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71) Applicant: SEIKO EPSON CORPORATION 4-1, Nishishinjuku 2-chome Shinjuku-ku Tokyo-to (JP)

(72) Inventor : Tanaka, Yuji c/o Seiko Epson Corporation, 3-5, Owa 3-chome Suwa-shi, Nagano-ken (JP) Inventor: Hayashi, Hiroko c/o Seiko Epson Corporation, 3-5, Owa 3-chome Suwa-shi, Nagano-ken (JP) Inventor: Itano, Masaaki c/o Seiko Epson Corporation, 3-5, Owa 3-chome Suwa-shi, Nagano-ken (JP) Inventor: Ouki, Yasuhiro c/o Seiko Epson Corporation, 3-5, Owa 3-chome Suwa-shi, Nagano-ken (JP)

(4) Representative: Lewin, John Harvey Elkington and Fife Prospect House 8 Pembroke Road Sevenoaks, Kent TN13 1XR (GB)

(54) Printing heads for use in ink jet printing and method for producing the same.

(57) A printing head for use in ink jet printing comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle, at least a part of the ink channel comprising an activation-energy-ray- hardening resin is disclosed. The resin in the printing head has a certain hardened state. The printing head has improved resistance to ink compositions containing acetylene glycol which sometimes damage the conventional printing heads comprising an activation-energy-ray-hardening resin.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to heads for use in ink jet printing, and more particularly to heads for use in ink jet printing, having improved resistance to inks containing acetylene glycol, glycol ether or the like.

Background Art

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In general, a printing head for use in an ink jet printing method comprises an orifice from which a printing ink is jetted; an ink channel, connected to the orifice, having a portion at which energy is applied to a printing ink so that the ink can be jetted; and an ink container in which a printing ink to be supplied to the ink channel is stored. There has been known, as a method for producing such a head for use in ink jet printing, a method in which an ink channel is formed by providing a minute groove in a substrate made of glass, a metal or the like by means of, for instance, cutting or etching, and by attaching thereto another substrate. Further, Japanese Laid-Open Patent Publication No. 43876/1982 discloses a method in which an activation-energy-ray-hardening resin is coated onto a first substrate and subjected to desired-pattern-wise exposure and then to development to form therein a groove for an ink channel, followed by attaching thereto a second substrate to finally form an ink channel. Furthermore, Japanese Laid-Open Patent Publication No. 191053/1992 discloses a method in which a head for use in ink jet printing is produced in the same way as the above method, by superposing several layers of resin compositions.

These methods using an activation-energy-ray-hardening resin are advantageous in that a minute channel for a liquid can be accurately formed with high yield and that the mass production of a head having such a channel can be easily attained.

On the other hand, a highly efficient ink containing acetylene glycol or the like has been recently used as an ink composition for ink jet printing.

However, when such an ink composition containing acetylene glycol, glycol ether or the like is applied to the above head produced by using an activation-energy-ray-hardening resin, there has been observed such a phenomenon that the resin used for the head is damaged by the ink composition. Due to this phenomenon, there has been a limitation on the use of the highly efficient ink composition containing acetylene glycol or the like to the printing head produced by using an activation-energy-ray-hardening resin.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a printing head comprising an activation-energy-ray-hard-ening resin, having resistance to highly efficient ink compositions containing acetylene glycol or the like.

We have now found that the hardened state of an activation-energy-ray-hardening resin used is closely related to the resistance to the ink compositions of the above type. The present invention has been accomplished on the basis of this finding.

According to the first embodiment of the present invention, there is provided a printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the ratio (S) of the infrared spectral absorbance of an absorption peak observed between 1600 and 1650 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.05 to 0.5.

According to the second embodiment of the present invention, there is provided a printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the ratio (J) of the infrared spectral absorbance of an absorption peak observed between 900 and 920 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.13 to 0.26.

According to the third embodiment of the present invention, there is provided a printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the hardened resin after immersed in a 1% acetylene glycol solution at a temperature of 70°C for 15 days shows a drop of 0.07 to 0.5 in the Vickers Hardness against the one before subjected to the immersion.

