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Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 359 365**  
**A1**

(12)

## EUROPEAN PATENT APPLICATION

(41) Application number: 89306750.4

(51) Int. Cl.<sup>5</sup>: **B41J 2/005**

(42) Date of filing: 03.07.89

(30) Priority: 05.07.88 US 215126

(43) Date of publication of application:  
21.03.90 Bulletin 90/12(84) Designated Contracting States:  
**DE FR GB NL**

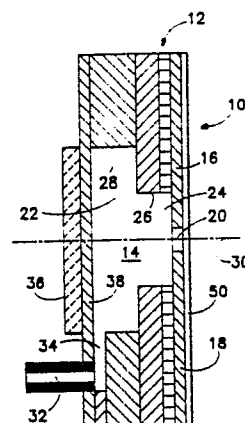
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(54) **Modified ink jet printing head and method for producing ink jet printed images.**

(57) A method is provided for modifying an ink jet printing head (10) which comprises applying a layer of a treated coating material (50) to the jet printing head surface area (18) surrounding each said drop discharge nozzle (20). This treated coated surrounding surface area maintains a phase change ink contact angle of at least about 50°, at an operating temperature of at least about 70° C. In this way, the ink jet printing head is capable of ejecting a plurality of individual drops of the phase change ink composition for forming undegraded, accurately placed printed images on a printing medium.



**FIG. 1**

## MODIFIED INK JET PRINTING HEAD AND METHOD FOR PRODUCING INK JET PRINTED IMAGES

### BACKGROUND OF THE INVENTION

This invention relates to a modified ink jet printing head and to a method for effectively and efficiently producing printed images from an ink composition on a printing medium.

Ink jet printers having one or more ink jet printheads with one or more ink jetting nozzles in each printhead for projecting drops of ink onto paper or other printing substrates to generate graphic images and text have become increasingly popular. To form color images, ink jet printers with multiple ink jetting nozzles are used, with each nozzle being supplied with ink of a different color. These colored inks are then applied, either alone or in combination, to the printing medium to make a finished color print. Typically, all of the colors needed to make the print are produced from combinations of cyan, magenta and yellow inks. Black ink may also be added to the above ink combination for printing textual material or for producing true four-color prints.

In common arrangements, the print medium is attached to a rotating drum or is advanced in a typewriter-like mechanism past the printheads with the ink jet heads being mounted on a traveling carriage that traverses the drum axially or, on the typewriter-like mechanism, in a boustrophedon manner. As the heads scan a helical or boustrophedan path over the printing medium, ink drops are projected from a minute external nozzle in each head toward the printing medium so as to form an image on the printing medium. A suitable control system synchronizes the generation of ink drops with the rotating drum or typewriter-like mechanism.

Various systems and methods are known for producing printed images on a recording substrate with aqueous based inks. A serious problem in printing images with ink jets that use aqueous based inks is wetting of the ink discharge surface. The presence of ink deposits on the ink discharge surface surrounding the drop discharge nozzle causes non-uniform ink ejection from the system which in turn degrades the quality of the printed image. Thus, methods have been provided which treat the discharge surface of an ink jet system with non-wetting materials thereby preventing deposits of ink from spreading out across the discharge surface from the drop discharge nozzles of the ink jet system. Thus, in U.S. 4,533,569, the interior surface area of a glass nozzle was cleaned with hydrofluoric acid and then coated with a blocking agent such as ethylene glycol, glycerine and

the like. Anti-wetting compounds such as long chain anionic non-wetting agents were applied to the fluid nozzles after ionic pretreatment to improve ink drop quality. U.S. 4,623,906 describes a three-layer coating for glass or silicon ink jet nozzles comprising silicon nitride and/or aluminum nitride. In U.S. Patent 4,343,013, the nozzle plate of an ink jet printer, which is made of glass, is coated with a material which is non-wetting relative to the aqueous characteristics of the ink composition. Compositions such as tetrafluoroethylene or certain silicone based materials are useful for this purpose since they have these aforementioned non-wetting characteristics. In U.S. Patent 4,368,476 a liquid repellant film layer of a fluorosilicon non-wetting compound is provided on the surface area surrounding the jet nozzle. In U.S. 4,643,948, an ink jet nozzle plate is coated with a non-wetting film comprising a partially fluorinated alkyl silane and a perfluorinated alkane, respectively. In U.S. 4,728,393, a nozzle plate of the electrostatic ink jet printer is polished to a mirror finish and then is completely coated with a thin layer of Teflon® resin. However, in this case, the Teflon® coating is employed for electrostatic control, not for ink drop formation. Ink drop formation is facilitated by the air-assist and mesa mechanisms. For this reason, the ink jet would work without the Teflon® coating. Other articles related to the wettability per se of fluorocarbon polymeric films include articles entitled "Highly Non-Wettable Surface of Plasma Polymer Vapor Deposition of Tetrafluoroethylene" by B.D. Washo, in the IBM TDB, Vol. 26, No. 4, Pg. 2074, and "Wettability of Perfluorocarbon Polymer Films: Effect of Roughness" by A.J.G. Allan, et al, in Journal of Polymer Science, Vol. XXXIX, Pg. 1.

