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### (54) Printing method

(57) Prints are produced without bleeding with an inkjet printer (1) that includes a print heating means (70) that heats media (30) from the back side of an inked surface of the media (30), and a preliminary heating means (40) that heats the media (30) from the back side of the inked surface before the media (30) is disposed at the position opposite the ink discharge face of a printhead

(14). The print heating means (70) and the preliminary heating means (40) heat the media (30) to make a surface temperature of the inked surface of the media (30) 40°C or more and 60°C or less. The printhead (14) discharges an ink that contains a binder resin, and the binder resin has a surface minimum filming temperature of 0°C or less.

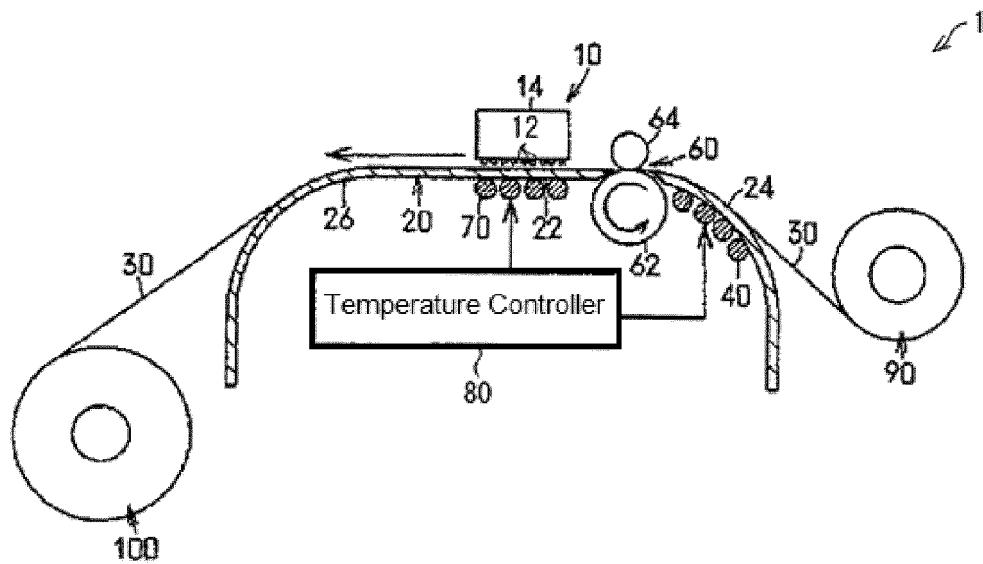


Fig. 1

**Description**

## BACKGROUND OF THE INVENTION

## 5 FIELD OF THE INVENTION

[0001] The present invention relates to a method for printing on a recording medium with an inkjet printer.

## DESCRIPTION OF THE BACKGROUND ART

10 [0002] Inkjet printers are known that prevents bleeding of a printed image with a preheater provided to heat a recording medium prior to printing, and a post-heater provided to heat a recording medium immediately after the printing, as described in JP-A-62-144955 (published June 29, 1987), and German Patent No. DE10056703C2 (published November 21, 2002). An inkjet printer provided with a preheater, a print heater, and a post-heater is also known, as described in 15 JP-A-2010-30313 (published February 12, 2010).

20 [0003] Referring to FIG. 4, the structure of an inkjet printer of related art such as JP-A-62-144955 and German Patent No. DE10056703C2 is described below. FIG. 4 is a side cross sectional view schematically illustrating the structure of an inkjet printer of related art. As illustrated in FIG. 4, an inkjet printer 3 expels droplets of ink through an array of nozzles 12 formed at the bottom surface of a printhead 14, causing the ink droplets to strike the surface of media 30 in dots on a platen 20. As a result, graphics and characters are printed as an array of ink dots on the surface of the media 30 by the inkjet printer 3. The ink droplets that struck the surface of the media 30 in dots as above permeate over a wide area around the impact positions of the ink droplets. This is problematic as it causes bleeding or blur in the graphics and characters printed as an array of ink dots on the surface of the media 30.

25 [0004] As a solution to such a problem, the inkjet printer 3 is provided with a preheater 40 and a post-heater 50. As illustrated in FIG. 4, the inkjet printer 3 uses the preheater 40 to heat the media 30 transported to a platen anterior portion 26, prior to printing. The post-heater 50 heats the media 30 immediately after the printing.

30 [0005] In this manner, the preheater 40 preliminarily heats the media 30 prior to printing to keep the media 30 warm and quickly dry the ink droplets that strike the surface of the media 30, and prevent the ink droplets from permeating over a wide area around the impact positions. The post-heater 50 quickly dries partially undried ink droplets remaining on the surface of the media 30, and prevents the ink droplets from permeating over a wide area around the impact positions. In this way, graphics and characters can be clearly printed as an array of ink dots on the surface of the media 30, without bleeding.

35 [0006] Inkjet printers generally use common water-soluble ink and lactate ink. However, water-soluble ink and lactate ink are unsatisfactory in terms of environment and media characteristics. Printers using water-soluble ink and lactate ink are thus not suited for printing graphics and characters on media for applications such as outdoor advertisement displays.

40 [0007] Latex ink, a dispersion or an emulsion of binder resin in water or water-soluble solvent, has sufficient environment and media characteristics, and is preferable for printing graphics and characters on media in application such as outdoor advertisement displays. However, latex ink has very high media diffusibility (wetting and spreading). Accordingly, the ink droplets that strike the media surface quickly diffuse over a wide area around the impact positions. The ink dots of latex ink thus cannot be clearly fixed at the impact positions of the ink on the media surface, and an array of ink dots cannot be clearly printed as graphics and characters without causing bleeding.

45 [0008] The inkjet printer 3 as described in JP-A-62-144955 and German Patent No. DE10056703C2 is not provided with a print heater that heats the placed ink droplets on the media 30 on site at a position below the scan range of the printhead 14, specifically opposite the ink discharge face of the printhead 14. Thus, when latex ink is used in the inkjet printer 3, the ink easily diffuses because the media 30 cannot have a sufficient surface temperature at the time when the ink strikes the media 30, even when the preheater 40 and the post-heater 50 heat the media 30 before and after the ink strikes the media 30.

50 [0009] The print heater can heat the ink droplets on site on the media 30 struck by the ink droplets, and can thus quickly dry the ink, and suppress diffusion of the ink on the media 30. However, because the print heater is provided opposite the ink discharge face of the printhead 14, the heat applied to the media 30 simultaneously solidifies the ink in the narrow diameter of the nozzles 12 in the printhead 14, and clogs the nozzles 12.

55 [0010] As the media used for inkjet printers, there has been development of media coated with various coating materials to prevent the placed ink droplets from permeating around the impact positions on the media surface, and fix the ink as small dots at the impact positions. However, such coated media are expensive, and are not practical for general purposes.

[0011] Various media are used for applications such as outdoor advertisement displays, including, for example, media that easily soften even under low-temperature heat (such as a vinyl chloride film), and media that do not easily soften even under high-temperature heat (such as a polyester film).

[0012] In the inkjet printer 3 as described in JP-A-62-144955 and German Patent No. DE10056703C2, the heat applied to the media 30 by the preheater 40 and the post-heater 50 shown in FIG. 4 is set to a constant, relatively high temperature, and is not adjustable. This is problematic when material such as a vinyl chloride film is used for the media 30, because such a film softens under the high-temperature heat of the preheater 40 and the post-heater 50, and cannot be smoothly transported on the platen 20. Specifically, the inkjet printer 3 cannot accommodate different media.

[0013] As a solution to such a problem, the inkjet printer described in JP-A-2010-30313 is provided with a preheater, a print heater, and a post-heater, and separately controls and drives each heater. However, use of the inkjet printer described in this publication is limited to solvent ink, and is not intended for various other inks.

## 10 SUMMARY OF THE INVENTION

[0014] The present invention has been made in view of these problems, and it is an object of the present invention to provide a printing method that enables an inkjet printer to clearly print with latex ink, without causing bleeding.

[0015] In order to solve the problems identified above, a printing method according to an embodiment of the present invention is a method for printing a recording medium with an inkjet printer that includes:

a printhead;  
 a driving means that moves and positions the recording medium and the printhead relative to each other;  
 a heating means provided at a position opposite an ink discharge face of the printhead, and that heats the recording medium from the back side of an inked surface of the recording medium positioned opposite the ink discharge face of the printhead by the driving means; and  
 a preliminary heating means that heats the recording medium from the back side of the inked surface before the recording medium is positioned opposite the ink discharge face of the printhead,  
 the method including:

heating the recording medium with the heating means and the preliminary heating means to make a surface temperature of the inked surface of the recording medium 40°C or more and 60°C or less; and  
 printing the recording medium by causing the printhead to discharge an ink that contains a solvent, a colorant, and a binder resin, wherein the binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less.

[0016] According this configuration, the inkjet printer is used to print the recording medium. In the inkjet printer, the driving means (driver) moves the printhead and the recording medium relative to each other to print the desired position of the recording medium. For printing, the preliminary heating means (heater) heats the recording medium from the back side of the inked surface before the recording medium is positioned opposite the ink discharge face of the printhead. The driver then transports the recording medium heated by the preliminary heater to the position opposite the ink discharge face of the printhead. The heating means (heater) provided opposite the ink discharge face of the printhead heats the transported recording medium from the back opposite the inked surface. The heater and the preliminary heater heat the recording medium in a manner that makes the surface temperature of the inked surface of the recording medium 40°C or more and 60°C or less.

[0017] The ink discharged from the printhead contains a solvent, a colorant, and a binder resin dispersed or emulsified in the solvent (hereinafter, such an ink is referred to as "latex ink"), and the binder resin has a surface minimum filming temperature of 0°C or less. The ink has excellent characteristics, particularly environment and media characteristics.

[0018] Droplets of the latex ink expelled through the nozzles of the printhead can strike the surface of the recording medium heated by the preliminary heater and the heater to a surface temperature of 40°C or more and 60°C or less. The ink droplets can thus quickly dry and fix without leaving time in the state of being fixed in dots at the impact positions, without diffusing over a wide area around the impact positions on the recording medium. Clear graphics and characters can thus be printed in the form of an array of latex ink dots on the surface of the recording medium without bleeding.

[0019] By heating the recording medium to a surface temperature of 40°C or more, the latex ink droplets that struck the surface of the recording medium can have a sufficient temperature under the transferred heat from the recording medium. On the other hand, by heating the recording medium to a surface temperature of 60°C or less, the recording medium will not be damaged by the applied heat, and can be smoothly transported onto the platen by the driver, even when a low heat-resistance film such as a vinyl chloride film is used as the recording medium. The present invention is thus applicable to essentially any recording medium, from low heat-resistance recording medium to high heat-resistance recording medium. The surface temperature range of 40°C to 60°C of the recording medium was found after the intensive studies conducted by the present inventor on the basis of the results of experiments in which graphics and characters were actually printed on the surface of various types of recording media with the latex ink using the inkjet printer according to the embodiment of the present invention.

[0020] The binder resin contained in the latex ink used in the present invention has a core-shell structure configured from an interior core portion and a surface shell portion. Because the binder resin has a surface minimum filming temperature (MFT) of 0°C or less, the latex ink can quickly start drying and fusing on the recording medium heated to a surface temperature of 40°C or more and 60°C or less.

5 [0021] By the stepwise heating with the preliminary heating means and the heating means, the surface temperature of the recording medium is finally brought to 40°C or more and 60°C or less, a suitable temperature range for drying and fusing the latex ink, by the time the ink strikes the recording medium. By heating the recording medium to a certain temperature in advance with the preliminary heating means, the surface of the recording medium can be brought to the desired temperature by the time the ink strikes the recording medium, even when the heating means alone fails to 10 sufficiently heat the recording medium to an appropriate temperature because of such factors as the thickness of the recording medium, and the ambient temperature of the inkjet printer.

15 [0022] Further, because the heater is disposed at a position opposite the ink discharge face of the printhead, heating the surface of the recording medium to 40°C or more and 60°C or less with the heater alone causes the ink to solidify and clog the narrow diameter of the nozzles in the printhead under the generated heat of the heater. In the embodiment 20 of the present invention, the surface temperature of the recording medium is brought to 40°C or more and 60°C or less by the stepwise heating with the preliminary heater and the heater by the time the ink strikes the recording medium. For example, by heating the recording medium to a certain temperature in advance with the preliminary heater, the surface of the recording medium can be heated to the desired temperature without generating high temperature in the heater. The ink can thus be prevented from solidifying and clogging the nozzles in the printhead under the generated heat of the heater.

[0023] The present invention can realize high image quality and fixing stability for the printed graphics and characters even for recording media used in outdoor advertisement displays and industrial applications that require high environment and media characteristics.

25 [0024] In the printing method according to the embodiment of the present invention, it is preferable that the binder resin have different minimum filming temperatures for a surface portion and an interior portion.

30 [0025] With this configuration, because the binder resin has different minimum filming temperatures for the surface and interior portions of the core-shell structure, drying and fusing can take place at different timings for the surface and interior portions of the binder resin, making it possible to provide separate functions. For example, the binder resin may be configured to dry and fuse on the surface first on the recording medium appropriately heated with the preliminary heater and the heater, before the interior dries and fuses under the heat of, for example, the drier that dries the recording medium struck by the ink.

35 [0026] The temperature used to dry the ink in inkjet printers of related art is typically set to about 80°C, whereas the actual drying temperature of the latex ink is believed to be about 50 to 60°C. By separately drying and fusing the surface and the interior of the binder resin, it is ensured that the latex ink is dried and fixed with the preliminary heater, and, for example, the post-heater, even when the heating temperature of the heater at the position opposite the ink discharge face of the printhead is set to a temperature that can avoid clogging of the ink.

40 [0027] In the printing method according to the embodiment of the present invention, it is preferable that the minimum filming temperature of the binder resin be lower in the surface portion than in the interior portion.

45 [0028] According to this configuration, because the minimum filming temperature of the binder resin in the latex ink is higher inside the resin than on the surface, the high-temperature storage stability of the latex ink can be improved. Because of the lower minimum filming temperature, the surface of the binder resin quickly starts drying and fusing on the recording medium heated with the preliminary heater and the heater. In this way, the binder resin surface having a lower minimum filming temperature can be clearly fixed without causing dot bleeding at the impact positions even when the latex ink is used that has very high diffusibility (wetting and spreading) for the recording medium, and that tends to quickly diffuse over a wide area around the impact positions of the ink droplets. The binding resin interior having a higher minimum filming temperature is then sufficiently dried and fused with, for example, the post-heater or the drier, and the latex ink that struck the recording medium can be sequentially dried, fused, and fixed in the direction of the transport of the recording medium.

50 [0029] In the printing method according to the embodiment of the present invention, it is preferable that the solvent be at least one of water and a hydrophilic solvent, and the latex ink contain the solvent in 50 weight% or more of the total weight of the latex ink.

[0030] According to this configuration, the impact of the ink on the environment can be relieved because of the high content of the water and/or hydrophilic solvent in the latex ink.

55 [0031] In the printing method according to the embodiment of the present invention, it is preferable that the heater and the preliminary heater be controlled to heat the recording medium at different temperatures.

[0032] According to this configuration, it is possible to separately control the temperature of the recording medium at and before arrival at the position opposite the ink discharge face of the printhead during the transport. The temperature of the recording medium can thus be accurately adjusted at the respective positions according to such factors as the

type and thickness of the recording medium, and the ambient temperature of the printer. This makes it possible to more accurately adjust the surface temperature of the recording medium in a temperature range of 40°C to 60°C by the time the ink droplets expelled from the ink discharge face of the printhead strike the recording medium.

**[0033]** In the printing method according to the embodiment of the present invention, it is preferable that the preliminary heater heat the inked surface of the recording medium to a surface temperature of 30°C or more and 50°C and less, and that the heater heat the inked surface of the recording medium to a surface temperature of 40°C or more and 60°C or less.

**[0034]** According to this configuration, the preliminary heater preliminarily heats the inked surface to a surface temperature of 30°C or more and 50°C or less before the recording medium is transported to the position opposite the ink discharge face of the printhead. The heater then heats the inked surface of the recording medium to a surface temperature of 40°C or more and 60°C or less when the recording medium transported after the preliminary heating reaches the position opposite the ink discharge face of the printhead. This ensures that the recording medium is always sufficiently heated to a surface temperature of 40°C or more and 60°C or less by the time the ink droplets expelled through the nozzles of the printhead strike the recording medium.

**[0035]** In the printing method according to the embodiment of the present invention, it is preferable that the heater and the preliminary heater be controlled to heat the recording medium at the same temperature.