Further, the present invention also provides a method for producing any one of the above printing heads,

comprising the steps of:

placing an activation-energy-ray-hardening resin on a first substrate,

irradiating the resin with activation energy rays to conduct desired-pattern-wise exposure,

removing the unhardened area of the resin to form a groove which will be an ink channel,

placing a second substrate on the resin provided on the first substrate to assemble a printing head, and irradiating the printing head with activation energy rays in such an amount as is required to make the resin into a hardened state which is defined in the above, respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

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In the drawings,

Fig. 1 is a partial cross-sectional view of a printing head according to the present invention;

Fig. 2(a) is a cross-sectional view of first substrate 11 on which first layer 13 of an activation-energy-ray-hardening resin is formed and which is subjected to desired-pattern-wise exposure (activation energy rays are indicated by arrows);

Fig. 2(b) is a cross-sectional view of the first substrate 11 on which unhardened areas of the first layer 13 are removed;

Fig. 2(c) is a cross-sectional view of the first substrate 11 to which the second substrate 12 is faced; and Fig. 2(d) is a cross-sectional view of the first substrate 11 and the second substrate 12 attached to first substrate 11 which are both irradiated with activation energy rays (activation energy rays are indicated by arrows).

DETAILED DESCRIPTION OF THE INVENTION

In this disclosure, an activation-energy-ray-hardening resin means a resin having a property that it is hardened due to polymerization or the like when irradiated with active energy rays, for instance, visible light, ultraviolet rays or electron beams. Resins having such a property have already been known, and can be utilized in the present invention. Many of these resins contain molecules having an ethylenically unsaturated bond or a functional group such as an epoxy group, and polymerization between the molecules proceeds through the functional group when activation energy rays are applied thereto. The resins are thus hardened due to this polymerization.

Specific examples of the resin which can be utilized in the present invention include those resins which contain a monomer having an ethylenically unsaturated bond. Examples of such a monomer include unsaturated monomers containing a carboxyl group, such as acrylic acid and methacrylic acid; unsaturated monomers containing a glycidyl group, such as glycidylacrylate and glycidylmethacrylate; hydroxyacryl esters of acrylic acid or methacrylic acid, such as hydroxyethylacrylate, hydroxyethylmethacrylate, hydroxypropylacrylate and hydroxypropylmethacrylate; and monomers having one or more ethylenically unsaturated bond, such as a monoester of acrylic acid or methacrylic acid and polyethylene glycol or polypropylene glycol.

Examples of another resin which can be utilized in the present invention include those resins which contain an epoxy group in the structure thereof. Specific examples of such a resin include epoxy resins such as of a bisphenol A type, of a novolak type, and of an alicyclic type. In addition, bisphenol A, bisphenol F, tetrahydroxyphenylmethane tetraglycidyl ether, resorcinol glycidyl ether and glycerol triglycidyl ether can also be utilized.

A commercially available resin can also be utilized in the present invention. Preferred examples of such a resin include "Photec SR-1300G", "Photec SR-3000", "Photec SR-2200G" and "Photec SR-2300G" (manufactured by Hitachi Chemical Co., Ltd.); "Ohdil PR-150", "Ohdil PR-155", "Ohdil SE-200" and "Ohdil SP-700" (manufactured by Tokyo Ohka Kogyo Co., Ltd.); and "A-400", "FH 5100" and "FH 6100" (manufactured by Fuji Hunt Electronics Technology Co., Ltd.).

The structure of a printing head according to the present invention, and the method for producing the printing head will now be explained by referring to the accompanying drawings.

Fig. 1 is a partial cross-sectional view of a printing head of the present invention. In the printing head 10, first substrate 11 and second substrate 12 which are made of glass, a resin, or a metal such as nickel or stainless steel are provided, and between these substrates are formed layers 13, 14 and 15 of an activation-energy-ray-hardening resin. In the resin layers are provided ink channel 16 and pressure chamber 17, which are connected to each other. The ink channel 16 is connected to an ink-supplying part (not illustrated), and an ink composition is thus supplied to the ink channel. Pressure-generating means 18 such as a piezoelectric element or an exothermic element is provided to the pressure chamber 17 so as to pressurize the ink composition in the pressure chamber 17. A droplet of the ink is jetted from ink nozzle 19 by the pressure generated by this pressure-generating means 18.

The printing head having the above structure may be produced by the following method.