In a different ink jet printing technology, non-aqueous, phase-change inks have been employed in place of aqueous based inks in ink jet systems. A phase change ink is solid at room temperature but becomes liquid at the operating temperature of the ink jet so that it may be jetted on a recording substrate in a predetermined pattern therefrom. The jetted ink pattern solidifies on the recording substrate. The problem of non-uniform ink drop ejection due to surface wetting as described above with respect to aqueous based inks can also be a problem with respect to phase change inks. This problem can conceptually and in practice be overcome by specifically configuring the structure of the ink jet nozzle. Some examples are mesas, ink puddles, squeeze tubes, and dissimilar liquid puddles. However, these configurations can be more costly to fabricate than is desirable, particularly for devices consisting of arrays of jets.

Therefore a need exists for an ink jet print head from which repeatable, uniform drops can be formed from ink compositions, including phase change ink compositions, and in turn in which the desired printed image characteristics can be formed on the printing medium without the need for a costly ink jet nozzle design.

## SUMMARY OF THE INVENTION

This invention meets the foregoing need for an ink jet printing head in which the previously-described desired ink drop properties can be produced from phase change ink compositions. By employing the method and system of the present invention, the essential printed image characteristics can be formed on a printing medium without the need for costly reconfiguring of the design of the phase change ink jet nozzle. More specifically, the printed images produced from phase change ink compositions by the method and the ink jet printing head of the present invention are undegraded and have excellent acuity because of the well formed and accurately placed ink drops.

In aqueous-based ink jet systems, ink drop quality can be improved by reducing the wettability of the discharge surfaces of the ink jet heads. This is accomplished by coating these surfaces with materials which inherently exhibit a significantly lower surface energy than the aqueous-based inks. The low surface energy of the coating material results in a relatively high ink contact angle which is well above the minimum angle required for reducing surface wettability near the ink discharge nozzle. Therefore, in the case of aqueous based inks, the conditions can be readily achieved for the production of high quality ink drops.

Applicants have now recognized that the large surface energy difference between many coating materials and aqueous-based inks, i.e., at least about 20 dynes/cm, do not inherently exist between these coatings and phase change inks. Therefore, most coating materials that substantially reduce discharge surface wettability for aqueous based inks will not perform similarly with phase change inks.

It has now been discovered by applicants that the above-described images can be formed with a phase change ink composition using an ink jet head having a nozzle plate that defines at least one discharge nozzle which does not have to be specifically configured. This is accomplished by increasing the ink contact angle in the area surrounding the discharge nozzles to a predetermined level thereby preventing substantial surface wetting of the surrounding area by the phase change ink

composition. This ink contact angle is increased by applying a layer of a selected coating material to the discharge surface of the ink jet head. By coating the discharge surface according to the teachings of the present invention, individual drops of the phase change ink fluid composition having a substantially uniform size and shape can be ejected in a predetermined pattern thereby forming thereon substantially undegraded, accurately placed printed images.

Thus, a method is provided for modifying an ink printing jet head as described above which comprises applying a layer of a coating material to the printing jet head surface area surrounding each said discharge nozzle. This coated surrounding surface area has an increased phase change ink contact angle of at least about  $50^\circ$ , at an operating temperature of at least about  $70^\circ\text{C}$ . The coated material is treated on the coated surrounding area for maintaining a high ink contact angle in the area surrounding the discharge nozzles. Thus, upon prolonged exposure of the surrounding area to the ink composition at an the operating temperture, the contact angle is at least about 20% greater than the ink contact angle for the surrounding area without treatment of the coated material. This prevents substantial surface wetting of the surrounding area by the ink composition. In this way, the ink printing jet head is capable of ejecting a plurality of above-described individual drops of the phase change ink composition for forming undegraded, accurately placed printed images on a printing medium.

The foregoing and other objects, features and advantages of the invention will become more readily apparent from the following detailed description of a preferred embodiment which proceeds with reference to the drawings.