**[0036]** According to this configuration, as the temperatures of the preliminary heater and the heater can be controlled in the same manner, the temperature control can be simplified.

**[0037]** In the printing method according to the embodiment of the present invention, it is preferable that the recording medium be one selected from the group consisting of a vinyl chloride sheet, a PET sheet, a tarpaulin sheet, and coated paper neither of which is coated with coating material, and uncoated polypropylene resin, uncoated glass, uncoated metal, and molded products thereof.

**[0038]** According to this configuration, high-quality graphics and characters can be printed with fixing stability, without bleeding, even when the recording medium is an all-purpose medium not coated with coating material or the like. Further, according to the foregoing configuration, it is possible to appropriately heat various types of recording media, including recording medium that soften under low temperature, and always allow such media to be smoothly transported. Specifically, no problem is posed in transporting different recording media, from low heat-resistance recording medium to high heat-resistance recording medium, and high-quality graphics and characters can be printed on such media with fixing stability, without bleeding.

**[0039]** In the printing method according to the embodiment of the present invention, it is preferable that the inkjet printer be adapted so that temperatures of the preliminary heater and the heater heating the recording medium are adjustably controlled with an operation panel provided for the printer, or with a printer-controlling host computer coupled to the printer.

**[0040]** According to this configuration, the heating temperatures of the preliminary heater and the heater can be adjustably controlled with an operation panel provided for the printer, or with a printer-controlling host computer, according to such factors as the type and thickness of the recording medium, and the ambient temperature of the printer. This makes it possible to always smoothly transport various types of recording media, for example, such as media that soften under low temperature, and print high image quality graphics and characters on such recording media with fixing stability, without bleeding.

**[0041]** In the method according to the embodiment of the present invention, it is preferable that the inkjet printer include a refresh mode unit that moves the printhead to a maintenance station, and causes the printhead to flush ink droplets through the nozzles to prevent the latex ink from solidifying and clogging the nozzles in the printhead.

**[0042]** According to this configuration, the refresh mode unit can be used to move the printhead to the maintenance station, and cause the printhead to flush ink droplets through the nozzles during the printing of graphics and characters with the latex ink. In this way, the latex ink can be prevented from solidifying and clogging the nozzles or other parts of the printhead. As a result, there will be no empty dots ("empty dots" describes the state where ink dots are absent in places ink dots are normally present), which might occur in part of the graphics and characters printed on the surface of the recording medium when the printhead is clogged.

**[0043]** In the method according to the embodiment of the present invention, it is preferable that the refresh mode unit provided in the inkjet printer move the printhead to the maintenance station at certain time intervals, and cause the printhead to flush ink droplets through the nozzles.

**[0044]** According to this configuration, the refresh mode unit can be used to move the printhead to the maintenance station at certain time intervals, and cause the printhead to forcibly flush ink droplets through the nozzles during the printing of graphics and characters with the latex ink. Because the printhead is moved to the maintenance station with the refresh mode unit during the printing of graphics and characters with the latex ink, it is ensured that the latex ink does not solidify and clog the nozzles in the printhead as might occur when ink droplets are not flushed through the nozzles of the printhead.

**[0045]** In the method according to the embodiment of the present invention, it is preferable that the inkjet printer include

a drier that dries the recording medium after the discharged ink droplets from the printhead strike the recording medium, and thereby dries the ink droplets adhering to the surface of the recording medium.

**[0046]** According to this configuration, the partially undried ink droplets adhering to the surface of the recording medium can be completely dried with the drier. The partially undried ink droplets adhering to the impact positions on the surface of the recording medium can be prevented from adhering to and contaminating other portions of the recording medium when the recording medium is wound into a roll or other form by, for example, the winder after the transport.

**[0047]** The printing method according to the embodiment of the present invention is a method for printing a recording medium with an inkjet printer. The method includes heating the recording medium with the heater and the preliminary heater to make a surface temperature of the inked surface of the recording medium 40°C or more and 60°C or less; and printing the recording medium by causing the printhead to discharge an ink that contains a solvent, a colorant, and a binder resin, wherein the binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less. The method enables graphics and characters to be clearly printed without bleeding.

#### BRIEF DESCRIPTION OF THE DRAWINGS

#### **[0048]**

FIG. 1 is a side cross sectional view schematically illustrating the structure of an inkjet printer according to an embodiment of the present invention.

FIG. 2 is a front view schematically illustrating the structure of an inkjet printer according to the embodiment of the present invention.

FIG. 3 is a side cross sectional view schematically illustrating the structure of an inkjet printer according to another embodiment of the present invention.

FIG. 4 is a side cross sectional view schematically illustrating the structure of an inkjet printer of related art.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0049]** A printing method according to an embodiment of the present invention is a method for printing a recording medium with an inkjet printer that includes:

a printhead;  
a driver that moves and positions the recording medium and the printhead relative to each other;  
a heater provided at a position opposite an ink discharge face of the printhead, and that heats the recording medium from the back side of an inked surface of the recording medium positioned opposite the ink discharge face of the printhead by the driver; and  
a preliminary heater that heats the recording medium from the back side of the inked surface before the recording medium is positioned opposite the ink discharge face of the printhead,  
the method comprising:

heating the recording medium with the heater and the preliminary heater to make a surface temperature of the inked surface of the recording medium 40°C or more and 60°C or less; and  
printing the recording medium by causing the printhead to discharge an ink that contains a solvent, a colorant, and a binder resin, wherein the binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less. Inkjet Printer 1

**[0050]** An example of the inkjet printer used in the printing method according to the embodiment of the present invention is described below with reference to FIGS. 1 and 2. FIG. 1 is a side cross sectional view schematically illustrating the structure of the inkjet printer according to the embodiment of the present invention. FIG. 2 is a front view schematically illustrating the structure of the inkjet printer according to the embodiment of the present invention.

**[0051]** As illustrated in FIGS. 1 and 2, an inkjet printer 1 includes a printhead 14, a printing section 10, a transport section 60, a print heater (heater) 70, and a preheater (preliminary heater) 40. The printing section 10 allows the printhead 14 to scan, and the transport section 60 transports media 30. The printing section 10 and the transport section 60 serve as a driving unit (driver) that moves and positions the media 30 and the printhead 14 relative to each other.

#### 55 Printhead 14

**[0052]** The printhead 14 is structured to expel droplets of latex ink (described later) through nozzles 12 arranged on the lower face of the printhead 14, using a method such as the piezo method. The printhead 14 is supported by a head

driving belt 16 constituting the printing section 10 as shown in FIG. 2 in a manner capable of freely scanning the printhead in transverse direction.

5 Printing Section 10

**[0053]** The printing section 10 allows the printhead 14 to scan in a direction orthogonal to the transport direction of the media 30 above a platen 20, moving and positioning the printhead 14 relative to the media 30.

10 Transport Section 60

**[0054]** The transport section 60 is configured from a feed roller 62 and a pressure roller 64 provided on opposite sides on the both sides of the platen 20. With the media 30 placed between the feed roller 62 and the pressure roller 64, the feed roller 62 is rotated forward (direction of arrow in FIG. 1) to transport the media 30 forward on the platen 20.

15 Print Heater 70

**[0055]** The print heater 70 is provided at a position opposite the ink discharge face of the printhead 14, and heats the media 30 from the back side of the inked surface of the media 30 disposed opposite the ink discharge face of the printhead 14 by the transport section 60. The print heater 70 is provided at a position opposite a platen central portion 22 with respect to the media 30. The print heater 70 heats the media 30 from the back surface opposite the inked surface to be struck by ink droplets, after the media 30 are transported to the platen central portion 22.

**[0056]** The print heater 70 may have any structure that heats the media 30 by the transferred heat via the platen 20 to the media 30 transported to the platen central portion 22. For example, an electrical heater using a ceramic or nichrome wire may be used as the print heater 70.

25 Preheater 40

**[0057]** The preheater 40 heats the media 30 from the back side of the inked surface before the media 30 are transported to the position opposite the ink discharge face of the printhead 14. The preheater 40 is provided at a position opposite a platen posterior portion 24 with respect to the media 30. The preheater 40 preliminarily heats the media 30 by heating the back surface opposite the inked surface to be struck by ink droplets, after the media 30 are transported to the platen posterior portion 24.

**[0058]** The preheater 40 may have any structure that preliminarily heats the media 30 by the transferred heat via the platen 20 to the media 30 transported to the platen posterior portion 24. For example, an electrical heater using a ceramic or nichrome wire may be used as the preheater 40.

Temperature Controller 80

**[0059]** The inkjet printer 1 may also include a temperature controller 80. The temperature controller 80 controls the heating temperatures of the preheater 40 and the print heater 70 in a manner that makes the surface temperature of the inked surface of the media 30 40 to 60°C by the time the discharged ink from the printhead 14 strikes the media 30. The temperature controller 80 may be configured from a combination of different components, such as a sensor that detects the generated heat temperatures of the preheater 40 and the print heater 70, and an electronic circuit that controls the generated heat temperatures.

**[0060]** The temperature controller 80 may be configured to independently control the heating temperatures of the preheater 40 and the print heater 70. Specifically, the temperature controller 80 may control the preheater 40 and the print heater 70 to have different heating temperatures. In this case, the temperature controller 80 can separately adjust the heating temperatures of the preheater 40 and the print heater 70 according to such factors as the type and thickness of the media 30, and the ambient temperature of the inkjet printer. This ensures that the surface temperature on the inked surface of the media 30 always falls in the desired temperature range of 40°C to 60°C by the accurate heating.

**[0061]** The temperature controller 80 may control the preheater 40 and the print heater 70 to have the same heating temperature. By using the same control for the temperatures of the preheater 40 and the print heater 70, the temperature control can be simplified.

**[0062]** Preferably, the temperature controller 80 controls the preheater 40 to heat the media 30 and make the surface temperature of the inked surface 30°C or more and 50°C or less, and controls the print heater 70 to heat the media 30 and make the surface temperature of the inked surface 40°C or more and 60°C or less. This ensures that the surface temperature always sufficiently falls in the 40°C to 60°C range at the time when ink droplets strike the media 30.

Media 30

[0063] The media 30 used in the inkjet printer 1 may be one selected from the group consisting of a vinyl chloride sheet, a PET sheet, a tarpaulin sheet, and coated paper neither of which is coated with coating material, and uncoated polypropylene resin, uncoated glass, uncoated metal, and molded products thereof.

[0064] The inkjet printer 1 can print high-quality graphics and characters with fixing stability, without bleeding, even when all-purpose media not coated with coating material or the like are used. Further, the inkjet printer 1 can appropriately heat various types of media, including media that soften under low temperature, and always allows such media to be smoothly transported. Specifically, the inkjet printer 1 does not pose any problem in transporting different media, from low heat-resistance media to high heat-resistance media, and can print high-quality graphics and characters on such media with fixing stability, without bleeding.

Host Computer 120

[0065] The inkjet printer 1 may also include a host computer 120. The host computer 120 controls the heating performed by the preheater 40 and the print heater 70, and the temperature control performed by the temperature controller 80. The host computer 120 also controls other print operations, including, for example, discharge of ink from the printhead 14, and transport of the media 30 by the transport section 60. The host computer 120 may be an operation panel provided for the inkjet printer 1.

Unwinder 90 and Winder 100

[0066] The inkjet printer 1 may also include an unwinder 90 and a winder 100. The unwinder 90 is provided posterior to the platen 20 (in the opposite direction of the arrowhead in FIG. 1). The unwinder 90 unwinds a roll of media 30, and sends the media 30 to the platen central portion 22.

[0067] The winder 100 is provided anterior to the platen 20 (the direction of the arrowhead in FIG. 1), and winds the media 30 into a roll after the media 30 are printed and sent forward past the platen anterior portion 26.

Refresh Mode Unit 140

[0068] As illustrated in FIG. 2, the inkjet printer 1 may include a refresh mode unit 140. The refresh mode unit 140 moves the printhead 14 to a maintenance station 130, and flushes ink droplets through the nozzles 12 of the printhead 14 into a pan 110 or the like provided in the maintenance station 130. In this way, the latex ink can be prevented from solidifying and clogging the nozzles 12. As a result, there will be no empty dots, which might occur in part of the graphics and characters printed on the surface of the media 30 when the printhead 14 is clogged.

[0069] The refresh mode unit 140 may move the printhead 14 to the maintenance station 130 and flush the ink during the printing of graphics and characters on the surface of the media 30 with the latex ink. Further, the refresh mode unit 140 may move the printhead 14 to the maintenance station 130 and flush the ink at certain time intervals during the printing of graphics and characters on the surface of the media 30 with the latex ink. This ensures that the latex ink does not solidify and clog the nozzles 12 in the printhead, which might occur when ink droplets are not flushed through the nozzles 12 of the printhead 14 during printing. The refresh mode unit 140 may be configured from an electronic circuit or the like of the host computer 120 controlling the printer.

Inkjet Printer 2

[0070] The inkjet printer 1 may be configured to further include a drier 150 as in the inkjet printer 2 shown in FIG. 3. FIG. 3 is a side cross sectional view schematically illustrating the structure of an inkjet printer according to another embodiment of the present invention.

Drier 150

[0071] As illustrated in FIG. 3, the inkjet printer 2 includes the drier 150 that dries the ink droplets adhered to the surface of the media 30 transported to the platen anterior portion 26. The drier 150 can dry the ink that remain partially undried on the surface of the media 30 struck by the ink discharged from the printhead 14. In this way, the partially undried ink droplets adhering to the surface of the media 30 wound into a roll from the platen anterior portion 26 by the winder 100 disposed in front thereof can be prevented from adhering to and contaminating other portions of the media 30.

[0072] The drier 150 may dry the ink droplets from the inked surface side of the media 30 as illustrated in FIG. 3, or from the back side of the inked surface of the media 30. The drier 150 may be realized by using, for example, a hot-air

drier, an infrared drier, or a heater drier that uses a ceramic or nichrome wire, either alone or in combination.

#### Printing Method

5 [0073] The following describes a printing method according to an embodiment of the present invention using the inkjet printer 1. First, the unwinder 90 unwinds a roll of the media 30 toward the platen posterior portion 24, and the transport section 60 transports the media 30 onto the platen posterior portion 24. The media 30 transported onto the platen posterior portion 24 are then preliminarily heated by the preheater 40 from the back side of the inked surface.

10 [0074] After being preliminarily heated, the media 30 are transported onto the platen central portion 22 by the transport section 60. At the platen central portion 22, the printing section 10 allows the printhead 14 to scan, and discharges the latex ink from the ink discharge face of the printhead 14 at the desired position. Here, the print heater 70 heats the media 30 from the back surface of the inked surface.

15 [0075] The temperature controller 80 controls the preheater 40 and the print heater 70 in such a manner that the surface temperature on the inked surface of the media 30 under the applied heat becomes 40°C or more and 60°C or less by the time the ink discharged from the printhead 14 strikes the media 30.

20 [0076] The ink droplets that struck the media 30 can thus quickly dry and fix without leaving time in the state of being fixed in dots at the impact positions, without diffusing over a wide area around the impact positions. Clear graphics and characters can thus be printed in the form of an array of ink dots on the surface of the media 30 without bleeding.

25 [0077] By heating the media 30 to a surface temperature of 40°C or more, the latex ink droplets that struck the surface of the media 30 can have a sufficient temperature under the transferred heat from the media 30. On the other hand, by heating the media 30 to a surface temperature of 60°C or less, the recording medium will not be damaged by the applied heat, and can be smoothly transported onto the platen 20 by the transport section 60, even when a low heat-resistance film such as a vinyl chloride film is used as the recording medium. The printing method according to the present embodiment is thus applicable to essentially any media 30, from low heat-resistance media 30 to high heat-resistance media 30. The surface temperature range of 40°C to 60°C of the media 30 was found after the intensive studies conducted by the present inventor on the basis of the results of experiments in which graphics and characters were actually printed on the surface of various types of media 30 with the latex ink using the inkjet printer according to the embodiment of the present invention.

30 [0078] The binder resin contained in the latex ink has a core-shell structure configured from an interior core portion and a surface shell portion. Because the binder resin has a surface minimum filming temperature (MFT) of 0°C or less, the latex ink can quickly start drying and fusing on the media 30 heated to a surface temperature of 40°C or more and 60°C or less. The latex ink will be described later in detail.