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The first layer 13 of an activation-energy-ray-hardening resin is firstly formed on the first substrate 11. This resin layer is then subjected to desired-pattern-wise exposure, for example, by using a pattern mask or by means of scanning exposure (Fig. 2(a)). The unexposed, unhardened area of the resin layer is removed by using, for example, a solvent to form a groove which will be an ink channel (This is a so called a developing process) (Fig. 2(b)). If necessary, a second layer of an activation-energy-ray-hardening resin (layer 15 in Fig. 2(b)) can be provided on the first layer 13 in the same way, and a groove can also be formed therein. The layer 15 can be formed by forming a layer of an activation-energy-ray-hardening resin on the layer 13 which has been hardened and developed, subjecting the layer to desired-pattern-wise exposure, and then removing unhardened area of the layer to form the layer 15. A groove which will finally be an ink channel is thus formed on the first substrate.

The second substrate 12 is attached to the first substrate 11 which is provided with the groove for an ink channel. It is noted that the second substrate 12 may also be one having thereon a groove of a desired pattern provided by using an activation-energy-ray-hardening resin in the same manner as in the first substrate (Fig. 2(c)).

These two substrates are attached to each other in the following manner. The two substrates are firstly faced each other as shown in Fig. 2(c). The attachment of the substrates may be conducted by using an adhesive agent. However, according to the preferred embodiment of the present invention, they are attached to each other without using any adhesive agent. The resin layer provided on the first substrate 11 (and the resin layer on the second substrate 12 if provided) is hardened to such a degree that the resin layer can have minimum hardness required to form a groove therein. The two substrates are then brought into close contact with each other with pressure, and heat and/or activation energy rays are applied thereto to further harden the resin. The two substrates can thus be firmly attached to each other. When no adhesive agent is employed, activation energy rays are to be applied from the outside of the first and/or second substrates (Fig. 2(d)). Hence, the activation energy rays are required to have high transmission like electron beams when the substrates are not transparent. Although the intensity of electron beams to be applied may be unlimited, when electron beams with very high intensity are applied, there is a possibility that the substrates are broken. It is therefore preferable to use an electron beam generator having an accelerating voltage of approximately 150 to 300 KeV. The method using no adhesive agent is very suitable for the production of excellent printing heads, because an adhesive agent may be clog an ink channel during the production process of printing heads.

In the above method, a printing head according to the present invention can be obtained by controlling the irradiation with activation energy rays so that the activation-energy-ray-hardening resin will finally be in the hardened state set forth below.

The printing head according to the first embodiment of the present invention comprises an ink channel connected to an ink-jetting nozzle, at least a part of the ink channel comprising an activation--energy-ray-hard-ening resin in the hardened state set forth below. Namely, the hardened state of the resin is such that the ratio (S) of the infrared spectral absorbance of an absorption peak observed between 1600 to 1650 cm⁻¹ to the one observed between 1360 to 1400 cm⁻¹ is in the range of 0.05 to 0.5, preferably 0.1 to 0.4. A printing head having an ink channel which comprises an activation-energy-ray-hardening resin having the value S, the ratio between the above two absorption peaks, in the range is extremely stable to an ink composition containing acetylene glycol or the like, which will be described later, and ensures good ink jet printing.

According to the more preferred embodiment of the first embodiment of the present invention, there is provided a printing head having a value T of 3 or more and 40 or less, preferably 5 or more and 30 or less, the value T being defined by the following equation:

$$T = (Ef/Ei) \times 100$$

wherein Ef represents the ethylenically unsaturated bond content of the resin in the head (that is, the resin after hardened by exposure), and Ei represents the ethylenically unsaturated bond content of the resin before hardened.

The value Ef and Ei can be obtained, for example, in the following manner. In the infrared spectrum, an ethylenically unsaturated bond shows an absorption peak in the range of approximately 1600 to 1650 cm⁻¹. On the other hand, in an activation-energy-ray-hardening resin, there is a functional group which undergoes no change in its structure before and after hardening by exposure. An alkyl group which is an example of a functional group of this type shows an absorption peak in the range of approximately 1360 to 1400 cm⁻¹ in the infrared spectrum. The values Ei and Ef can be respectively obtained by calculating the ratios of the absorbances of the ethylenically unsaturated bond in the resin before and after hardened to the absorbance of the absorption peak attributed to an alkyl group.

A printing head having a value T in the above range ensures more excellent ink jet printing.