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is a vertical sectional view of an ink jet head modified in accordance with the present invention.

FIG. 2 is a perspective view of an electron beam evaporation system employed to apply the coating material to the ink jet head of this invention.

FIG. 3 is a graphical representation of ink drop repetition rate vs. time-of-travel of the ink drops to a point 1 mm. from discharge nozzle for ink jet heads with and without the application of selected coating material.

## DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Referring now to FIG. 1, an ink jet head 10 for printing a phase change ink composition onto a printing medium is depicted. The ink jet head 10 includes a body portion 12 within which a single compartment ink chamber 14 is provided. The ink chamber 14 is enclosed by a plate 16 which forms a chamber wall. The outer portion of the nozzle plate 16 forms a discharge surface 15. An external ink jet drop discharge nozzle defined by nozzle plate 16, which forms the surrounding area for discharge nozzle 20, passes from the ink chamber 14 to the exterior of the ink jet head 10. Although a single nozzle 20 can be provided in the nozzle plate 16, a plurality of discharge nozzles and associated ink chambers are preferably furnished. Ink chamber 14, comprised of sections 22 and 24, is, but need not be, of generally circular cross sectional configuration. Section 24 is positioned adjacent to the wall 16 and the external ink nozzle 20, and is bounded by an interior wall 26 of ink jet head body 12. Section 22 is of greater diameter than section 24, and is bounded by an interior wall 28. The sections 22, 24 as depicted are, but need not be, symmetrical about the axis 30.

A melted phase change ink is delivered to an ink receiving inlet 32, flows through an ink passageway 34, and fills the ink chamber 14 within ink jet head 10. The end of ink chamber 14 opposite to external ink nozzle 20 is closed by a flexible membrane 38, such as of stainless steel. A piezoelectric ceramic disc 36, metalized on both sides and bonded to membrane 38, comprises one form of a pressure pulse generating actuator. However, other configurations using piezoelectric ceramics can be used herein. In response to electrical pulses applied across the piezoelectric disc, a pressure pulse is generated in ink chamber 14. This causes the ejection of an ink drop from the ink external nozzle 20. Ink drops are propelled towards the printing medium where they create the requisite printed image.

The discharge surface 18 of the nozzle plate 16 has a layer of coating material 50 selectively applied to the ink jet head in the area surrounding, as well as into, discharge nozzle 20 for purposes of preventing substantial surface wetting of the surrounding area by the drops of the phase change ink composition being discharged from the nozzle 20.

Through the use of surface coating layer 50, surface wetting is substantially decreased and the contact angle of the ink composition on the coating is substantially increased. Typically, the contact angle is measured using the procedure described in ASTM D724-45. Furthermore, the contact angle is substantially maintained on prolonged exposure of the surrounding area to the phase change ink composition at the phase change ink operating

temperature, typically at an operating temperature of at least about 70°C, preferably at least about 100°C, and most preferably at least about 150°C. Thus, the contact angle of the ink composition produced by employing the present invention with respect to the coating layer 50 is maintained at least about 50°, preferably at least about 55°, and more preferably at least about 60°. Coating materials were evaluated by measuring the contact angle of the phase change inks after soaking (or aging) the coating materials in the phase change inks at the 150°C temperature for a period of time of at least 24 hours. The angle between a given phase change ink and coating material was measured with a goniometer manufactured by Rame'-Hart Inc, bearing Model No. 100-00-115.

In order to maximize the contact angle, a minimum difference should be maintained between the surface energy of the coating material and the surface tension of the phase change ink composition, respectively. More specifically, the surface energy of the coating material is preferably lower than the surface energy of the phase change ink composition by at least about 4 dynes/cm, and more preferably at least about 6 dynes/cm. The surface energy of the coating material and the surface tension of the phase change ink composition are preferably measured on a goniometer, such as described above.

The material generally employed as the coating layer 50 is a polymeric material, preferably a fluorocarbon polymer, having the requisite ink contact angle and surface energy levels described above. The fluorocarbon polymers of choice are the Dupont trademarked Teflon® polymers, particularly Teflon® PTFE (polytetrafluoroethylene), Teflon® PFA (polyperfluoroalkoxybutadiene), or a fluorocarbon dispersion, such as a dispersion of either Teflon® PTFE or PFA. The preferred dispersion is a colloidal fluorocarbon polymer dispersed in electroless nickel, such as the above-described Teflon® PTFE dispersed in Richardson Industries' "Dynaplate" formulations 75-A and 75-R.