35 [0079] By the stepwise heating with the preheater 40 and the print heater 70, the surface temperature of the media 30 is finally brought to 40°C or more and 60°C or less, a suitable temperature range for drying and fusing the latex ink, by the time the ink strikes the media 30. By heating the media 30 to a certain temperature in advance with the preheater 40, the surface of the media 30 can be brought to the desired temperature by the time the ink strikes the media 30, even when the print heater 70 alone fails to sufficiently heat the media 30 to an appropriate temperature at the platen central portion 22 because of such factors as the thickness of the media 30, and the ambient temperature of the inkjet printer 1.

40 [0080] Further, because the print heater 70 is disposed at the position opposite the ink discharge face of the printhead 14, heating the surface of the media 30 to 40°C or more and 60°C or less with the print heater 70 alone causes the ink to solidify and clog the narrow diameter of the nozzles in the printhead 14 under the generated heat of the print heater 70. In the printing method according to the present embodiment, the surface temperature of the media 30 is brought to 40°C or more and 60°C or less by the stepwise heating with the preheater 40 and the print heater 70 by the time the ink strikes the media 30. For example, by heating the media 30 to a certain temperature in advance with the preheater 40, the surface of the media 30 can be brought to the desired temperature without generating high temperature in the print heater 70. The ink can thus be prevented from solidifying and clogging the nozzles in the printhead 14 under the generated heat of the print heater 70.

45 [0081] The media 30 with the graphics and characters printed on the surface in the form of an array of latex ink dots are then transported from the platen central portion 22 to the platen anterior portion 26 by the transport section 60. The winder 100 disposed anterior to the platen 20 then winds the media 30 into a roll, and the printing is finished.

#### Latex Ink

55 [0082] The ink used in the printing method according to the present embodiment contains a solvent, a colorant, and a binder resin. The binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less. Such an ink containing a solvent, a colorant, and a binder resin dispersed and emulsified in the solvent is called a latex ink. The latex ink is an emulsion containing a solvent, a colorant, and a binder resin, the binder resin being dispersed or emulsified in the solvent.

## Solvent

[0083] The solvent contained in the latex ink is preferably at least one of water and a water-soluble organic solvent.

[0084] Specific examples of the water-soluble organic solvent include polyalcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetraethylene glycol, polyethylene glycol, polypropylene glycol, 1,3-butanediol, 3-methyl-1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pantanediol, 1,6-hexanediol, glycerol, 1,2,6-hexanetriol, 1,2,4-butanetriol, 1,2,3-butanetriol, 2-methyl-2,4-pantanediol, methylpentanetriol, and 3-methoxy-3-methyl-1-butanediol; polyalcohol alkyl ethers such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, and propylene glycol monoethyl ether; polyalcohol aryl ethers such as ethylene glycol monophenyl ether, ethylene glycol mono benzyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monobutyl ether, diethylene glycol isobutyl ether, triethylene glycol isobutyl ether, and diethylene glycol isopropyl ether; nitrogen-containing heterocyclic compounds such as 2-pyrrolidone, N-methyl-2-pyrrolidone, N-hydroxyethyl-2-pyrrolidone, 1,3-dimethyl imidazolidinone,  $\epsilon$ -caprolactam, and  $\gamma$ -butyrolactone; amides such as formamide, N-methylformamide, and N,N-dimethylformamide; amines such as monoethanolamine, diethanolamine, triethanolamine, monoethylamine, diethylamine, and triethylamine; sulfur-containing compounds such as dimethyl sulfoxide, sulfolane, thiodiethanol, and thioglycol; propylene carbonate, ethylene carbonate, trimethylolpropane, tetramethylurea, and urea.

[0085] Particularly preferred among these water-soluble organic solvents are glycerine, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pantanediol, tetraethylene glycol, 1,6-hexanediol, 2-methyl-2,4-pantanediol, polyethylene glycol, 1,2,4-butanetriol, 1,2,6-hexanetriol, thioglycol, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-hydroxyethyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone. These water-soluble organic solvents have excellent solubility, and excel in preventing an expulsion characteristics failure due to moisture evaporation.

[0086] The latex ink may contain the water-soluble organic solvents either alone or in a combination of two or more kinds thereof.

[0087] The solvent content in the latex ink may be appropriately set according to such factors as the purpose of printing, and is preferably, for example, 50 weight% or more, more preferably 60 weight% or more, most preferably 70 weight% or more of the total amount of the latex ink. Preferably, the latex ink has a higher solvent content than the common aqueous inkjet ink, because the latex ink is generally recognized as an environmentally friendly eco-ink.

## Colorant

[0088] The colorant contained in the latex ink may be appropriately selected according to such factors as the purpose of printing. Examples of the colorant include dyes such as water-soluble dye, oil-soluble dye, and dispersion dye, and pigments. From the standpoint of desirable adsorbability and enclosure, the colorant is preferably an oil-soluble dye or a dispersion dye. Pigments are preferably used from the standpoint of the lightfastness of the produced image.

[0089] For efficient dissolving in the latex ink, the colorant is preferably one that easily dissolves in the water-soluble organic solvent. For example, the colorant is preferably one that dissolves in 2 g/L or more, more preferably 20 to 600 g/L in a ketone solvent.

[0090] The colorant content in the latex ink is preferably 10 to 200 weight parts, more preferably 25 to 150 weight parts with respect to 100 weight parts of the latex ink.

[0091] Preferably, the colorant contained in the latex ink is polymer grafted. Examples of such polymer grafted colorants include polymer grafted colorants represented by Synthesis Example 1 (carbon black), Synthesis Example 2 (yellow pigment), Synthesis Example 3 (magenta pigment), and Synthesis Example 4 (cyan pigment) of Examples below.

[0092] The colorant contained in the latex ink is more preferably one that contains polymer. Examples of such colorants containing polymer include polymer-containing colorants represented by Synthesis Example 5 (synthetic resin), Synthesis Example 6 (phthalocyanine), Synthesis Example 7 (quinacridone), Synthesis Example 8 (monoazo yellow pigment), and Synthesis Example 9 (carbon black) of Examples below.

[0093] A resin coated colorant also may preferably be used as the colorant contained in the latex ink. The resin coated colorant is a polymer emulsion containing a water-insoluble or poorly water-soluble colorant in polymer fine particles. As used herein, "containing a colorant" means the state of the colorant being enclosed in the polymer fine particles, and/or the state of the colorant being adsorbed to the surfaces of polymer fine particles. Here, it is not necessarily required that all the colorant mixed in the latex ink is enclosed in or adsorbed to the polymer fine particles, and the colorant may be dispersed in the emulsion to such an extent that it is not detrimental to the advantages of the present invention. The colorant is not particularly limited, as long as it is water-insoluble or poorly water-soluble, and can be adsorbed to the polymer.

[0094] As used herein, the colorant is water-insoluble or poorly water-soluble when 10 weight parts or more of the

colorant does not dissolve in 100 weight parts of 20°C water. The colorant is also deemed as water soluble when separation or sedimentation of the colorant is not observed in the surface layer or bottom layer of an aqueous solution by visual inspection under the same conditions.

**[0095]** The polymer used to form the polymer emulsion may be, for example, a vinyl polymer, a polyester polymer, or a polyurethane polymer. Vinyl polymers and polyester polymers are particularly preferred. Specific examples of such polymers include the polymers disclosed in JP-A-2000-53897 (Reference Literature 1), and JP-A-2001-139849 (Reference Literature 2).

**[0096]** The colorant used in the present invention is more preferably a pigment. However, a dye also may be used for the resin coated colorant. Some examples of such water-soluble dyes are presented below. Preferably, water-soluble dyes having excellent water resistance and excellent lightfastness are used.

#### Pigment

**[0097]** Carbon black as a black pigment represents an example of the pigment used as the colorant. Examples of color pigments include anthraquinone, phthalocyanine blue, phthalocyanine green, diazo, monoazo, pyranthrone, perylene, heterocyclic yellow, quinacridone, and (thio)indigoid. Representative examples of phthalocyanine blue include copper phthalocyanine blue, and derivatives thereof (pigment blue 15). Representative examples of quinacridone include pigment orange 48, pigment orange 49, pigment red 122, pigment red 192, pigment red 202, pigment red 206, pigment red 207, pigment red 209, pigment violet 19, and pigment violet 42. Representative examples of anthraquinone include pigment red 43, pigment red 194 (perinone red), pigment red 216 (brominated pyranthrone red), and pigment red 226 (pyranthrone red). Representative examples of perylene include pigment red 123 (vermillion), pigment red 149 (scarlet), pigment red 179 (maroon), pigment red 190 (red), pigment violet, pigment red 189 (yellow shaded red), and pigment red 224. Representative examples of thioindigoid include pigment red 86, pigment red 87, pigment red 88, pigment red 181, pigment red 198, pigment violet 36, and pigment violet 38. Representative examples of heterocyclic yellow include pigment yellow 117, and pigment yellow 138.

**[0098]** Other examples of the appropriate pigments include those described in The Color Index, the 3rd Ed. (The Society of Dyers and Colorists, 1982).

**[0099]** The pigment contained in the latex ink may be a pigment that has at least one hydrophilic group attached to the pigment surface either directly or via some other atom group, and that can be stably dispersed without using a dispersant. The pigment with the surface-introduced hydrophilic group is preferably an ionic pigment, preferably an anionic or cationic pigment.

**[0100]** Examples of the anionic hydrophilic group include -COOM, -SO<sub>3</sub>M, -PO<sub>3</sub>HM, -PO<sub>3</sub>M<sub>2</sub>, -SO<sub>2</sub>NH<sub>2</sub>, and -SO<sub>2</sub>NHCOR (in the formulae, M represents a hydrogen atom, alkali metal, or ammonium or organic ammonium, and R represents alkyl of 1 to 12 carbon atoms, optionally substituted phenyl, or optionally substituted naphthyl). Pigments with the -COOM or -SO<sub>3</sub>M attached to the pigment surface are particularly preferred. The method used to obtain an anionic pigment is not particularly limited, and may be performed by using, for example, a method in which the pigment is subjected to oxidation treatment with sodium hypochlorite, a method involving sulfonation, or a method involving reaction with a diazonium salt.

**[0101]** The hydrophilic group attached to the cationic color pigment surface may be, for example, a quaternary ammonium group. More preferably, pigments in which at least one of the quaternary ammonium groups below is attached to the pigment surface are used.

#### Dispersant

**[0102]** When the colorant contained in the latex ink is a pigment, a pigment dispersion may be used in which the pigment is dispersed in the solvent using a dispersant.

**[0103]** Known dispersants used for preparation of pigment dispersions are preferably used. Examples include polymer dispersants such as polyacrylic acid, polymethacrylic acid, acrylic acid-acrylonitrile copolymer, vinyl acetate-acrylic acid ester copolymer, acrylic acid-acrylic acid alkyl ester copolymer, styrene-acrylic acid copolymer, styrene-methacrylic acid copolymer, styrene-acrylic acid-acrylic acid alkyl ester copolymer, styrene- $\alpha$ -methylstyrene-acrylic acid copolymer, styrene- $\alpha$ -methylstyrene-acrylic acid copolymer-acrylic acid alkyl ester copolymer, styrene-maleic acid copolymer, vinylnaphthalene-maleic acid copolymer, vinyl acetate-ethylene copolymer, vinyl acetate-fatty acid vinyl ethylene copolymer, vinyl acetate-maleic acid ester copolymer, vinyl acetate-crotonic acid copolymer, and vinyl acetate-acrylic acid copolymer.

**[0104]** The nonionic or anionic dispersants used to disperse the pigment may be appropriately selected according to the type of the pigment, or ink formulation. Examples of the nonionic dispersants include polyoxyethylene alkyl ether (such as polyoxyethylene lauryl ether, polyoxyethylene myristyl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, and polyoxyethylene oleyl ether), polyoxyethylene alkyl phenyl ether (such as polyoxyethylene octyl phenyl

ether, and polyoxyethylene nonyl phenyl ether), polyoxyethylene  $\alpha$  naphthyl ether, polyoxyethylene  $\beta$  naphthyl ether, polyoxyethylene monostyryl phenyl ether, polyoxyethylene distyryl phenyl ether, polyoxyethylene alkyl naphthyl ether, polyoxyethylene monostyryl naphthyl ether, polyoxyethylene distyryl naphthyl ether, and polyoxyethylene polyoxypropylene block copolymer.

5 [0105] It is also possible to use dispersants in which the polyoxyethylene of the foregoing dispersants is partially replaced with polyoxypropylene, and dispersants in which a compound having an aromatic ring, such as polyoxyethylene alkyl phenyl ether, is condensed with a compound such as formalin.

10 [0106] The nonionic dispersant has an HLB of preferably 12 to 19.5, more preferably 13 to 19. With a nonionic dispersant having an HLB of 12 or more, the dispersant can have improved affinity for the dispersion medium, and dispersion stability improves. With a nonionic dispersant having an HLB of 19.5 or less, the dispersant is more easily adsorbed to the pigment, and dispersion stability improves. When more than one nonionic dispersant is used as a mixture, the HLB of the mixture may be adjusted to 12 or more and 19.5 or less.

15 [0107] Examples of the anionic dispersants include polyoxyethylene alkyl ether sulfate, polyoxyethylene alkyl phenyl ether sulfate, polyoxyethylene monostyryl phenyl ether sulfate, polyoxyethylene distyryl phenyl ether sulfate, polyoxyethylene alkyl ether phosphate, polyoxyethylene alkyl phenyl ether phosphate, polyoxyethylene monostyryl phenyl ether phosphate, polyoxyethylene distyryl phenyl ether phosphate, polyoxyethylene alkyl ether carboxylate, polyoxyethylene alkyl phenyl ether carboxylate, polyoxyethylene monostyryl phenyl ether carboxylate, polyoxyethylene distyryl phenyl ether carboxylate, naphthalene sulfonate formalin condensation product, melamine sulfonate formalin condensation product, dialkyl sulfosuccinate, dialkyl sulfosuccinate, polyoxyethylene dialkylsulfosuccinate, alkyl sulfoacetate,  $\alpha$ -olefin sulfonate, alkylbenzene sulfonate, alkylnaphthalene sulfonate, alkyl sulfonate, N-acylamino acid salt, acylated peptide, and soap. Particularly preferred are polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, and sulfate or phosphate of polyoxyethylene distyryl phenyl ether.

20 [0108] The dispersant is added in preferably 10 weight% or more and 50 weight% or less of the total pigment weight. When the dispersant is added in 10 weight% or more of the total pigment weight, the pigment dispersion and the ink can maintain preservation stability, and the dispersion time can be reduced. When the dispersant is added in 50 weight% or less of the total pigment weight, ink viscosity can be lowered, and discharge stability can improve.

25 [0109] The polymer dispersants, the nonionic dispersants, and the anionic dispersants may be used either alone or in a combination of two or more kinds thereof as may be appropriately decided according to intended use.

### 30 Dye

[0110] Specific examples of acidic dyes and food dyes as the colorant contained in the latex ink include C.I. acid yellow 17, 23, 42, 44, 79, 142; C.I. acid red 1, 8, 13, 14, 18, 26, 27, 35, 37, 42, 52, 82, 87, 89, 92, 97, 106, 111, 114, 115, 134, 186, 249, 254, 289; C.I. acid blue 9, 29, 45, 92, 249; C.I. acid black 1, 2, 7, 24, 26, 94; C.I. food yellow 3, 4; C.I. food red 7, 9, 14; and C.I. food black 1, 2.

35 [0111] Examples of direct dyes include C.I. direct yellow 1, 12, 24, 26, 33, 44, 50, 86, 120, 132, 142, 144; C.I. direct red 1, 4, 9, 13, 17, 20, 28, 31, 39, 80, 81, 83, 89, 225, 227; C.I. direct orange 26, 29, 62, 102; C.I. direct blue 1, 2, 6, 15, 22, 25, 71, 76, 79, 86, 87, 90, 98, 163, 165, 199, 202; and C.I. direct black 19, 22, 32, 38, 51, 56, 71, 74, 75, 77, 154, 168, 171.

40 [0112] Examples of basic dye include C.I. basic yellow 1, 2, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 40, 41, 45, 49, 51, 53, 63, 64, 65, 67, 70, 73, 77, 87, 91; C.I. basic red 2, 12, 13, 14, 15, 18, 22, 23, 24, 27, 29, 35, 36, 38, 39, 46, 49, 51, 52, 54, 59, 68, 69, 70, 73, 78, 82, 102, 104, 109, 112; C.I. basic blue 1, 3, 5, 7, 9, 21, 22, 26, 35, 41, 45, 47, 54, 62, 65, 66, 67, 69, 75, 77, 78, 89, 92, 93, 105, 117, 120, 122, 124, 129, 137, 141, 147, 155; and C.I. basic black 2, 8.