Due to the definition of the value Ef, there is a case where the value Ef is equal to the value S. The value

T is therefore more preferable in the sense of further restricting the value S. However, as is clear also from Examples described later, even a printing head comprising a resin in the hardened state defined by the value S, which is obtained from the resin after hardened by exposure, can also bring about good results. Therefore, a printing head comprising a hardened resin which has either a value S or a value T in the above range is included in the scope of the present invention.

A printing head according to the second embodiment of the present invention comprises an ink channel connected to an ink-jetting nozzle, at least a part of the ink channel comprising an activation-energy-ray-hard-ening resin in the hardened state set forth below. Namely, the hardened state of the resin is such that the ratio (J) of the infrared spectral absorbance of an absorption peak observed between 900 and 920 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.13 to 0.26, preferably 0.15 to 0.24. A printing head having an ink channel which comprises an activation-energy-ray-hardening resin having a value J, a ratio between the above two absorption peaks, in the range is extremely stable to an ink composition containing acetylene glycol or the like, which will be described later, and ensures good ink jet printing.

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According to the more preferred embodiment of the second embodiment of the present invention, there is provided a printing head having a value K of 40 or more and 70 or less, preferably 45 or more and 60 or less, the value K being defined by the following equation:

$$K = (Pf/Pi) \times 100$$

wherein Pf represents the epoxy group content of the resin contained in the head (that is, the resin after hardened by exposure), and Pi represents the epoxy group content of the resin before hardened.

The values Pf and Pi can be obtained, for example, in the following manner. In the infrared spectrum, an epoxy group shows an absorption peak in the range of approximately 900 to 920 cm⁻¹. Therefore, as in the case of the value T, the values Pi and Pf can be respectively obtained by calculating the ratios of the absorbances attributed to an epoxy group in the resin before and after hardened to the absorbance attributed to a functional group which undergoes no change in its structure before and after the resin is hardened by exposure.

A printing head having a value K in the above range ensures more excellent ink jet printing.

Due to the definition of the value Pf, there is a case where the value Pf is equal to the value J. The value K is therefore more preferable in the sense of further restricting the value J. However, as is clear also from Examples described later, even a printing head comprising a resin in the hardened state defined by the value J, which is obtained from the resin after hardened by exposure, can also bring about good results. Therefore, a printing head comprising a hardened resin which has either a value K or a value J in the above range is included in the scope of the present invention.

In the present invention, a printing head which fulfills the requirements in the first and second embodiments at the same time is preferred. Namely, a preferable printing head is one comprising a hardened resin whose S value is in the range of 0.05 to 0.5 and, at the same time, whose J value is in the range of 0.13 to 0.26.

Furthermore, according to another preferred embodiment of the present invention, when electron beams are applied from either the first substrate side or the second substrate side in the first or second embodiment, the sum total of the product of the density and the thickness of the substrate to which the electron beams are applied, and the product of the density and the thickness of the resin layer is preferably 1 kg·m/m³ or less, more preferably 0.7 kg·m/m³ or less. A printing head which fulfills such a condition can be efficiently hardened when electron beams are applied thereto. In the case where electron beams are applied from both the first substrate side and the second substrate side as shown in Fig. 2(d), the sum total of the product of the density and the thickness of the first and second substrate, and the product of the density and the thickness of the resin layer is preferably 2.0 kg·m/m³ or less, more preferably 1.4 kg·m/m³ or less. In the second substrate 12 of the printing head shown in Fig. 1, thin portions 20 are provided so as not to impair the mechanical strength of the printing head. It is also preferable to substantially decrease the above sum total by Providing such a thin portion 20.

A printing head according to the third embodiment of the present invention comprises an ink channel connected to an ink-jetting nozzle, at least a part of the ink channel comprising an activation-energy-ray-hardening resin in the hardened state set forth below. Namely, the hardened state of the resin is such that the hardened resin after immersed in a 1% acetylene glycol solution at a temperature of 70°C for 15 days shows a drop of 0.07 to 0.5 in the Vickers hardness against the one before subjected to the immersion. A printing head having an ink channel which comprises a resin in such a hardened state is extremely stable to an ink composition containing acetylene glycol or the like, which will be described later, and ensures good ink jet printing.

It is more preferable also in the third embodiment of the present invention that the values T and K be in the above respective ranges.

The printing heads according to the present invention are extremely stable to ink compositions containing acetylene glycol or the like, of which use to conventional printing heads produced by using an activation-en-

ergy-ray-hardening resin has been difficult, and ensure good ink jet printing.