Various methods can be employed for applying the coating material 50 to the ink jet head 10. These methods can include thermal evaporation of the fluorocarbon polymers, dip, spray or spin coating of aqueous fluorocarbon dispersions with subsequent thermal curing, deposition of fluoropolymers onto the substrate by plasma polymerization of precursor monomers, and deposition of inclusions of colloidal fluorocarbons in electroless nickel. The preferred methods are the thermal evaporation of fluorocarbon resins and the deposition of colloidal fluorocarbons in electroless nickel.

In order to better maintain a low surface energy of the coating 50 upon prolonged ink exposure, the polymeric material is annealed by heating subse-

quent to deposition. This controlled heating often takes the form of a heating cycle in which the coating layer 50 is subjected to a plurality of individual heating steps, at a plurality of individual annealing temperatures, for a period of time to complete the annealing process. The preferred annealing temperature during the individual heating steps is from about 150°C to 500°C, and more preferably from about 200°C to 400°C.

Although most phase change ink compositions can be employed within the scope of this invention, the preferred phase change ink compositions are those which are effective at the aforementioned elevated operating temperatures. As an example, the phase change ink compositions can comprise a phase change ink carrier composition, preferably including a fatty amide-containing resin material along with a tackifier and a plasticizer, and a coloring material. The preferred fatty amide resin material is a combination of a tetraamide compound and stearyl stearamide.

#### EXAMPLE 1

This example illustrates a phase change ink printing jet head apparatus of the present invention, including a nozzle plate coated with a layer of coating material. It also sets forth a method of this invention for producing substantially undegraded, accurately placed phase change ink composition printed images. The subject coated apparatus is compared to the same printing jet head having an uncoated nozzle plate.

Thus, an experiment was conducted in which the printing jet head depicted in FIG. 1, with and without a coating layer 50 of Teflon® PFA (polyperfluoroalkoxybutadiene), applied as described in EXAMPLE 2, was employed to produce phase change ink drops. The jet heads had identical structural geometries and were built as a layered structure of chemically etched stainless steel plates that were bonded together into a monolithic unit.

The jets were characterized in terms of the drop formation process and the maximum number of drops that could be ejected per second before jet failure occurred. These characteristics were viewed from the ink aperture to an axial location approximately 1 mm downstream of the aperture with an imaging system, an electronic delay circuit, and a strobe light. The imaging system consisted of a microscope placed perpendicular to the trajectory of the ink drops. This microscope was connected to a video camera that in turn was connected to a monitor. System magnification was approximately 250X. The strobe light backlit the

drops. This unit was controlled by a delay circuit that was triggered by the drive signal to this jet. The drive waveform that was used for these measurements was one cycle of a sinusoidal wave with a period of 60 microseconds. With this delay circuit, temporal measurements of the drop formation process could be made.

A fatty amide ink composition was used which comprised the following: 39.2% of a tetra-amide manufactured by Union Camp, 49.0% Stearyl Stearamide, 9.8% of Foral 105 tackifier manufactured by Hercules Inc., and 2% of Sanicizer 278 plasticizer manufactured by Monsanto Company. An operating temperature of 160°C was used with each jet. The Union Camp tetraamide is produced by the reaction of one mole of dimer acid, 2 moles of ethylene diamine and 2 moles of stearic acid. For the coated and annealed surface, the contact angle was at least about 60° when the ink and surface were heated to 150°C. For the uncoated surface, the contact angle was at most about 20° at 150°C.

The voltage for each jet was set so that when each jet produced drops at a rate of 1000 drops per second, each drop reached a point one mm downstream of the nozzle in 350 microseconds. A one mm distance was chosen because it is representative of how far the print medium is from the jet nozzle in a printer application. As the rate of ejection was increased, any variation in either time required for the drops to reach one mm or in the size or shape of the drops was noted.

Figure 3 is a comparison of the performance of the two jets. The graph indicates that the jet having a discharge nozzle without a coating disposed thereon cannot produce as many drops per second as a jet having a discharge nozzle with such a coating. At about 2000 drops/sec., the jet without the coating failed to operate due to the meniscus wetting over the area surrounding the nozzle. The jet with the coating operated to more than 10,000 drops/s. For both jets, single drops were produced at every repetition rate up to the point at which the jet failed.

The maximum drop production rate at which the jet can operate directly affects the architecture of the print engine. The time required for a printer to produce a copy is directly related to the number of jets that are available for printing, as well as to the maximum number of drops per second that can be produced from each jet. If one thinks of the data in these terms, one might conclude that for a given copy time a printer having jets without the coating would require five times as many jets as a printer having jets with the coating. Otherwise, the copy time for the former printer would be about five times as great as for the latter.