45 [0113] Examples of reactive dyes include C.I. reactive black 3, 4, 7, 11, 12, 17; C.I. reactive yellow 1, 5, 11, 13, 14, 20, 21, 22, 25, 40, 47, 51, 55, 65, 67; C.I. reactive red 1, 14, 17, 25, 26, 32, 37, 44, 46, 55, 60, 66, 74, 79, 96, 97; and C.I. reactive blue 1, 2, 7, 14, 15, 23, 32, 35, 38, 41, 63, 80, 95.

50 [0114] The pigments and dyes as the colorant contained in the latex ink may be appropriately selected according to such factors as the purpose of printing, and may be used either alone or in a combination of two or more kinds thereof.

### 55 Binder Resin

[0115] The binder resin contained in the latex ink has a core-shell structure configured from a core portion (inside) and a shell portion (surface) covering the core portion. The shell portion has a minimum filming temperature (MFT) of 0°C or less. The latex ink can thus quickly starts drying and fusing on the media 30 heated to a surface temperature of 40°C or more and 60°C or less.

55 [0116] The binder resin may have different minimum filming temperatures for the shell portion and the core portion.

[0117] In this way, drying and fusing can take place at different timings for the shell portion and the core portion of the binder resin, making it possible to provide separate functions. For example, the binder resin may be configured to dry

and fuse on the shell portion first on the media 30 appropriately heated by the preheater 40 and the print heater 70, before the core portion is dried and fused under the heat of, for example, the drier 150 that dries the recording medium struck by the ink.

[0118] The temperature used to dry the ink in inkjet printers of related art is typically set to about 80°C, whereas the actual drying temperature of the latex ink is believed to be about 50 to 60°C. By separately drying and fusing the shell portion and the core portion of the binder resin, it is ensured that the latex ink is dried and fused with the preheater 40, and, for example, the drier, even when the heating temperature of the print heater 70 at the position opposite the ink discharge face of the printhead is set to a temperature that can avoid clogging of the ink.

[0119] Another reason for having different minimum filming temperatures for the shell portion and the core portion of the binder resin is to further improve the preservation stability of the binder resin. Specifically, by taking advantage of the characteristics of the high MFT phase and low MFT phase of different minimum filming temperatures (MFT; hereinafter, simply "MFT"), it is possible to improve both the fixability and the preservability of the ink while keeping good balance between these two properties. The latex ink according to the embodiment of the present invention containing the binder resin of such a configuration is also desirable in terms of reliability, print quality (such as bleeding), abrasion resistance, and discharge stability.

[0120] Further, because of the low MFT of the shell portion, the ink immediately films after being discharged and striking the media 30, and can thus accommodate high-speed printing.

[0121] The MFT of the shell portion is not limited, as long as it is lower than the MFT of the core portion, and is preferably 0°C or less. The shell portion with the MFT of 0°C or less (hereinafter, also referred to as "low MFT phase") films at ordinary temperature, and can improve fixability of the placed ink. The MFT of the low MFT phase is not limited, as long as it is 0°C or less. However, a temperature of -20°C or more and 0°C or less is preferred for improved effects.

[0122] The MFT of the core portion is not limited, as long as it is higher than the MFT of the shell portion, and is preferably 10°C or more. The core portion with the MFT of 10°C or more (hereinafter, also referred to as "high MFT phase") helps to spread the binder resin particles on the media 30, and fix the pigment colorant over the recording medium. The high MFT phase of 10°C or more is preferred, because it allows the binding of the paper fiber to automatically proceed without having the need to subject the image supporting medium on which an image is formed to processes such as heating and drying. The MFT of the high MFT phase is thus preferably 10°C or more, and is further preferably 20°C or more for improved effects.

[0123] As used herein, "minimum filming temperature (MFT)" is defined as the minimum temperature at which an aqueous emulsion prepared by dispersing the binder resin in water and cast onto a metal plate such as aluminum forms a transparent continuous film under increasing temperatures.

[0124] Specifically, MFT is the value measured with an MFT measurement device such as a filming temperature tester (Imoto Machinery Co., Ltd.), and a TP-801 MFT tester (Tester Sangyo Co., Ltd.). The measurement method specified by JIS K6828-1996 also may be used. Further, MFT can be adjusted, for example, by controlling the Tg (glass transition point) of the binder resin particles, more specifically by varying the proportion (added ratio) of the constituent monomer of the binder resin particles, when the binder resin particles are copolymer. Further, low MFT binder resin particles may be prepared by adding a filming auxiliary agent to high MFT binder resin particles. Here, the filming auxiliary agent is added, because it can lower the filming temperature, specifically the MFT of the binder resin particles.

[0125] Examples of the binder resin include "polymer emulsion" particles. By "polymer emulsion", it means an emulsion in which a polymer is dispersed or emulsified as an independent phase in the presence of a surfactant in a solvent having an aqueous continuous phase. The polymer emulsion is obtained by the emulsion polymerization of an ethylenic unsaturated monomer. The polymer emulsion is preferably a vinyl polymer emulsion from the standpoint of dispersion stability. The polymer in the polymer emulsion may be used alone or in a combination of two or more kinds thereof.

[0126] From the standpoint of accelerating the drying of the ink printed on media, the polymer of the polymer emulsion preferably has the constituting unit represented by the following formula (1).



[0127] In the formula (1), R<sup>1</sup> represents a hydrogen atom or methyl group. R<sup>2</sup> represents optionally substituted arylalkyl group of 7 to 22, preferably 7 to 18, further preferably 7 to 12 carbon atoms, or aryl group of 6 to 22, preferably 6 to 18, further preferably 6 to 12 carbon atoms. The substituents may contain a heteroatom. Examples of the heteroatom include a nitrogen atom, an oxygen atom, and a sulfur atom.

[0128] Specific examples of R<sup>2</sup> include benzyl group, phenethyl group (phenylethyl group), phenoxyethyl group, diphenylmethyl group, and trityl group.

[0129] Specific examples of the substituents include alkyl group, alkoxy group, or acyloxy group of preferably 1 to 9 carbon atoms, hydroxy group, ether group, ester group, and a nitro group.

[0130] From the standpoint of developing high glossiness, the constituting unit represented by formula (1) is particularly preferably one derived from benzyl(meth)acrylate.

**[0131]** The constituting unit represented by formula (1) is preferably obtained by polymerizing the monomer represented by the following formula (1-1).



(In the formula (1-1),  $R^1$  and  $R^2$  are the same as in formula (1).)

**[0132]** Specifically, a polymer having the constituting unit represented by formula (1) can be synthesized by polymerizing compounds such as phenyl (meth) acrylate, benzyl (meth) acrylate, 2-phenylethyl(meth)acrylate, phenoxyethyl(meth)acrylate, 1-naphthalyl acrylate, 2-naphthalyl (meth)acrylate, phthalimidemethyl(meth)acrylate, p-nitrophenyl(meth)acrylate, 2-hydroxy-3-phenoxypropyl(meth)acrylate, 2-methacryloyloxyethyl-2-hydroxypropylphthalate, and 2-acryloyloxyethyl phthalic acid. Particularly preferred is benzyl(meth)acrylate. The constituting unit derived from these (meth)acrylates may be used alone or in a combination of two or more kinds thereof.

**[01331]** As used herein, "(meth) acryl" means "acryl", "(meth) acryl", or a mixture of these.

[0134] The preferred monomer configurations of the binder resin contained in the latex ink are described below in detail.

**[0135]** It is particularly preferable that the binder resin contains (b) a macromonomer-derived constituting unit, (c) a hydrophobic monomer-derived constituting unit, (d) a hydroxyl group-containing monomer-derived constituting unit, and (e) an oxyalkylene group-containing monomer-derived constituting unit.

(a) A salt forming group-containing monomer-derived constituting unit, (b) the macromonomer-derived constituting unit, (c) the hydrophobic monomer-derived constituting unit, (d) the hydroxyl group-containing monomer-derived constituting unit, (e) and the oxyalkylene group-containing monomer-derived constituting unit may be contained alone. However, it is more preferable to contain more than one of (a) to (e), further preferably all of (a) to (e).

**[0136]** The binder resin more preferably contains (a) the salt forming group-containing monomer-derived constituting unit. In this way, polymer dispersibility can improve. (a) The salt forming group-containing monomer-derived constituting unit may be obtained by polymerizing a salt forming group-containing monomer. After polymerization, a salt forming group (anionic group or cationic group) may be introduced to the polymer chain. Examples of the salt forming group include anionic groups such as a carboxyl group, a sulfonic acid group, and a phosphoric acid group; and cationic groups such as an amino group, and an ammonium group.

(a) The salt forming group-containing monomer is more preferably (a-1) an anionic monomer, or (a-2) a cationic monomer.

**[0137]** Examples of (a-1) anionic monomer include an unsaturated carboxylic acid monomer, an unsaturated sulfonic acid monomer, and an unsaturated phosphoric acid monomer.

**[0138]** Examples of the unsaturated carboxylic acid monomer include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, and 2-methacryloyloxyethyl succinic acid.

**[0139]** Examples of the unsaturated sulfonic acid monomer include styrene sulfonic acid, 2-acrylamide-2-methyl propane sulfonic acid, 3-sulfopropyl(meth)acrylic acid ester, and bis-(3-sulfopropyl)-itaconic acid ester.

**[0140]** Examples of the unsaturated phosphoric acid monomer include vinylphosphonic acid, vinylphosphate, bis(methacryloxyethyl) phosphate, diphenyl-2-acryloyloxyethyl phosphate, diphenyl-2-methacryloyloxyethyl phosphate, and dibutyl-2-acryloyloxyethyl phosphate.

**[0141]** From the standpoint of ink viscosity and dischargeability, (a-1) anionic monomer is preferably an unsaturated carboxylic acid monomer, more preferably acrylic acid, or methacrylic acid.

**[0142]** Examples of (a-2) cationic monomer include unsaturated tertiary amine-containing vinyl monomer, and an unsaturated ammonium salt-containing vinyl monomer.

**[0144]** Examples of the unsaturated ammonium salt-containing monomer include N,N-dimethylaminoethyl(meth)acrylate quaternary monomer, N,N-diethylaminoethyl(meth)acrylate quaternary monomer, and N,N-dimethylaminopropyl(meth)acrylamide, vinylpyrrolidone, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-6-vinylpyridine, and 5-ethyl-2-vinylpyridine.

(c-2) Cationic monomer is more preferably N,N-dimethylaminopropyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate quaternary monomer, and N,N-dimethylaminopropyl(meth)acrylate quaternary monomer.

(a) The salt forming group-containing monomer may be used either alone or in a combination of two or more kinds

thereof.

[0145] The binder resin more preferably contains (b) macromonomer-derived constituting unit. (b) Macromonomer-derived constituting unit is used to improve preservation stability and abrasion resistance, and may be obtained by polymerizing a macromonomer having a polymerizable functional group at one of the terminals.

[0146] Preferred as (b) macromonomer are (b-1) styrene macromonomer having a polymerizable functional group at one of the terminals, (b-2) alkyl (meth)acrylate macromonomer having a polymerizable functional group at one of the terminals, and (b-3) silicone macromonomer having a polymerizable functional group at one of the terminals. The polymerizable functional group present at one of the terminals is preferably an acryloyloxy group or a methacryloyloxy group, and the polymer having a macromonomer-derived constituting unit may be obtained by copolymerizing such monomers.

[0147] Examples of (b-1) styrene macromonomer having a polymerizable functional group at one of the terminals include a styrene homopolymer having a polymerizable functional group at one of the terminals, and a copolymer of styrene and other monomer with a polymerizable functional group attached to one of the terminals. Examples of other monomer include (i) acrylonitrile, (ii) (meth)acrylic acid esters having alkyl group and 1 to 22 carbon atoms, preferably 1 to 18 carbon atoms, and optionally hydroxyl group, and (iii) aromatic ring-containing monomers other than styrene.

[0148] Examples of (ii) (meth)acrylic acid esters include methyl(meth)acrylate, ethyl(meth)acrylate, (iso)propyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, (iso or tert-)butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, (iso)octyl(meth)acrylate, (iso)decyl(meth)acrylate, and (iso)stearyl(meth)acrylate.

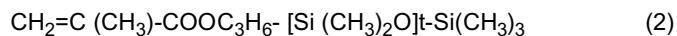
[0149] As used herein, "(iso or tert-)" and "(iso)" are inclusive of both the presence of a branched structure as represented by "iso" or "tert-", and the absence of such a structure (normal).

[0150] Examples of (iii) aromatic ring-containing monomers other than styrene include vinyl monomers having an aromatic ring and 6 to 22 carbon atoms, such as  $\alpha$ -methylstyrene, vinyl toluene, vinyl naphthalene, ethylvinylbenzene, 4-vinyl biphenyl, 1,1-diphenylethylene, benzyl(meth)acrylate, phenoxyethyl(meth)acrylate, 2-hydroxy-3-phenoxypropylacrylate, and 2-methacryloyloxyethyl-2-hydroxypropylphthalate.

[0151] From the standpoint of preservation stability, the content of the styrene-derived constituting unit in (b-1) styrene macromonomer is preferably 60 weight% or more, more preferably 70 weight% or more, particularly preferably 90 weight% or more. Examples of commercially available products of (b-1) styrene macromonomer include AS-6, AS-6S, AN-6, AN-6S, HS-6, and HS-6S (Toagosei Co., Ltd.).

[0152] Examples of (b-2) alkyl (meth)acrylate macromonomer having a polymerizable functional group at one of the terminals include alkyl(meth)acrylate homopolymer having a polymerizable functional group at one of the terminals, and a copolymer of alkyl(meth)acrylate and other monomer with a polymerizable functional group attached to one of the terminals. Preferred are alkyl(meth)acrylate macromonomers of 1 to 8 carbon atoms, including, for example, methylmethacrylate macromonomer, butylacrylate macromonomer, and isobutylmethacrylate macromonomer.

[0153] (b-3) Silicone macromonomer having a polymerizable functional group at one of the terminals is preferably the macromonomer represented by the following formula (2).



(in the formula (2), t represents a number 8 to 40).

[0154] From the standpoint of increasing copolymerization ratio and maintaining low viscosity for improved dispersion stability, the number average molecular weight of (b) macromonomer is preferably 1,000 to 10,000, more preferably 2,000 to 8,000.

[0155] The number average molecular weight of the macromonomer is as measured by gel permeation chromatography using polystyrene as standard substance, and a solvent, for which tetrahydrofuran containing 50 mmol/L of acetic acid is used.

(b) Macromonomer may be used either alone or in a combination of two or more kinds thereof.

[0156] The binder resin more preferably contains (c) hydrophobic monomer-derived constituting unit.

(c) Hydrophobic monomer-derived constituting unit is used for preservation stability and abrasion resistance, and may be obtained by polymerizing a hydrophobic monomer. After polymerization, a hydrophobic monomer may be introduced to the polymer chain.

(c) Hydrophobic monomer is preferably (c-1) (meth)acrylate having alkyl group of 1 to 22 carbon atoms, or (c-2) aromatic group-containing monomer represented by the following formula (3).



5 (In the formula, R<sup>3</sup> represents a hydrogen atom, or alkyl group of 1 to 5 carbon atoms, and R<sup>4</sup> represents an aromatic group-containing hydrocarbon group of 6 to 22 carbon atoms.)

[0156] Examples of (c-1) (meth)acrylate having alkyl of 1 to 22 carbon atoms include methyl(meth)acrylate, ethyl(meth)acrylate, (iso)propyl(meth)acrylate, (iso or tert-)butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, (iso)octyl(meth)acrylate, (iso)decyl(meth)acrylate, (iso)dodecyl(meth)acrylate, (iso)stearyl(meth)acrylate, and behenyl(meth)acrylate.

[0157] From the standpoint of abrasion resistance, (c-2) aromatic group-containing monomer represented by the formula (3) is preferably at least one selected from styrene, vinyl naphthalene,  $\alpha$ -methylstyrene, vinyl toluene, ethylvinylbenzene, 4-vinyl biphenyl, and 1,1-diphenylethylene. From the standpoint of abrasion resistance and preservation stability, styrene,  $\alpha$ -methylstyrene, and vinyl toluene are more preferred.

15 (c) Hydrophobic monomer may be used either alone or in a combination of two or more kinds thereof.

[0158] The binder resin preferably contains (d) hydroxyl group-containing monomer-derived constituting unit.