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Ink compositions containing acetylene glycol represented, for example, by the following formula can be mentioned as the ink compositions of which use to conventional printing heads has been limited:

$$R^{1} - C - C = C - C - R^{2}$$

$$CH_{2} - CH_{2}$$

$$CH_{2} - CH_{2}$$

$$O + CH_{2} - CH_{2$$

wherein R^1 , R^2 , R^3 and R^4 represent independently a lower alkyl group, preferably a C_{1-6} alkyl group, more preferably a C_{1-4} alkyl group, and the total number of n and m is from 0 to 30, preferably from 3 to 10.

More specific examples of such acetylene glycol are shown in the following table:

	R ¹	R ²	R³	R ⁴	n+m
No. 1	iso-butyl	methyl	methyl	iso-butyl	10
No. 2	iso-butyl	methyl	methyl	iso-butyl	3.5
No. 3	ethyl	methyl	methyl	ethyl	10
No. 4	methyl	methyl	methyl	methyl	0
No. 5	ethyl	methyl	methyl	ethyl	0
No. 6	iso-butyl	methyl	methyl	iso-butyl	0

When an ink composition containing such acetylene glycol is applied to a conventional printing head, the resin in the printing head is dissolved or swollen, and, in addition, the resin layer is flaked off to damage the printing head. For this reason, it has been difficult to use the ink compositions of this type with conventional printing heads. However, the printing heads according to the present invention are extremely stable to the ink compositions, so that they can achieve good ink jet printing.

In addition to the above, the ink compositions which are so difficult to apply to the conventional printing heads include that containing as an organic solvent glycol-ether such as triethylene glycol monobutyl ether, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monobutyl ether or propylene glycol monobutyl ether.

There is no particular limitation on the formulation of ink compositions containing the acetylene glycol, glycol ether or the like, which can be applied to the printing heads according to the present invention. However, those ink compositions which contain 0.1 to 10% by weight, particularly 0.5 to 5% by weight of an organic solvent such as acetylene glycol are preferred.

The printing heads according to the present invention have a wide range of application, and can achieve good ink jet printing along with various ink compositions containing a variety of colorants, an organic solvent and an additive.

For instance, either a dye or a pigment can be used as the colorant. A coloring dye, a direct dye or a reactive dye can be used as a dye; and carbon black or an organic pigment of various types can be used as a pigment. The amount of a colorant to be added is determined in consideration of, for example, the density of printed images. It is however preferable that the amount of a colorant be approximately 0.5 to 10% of the total weight of the ink composition.

The printing heads according to the present invention ensure good ink jet printing to ink compositions prepared by using an organic solvent selected from alcohols having approximately 1 to 4 carbon atoms, such as

methanol, ethanol and propanol, ketones and ethers.

A wetting agent plays an important role in an ink composition for ink jet printing. The printing heads according to the present invention also ensure good ink jet printing to ink compositions containing a variety of wetting agents. Examples of the wetting agent include polyhydric alcohols such as glycerol, ethylene glycol, diethylene glycol, triethylene glycol and propylene glycol; nitrogen-containing compounds such as dimethylformamide, 1,3-dimethyl-2-imidazolidinone, 2-pyrrolidone and n-methyl-2-pyrrolidone; urea; and sugars.

Further, the printing heads according to the present invention also ensure good ink jet printing to ink compositions containing other additives such as a preservative, an antifungal agent, a chelating agent, a surface active agent.

The present invention will now be explained more specifically by referring to the following Examples. However, the present invention is not limited to or limited by these examples.

Production of Printing Heads

Printing heads according to the present invention were prepared in the following manner. An activation-energy-ray-hardening resin ("Ohdil PR-155" manufactured by Tokyo Ohka Kogyo Co., Ltd.) was coated onto the surface of a first substrate made of stainless steel, having a thickness of 100 μm . Then, the resin layer was subjected to desired-pattern-wise exposure (wavelength: 365 nm, exposure dose: 90 mJ/cm²) four times. The unhardened area of the resin layer was removed by using a solvent to form a groove which would be an ink channel. As a result, the thickness of the resin layer became 400 μm . A second substrate made of nickel, having a thickness of 30 μm was placed on and attached to this resin layer. This attachment was conducted in such a manner that the first substrate and the second substrate were brought into close contact with each other with the application of pressure 800 g/cm³ and heat 150°C, and then electron beams were applied thereto from both the first substrate side and the second substrate side. By changing the exposure dose of the electron beams applied, printing heads in which the resin was in various hardened states were obtained.