The difference between the absolute maximum

and absolute minimum (which defines the range) time for the drops to reach one mm, as a function of repetition rate, also affects print engine architecture, since this range as a function of repetition rate is a direct measure of one type of drop placement error. This error limits the maximum, meaningful addressability (which will be defined as the number of dot locations per inch, where dot location refers to theoretical bit map locations rather than physical dot locations on the media) at which the jet can be used to print. An expression for this maximum addressability, in the direction of the printing, due to drop-time-to-media variations can be written as:

$$nD = 1 (V\Delta t)$$

where  $n$  is a positive number that reflects a tolerance on drop placement,  $D$  is the number of dot locations per inch,  $V$  is the relative velocity between the media and jet during drop ejection, and  $\Delta t$  is the range of time to reach the printing medium over the repetition rates at which the jet will print. A typical value for  $n$  might be three for a maximum allowable drop placement error of one-third of a dot location. If the error were larger than this, for instance, then even though the same number of dots could be located in an inch, the information contained in these dots would not be meaningful on the media. Therefore the maximum, meaningful addressability would be less. From this equation, for a given  $n$  and  $V$ , as  $\Delta t$  increases the addressability decreases. If the addressability is constant, one could lower the relative velocity in order to compensate for an increase in  $\Delta t$ . This smaller  $V$  will result in a longer copy time unless more jets are used to accomplish the same level of printing.

In FIG. 3, we see that the time-to-one mm increases rapidly for the uncoated jet until the jet fails. The range of  $\Delta t$  for this uncoated jet is about 120 microseconds. The range of  $\Delta t$  for the coated jet is only 25 microseconds. Therefore the presence of the coating improved the  $\Delta t$  by about five fold. From the previous discussion, this five fold difference in  $\Delta t$  means that for a given  $n$  and  $V$ , the addressability of the coated jet is five times that of the uncoated jet. Otherwise, the copy time of the coated jet would be five times less than that of the uncoated jet. Likewise, five times fewer coated jets are needed to achieve the same copy time and addressability as with the uncoated jets.

## EXAMPLE 2

This example illustrates a preferred method of application of a coating material of the present invention. Several commercial electron beam evaporators that are similar to our system are commercially

available for applying the coating layer. One such device is the CHA Industries electron beam evaporator, Model # SE 600. As depicted in FIG. 2, the coating material was applied to a sample coupon 70, made of stainless steel of the type used in the manufacture of ink jet discharge heads, by an electron beam evaporation system 60 comprising a bell jar 62 that seals onto and is supported by base 64 in order to form an enclosed vacuum deposition chamber 66. The polymeric coating material source was polyperfluoroalkoxybutadiene in the form of Teflon® PFA rod 68 located in a metal holding cup 72. The deposition chamber 66 was evacuated by a pump (not shown) in communication with chamber 66. A sample rack 74 was attached toward the top of the bell jar 62. The sample coupon 70 was set on rack 74 immediately above the rod 68. An electron beam source 76 was located immediately below the holding cup 72.

The chamber 66 was evacuated to an initial pressure of about  $5 \times 10^{-6}$  Torr. and a pressure during the evaporation of about  $5 \times 10^{-4}$  Torr. The electron beam power was maintained during the run at about 300 watts. The sample coupons were heated to a temperature of about  $120^\circ\text{C}$  by an infrared lamp 78 located above the sample coupons within the bell jar. Though the electron beam source is located below the holder, the beam was emitted at an angle and then focused with a magnetic field so that it was bent into the holder. The polymeric rod 68 was heated to a range of between  $300\text{--}600^\circ\text{C}$  by the electron beam source 76 which vaporized the polytetrafluoroethylene material the vapor of which then condensed onto the sample coupon for purposes of coating same. Coatings of about 400-600 nm thickness were obtained by this method.

The coated samples were subsequently annealed in a belt furnace under a nitrogen atmosphere for a total period of time of about 1.75 hours over the entire cure cycle. The belt furnace was divided into five temperature zones of substantially equal size. Thus, the belt was driven at a constant rate of speed so that the sample has a subsequently equal residence time in each temperature zone. The temperature in each zone can be the same or different than an adjacent zone. In this example, the cure cycle comprises a temperature sequence of  $200^\circ\text{--}400^\circ\text{--}400^\circ\text{--}400^\circ\text{--}200^\circ\text{C}$ .