[0159] Containing (d) hydroxyl group-containing monomer-derived constituting unit improves the dispersion stability of the binder resin, and quickly improves marker resistance upon printing. (d) Hydroxyl group-containing monomer-derived constituting unit may be obtained by polymerizing a hydroxyl group-containing monomer. Examples include 2-hydroxyethyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, polyethylene glycol (n = 2 to 30; here and below, n represents the average number of moles of oxyalkylene group added) (meth)acrylate, polypropylene glycol (n = 2 to 30) (meth)acrylate, poly(ethylene glycol (n = 1 to 15)-propylene glycol (n = 1 to 15)) (meth) acrylate, and polyethylene glycol methacrylate 2-ethylhexyl ether. Preferred are 2-hydroxyethyl (meth)acrylate, polyethylene glycol monomethacrylate, polyethylene glycol methacrylate 2-ethylhexyl ether, and polypropylene glycol methacrylate.

25 (d) Hydroxyl group-containing monomer may be used either alone or in a combination of two or more kinds thereof.

[0160] The binder resin preferably contains (e) oxyalkylene group-containing monomer-derived constituting unit.

[0161] Examples of (e) oxyalkylene group-containing monomer include the monomer represented by the following formula (4).



35 (In the formula (4), R<sup>5</sup> represents a hydrogen atom, or alkyl group of 1 to 5 carbon atoms, R<sup>6</sup> represents a bivalent hydrocarbon group of 1 to 30 carbon atoms with an optional heteroatom, R<sup>7</sup> represents a monovalent hydrocarbon group of 1 to 30 carbon atoms with an optional heteroatom, and p represents the average number of moles added, and is 1 to 60, preferably 1 to 30.)

[0162] With the binder resin containing (e) oxyalkylene group-containing monomer-derived constituting unit, the discharge stability of aqueous ink can improve. (e) Oxyalkylene group-containing monomer-derived constituting unit may be obtained by polymerizing the monomer represented by the formula (4).

[0163] Examples of the heteroatom optionally contained in R<sup>6</sup> or R<sup>7</sup> in formula (4) include a nitrogen atom, an oxygen atom, a halogen atom, and a sulfur atom.

[0164] Representative examples of the group represented by R<sup>6</sup> or R<sup>7</sup> include an aromatic group of 6 to 30 carbon atoms, a heterocyclic group of 3 to 30 carbon atoms, and alkylene group of 1 to 30 carbon atoms. These may be optionally substituted, and may be used in a combination of two or more kinds thereof. Examples of the substituents include an aromatic group, a heterocyclic group, alkyl group, a halogen atom, and an amino group.

[0165] Examples of R<sup>6</sup> include optionally substituted phenylene group of 1 to 24 carbon atoms, aliphatic alkylene group of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, alkylene group of 7 to 30 carbon atoms having an aromatic ring, and alkylene group of 4 to 30 carbon atoms having a hetero ring. Particularly preferred examples of the R<sup>6</sup>O group include oxyethylene group, oxy(iso)propylene group, oxytetramethylene group, oxyheptamethylene group, oxyhexamethylene group, and oxyalkylene group or oxyphenylene group of 2 to 7 carbon atoms formed by one or more of these oxyalkylene groups.

[0166] Examples of R<sup>7</sup> include phenyl group, aliphatic alkyl group of 1 to 30, preferably 1 to 20 carbon atoms, alkyl group of 7 to 30 carbon atoms having an aromatic ring, and alkyl group of 4 to 30 carbon atoms having a hetero ring. More preferred examples of R<sup>7</sup> include alkyl group of 1 to 12 carbon atoms such as methyl group, ethyl group, (iso)propyl group, (iso)butyl group, (iso)pentyl group, (iso)hexyl group, (iso)octyl group, (iso)decyl group, and (iso)dodecyl group, and phenyl group.

[0167] Specific examples of (e) oxyalkylene group-containing monomer include methoxypolyethylene glycol ( $p = 1$  to 30 in formula (4)) (meth)acrylate, methoxypolytetramethylene glycol ( $p = 1$  to 30) (meth) acrylate, ethoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, (iso)propoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, butoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, octoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, phenoxypropoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, methoxypolypropylene glycol ( $p = 1$  to 30) (meth)acrylate, methoxy(ethylene glycol-propylene glycol copolymer) ( $p = 1$  to 30; 1 to 29 for the ethylene glycol moiety) (meth) acrylate, and phenoxy(ethylene glycol-propylene glycol copolymer) ( $p = 1$  to 30; 1 to 29 for the ethylene glycol moiety) (meth)acrylate. More preferred are methoxypolyethylene glycol ( $p = 1$  to 30) (meth) acrylate, octoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, phenoxypropoxypolyethylene glycol ( $p = 1$  to 30) (meth)acrylate, and phenoxy(ethylene glycol-propylene glycol copolymer) ( $p = 1$  to 30; 1 to 29 for the ethylene glycol moiety) (meth)acrylate.

(d) Oxyalkylene group-containing monomer may be used either alone or in a combination of two or more kinds thereof.

[0168] The binder resin contained in the latex ink contains the monomer represented by the formula (1-1), and preferably further contains the salt forming group-containing monomer (a). More preferably, the binder resin further contains macromonomer (b). Most preferably, the binder resin further contains hydrophobic monomer (c). Preferably, the binder resin is obtained by copolymerizing a monomer mixture that contains at least one selected from the group consisting of hydroxyl group-containing monomer (d), and oxyalkylene group-containing monomer (e) (hereinafter, such a mixture will be referred to as "monomer mixture").

[0169] From the standpoint of improving the abrasion resistance and glossiness of the ink, and dispersion stability, the content of the monomer represented by formula (1-1) in the monomer mixture, or the content of the constituting unit represented by the formula (1) in the polymer is preferably 10 to 80 weight%, further preferably 25 to 80 weight%, particularly preferably 25 to 75 weight%.

[0170] From the standpoint of improving the print density and the glossiness of the ink, and desirable dispersion stability, the content of (a) salt forming group-containing monomer in the monomer mixture (unneutralized content; hereinafter calculated as unneutralized content for the salt forming group-containing monomer), or the content of the constituting unit derived from (a) salt forming group-containing monomer in the polymer is preferably 3 to 30 weight%, further preferably 5 to 25 weight%, particularly preferably 5 to 20 weight%.

[0171] From the standpoint of improving the dispersibility and the glossiness of the polymer, the weight ratio of [constituting unit represented by formula (1) / (a) salt forming group-containing monomer-derived constituting unit] is preferably 10/1 to 1/1, further preferably 5/1 to 1/1.

[0172] The binder resin containing the silicone macromonomer or styrene macromonomer generally has excellent dispersion stability. Conceivably, this is due to reasons related to the molecular structure. Specifically, in contrast to the random orientation of the side chains which is more likely to occur in polymers polymerized from a simple monomer, the side chains are more likely to orient themselves in the same pattern in the case of the macromonomer.

[0173] From the standpoint of the preservation stability and the abrasion resistance of the ink, the content of (b) macromonomer in the monomer mixture, or the content of the constituting unit derived from (b) macromonomer in the polymer is preferably 0 to 50 weight%, further preferably 5 to 35 weight%, particularly preferably 5 to 30 weight%. When (b) macromonomer is silicone macromonomer or styrene macromonomer, it is preferable that the content of (b) macromonomer is 30 weight% or less with respect to the total amount of the monomer mixture forming the binder resin. A macromonomer content of 30 weight% or less is preferable, because the binder resin is required to have various functions other than dispersion stability, including, for example, ink filming, adhesion, abrasion resistance, glossiness, reactivity, and preservation stability, and each of these functions is dependent on the mixed monomer. Considering realizing these functions with other monomers, the macromonomer content is preferably 30 weight% or less.

[0174] From the standpoint of improving the preservation stability, abrasion resistance, and glossiness of the polymer, the weight ratio of [constituting unit represented by formula (1) / (b) macromonomer-derived constituting unit] is preferably 10/1 to 1/1, further preferably 5/1 to 1/1.

[0175] From the standpoint of the preservation stability and abrasion resistance of the ink, the content of (c) hydrophobic monomer in the monomer mixture, or the content of the constituting unit derived from (c) hydrophobic monomer in the polymer is preferably 0 to 40 weight%, further preferably 0 to 20 weight%.

[0176] From the standpoint of dispersion stability for the ink, the content of (d) hydroxyl group-containing monomer in the monomer mixture, or the content of the constituting unit derived from (d) hydroxyl group-containing monomer in the polymer is preferably 0 to 40 weight%, further preferably 0 to 20 weight%.

[0177] From the standpoint of discharge stability of the ink, the content of (e) oxyalkylene group-containing monomer in the monomer mixture, or the content of the constituting unit derived from (e) oxyalkylene group-containing monomer in the polymer is preferably 0 to 50 weight%, further preferably 10 to 40 weight%.

[0178] When the binder resin has a salt forming group, the salt forming group derived from the salt forming group-containing monomer is used after being neutralized with a neutralizing agent (described later). The degree of neutralization

of the salt forming group is preferably 10 to 200%, more preferably 20 to 150%, particularly preferably 50 to 150%.

[0179] The degree of neutralization may be determined by using the following equation, when the salt forming group is an anionic group.

$$5 \quad \{ [\text{Neutralizing agent weight (g)}/\text{equivalence of neutralizing agent}] / [\text{polymer acid number (KOHmg/g)} \times \text{polymer weight (g)} / (56 \times 1000)] \} \times 100$$

10 [0180] The degree of neutralization may be determined by using the following equation, when the salt forming group is a cationic group.

$$15 \quad \{ [\text{Neutralizing agent weight (g)}/\text{equivalence of neutralizing agent}] / [\text{polymer amine number (HCLmg/g)} \times \text{polymer weight (g)} / (36.5 \times 1000)] \} \times 100$$

20 [0181] Acid number and amine number may be determined by calculation from the constituting unit of water-insoluble vinyl polymer. It is also possible to use a method that involves titration of a solution prepared by dissolving the polymer in a suitable solvent (for example, methyl ethyl ketone).

25 [0182] From the standpoint of ink glossiness, the weight-average molecular weight of the binder resin is preferably 5,000 to 500,000, further preferably 10,000 to 400,000, particularly preferably 10,000 to 300,000.

[0183] The weight-average molecular weight of the binder resin is measured by gel chromatography, using polystyrene as standard substance, and a solvent, for which dimethylformamide containing 60 mmol/L of phosphoric acid and 50 mmol/L of lithium bromide is used.

30 [0184] The average particle diameter of the binder resin particles is preferably 0.16  $\mu\text{m}$  or less as measured in the latex ink.

[0185] The content of the binder resin in the latex ink is preferably 8 to 20 weight%, more preferably 8 to 12 weight% in terms of a solid content with respect to the total amount of the latex ink.

35 [0186] More preferably, the binder resin contains at least one water dispersible resin selected from the group consisting of aqueous polyester resin, aqueous polyurethane resin, aqueous acrylic resin, and aqueous vinyl chloride resin. This improves the dispersibility of the binder resin for water and water-soluble organic solvent.

40 [0187] Examples of commercially available binder resin products include Superflex 470 (NV 38%, Dai-Ichi Kogyo Seiyaku Co., Ltd.) in the case of urethane dispersion, Superflex 126 (solid content 30%, Dai-Ichi Kogyo Seiyaku Co., Ltd.) in the case of polyurethane dispersion, Elitel KA-5071S (solid content 30%, Unitika) in the case of polyester emulsion, and Joncryl 63 (solid content 30%, BASF) and styrene acrylic emulsion (solid content 46%, BASF) in the case of aqueous acrylic resin. Vinyl chloride-vinyl acetate copolymer products are in practical use, as represented by Solbin CL (Nissin Chemical Co., Ltd.).

45 [0188] The binder resin may be an emulsion polymerization polymer. The emulsion polymerization polymer is a polymer obtained by the emulsion polymerization of a monomer mixture containing the monomer represented by the formula (1-1), and, as required, (a) salt forming group-containing monomer, (b) macromonomer, (c) hydrophobic monomer, (d) hydroxyl group-containing monomer, and/or (e) oxyalkylene group-containing monomer in the presence of a surfactant and/or reactive surfactant, using an ordinary method.

[0189] The reactive surfactant, with its one or more radically polymerizable unsaturated double bonds contained within the molecule, has excellent monomer emulsifiability, and is useful for the production of a water dispersion having excellent stability.

50 [0190] The reactive surfactant is preferably an anionic or nonionic surfactant having at least one hydrophobic group such as linear or branched alkyl group of 8 to 30, preferably 12 to 22 carbon atoms, and alkenyl group, and at least one hydrophilic group such as an ionic group, and an oxyalkylene group.

[0191] Specific examples of the reactive surfactant include Latemul S-120P, S-180A (Kao Corporation), and Eleminol JS-2 (Sanyokasei Co., Ltd.) in the case of sulfosuccinic acid ester surfactant, and Aqualon HS-10 and RN-20 (Dai-Ichi Kogyo Seiyaku Co., Ltd.) in the case of alkyl phenol ether surfactant.

55 [0192] From the standpoint of the preservation stability, glossiness, and abrasion resistance of the water dispersion, the D50 (the cumulative 50% value as calculated from the smaller particle side in the scattering intensity frequency

distribution) of the emulsion polymerization polymer (core portion) obtained as above is preferably 500 nm or less, further preferably 300 nm or less, particularly preferably 100 nm or less. For ease of production, the lower limit is preferably 10 nm or more, further preferably 20 nm or more. Taken together, 10 to 500 nm is preferable, 50 to 300 nm is further preferable, and 60 to 250 nm is particularly preferable. The core portion is preferably 50 to 200 nm, because the shell portion should preferably be thinner than the core portion to meet the reactivity and deposition requirements.

**[0193]** From the standpoint of reducing coarse particles and improving preservation stability of the dispersion, the D90 (the cumulative 90% value as calculated from the smaller particle side in a scattering intensity frequency distribution) of the emulsion polymerization polymer is preferably 2,000 nm or less, further preferably 1,000 nm or less, particularly preferably 500 nm or less. For ease of production, the lower limit is preferably 20 nm or more, further preferably 50 nm or more.

**[0194]** D50 and D90 may be measured by using a laser particle analysis system ELS-8000 (Otsuka Electronics Co., Ltd.).

**[0195]** The latex ink may further include a penetrant. Examples of the penetrant include polyol, preferably polyol of 7 to 11 carbon atoms, further preferably 2-ethyl-1,3-hexanediol, and 2,2,4-trimethyl-1,3-pentanediol.

**[0196]** The content of the penetrant in the latex ink is preferably 0.1 weight% to 20 weight%, more preferably 0.1 weight% to 10 weight%, further preferably 0.1 weight% to 7 weight%, particularly preferably 0.5 weight% to 10 weight%. A penetrant content of 0.1 weight% or more increases permeability to the media 30, and suppresses contamination as might occur when the media 30 is rubbed against rollers during the transport, or when the ink adheres to the conveyer belt during the transport for printing. This makes it possible to accommodate faster printing. With a penetrant content of 20 weight% or less, the print dot diameter can be reduced, and the characters can have narrower widths, making it possible to improve the image resolution.

**[0197]** In the latex ink, the weight mixture ratio of 2-ethyl-1,3-hexanediol or 2,2,4-trimethyl-1,3-pentanediol to the binder resin is preferably 1:1 to 1:5. 2-Ethyl-1,3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol are oily substances with 8 weight% or less solubility to water. Accordingly, there is a limit to the mixed proportion in the binder resin. The preferred mixed proportion is 1:1 to 1:5, preferably the same or greater proportion than the proportion of the binder resin.

**[0198]** The penetrant serves as a thickener. Because of the low solubility to water, the penetrant, when added in a content reaching the solubility limit, rapidly precipitates as an oily component as the moisture evaporates. The precipitation of the oily component promotes precipitation of components other than the colorant, such as the binder resin, in the latex ink, causing the ink to rapidly gel.

**[0199]** Aside from the components described above, the latex ink also may contain additives such as a mildew-proofing agent, an anti-rusting agent, a pH adjuster, a wetting agent, a surfactant, a water-soluble ultraviolet absorber, and a water-soluble infrared absorber.

**[0200]** Examples of the mildew-proofing agent include 1,2-benzisothiazolin-3-one. By containing the mildew-proofing agent, the latex ink can have excellent mildew-proofing effect while ensuring reliability such as preservation stability, and discharge stability. The effect becomes particularly sufficient when combined with the wetting agent, even in contents traditionally considered difficult to suppress bacteria or mold generation.