The hardened states of the resin in the printing heads thus obtained are as shown in the following tables. Drops in Vickers hardness and Young's modulus shown in the table were obtained by the following manner. A sample film (size: $5 \text{ mm} \times 10 \text{ mm}$; thickness: $200 \, \mu\text{m}$) was prepared from the same active-energy-ray-hardening resin as was used for preparing the above printing head, by making it into the same hardened state as in the above printing head. The sample was immersed in 1% acetylene glycol solution at 70°C for 15 days. The Vickers hardness values and the Young's modulus values of the sample before and after immersed were measured by an apparatus "Matsuzawa Seiki Co., Ltd." manufactured by Micro Hardness Tester Model DMH-1 and an apparatus "TMA=100" manufactured by Seiko Instruments Inc., respectively. The drop in the Vickers hardness and drop in the Young's modulus are measured by the equations set forth below.

Drop in Vickers hardness = 1 - Vickers hardness after immersed Vickers hardness before immersed Vickers hardness before immersed Young's modulus after immersed Young's modulus before immersed

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Table 1

			S	Т	Drop in Vickers hardness	Drop in Young's modulus
5	Example	A1	0.47	38	0.48	0.38
		A2	0.42	34	0.33	0.32
		А3	0.39	28	0.32	0.19
10		A4	0.31	19	0.21	0.10
		A 5	0.18	10	0.18	0.08
		A6	0.11	5	0.11	0.06
15		A7	0.07	7	0.38	0.28
		A8	0.25	25	0.11	0.08
		A9	0.09	12	0.19	0.25
20		A10	0.41	31	0.44	0.33
		A11	0.06	5	0.08	0.09
		A12	0.18	11	0.20	0.12
25		A13	0.32	24	0.25	0.18
		A14	0.48	35	0.45	0.35
	Comparative Example	A1	0.04	2	0.08	0.04
30		A2	0.53	45	0.65	0.55
		А3	0.62	52	0.69	0.49
		A4	0.65	60	0.80	0.70
35		A 5	0.03	2	0.05	0.02
		A6	0.55	42	0.63	0.52

Table 2

			J	К	Drop in Vickers hardness	Drop in Young's modulus
5	Example	B1	0.14	48	0.24	0.15
		B2	0.17	55	0.30	0.18
		В3	0.17	75	0.35	0.21
10		B4	0.2	66	0.41	0.17
		B5	0.2	30	0.28	0.14
		В6	0.22	56	0.31	0.25
15		В7	0.23	73	0.44	0.35
		В8	0.24	45	0.25	0.16
		В9	0.24	52	0.32	0.18
20		B10	0.25	60	0.48	0.33
	Comparative Example	B1	0.05	55	0.03	0.02
		B2	0.12	32	0.06	0.04
25		В3	0.28	45	0.55	0.45
		B4	0.33	82	0.65	0.70

Table 3

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			S	J	Drop in Vickers hardness	Drop in Young's modulus
	Example	C1	0.09	0.16	0.21	0.13
35		C2	0.33	0.21	0.18	0.08
		СЗ	0.24	0.18	0.15	0.06
		C4	0.47	0.14	0.29	0.18
40		C5	0.11	0.25	0.21	0.12
		C6	0.07	0.22	0.26	0.15
		C7	0.29	0.13	0.27	0.16
45		C8	0.42	0.17	0.20	0.12
		C9	0.19	0.15	0.10	0.05
		C10	0.39	0.20	0.24	0.10
50	Comparative Example	C1	0.73	0.09	0.55	0.45
		C2	0.02	0.34	0.53	0.44
		С3	0.61	0.31	0.88	0.80

The density of the first substrate, that of the second substrate, and that of the resin were approximately 7.9×10^3 kg/m³, approximately 8.85 kg/m³ and 1000 kg/m³, respectively. Therefore, the sum total of the product of the density and the thickness of the first substrate, that of the second substrate, and that of the resin layer

was 1.87 kg/m³.

Evaluation of Printing Heads

5 (Ink Compositions)

In order to evaluate the printing heads thus obtained, ink compositions having the following formulations were prepared.

In the following formulations, "%" means "% by weight"; and Acetylene glycols Nos. 1, 2, 5 and 6 are those having the structures which are given in the table shown previously.