The effect of a surface coating on the ink discharge surface surrounding the nozzle of a phase change ink jet was determined by comparing the ink wetting properties of coated and uncoated sample coupons made of stainless steel of the type used in the manufacture of ink jet discharge heads. The wetting properties of two samples, one PFA coated and one uncoated sample, were as follows:

a. The contact angle of the phase change ink on the annealed coated surface, measured at 150°C, was determined to be about 68° before aging. The surface tension of the melted phase change ink at 150°C was about 24.5 dynes/cm. The surface energy of the unaged coated surface was determined to be 16 dynes/cm. The contact angle of the phase change ink on the uncoated sample, measured under the same conditions, was only about 20°.

b. After aging the samples by soaking in the ink at 150°C for 72 hours, the contact angle of the annealed coated layer surface, measured at 150°C, was determined to be about 60°. The surface tension of the melted phase change ink at 150°C was also about 24.5 dynes/cm, and the surface energy of the aged coated surface was measured and determined to be about 20 dynes/cm. After aging, the contact angle of the uncoated sample, measured under the same conditions, was about 15°.

c. Samples which were coated with Teflon® PFA as described in EXAMPLE 2 above were aged by soaking same in the ink at 150°C for 72 hours. These coated samples were not annealed prior to aging. The contact angle of the phase change ink on these samples was determined to be about 72 degrees before aging and 40-43 degrees after aging.

Therefore, it has been demonstrated herein that ink jet heads coated with treated (annealed), aged fluorocarbon polymer will maintain a high contact angle, even upon prolonged exposure to phase change inks at operating temperatures, and in turn less degraded, more accurately placed printed images of the type previously set forth, than their untreated counterparts.

### EXAMPLE 3

EXAMPLE 2 was repeated employing a composite, coating layer of a fluorocarbon polymeric dispersion, in this case a dispersion of the polymer in electroless nickel.

In this experiment, a commercial electroless nickel mixture was utilized in the form of a Richardson Industries Dynaplate formulation. A boro-nickel composite was used herein, although most of these formulations are phosphate nickel based. A mixture of 150 ml/liter of Richardson Industries 752A preparation, 50 ml/liter of Richardson Industries 752A preparation, and 800 ml of distilled water were mixed with 50 ml of a DuPont 30 submicro PTFE emulsion, and were used as the coating material.

Stainless steel sample coupons were immersed in the above coating mixture at 85-90°C

for a period of 10 to 30 minutes and produced coating in the order of .0001" to .0004" thickness. The coupons were then annealed under nitrogen at 300°C for one hour.

The contact angle of the ink on the sample before aging was 60°, and was 58° after aging. The aging was conducted in the same manner as in EXAMPLE 2.

Therefore, it has been demonstrated that ink jet heads coated with other treated, unaged and aged fluorocarbon polymer, and more particularly the fluorocarbon polymeric dispersion described above, can be fabricated which will produce the requisite contact angle, and therefore the undegraded, accurately placed printed images of the type previously set forth, even from phase change ink compositions.

Having illustrated and described the principles of our invention in a preferred embodiment thereof, it should be readily apparent to those skilled in the art that the invention can be modified in arrangement and detail without departing from such principles. We claim all modifications coming within the spirit and scope of the accompanying claims.

### Claims

1. An ink jet printing head, comprising a body portion (12) having a discharge surface (18) defining at least one discharge nozzle (20) through which in use to eject individual drops of a phase change ink composition onto an adjacent printing medium to form a printed image, and a layer (50) of a coating material applied to the discharge surface (18) surrounding the discharge nozzle (20) to provide, in the area surrounding the nozzle, a contact angle of at least 50° to said ink composition at an operating temperature of at least 70°C, thereby preventing substantial surface wetting of the surrounding area by said ink composition.

2. The ink jet printing head of claim 1, wherein said coating material comprises an annealed fluorocarbon polymer.

3. The ink jet printing head of claim 2, wherein said fluorocarbon polymer comprises polytetrafluoroethylene, polyperfluoroalkoxybutadiene or a dispersion of polytetrafluoroethylene and polyperfluoroalkoxybutadiene.

4. The ink jet printing head of claim 2 or claim 3, wherein said fluorocarbon polymer is one which has been annealed by subjecting the layer (50) to a plurality of individual heating steps at a plurality of individual annealing temperatures.

5. The ink jet printing head of any preceding claim, wherein the difference in the surface energy of said coating material and the surface tension of

said ink composition is at least about 6 dynes/cm.