**[0201]** By limiting the content of the 1,2-benzisothiazolin-3-one, it is possible to prevent phenomena such as particle aggregation, and ink thickening. The performance of the ink can thus last over extended time periods. When the latex ink contains 1,2-benzisothiazolin-3-one as a mildew-proofing agent, the content of this component as an active ingredient amount is preferably 0.01 to 0.04 weight parts of the total ink amount. A sufficient mildew-proofing effect can be obtained when the content is 0.01 weight parts or more. With a content of 0.04 weight parts or less, particle aggregation can be suppressed in long storage (for example, 2 years at room temperature, and 1 to 3 months at 50 to 60°C). It is also possible to solve the problem that the ink viscosity increases by 50% to 100% from the initial viscosity. This improves the long-term preservation stability. The initial print performance can thus last over extended time periods.

**[0202]** Any material may be used as the pH adjuster, as long as the pH can be brought to 7 or more without having adverse effects on the prepared ink.

**[0203]** Examples of such material include amines (such as diethanolamine, and triethanolamine), hydroxides of alkali metal elements (such as lithium hydroxide, sodium hydroxide, and potassium hydroxide), ammonium hydroxide, quaternary ammonium hydroxide, quaternary phosphonium hydroxide, carbonates of alkali metals (such as lithium carbonate, sodium carbonate, and potassium carbonate), and aminopropanediol derivatives. The aminopropanediol derivatives are water-soluble organic basic compounds, for example, such as 1-amino-2,3-propanediol, 1-methylamino-2,3-propanediol, 2-amino-2-methyl-1,3-propanediol, and 2-amino-2-ethyl-1,3-propanediol. Particularly preferred examples include 2-amino-2-ethyl-1,3-propanediol.

**[0204]** Examples of the anti-rusting agent include acidic sulfite, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, and dicyclohexylammonium nitrite.

**[0205]** Examples of the surfactant include a polyalkylene glycol surfactant. The polyalkylene glycol surfactant is an ethylene oxide adduct, and can remain effective even when a part of the ethylene oxide is substituted with alkylene oxide such as propylene oxide and butylene oxide to the extent that the water solubility is maintained. Percentage

substitution is preferably 50% or less. The HLB (hydrophilic-lipophilic balance) of the polyalkylene glycol surfactant is preferably 13 to 19. Dispersibility can further improve when the HLB is adjusted to fall within this range.

[0206] The latex ink can be obtained by selecting the foregoing materials as the solvent, the colorant, and the binder resin, and by mixing these components. The order of mixing the materials is not particularly limited. The materials are mixed preferably at a temperature of 5 to 50°C.

[0207] The latex ink may further contain additives such as a wetting agent, a dispersant, a defoaming agent, a mildew-proofing agent, and a chelating agent, as required. The method used to mix these components is not particularly limited.

[0208] From the standpoint of ink properties such as print density, abrasion resistance, and glossiness, the weight ratio of the binder resin to the colorant [binder resin/colorant] in the latex ink is preferably 1/10 to 10/1, further preferably 1/5 to 5/1, particularly preferably 1/3 to 3/1, most preferably 1/2 to 2/1.

[0209] The surface tension (20°C) of the latex ink is preferably 30 to 70 mN/m, further preferably 35 to 68 mN/m in terms of a water dispersion (colorant dispersion), and is preferably 25 to 50 mN/m, further preferably 27 to 45 mN/m in terms of an ink.

[0210] The viscosity (20°C) of the water dispersion at the solid content of 10 weight% is preferably 2 to 6 mPa·s, further preferably 2 to 5 mPa·s to provide a desirable ink viscosity. The viscosity (20°C) of the latex ink is preferably 2 to 12 mPa·s, further preferably 2.5 to 10 mPa·s to maintain desirable dischargeability. The pH of the latex ink is preferably 4 to 10.

#### Additional Remarks

[0211] In order to solve the problems identified above, the printing method according to the embodiment of the present invention is a method for printing the media 30 with the inkjet printer 1 that includes:

the printhead 14;

the driver that moves and positions the printhead 14 and the media 30 relative to each other;

the print heater 70 provided at a position opposite an ink discharge face of the printhead 14, and that heats the media 30 from the back side of an inked surface of the media 30 disposed opposite the ink discharge face of the printhead 14 by the driver; and

the preheater 40 that heats the media 30 from the back side of the inked surface before the media 30 is positioned opposite the ink discharge face of the printhead 14,

the method including:

heating the media 30 with the print heater 70 and the preheater 40 to make a surface temperature of the inked surface of the media 30 40°C or more and 60°C or less; and

printing the media 30 by causing the printhead 14 to discharge an ink that contains a solvent, a colorant, and a binder resin, wherein the binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less.

[0212] According this configuration, the inkjet printer 1 is used to print the media 30. In the inkjet printer 1, the driver moves the printhead 14 and the media 30 relative to each other to print the desired position of the media 30. For printing, the preheater 40 heats the media 30 from the back side of the inked surface before the media 30 is positioned opposite the ink discharge face of the printhead 14. The driver then transports the media 30 heated by the preheater 40 to the position opposite the ink discharge face of the printhead 14. The print heater 70 provided opposite the ink discharge face of the printhead 14 heats the media 30 from the back side of the inked surface. The print heater 70 and the preheater 40 heat the media 30 in a manner that makes the surface temperature of the inked surface of the media 30 40°C or more and 60°C or less.

[0213] The ink discharged from the printhead 14 contains a solvent, a colorant, and a binder resin dispersed or emulsified in the solvent, (hereinafter, such an ink is referred to as "latex ink"), and the binder resin has a surface minimum filming temperature of 0°C or less. The ink has excellent characteristics, particularly environment and media characteristics.

[0214] Droplets of the latex ink expelled through the nozzles of the printhead 14 can strike the surface of the media 30 heated by the preheater 40 and the print heater 70 to a surface temperature of 40°C or more and 60°C or less. The ink droplets can thus quickly dry and fix without leaving time in the state of being fixed in dots at the impact positions, without diffusing over a wide area around the impact positions on the media 30. Clear graphics and characters can thus be printed in the form of an array of latex ink dots on the surface of the media 30 without bleeding.

[0215] By heating the media 30 to a surface temperature of 40°C or more, the latex ink droplets that struck the surface of the media 30 can have a sufficient temperature under the transferred heat from the media 30. On the other hand, by heating the media 30 to a surface temperature of 60°C or less, the media 30 will not be damaged by the applied heat, and can be smoothly transported onto the platen by the driver, even when a low heat-resistance film such as a vinyl

chloride film is used as the media 30. The present invention is thus applicable to essentially any media 30, from low heat-resistance media 30 to high heat-resistance media 30. The surface temperature range of 40°C to 60°C of the media 30 was found after the intensive studies conducted by the present inventor on the basis of the results of experiments in which graphics and characters were actually printed on the surface of various types of media 30 with the latex ink using the inkjet printer 1 according to the embodiment of the present invention.

**[0216]** The binder resin contained in the latex ink used in the present invention has a core-shell structure configured from an interior core portion and a surface shell portion. Because the binder resin has a surface minimum filming temperature (MFT) of 0°C or less, the latex ink can quickly start drying and fusing on the media 30 heated to a surface temperature of 40°C or more and 60°C or less.

**[0217]** By the stepwise heating with the preheater 40 and the print heater 70, the surface temperature of the media 30 is finally brought to 40°C or more and 60°C or less, a suitable temperature range for drying and fusing the latex ink, by the time the ink strikes the media 30. By heating the media 30 to a certain temperature in advance with the preheater 40, the surface of the media 30 can be brought to the desired temperature by the time the ink strikes the media 30, even when the print heater 70 alone fails to sufficiently heat the media 30 to an appropriate temperature because of such factors as the thickness of the media 30, and the ambient temperature of the inkjet printer 1.

**[0218]** Further, because the print heater 70 is disposed at a position opposite the ink discharge face of the printhead 14, heating the surface of the media 30 to 40°C or more and 60°C or less with the print heater 70 alone causes the ink to solidify and clog the narrow diameter of the nozzles in the printhead 14 under the generated heat of the print heater 70. In the embodiment of the present invention, the surface temperature of the media 30 is brought to 40°C or more and 60°C or less by the stepwise heating with the preheater 40 and the print heater 70 by the time the ink strikes the media 30. For example, by heating the media 30 to a certain temperature in advance with the preheater 40, the surface of the media 30 can be heated to the desired temperature without generating high temperature in the print heater 70. The ink can thus be prevented from solidifying and clogging the nozzles in the printhead 14 under the generated heat of the print heater 70.

**[0219]** The present invention can realize high image quality and fixing stability for the printed graphics and characters even for media 30 used in outdoor advertisement displays and industrial applications that require high environment and media characteristics.

**[0220]** In the printing method according to the embodiment of the present invention, the binder resin has different minimum filming temperatures for a surface portion and an interior portion.

**[0221]** With this configuration, because the binder resin has different minimum filming temperatures for the surface and interior portions of the core-shell structure, drying and fusing can take place at different timings for the surface and interior portions of the binder resin, making it possible to provide separate functions. For example, the binder resin may be configured to dry and fuse on the surface first on the media 30 appropriately heated with the preheater 40 and print heater 70, before the interior dries and fuses under the heat of, for example, the drier that dries the media 30 struck by the ink.

**[0222]** The temperature used to dry the ink in inkjet printers of related art is typically set to about 80°C, whereas the actual drying temperature of the latex ink is believed to be about 50 to 60°C. By separately drying and fusing the surface and the interior of the binder resin, it is ensured that the latex ink is dried and fixed with the preheater 40, and, for example, the post-heater, even when the heating temperature of the print heater 70 at the position opposite the ink discharge face of the printhead 14 is set to a temperature that can avoid clogging of the ink.

**[0223]** In the printing method according to the embodiment of the present invention, the minimum filming temperature of the binder resin is lower in the surface portion than in the interior portion.

**[0224]** According to this configuration, because the minimum filming temperature of the binder resin in the latex ink is higher inside the resin than on the surface, the high-temperature storage stability of the latex ink can be improved. Because of the lower minimum filming temperature, the surface of the binder resin quickly starts drying and fusing on the media 30 heated with the preheater 40 and the print heater 70. In this way, the binder resin surface having a lower minimum filming temperature can be clearly fixed without causing dot bleeding at the impact positions even when the latex ink is used that has very high diffusibility (wetting and spreading) for the media 30, and that tends to quickly diffuse over a wide area around the impact positions of the ink droplets. The binding resin interior having a higher minimum filming temperature is then sufficiently dried and fused with, for example, the post-heater or the drier, and the latex ink that struck the media 30 can be sequentially dried, fused, and fixed in the direction of the transport of the media 30.

**[0225]** In the printing method according to the embodiment of the present invention, the solvent is at least one of water and a hydrophilic solvent, and the latex ink contains the solvent in 50 weight% or more of the total weight of the latex ink.

**[0226]** According to this configuration, the impact of the ink on the environment can be relieved because of the high content of the water and/or hydrophilic solvent in the latex ink.

**[0227]** In the printing method according to the embodiment of the present invention, the print heater 70 and the preheater 40 are controlled to heat the media 30 at different temperatures.

**[0228]** According to this configuration, it is possible to separately control the temperature of the media 30 at and before

arrival at the position opposite the ink discharge face of the printhead 14 during the transport. The temperature of the media 30 can thus be accurately adjusted at the respective positions according to such factors as the type and thickness of the media 30, and the ambient temperature of the printer. This makes it possible to more accurately adjust the surface temperature of the media 30 in a temperature range of 40°C to 60°C by the time the ink droplets expelled from the ink discharge face of the printhead 14 strike the media 30.

**[0229]** In the printing method according to the embodiment of the present invention, the preheater 40 heats the inked surface of the media 30 to a surface temperature of 30°C or more and 50°C and less, and the print heater 70 heats the inked surface of the media 30 to a surface temperature of 40°C or more and 60°C or less.

**[0230]** According to this configuration, the preheater 40 preliminarily heats the inked surface to a surface temperature of 30°C or more and 50°C or less before the media 30 are transported to the position opposite the ink discharge face of the printhead 14. The print heater 70 then heats the inked surface of the media 30 to a surface temperature of 40°C or more and 60°C or less when the media 30 transported after the preliminary heating reaches the position opposite the ink discharge face of the printhead 14. This ensures that the media 30 are always sufficiently heated to a surface temperature of 40°C or more and 60°C or less by the time the ink droplets expelled through the nozzles of the printhead 14 strike the media 30.

**[0231]** In the printing method according to the embodiment of the present invention, the print heater 70 and the preheater 40 are controlled to heat the media 30 at the same temperature.

**[0232]** According to this configuration, by using the same control for the temperatures of the preheater 40 and the print heater 70, the temperature control can be simplified.

**[0233]** In the printing method according to the embodiment of the present invention, the media 30 may be one selected from the group consisting of a vinyl chloride sheet, a PET sheet, a tarpaulin sheet, and coated paper neither of which is coated with coating material, and uncoated polypropylene resin, uncoated glass, uncoated metal, and molded products thereof.

**[0234]** According to this configuration, high-quality graphics and characters can be printed with fixing stability, without bleeding, even when the media 30 are all-purpose media not coated with coating material or the like. Further, according to the foregoing configuration, it is possible to appropriately heat various types of media 30, including media 30 that soften under low temperature, and always allow such media to be smoothly transported. Specifically, no problem is posed in transporting different media 30, from low heat-resistance media 30 to high heat-resistance media 30, and high-quality graphics and characters can be printed on such media with fixing stability, without bleeding.

**[0235]** In the printing method according to the embodiment of the present invention, the inkjet printer 1 is adapted so that temperatures of the preheater 40 and the print heater 70 heating the media 30 are adjustably controlled with an operation panel provided for the printer, or with a printer-controlling host computer coupled to the printer.

**[0236]** According to this configuration, the heating temperatures of the preheater 40 and the print heater 70 can be adjustably controlled with an operation panel provided for the printer, or with a printer-controlling host computer, according to such factors as the type and thickness of the media 30, and the ambient temperature of the printer. This makes it possible to always smoothly transport various types of media 30, for example, such as media that soften under low temperature, and print high image quality graphics and characters on such media 30 with fixing stability, without bleeding.

**[0237]** In the method according to the embodiment of the present invention, the inkjet printer 1 includes a refresh mode unit that moves the printhead 14 to a maintenance station, and causes the printhead 14 to flush ink droplets through the nozzles to prevent the latex ink from solidifying and clogging the nozzles in the printhead 14.

**[0238]** According to this configuration, the refresh mode unit can be used to move the printhead 14 to the maintenance station, and cause the printhead 14 to flush ink droplets through the nozzles during the printing of graphics and characters with the latex ink. In this way, the latex ink can be prevented from solidifying and clogging the nozzles or other parts of the printhead 14. As a result, there will be no empty dots ("empty dots" describes the state where ink dots are absent in places ink dots are normally present), which might occur in part of the graphics and characters printed on the surface of the media 30 when the printhead 14 is clogged.

**[0239]** In the method according to the embodiment of the present invention, the refresh mode unit provided in the inkjet printer 1 moves the printhead 14 to the maintenance station at certain time intervals, and causes the printhead 14 to flush ink droplets through the nozzles.

**[0240]** According to this configuration, the refresh mode unit can be used to move the printhead 14 to the maintenance station at certain time intervals, and cause the printhead 14 to forcibly flush ink droplets through the nozzles during the printing of graphics and characters with the latex ink. Because the printhead 14 is moved to the maintenance station with the refresh mode unit during the printing of graphics and characters with the latex ink, it is ensured that the latex ink does not solidify and clog the nozzles in the printhead 14 as might occur when ink droplets are not flushed through the nozzles of the printhead 14.

**[0241]** In the method according to the embodiment of the present invention, the inkjet printer 1 includes a drier that dries the media 30 after the discharged ink droplets from the printhead 14 strike the media 30, and thereby dries the ink droplets adhering to the surface of the media 30.

[0242] According to this configuration, the partially undried ink droplets adhering to the surface of the media 30 can be completely dried with the drier. The partially undried ink droplets adhering to the impact positions on the surface of the media 30 can be prevented from adhering to and contaminating other portions of the media 30 when the media 30 are wound into a roll or other form by, for example, the winder after the transport.

5 [0243] The present invention is not limited to the description of the embodiments above, but may be altered in many ways within the scope of the claims. An embodiment based on a proper combination of technical means disclosed in different embodiments is encompassed in the technical scope of the present invention.

## EXAMPLES

10 [0244] Examples and Comparative Examples of the present invention are described below. It should be noted that the present invention is not limited by the following descriptions. The amount of each component given in Examples and Comparative Examples is by weight.