Ink Composition I	
Acid Red 289	3%
Diethylene glycol	10%
Glycerol	15%
Acetylene glycol No. 1	1.5%
Water	q.s. to 100%

Ink Composition II	
Direct Blue 199	4%
2	
Glycerol	20%
Triethylene glycol	10%
Ethanol	5%
Acetylene glycol No. 5	2%
Water	q.s. to 100%

Ink Composition III	
Direct Yellow 86	2%
Glycerol	5%
Urea	5%
2-Pyrrolidone	5%
Acetylene glycol No. 1	1%
Acetylene glycol No. 6	0.4%
Water	q.s. to 100%

	EP 0 624 474 A2		
	Ink Composition IV		
	Food Black 2	4%	
5	Diethylene glycol	10%	
	1,3-Propane diol	4%	
	n-Propanol	4%	
10	Acetylene glycol No. 1	2%	
	Acetylene glycol No. 2	2%	
	Water	q.s. to 100%	
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	Ink Composition V		
	Direct Black 154	4%	
20	Glycerol	4%	
	Ethylene glycol	2%	
	Ethanol	5%	

Water

Ink Composition VI	
Direct Yellow 86	2%
Glycerol	3%
2-Pyrrolidone	3%
Water	q.s. to 100%

q.s. to 100%

Ink Composition VII	
Food Black 2	4%
Diethylene glycol	10%
1,3-Propane diol	5%
n-Propanol	4%
Water	q.s. to 100%

Ink Composition VIII	
Direct Blue 199	2%
Diethylene glycol	15%
Triethylene glycol monobutyl ether	10%
Water	q.s. to 100%

Ink Composition IX	
Acid Red 289	2%
Glycerol	10%
Diethylene glycol monobutyl ether	10%
Acetylene glycol No. 5	1%
Water	q.s. to 100%

Ink Composition X	
Acid Yellow 23	2%
2-Pyrrolidone	10%
Dipropylene glycol monobutyl ether	5%
Water	q.s. to 100%

Items and Methods of Evaluation

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Evaluation 1: Change in Young's Modulus

A sample film (size: 5 mm \times 10 mm; thickness: 200 μ m) was prepared from the same activation-energy-ray-hardening resin as was used for preparing the above-described printing head, by making it into the same hardened state as in the above printing head.

This sample was immersed in the above ink composition at 70°C for 15 days. The Young's modulus values of the sample before and after immersed were measured by an apparatus "TMA-100" manufactured by Seiko Instruments Inc. The ratio of the Young's modulus of the sample after the immersion to the one before the immersion was evaluated in accordance with the following criteria:

1 - 0.8 or more: excellent (③) less than 0.8 but 0.6 or more: good (○) less than 0.6: poor (x)

Evaluation 2: Degree of Swelling

The same sample as was used in Evaluation 1 was employed. The ratios of the thickness, the length and the width of the sample after the above immersion to those of the sample before the immersion were respectively obtained. The average of these three ratios was obtained, and evaluated in accordance with the following criteria:

1 - 0.95 or more: excellent (((iii))) less than 0.95 but 0.85 or more: good (()) less than 0.85: poor (x)

Evaluation 3: Flaking

The above printing head was immersed in the above ink composition at a surrounding temperature of 70°C for 15 days. Thereafter, the printing head was visually observed as to whether the substrates or the resin layer was flaked off or not, and evaluated in accordance with the following criteria:

No flaking was observed: good (○)

Flaking was slightly observed: slightly poor (Δ)

The substrates or the resin layer was completely flaked off: poor (x)

Evaluation 4: Printing Test

The above printing head was mounted on a printer, and the ink composition was charged in it. After printing was once conducted, the printer filled with the ink composition was allowed to stand at a surrounding temperature of 50°C for one month. Thereafter, printing was restarted, and the printed images obtained were evaluated in accordance with the following standard. It is noted that the response frequency of the printing head was 7.2 kHz and/or 4 kHz while the printing was conducted.

Printed images comparable to those obtained initially were obtained: good (O)

Unevenness was observed in the printed images: poor (x)

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45	Ink Composition	Evaluation Printing Head	Example C1 C2 C3 C4 C5 C6 C7 C8 C9	Comparative Example Cl C2 C3
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Claims

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1. A printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected

to the ink-jetting nozzle,

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at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the ratio (S) of the infrared spectral absorbance of an absorption peak observed between 1600 and 1650 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.05 to 0.5.