6. An ink jet printer wherein there is provided one or more printing heads as claimed in any preceding claim.

7. A method for modifying an ink jet printing head which method comprises applying a layer of a coating material to a printing head surface area about a discharge nozzle of the printing head through which nozzle in use to eject individual drops of a phase change ink composition onto an adjacent printing medium to form a printed image, and annealing the coating material of the so-applied layer, whereby the phase change ink composition contact angle of the printing head surface about the discharge nozzle at a temperature of 70°C is at least 50° so as to prevent substantial surface wetting of the surrounding area by said ink composition.

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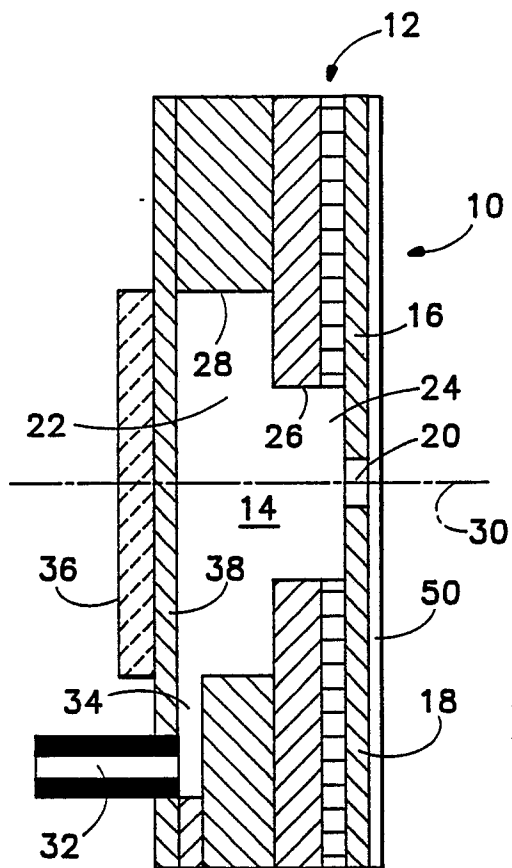