15 Production of Resin Dispersion Colorant

### Production Example 1 (Phthalocyanine Pigment Dispersion)

20 [0245] C.I. pigment cyan 15:3 (150 g), SOLSPERSE 43000 (polymer-type dispersant, Lubrizol; 3.0 %), SOLSPERSE 44000 (polymer-type dispersant, Lubrizol; 3.0%), and distilled water (738 g) were mixed. After being predispersed, the mixture was dispersed under circulation for 20 hours using a disc-type bead mill (Shinmaru Enterprises; KDL type; media: 0.3-mm Ø zirconia ball) to obtain phthalocyanine pigment dispersion (C-1).

### Production Example 2 (Dimethylquinacridone Pigment Dispersion)

25 [0246] Dimethylquinacridone pigment dispersion (M-1) was obtained by using the same procedures used in Production Example 1, except that C.I. pigment cyan 15:3 was changed to C.I. pigment red 122, and that SOLSPERSE 43000 and SOLSPERSE 44000 were both used in 3.38%.

30 Production Example 3 (Monoazo Yellow Pigment Dispersion)

[0247] Monoazo Yellow Pigment Dispersion (Y-1) was obtained by using the same procedures used in Production Example 1, except that C.I. pigment cyan 15: 3 was changed to C.I. pigment yellow 74, and that SOLSPERSE 43000 and SOLSPERSE 44000 were both used in 1.3%.

35 Production Example 4 (Carbon Black Pigment Dispersion)

[0248] Carbon black pigment dispersion (B-1) was obtained by using the same procedures used in Production Example 1, except that C.I. pigment cyan 15:3 was changed to C. carbon black, and that SOLSPERSE 43000 and SOLSPERSE 44000 were both used in 2.3%.

## Production of Polymer Grafted Colorant

### Synthesis Example 1 (Cyan Pigment Dispersion)

45 [0249] A surface modified cyan pigment was prepared by using the same procedures used in Synthesis Example 2, except that C.I. pigment cyan 15:3 was used instead of C.I. pigment yellow 128. As in Synthesis Example 2, the surface modified colored pigment was easily dispersed in the aqueous vehicle by being stirred, and desalted and concentrated through an ultrafiltration membrane to obtain cyan pigment dispersion (C-2) having a pigment concentration of 15%.

50 Synthesis Example 2 (Magenta Pigment Dispersion)

[0250] A surface modified magenta pigment was prepared by using the same procedures used in Synthesis Example 1, except that pigment red 122 was used instead of C.I. pigment yellow 128. As in Synthesis Example 2, the surface modified colored pigment was easily dispersed in the aqueous vehicle by being stirred, and desalted and concentrated through an ultrafiltration membrane to obtain magenta pigment dispersion (M-2) having a pigment concentration of 15%.

## Synthesis Example 3 (Yellow Pigment Dispersion)

5 [0251] C.I. pigment yellow 128 used as a yellow pigment was subjected to a low-temperature plasma treatment to produce a carboxylic acid group-introduced pigment. A dispersion of the pigment in ion-exchange water was desalinated and concentrated through an ultrafiltration membrane to obtain yellow pigment dispersion (Y-2) having a pigment concentration of 15%.

## Synthesis Example 4 (Carbon Black Pigment Dispersion)

10 [0252] A carbon black (90 g) having a CTAB specific surface area of 150 m<sup>2</sup>/g, and a DBP oil absorption of 100 ml/100 g was added to a 2.5 N sodium sulfate solution (3,000 ml). The mixture was stirred at a temperature of 60°C and a rotation speed of 300 rpm to allow reaction to proceed for 10 hours as an oxidation treatment. The reaction mixture was filtered, and the separated carbon black was neutralized with a sodium hydroxide solution, and filtered by ultrafiltration. The resulting carbon black (B-2) was water washed, dried, and dispersed in deionized water in such a way that the 15 content is 20 weight%.

## Synthesis Example of Polymer-Containing Colorant

## Synthesis Example 5 (Preparation of Polymer Dispersion)

20 [0253] Inside of a 1-L flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, a reflux tube, and a dripping funnel was sufficiently displaced with nitrogen gas. The flask was then charged with styrene (11.2 g), acrylic acid (2.8 g), lauryl methacrylate (12.0 g), polyethylene glycol methacrylate (4.0 g), styrene macromer (AS-6; Toagosei Co., Ltd.; 4.0 g), and mercaptoethanol (0.4 g). The temperature of the mixture was then increased to 65°C.

25 [0254] Then, a mixed solution of styrene (100.8 g), acrylic acid (25.2 g), lauryl methacrylate (108.0 g), polyethylene glycol methacrylate (36.0 g), hydroxyethyl methacrylate (60.0 g), styrene macromer (AS-6; Toagosei Co., Ltd.; 36.0 g), mercaptoethanol (3.6g), azobis dimethylvaleronitrile (2.4 g), and methyl ethyl ketone (18 g) was dropped into the flask for 2.5 hours while stirring the mixture.

30 [0255] Thereafter, a mixed solution of azobis dimethylvaleronitrile (0.8 g) and methyl ethyl ketone (18 g) was dropped into the flask for 0.5 hours while stirring the mixture. After aging the mixture at 65°C for 1 hour, azobis dimethylvaleronitrile (0.8 g) was added, and the mixture was further aged for 1 hour. After the reaction, methyl ethyl ketone (364 g) was added to the flask to give a polymer solution (800 g) having a solid content of 50%.

## Synthesis Example 6 (Phthalocyanine Pigment-Containing Polymer Fine Particle Dispersion)

35 [0256] The polymer solution (28 g) obtained in Synthesis Example 5, a phthalocyanine pigment (26 g), a 1 mol/L potassium hydroxide solution (13.6 g), methyl ethyl ketone (20 g), and ion-exchange water (30 g) were thoroughly stirred, and kneaded with a three-roller mill. The resulting paste was charged into ion-exchange water (200 g). After thoroughly stirring the mixture, methyl ethyl ketone and water were evaporated with an evaporator to give cyan-colored polymer 40 fine particle dispersion (C-3).

## Synthesis Example 7 (Dimethylquinacridone Pigment-Containing Polymer Fine Particle Dispersion)

45 [0257] Magenta-colored polymer fine particle dispersion (M-3) was obtained by using the same procedures used in Synthesis Examples 5 and 6, except that the phthalocyanine pigment was changed to pigment red 122.

## Synthesis Example 8 (Monoazo Yellow Pigment-Containing Polymer Fine Particle Dispersion)

50 [0258] Yellow polymer fine particle dispersion (Y-3) was obtained by using the same procedures used in Synthesis Examples 5 and 6, except that the phthalocyanine pigment was changed to pigment yellow 74.

## Synthesis Example 9 (Carbon Black Pigment-Containing Polymer Fine Particle Dispersion)

55 [0259] Black polymer fine particle dispersion (B-3) was obtained by using the same procedures used in Synthesis Examples 5 and 6, except that the phthalocyanine pigment was changed to carbon black.

## Synthesis of Binder Resin Core Portion

[0260] Synthesis Examples for the core portion of the core-shell binder resin contained in the latex ink according to the present invention are described below.

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## Synthesis Example 10

[0261] Inside of a flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, a reflux tube, and a dripping funnel was sufficiently displaced with nitrogen gas. The flask was then charged with Aqualon RN-20 (alkyl phenol ether reactive surfactant; Dai-Ichi Kogyo Seiyaku Co., Ltd.; 10 g), potassium persulfate (1 g), and deionized water (286 g). The temperature of the mixture was then increased to 65°C.

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[0262] Then, a mixed solution of methyl methacrylate (150 g), 2-ethylhexyl acrylate (100 g), acrylic acid (20 g), vinyl-triethoxysilane (20 g), Aqualon RN-20 (10 g), potassium persulfate (4 g), and deionized water (398.3 g) was dropped into the flask for 2.5 hours while stirring the mixture. The mixture was aged under heat at 80°C for 3 hours, cooled, and brought to pH 7 to 8 with potassium hydroxide. The resin had an average particle diameter of 130 nm as measured by using a microtrack UPA. The minimum filming temperature (MFT) was 10°C.

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## Synthesis Example 11

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[0263] Inside of a flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, a reflux tube, and a dripping funnel was sufficiently displaced with nitrogen gas. The flask was then charged with Aqualon RN-20 (alkyl phenol ether reactive surfactant; Dai-Ichi Kogyo Seiyaku Co., Ltd.; 10 g), potassium persulfate (1 g), and deionized water (286 g). The temperature of the mixture was then increased to 65°C. Then, a mixed solution of methyl methacrylate (150 g), 2-ethylhexyl acrylate (100 g), acrylic acid (20 g), hexyltrimethoxysilane (40 g), Aqualon RN-20 (10 g), potassium persulfate (4 g), and deionized water (398.3 g) was dropped into the flask for 3 hours while stirring the mixture. The mixture was aged under heat at 80°C for 3 hours, cooled, and brought to pH 7 to 8 with potassium hydroxide. The resin had an average particle diameter of 148 nm as measured by using a microtrack UPA. The minimum filming temperature (MFT) was 10°C.

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## Synthesis Example 12

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[0264] Inside of a flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, a reflux tube, and a dripping funnel was sufficiently displaced with nitrogen gas. The flask was then charged with deionized water (100 g), sodium dodecylbenzene sulfonate (3g), and polyethylene glycol nonyl phenyl ether (1 g). The temperature of the mixture was increased to 60°C after adding ammonium persulfate (1 g) and sodium bisulfite (0.2 g).

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[0265] Thereafter, butyl acrylate (30 g), methyl methacrylate (40 g), butyl methacrylate (19 g), a vinylsilanetriol potassium salt (10 g), and 3-methacryloxypropyl methyldimethoxysilane (1 g) were dropped into the flask for 3 hours while stirring the mixture. Here, the polymerization reaction mixture was brought to pH 7 with an ammonia aqueous solution for polymerization. The resin had an average particle diameter of 160 nm as measured by using a microtrack UPA. The minimum filming temperature (MFT) was 15°C.

## Synthesis of Binder Resin Shell Portion

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[0266] Synthesis Examples for the shell portion of the core-shell binder resin contained in the latex ink according to the present invention are described below.

## Synthesis Example 13 (For Example)

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[0267] A glass reaction vessel equipped with a stirrer, a thermometer, reflux condenser, and a nitrogen conduit was charged with ion-exchange water (100 g), an ether sulfate type reactive surfactant (reactive surfactant Latemul PD-104, active ingredient 20%; Kao Corporation; 8 g) as a reactive surfactant, and potassium persulfate (0.24g). After nitrogen displacement, the temperature was brought to 70°C in a hot-water bath.

55

[0268] The emulsion (P-10) (100 g; solid content 45%) synthesized in Synthesis Example 10 was then added and stirred in the mixture. Then, a monomer mixture (30 g) of (c) styrene/(a) acrylic acid/(c) 2-ethylhexyl acrylate/(c) butylacrylate = 32/2/24/42 was dropped into the mixture for 2 hours, and the mixture was aged at 80°C for 2 hours to obtain a water dispersion containing emulsion (P-13). The emulsion had an average particle diameter of 200 nm. An appropriate amount of ion-exchange water was added to adjust the solid content (active ingredient content) in the core-shell emulsion solution to 45%. The minimum filming temperature (MFT) of the shell portion was 0°C.

## Synthesis Example 14 (For Example)

**[0269]** A water dispersion containing emulsion (P-14) was obtained by using the same procedures used in Synthesis Example 13, except that (c) styrene/ (a) acrylic acid/ (c) 2-ethylhexyl acrylate = 49/2/49 was used as a monomer mixture, and that the emulsion dispersion (P-11) (100 g; solid content 45%) synthesized in Synthesis Example 11 was added to the monomer mixture. The obtained water-insoluble emulsion had an average particle diameter of 200 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was -10°C.

## Synthesis Example 15 (For Example)

**[0270]** A water dispersion containing emulsion (P-15) was obtained by using the same procedures used in Synthesis Example 12, except that a monomer mixture (200 g in total) of (c) benzylmethacrylate/(a) methacrylic acid/(b) styrene macromer (AS-6; Toagosei Co., Ltd.)/(e) polyethylene glycol methacrylate 2-ethylhexyl ether (NKEster EH-4G; Shin-Nakamura Chemical Co., Ltd.) = 44/16/15/25 (active ingredient weight ratio) was used, and that the emulsion dispersion (P-12) (100 g; solid content 45%) synthesized in Synthesis Example 12 was added to the monomer mixture. The obtained emulsion (P-15) had an average particle diameter of 200 nm. The solid content (active ingredient content) of the water-insoluble emulsion solution was 45%. The minimum filming temperature (MFT) of the shell portion was 0°C.

## Synthesis Example 16 (For Example)

**[0271]** A water dispersion containing emulsion (P-24) was obtained by using the same procedures used in Synthesis Example 13, except that the monomer composition was changed to (c) styrene/(a) N,N-dimethylaminoethyl(meth)acrylate/(c) 2-ethylhexyl acrylate = 74/2/24. The obtained emulsion (P-16) had an average particle diameter of 200 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was -13°C.

## Synthesis Example 17 (For Example)

**[0272]** A water dispersion containing emulsion (P-17) was obtained by using the same procedures used in Synthesis Example 14, except that a monomer mixture of (c) styrene/(a) N,N-dimethylaminopropyl(meth)acrylamide/(c) 2-ethylhexyl acrylate = 32/2/66 was used. The obtained emulsion (P-17) had an average particle diameter of 200 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was 0°C.

## Synthesis Example 18 (For Example)

**[0273]** A water dispersion containing emulsion (P-18) was obtained by using the same procedures used in Synthesis Example 15, except that the monomer composition was changed to (c) benzylmethacrylate/ (a) vinylpyrrolidone/ (b) styrene macromer (AS-6; Toagosei Co., Ltd.)/(e) polyethylene glycol methacrylate 2-ethylhexyl ether (NKEster EH-4G; Shin-Nakamura Chemical Co., Ltd.). The obtained emulsion (P-18) had an average particle diameter of 200 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was 0°C.

## Synthesis Example 19 (For Comparative Example)

**[0274]** A water dispersion containing emulsion (P-19) was obtained by using the same procedures used in Synthesis Example 15, except that a monomer mixture of (c) styrene/(a) acrylic acid/(c) 2-ethylhexyl acrylate/(c) butyl acrylate = 49/2/24/25 was used, and that polyoxyethylene alkyl ether sodium sulfate (unreactive surfactant Latemul E-118B, active ingredient content 26%; Kao Corporation; 62 g) was used as a non-reactive surfactant. The obtained emulsion (P-19) had an average particle diameter of 215 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was 30°C.

## Synthesis Example 20 (For Comparative Example)

**[0275]** A water dispersion containing emulsion (P-20) was obtained by using the same procedures used in Synthesis Example 13, except that a monomer mixture of (c) styrene/(a) acrylic acid/(c) 2-ethylhexyl acrylate = 19/2/79 was used. The obtained emulsion (P-20) had an average particle diameter of 230 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was 25°C.

## Synthesis Example 21 (For Comparative Example)

5 [0276] A water dispersion containing emulsion (P-21) was obtained by using the same procedures used in Synthesis Example 14, except that a monomer mixture of (c) styrene/(a) N,N-dimethylaminoethyl(meth)acrylate/(c) 2-ethylhexyl acrylate = 89/2/9 was used. The obtained emulsion (P-21) had an average particle diameter of 95 nm, and a solid content (active ingredient content) of 45%. The minimum filming temperature (MFT) of the shell portion was 30°C.

## Particle Diameter Measurement

10 [0277] Particle diameter was measured using a laser particle analysis system ELS-8000 (Cumulant Analyzer; Otsuka Electronics Co., Ltd.) under the following settings.

[0278] Temperature: 25°C

[0279] Incident light-detector angle: 90°

[0280] Cumulated number: 100

15 [0281] Dispersion solvent refractive index: 1.333 Production Examples of Latex Ink

[0282] A latex ink was produced by mixing components such as water, a water-soluble organic solvent, a colorant, a binder resin, a wetting agent, and a surfactant.