2. A printing head according to Claim 1, having a value T of 3 or more and 40 or less, the value T being defined by the following equation;

$$T = Ef/Ei \times 100$$

wherein Ef represents the ethylenically unsaturated bond content of the resin in the head, that is, the resin after hardened by exposure, and Ei represents the ethylenically unsaturated bond content of the resin before hardened.

3. A printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the ratio (J) of the infrared spectral absorbance of an absorption peak observed between 900 and 920 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.13 to 0.26.

4. A printing head according to Claim 3, having a value K of 40 or more and 70 or less, the value K being defined by the following equation:

$$K = Pf/Pi \times 100$$

wherein Pf represents the epoxy group content of the resin in the head, that is, the resin after hardened by exposure, and Pi represents the epoxy group content of the resin before hardened.

5. A printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the ratio (S) of the infrared spectral absorbance of an absorption peak observed between 1600 and 1650 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.05 to 0.5, and that the ratio (J) of the infrared spectral absorbance of an absorption peak observed between 900 and 920 cm⁻¹ to the one observed between 1360 and 1400 cm⁻¹ is in the range of 0.13 to 0.26.

- 6. A printing head according to any one of Claims 1 to 5, wherein the activation-energy-ray-hardening resin is in such a hardened state that the hardened resin after immersed in 1% acetylene glycol solution at 70°C for 15 days shows a drop of 0.05 to 0.4 in the Young's modulus against that of the hardened resin before immersed.
- **7.** A printing head for use in ink jet printing, comprising an ink-jetting nozzle and an ink channel connected to the ink-jetting nozzle,

at least a part of the ink channel comprising an activation-energy-ray-hardening resin,

the activation-energy-ray-hardening resin being in such a hardened state that the hardened resin after immersed in 1% acetylene glycol solution at 70°C for 15 days shows a drop of 0.07 to 0.5 in the Vickers hardness against that of the hardened resin before immersed.

8. A printing head according to Claim 7, having a value T of 3 or more and 40 or less, the value T being defined by the following equation:

$$T = Ef/Ei \times 100$$

wherein Ef represents the ethylenically unsaturated bond content of the resin in the head, that is, the resin after hardened by exposure, and Ei represents the ethylenically unsaturated bond content of the resin before hardened.

9. A printing head according to Claim 3, having a value K of 40 or more and 70 or less, the value K being defined by the following equation:

$$K = Pf/Pi \times 100$$

wherein Pf represents the epoxy group content of the resin in the head, that is, the resin after hardened by exposure, and Pi represents the epoxy group content of the resin before hardened.

10. A method for producing a printing head for use in ink jet printing which is defined by any one of Claims 1 to 9, comprising the steps of: placing an activation-energy-ray-hardening resin on a first substrate, irradiating the resin with activation energy rays to conduct desired-pattern-wise exposure, removing the unhardened area of the resin to form a groove which will be an ink channel, 5 placing a second substrate on the resin provided on the first substrate to assemble a printing head, and irradiating the printing head with activation energy rays in such an amount as is required to make the resin into a hardened state which is defined by any one of Claims 1 to 9. 10 11. A method according to Claim 10, wherein the activation energy rays irradiated with after the second substrate is placed are electron beams. 12. A method according to Claim 11, wherein the irradiation with activation energy rays is conducted from either the first substrate side or the second substrate side, and the sum total of the product of the density 15 and the thickness of the substrate to which the activation energy rays are applied, and the product of the density and the thickness of the resin layer is 1 kg·m/m³ or less. 13. A method according to Claim 11, wherein the irradiation with activation energy rays is conducted from both the first substrate side and the second substrate side, and the sum total of the product of the density 20 and the thickness of the two substrate and the product of the density and the thickness of the resin layer is 2 kg·m/m3 or less. 25 30 35 40 45 50 55

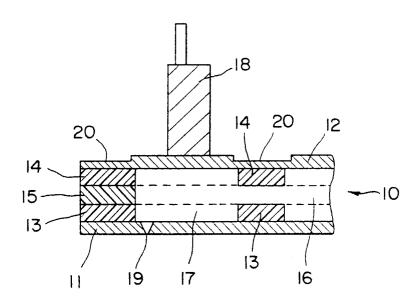


FIG. 1

