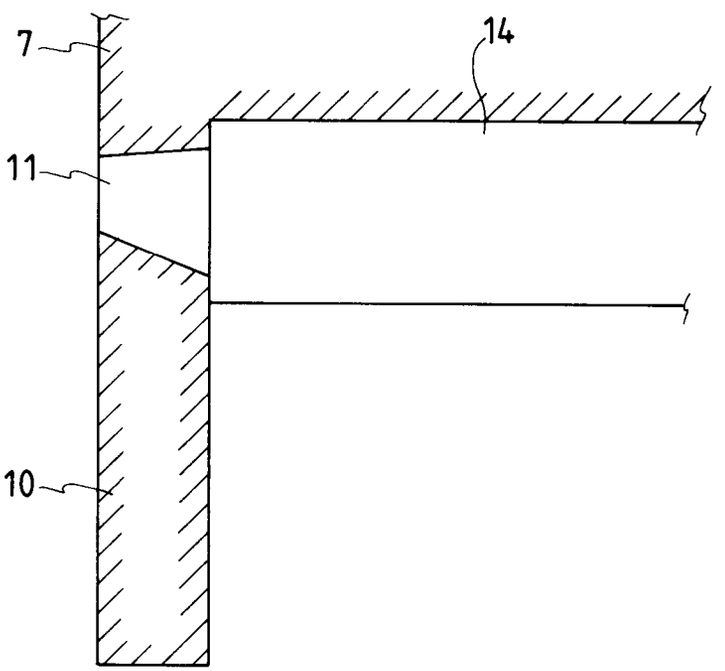


FIG. 10

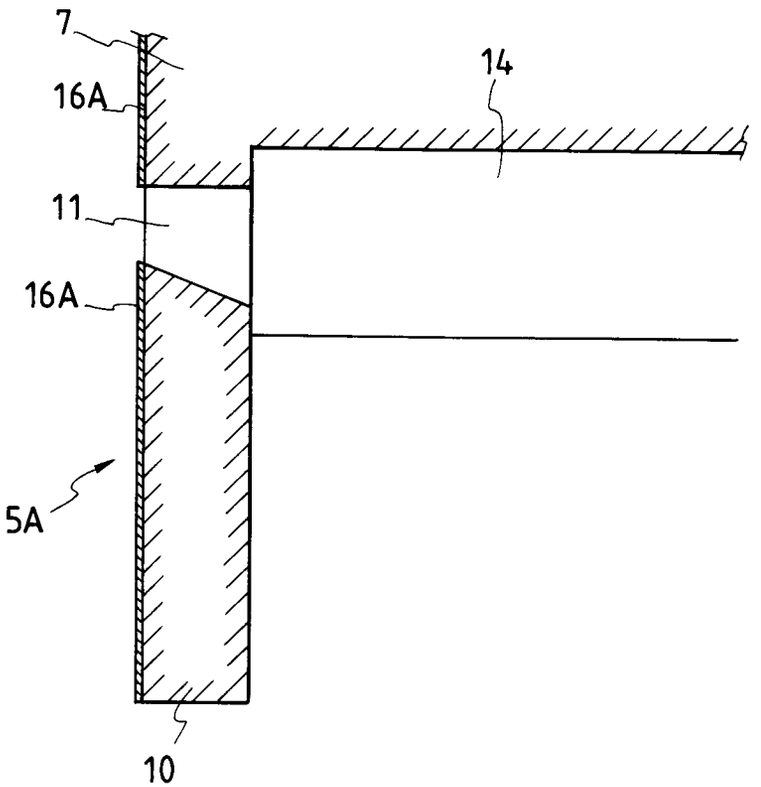
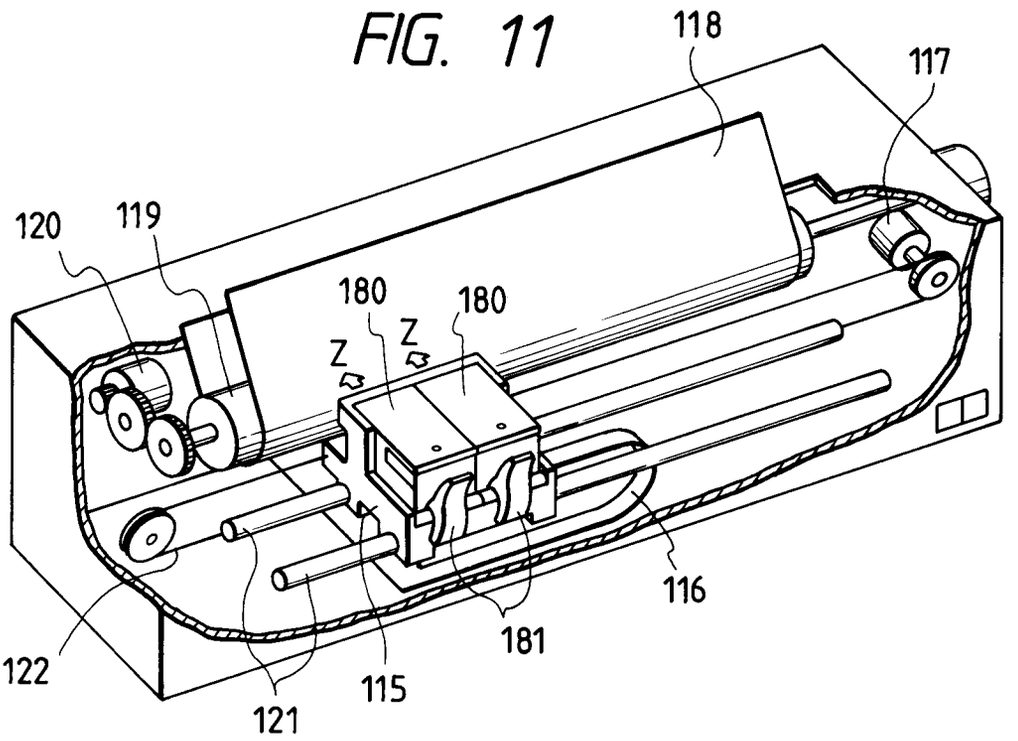

7
16A
14
11
16A
5A
10

FIG. 11


118
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121

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0353

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	JP-A-2 153 744 (MASUDA ET AL.) 13 June 1990	1-5, 7-12, 17, 20, 41-43	B41J2/16
P,X	& US-A-5 017 946 (...)		
A	US-A-4 897 475 (SCHROEPFER ET AL.) * the whole document *	1, 3-5, 7-11, 41-43	
D	& JP-A-1 131 215 (...)		
D,X	PATENT ABSTRACTS OF JAPAN vol. 10, no. 336 (M-535)(2392) 14 November 1986 & JP-A-61 141 565 (RICOH CO LTD) 28 June 1986 * abstract *	14, 15	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 12 (M-269)(1449) 19 January 1984 & JP-A-58 175 666 (FUJITSU K.K.) 14 October 1983 * abstract *	1-43	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 158 (M-591)(2605) 22 May 1987 & JP-A-61 291 148 (RICOH CO LTD) 20 December 1986 * abstract *	1-43	B41J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 APRIL 1992	JOOSTING T.E.

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