FIG. 1

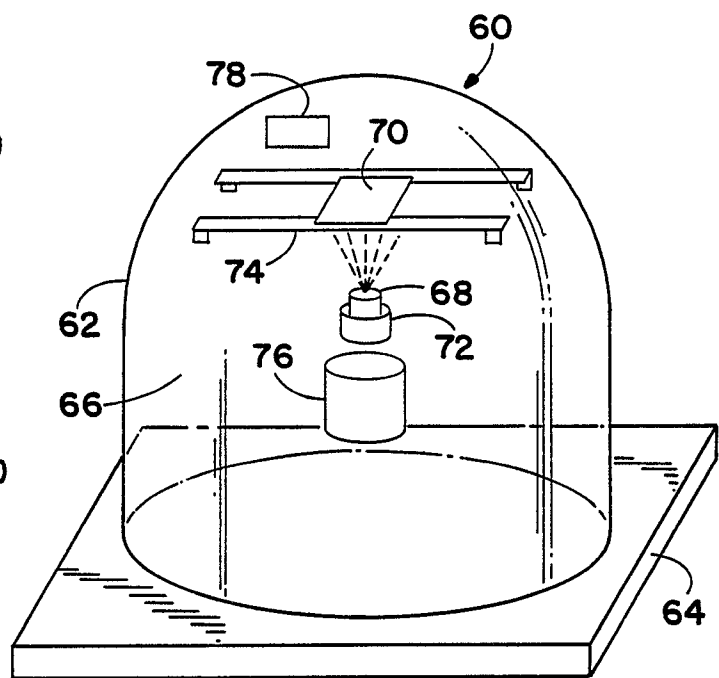


FIG. 2

### TWO IMPROVEMENTS TO HOT MELT INK DROP EJECTION DUE TO FLUOROPOLYMER SURFACE COATING

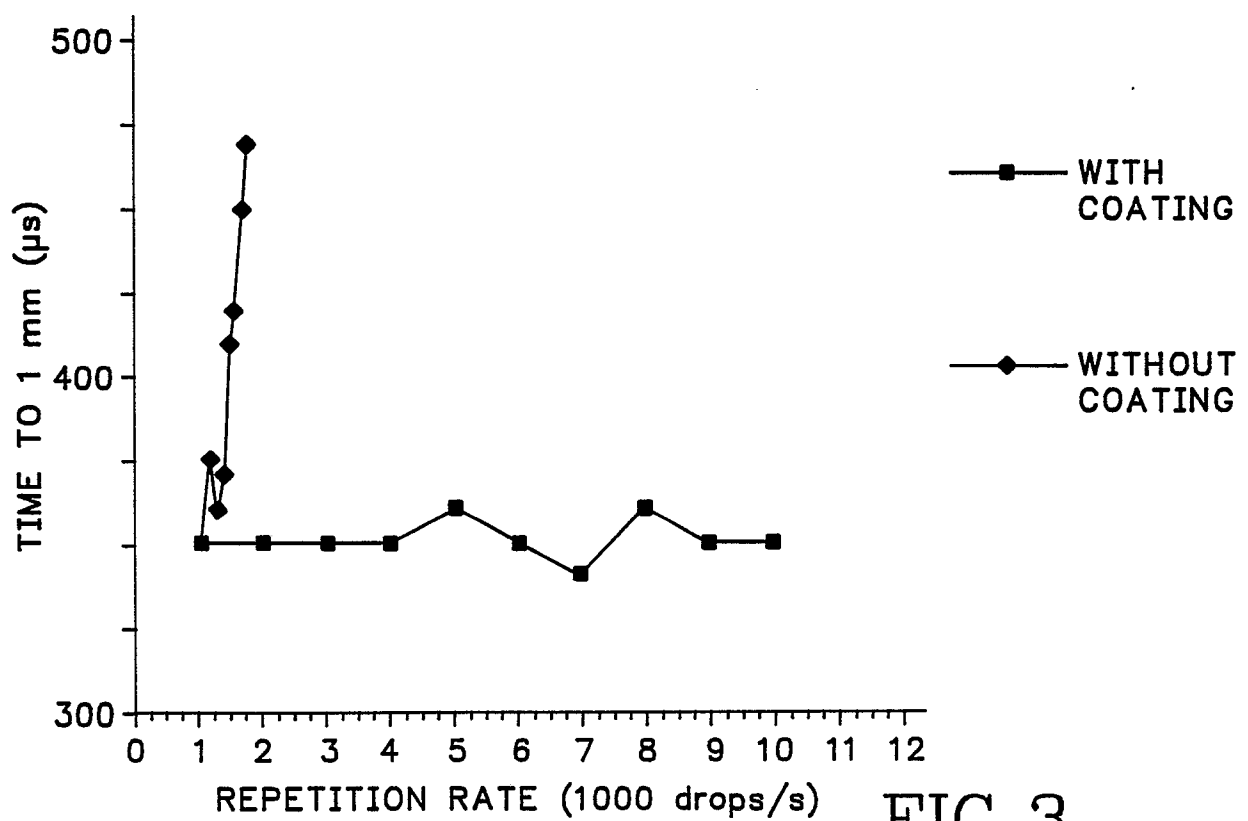


FIG. 3



| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                     |                                                                                         |                                                                                                                                                                                                                                                                                  | EP 89306750.4                                 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| Category                                                                                                                                                                                                                | Citation of document with indication, where appropriate, of relevant passages           | Relevant to claim                                                                                                                                                                                                                                                                | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| D, A                                                                                                                                                                                                                    | <u>US - A - 4 728 392</u><br>(MIURA)<br>* Column 8, line 59 - column 10, line 5 *<br>-- | 1-3,7                                                                                                                                                                                                                                                                            | B 41 J 2/005                                  |
| D, A                                                                                                                                                                                                                    | <u>US - A - 4 643 948</u><br>(DIAZ)<br>* Totality *<br>--                               | 1-3,7                                                                                                                                                                                                                                                                            |                                               |
| A                                                                                                                                                                                                                       | <u>US - A - 4 555 062</u><br>(YOU)<br>--                                                |                                                                                                                                                                                                                                                                                  |                                               |
| A                                                                                                                                                                                                                       | <u>EP - A1 - 0 213 240</u><br>(EXXON)<br>-----                                          |                                                                                                                                                                                                                                                                                  |                                               |
| The present search report has been drawn up for all claims                                                                                                                                                              |                                                                                         |                                                                                                                                                                                                                                                                                  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)         |
|                                                                                                                                                                                                                         |                                                                                         |                                                                                                                                                                                                                                                                                  | B 41 J<br>G 01 D                              |
| Place of search<br>VIENNA                                                                                                                                                                                               |                                                                                         | Date of completion of the search<br>10-10-1989                                                                                                                                                                                                                                   | Examiner<br>WITTMANN                          |
| CATEGORY OF CITED DOCUMENTS                                                                                                                                                                                             |                                                                                         |                                                                                                                                                                                                                                                                                  |                                               |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |                                                                                         | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br><br>& : member of the same patent family, corresponding document |                                               |