## Ink Production Example (1-1)

20 [0283] Cyan Pigment Dispersion (C-1) of Production Example 1: 6 wt%  
(solid content)

25 [0284] Binder resin (P-13) (solid content 45%): 10 wt%

3-Methyl-1,3-butanediol: 15 wt%

Glycerine: 15 wt%

Polyalkylene glycol surfactant (Adeka): 1 wt%

2-Ethyl-1,3-hexanediol: 2 wt%

30 Total 100% with ion-exchange water

## Ink Production Example (1-2)

35 [0285] Magenta pigment dispersion (M-1) of Production Example 2: 6 wt% (solid content)

Binder resin (P-14) (solid content 45%): 10 wt%

Triethylene glycol isobutyl ether: 2 wt%

Glycerine: 20 wt%

Polyalkylene glycol surfactant (Adeka): 1 wt%

2-Ethyl-1,3-hexanediol: 2 wt%

40 Total 100% with ion-exchange water

## Ink Production Example (1-3)

45 [0286] Yellow pigment dispersion (Y-1) of Production Example 3: 6 wt%

(solid content)

[0287] Binder resin (P-15) (solid content 45%): 10 wt%

1,3-Butanediol: 20 wt%

50 Glycerine: 20 wt%

2-Pyrrolidone: 1 wt%

Polyalkylene glycol surfactant (Adeka): 1 wt%

2,2,4-Trimethyl-1,3-pentanediol: 2 wt%

55 Total 100% with ion-exchange water

## Ink Production Example (1-4)

[0288] Carbon black pigment dispersion (B-1) of Production Example 4: 9 wt% (solid content)

Binder resin (P-16) (solid content 45%): 10 wt%

3-Methyl-1,3-butanediol: 20 wt%

Glycerine: 15 wt%

2-Pyrrolidone: 2 wt%

5 Polyalkylene glycol surfactant (Adeka): 1 wt%

2-Ethyl-1,3-hexanediol: 2 wt%

Total 100% with ion-exchange water

[0289] Other Ink Production Examples

10 Ink Production Example (2-1)

[0290] A latex ink was produced by preparing the same composition except that the cyan pigment dispersion (C-1) was changed to (C-2), and that the binder resin (P-13) was changed to (P-17).

15 Ink Production Example (2-2)

[0291] A latex ink was produced by preparing the same composition except that the magenta pigment dispersion (M-1) was changed to (M-2), and that the binder resin (P-14) was changed to (P-18).

20 Ink Production Example (2-3)

[0292] A latex ink was produced by preparing the same composition except that the yellow pigment dispersion (Y-1) was changed to (Y-2), and that the binder resin (P-15) was changed to (P-13).

25 Ink Production Example (2-4)

[0293] A latex ink was produced by preparing the same composition except that the carbon black pigment dispersion (B-1) was changed to (B-2), and that the binder resin (P-16) was changed to (P-14).

30 Ink Production Example (3-1)

[0294] A latex ink was produced by preparing the same composition except that the cyan pigment dispersion (C-1) was changed to (C-3), and that the binder resin (P-13) was changed to (P-15).

35 Ink Production Example (3-2)

[0295] A latex ink was produced by preparing the same composition except that the magenta pigment dispersion (M-1) was changed to (M-3), and that the binder resin (P-14) was changed to (P-16).

40 Ink Production Example (3-3)

[0296] A latex ink was produced by preparing the same composition except that the yellow pigment dispersion (Y-1) was changed to (Y-3), and that the binder resin (P-15) was changed to (P-17).

45 Ink Production Example (3-4)

[0297] A latex ink was produced by preparing the same composition except that the carbon black pigment dispersion (B-1) was changed to (B-3), and that the binder resin (P-16) was changed to (P-18).

50 Ink Production Example (4-1)

[0298] A latex ink was produced by preparing the same composition except that cyan pigment dispersion (C-1) and binder resin (P-19) were used.

55 Ink Production Example (4-2)

[0299] A latex ink was produced by preparing the same composition except that magenta pigment dispersion (M-1) and binder resin (P-20) were used.

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### Ink Production Example (4-3)

**[0300]** A latex ink was produced by preparing the same composition except that yellow pigment dispersion (Y-1) and binder resin (P-21) were used.

5

### Ink Production Example (4-4)

**[0301]** A latex ink was produced by preparing the same composition except that carbon black pigment dispersion (B-1) and binder resin (P-21) were used.

10

**[0302]** Table 1 presents the combination of ink color material and binder resin for each Production Example. Table 2 presents the physical properties of each ink.

Table 1

Production Example	Dispersion	Binder resin	Production Example	Dispersion	Binder resin
1-1	C-1	P-13	3-1	C-3	P-15
1-2	M-1	P-14	3-2	M-3	P-16
1-3	Y-1	P-15	3-3	Y-3	P-17
1-4	B-1	P-16	3-4	B-3	P-18
2-1	C-2	P-17	4-1	C-1	P-19
2-2	M-2	P-18	4-2	M-1	P-20
2-3	Y-2	P-13	4-3	Y-1	P-21
2-4	B-2	P-14	4-4	B-1	P-21

Table 2

Production Example	Surface tension (mN/m)	Viscosity (mPa·s)	Production Example	Surface tension (mN/m)	Viscosity (mPa·s)
1-1	25.6	9.11	3-1	27.9	9.00
1-2	27.4	8.98	3-2	26.5	9.01
1-3	26.1	8.76	3-3	27.4	8.78
1-4	27.3	8.56	3-4	28.3	8.94
2-1	26.4	8.74	4-1	27.7	8.84
2-2	27.1	8.88	4-2	26.6	8.86
2-3	26.5	8.43	4-3	27.3	8.79
2-4	27.1	8.97	4-4	27.2	8.93

45

### Inks Used in Examples and Comparative Examples

**[0303]** In Examples and Comparative Examples, the inks were used in the combinations presented in Table 3.

Table 3

Ink	Cyan	Magenta	Yellow	Black
Example 1	1-1	1-2	1-3	1-4
Example 2	2-1	2-2	2-3	2-4
Example 3	3-1	3-2	3-3	3-4
Comparative Example 1	4-1	4-2	4-3	4-4

## Evaluation of Print Image Quality

[0304] GEN5 (Ricoh) was attached to the head of an inkjet printer (JV33; Mimaki Engineering Co., Ltd.). The inks of Production Examples 1-1 to 4-4 were used to print different media under the conditions below, and the prints were reeled into a media paper core. The reeled print surface was then checked by visual inspection for bleeding. The printing speed is shown in Table 4. The print density was set according to the amount of the ink applied per unit area.

Table 4

	Printing speed		Maximum density			
	Draft (m <sup>2</sup> /h)	Fine (m <sup>2</sup> /h)	Draft (35°C)	Draft (40°C)	Fine (35°C)	Fine (40°C)
Example 1	80.7	40.5	240%	240%	270%	270%
Example 2	84.3	41.3	240%	230%	270%	280%
Example 3	79.6	40.5	240%	230%	260%	280%
Comparative Example 1	22.6	11.2	120%	110%	170%	180%

## Print Conditions

[0305] Printing Speed:

- (1) Draft: 540 x 1080 dpi/high speed mode
- (2) Fine: 720 x 1080 dpi/high speed mode Heater temperature:
  - (i) Preheater: OFF to 45°C
  - (ii) Print heater: OFF to 45°C
  - (iii) Post-heater: OFF to 50°C

## Print Image Quality Evaluation Method

[0306] The image characteristics of the print image were evaluated with respect to feathering, color bleed, beading, image density, and gloss. The image was also evaluated for abrasion resistance as a measure of image reliability. The results are presented in Table 5.

## Evaluation of Image Characteristics

## Feathering and Color Bleed Evaluation

[0307] The presence or absence of feathering and color bleed was observed by visual inspection for each Example and Comparative Example, and the results were evaluated according to the following criteria.

## Evaluation Criteria

[0308] Excellent: No bleeding in all paper media; clear printing Good: Spiked bleeding in some of the paper media (recycled paper)

Acceptable: Spiked bleeding in all of the paper media Poor: Serious bleeding blurring the contour of characters Beading Evaluation

[0309] The extent of beading in green solid image portions was observed in visual inspection for each Example and Comparative Example, and the results were evaluated according to the following criteria.

## Evaluation Criteria

[0310]

- 5: Uniform printing without beading
- 4: Slight beading was observed, but was hardly noticeable

- 3: Beading was observed, but was not detrimental to image quality
- 2: Clear beading was observed
- 1: Severe beading was observed

5      Image Density Evaluation

**[0311]** The optical density in magenta solid image portions was measured for each Example and Comparative Example using X-Rite 932, and the results were evaluated according to the following criteria.

10     Evaluation Criteria

- [0312]** Excellent: Magenta image density of 1.6 or more
- Good: Magenta image density of 1.3 or more
- Acceptable: Magenta image density of 1.0 or more
- 15     Poor: Magenta image density of less than 1.0

Gloss Evaluation

**[0313]** The extent of the gloss in image portions was observed by visual inspection for each Example and Comparative Example, and the results were evaluated according to the following criteria.

Evaluation Criteria

- [0314]** Excellent: High glossiness was observed
- 25     Good: Glossiness was observed
- Poor: No glossiness was observed

Image Reliability Evaluation

Evaluation of Abrasion Resistance

**[0315]** For image evaluation, square (3 cm x 3 cm) samples of black, cyan, magenta, yellow, red, green, and blue were prepared. After 24 hours from printing, the sample of each color was rubbed 5 times in strokes with a white cotton cloth (JISL 0803; cotton 3) attached to a friction block via a double-sided adhesive foam tape (#4016; t = 1.6; 3M), using a clock meter (CM-1). The density of the color material adhered to the cotton cloth was then measured with a spectro-densitometer (Model-938; X-Rite).

Evaluation Criteria

- [0316]** Excellent: Density of color material adhered to cotton cloth was less than 0.05
- 40     Good: Density of color material adhered to cotton cloth was 0.05 or more and less than 0.1
- Poor: Density of color material adhered to cotton cloth was 0.1 or more

**[0317]** The results of the image characteristic and image reliability evaluations are presented in Table 5.

Table 5

	Feathering	Color bleed	Beading	Density	Gloss	Abrasion resistance
Example 1	Excellent	Excellent	5.0 (Excellent)	Excellent	Excellent	Excellent
Example 2	Excellent	Excellent	4.5 (Excellent)	Excellent	Excellent	Excellent
Example 3	Excellent	Excellent	4.5 (Excellent)	Excellent	Excellent	Excellent
Comparative Example 1	Good	Good	1.5 (Acceptable)	Acceptable	Acceptable	Acceptable

## Evaluation of Latex Ink Preservation Stability

[0318] Each latex ink (100 ml) was placed in a glass container, sealed, and stored under the following conditions. Each sample was then evaluated for changes in surface tension and viscosity. The results are presented in Table 7.

5

## Storage Conditions

## [0319]

- 10 (i) Ordinary temperature (25°C) for 28 days
- (ii) High temperature (50°C) for 14 days
- (iii) Low temperature (0°C) for 28 days
- (iv) Cycle test (0 to 50°C); stored for 14 days by varying the temperature every 24 hours

15 [0320] The surface tension and viscosity changes of each sample are presented in Table 7. The physical properties hardly changed in each ink.

Table 6

	(i)	(ii)	(iii)	(iv)
20 Production Example	Surface tension (mN/m)/ viscosity (mPa·s)			
25 1-1	25.6/9.12	25.9/9.16	25.6/9.03	25.7/9.43
26 1-2	27.3/9.10	27.1/9.31	27.0/9.09	27.3/9.57
27 1-3	26.2/8.12	26.5/8.32	26.1/8.83	26.4/8.62
28 1-4	27.1/8.81	26.8/8.89	26.6/8.83	26.7/9.02
29 2-1	26.3/9.12	26.6/9.21	26.3/9.03	26.4/90.9
30 2-2	27.4/8.61	27.8/8.83	27.7/8.78	27.6/8.89
31 2-3	26.7/9.02	26.9/9.11	26.5/9.02	26.6/9.89
32 2-4	27.1/9.02	27.0/26.8	27.5/18.9	27.4/25.5
33 3-1	27.9/8.98	27.7/18.9	27.7/19.1	27.4/21.6
34 3-2	26.6/9.00	26.6/9.12	26.7/8.97	26.8/9.34
35 3-3	27.4/9.10	27.6/9.31	27.4/8.57	27.5/9.31
36 3-4	28.2/9.11	28.6/9.20	28.7/9.10	28.9/9.43
37 4-1	27.8/8.99	27.6/22.1	27.2/14.3	27.8/23.1
38 4-2	26.6/9.11	26.5/9.02	26.6/9.04	26.5/9.32
39 4-3	27.3/8.89	27.4/21.8	27.2/19.4	27.6/26.3
40 4-4	27.1/8.78	27.0/20.6	27.7/15.8	27.6/24.2

## Printing Method Evaluation

50 [0321] The inks of Examples 1 to 3 and Comparative Example 1 were used to print graphics and characters on surfaces of various media using the inkjet printer 1, and the results were assessed in view of the foregoing test results. In each example, the inkjet printer was used in an ordinary temperature room at a room temperature of about 15 to 20°C. In the tables, the media heating temperature of the preheater is the temperature on the surface of the media transported to the platen posterior portion and heated by the preheater. The media heating temperature of the print heater is the temperature on the surface of the media heated by the print heater and struck by the ink droplets expelled from the printhead after being transported to the platen central portion. In each table, the image quality represents the result of the comprehensive evaluation of the image characteristics (feathering, color bleed, beading, image density, and gloss)

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in scale of 1 to 10, where 10 is the highest score. In each table, "OFF" means that the preheater or the print heater is turned off, and not heating the media.

Ink of Example 1

5

**[0322]** MacMarc: 9829-00 (product name) was used as media.

Table 7

	1	2	3	4	5	6
Media heating temperature of preheater	OFF	35°C	40°C	45°C	45°C	OFF
Media heating temperature of print heater	OFF	35°C	40°C	45°C	OFF	45°C
Media heating temperature of post-heater	OFF	45°C	45°C	45°C	45°C	45°C
Image quality	4	6	6	6	6	6

Ink of Example 2

20

**[0323]** Transparent PVC Film P-245RC: LINTEC (product name) was used as media.

Table 8

	1	2	3	4	5	6
Media heating temperature of preheater	OFF	35°C	40°C	45°C	45°C	OFF
Media heating temperature of print heater	OFF	35°C	40°C	45°C	OFF	45°C
Media heating temperature of post-heater	OFF	45°C	45°C	45°C	45°C	45°C
Image quality	4	7	7	8	6	7

30

Ink of Example 3

35

**[0324]** PVC Viewcal 880C: LINTEC (product name) was used as media.

Table 9

	1	2	3	4	5	6
Media heating temperature of preheater	OFF	35°C	40°C	45°C	45°C	OFF
Media heating temperature of print heater	OFF	35°C	40°C	45°C	OFF	45°C
Media heating temperature of post-heater	OFF	45°C	45°C	45°C	OFF	45°C
Image quality	4	5	5	6	4	6

45

Ink of Comparative Example 1

50

**[0325]** MacMarc: 9829-00 (product name) was used as media.

Table 10

	1	2	3	4	5	6
Media heating temperature of print heater	OFF	35°C	40°C	45°C	OFF	45°C
Media heating temperature of post-heater	OFF	45°C	45°C	45°C	45°C	45°C
Image quality	2	5	4	4	3	4

55

**[0326]** The results from using the inks of Examples 1 to 3 and Comparative Example 1 confirmed that the image quality

of graphics and characters printed on media surface improves when the latex ink containing a binder resin having a surface minimum filming temperature of 0°C or less is used in the printing method that preliminarily heats the media with the preheater before printing graphics and characters, and that uses the print heater to heat the media to be struck by the ink droplets expelled from the printhead.

5 [0327] As described above, the printing method according to the embodiment of the present invention is preferable for printing high-image-quality graphics and characters on media surface with fixing stability in applications such as in outdoor advertisement displays required to satisfy environment and media characteristics. The printing method according to the embodiment of the present invention is also preferable for printing graphics and characters on media surface in industrial applications where abrasion resistance is required.

10

## Claims

1. A method for printing a recording medium with an inkjet printer that includes:

15 a printhead;  
 a driving means for that moves and positions the recording medium and the printhead relative to each other;  
 a heating means provided at a position opposite an ink discharge face of the printhead, and that heats the recording medium from the back side of an inked surface of the recording medium positioned opposite the ink discharge face of the printhead by the driving means; and  
 20 a preliminary heating means that heats the recording medium from the back side of the inked surface before the recording medium is positioned opposite the ink discharge face of the printhead,  
 the method comprising:

25 heating the recording medium with the heating means and the preliminary heating means to make a surface temperature of the inked surface of the recording medium 40°C or more and 60°C or less; and  
 printing the recording medium by causing the printhead to discharge an ink that contains a solvent, a colorant, and a binder resin, wherein the binder resin is dispersed or emulsified in the solvent, and has a surface minimum filming temperature of 0°C or less.

30 2. The printing method according to claim 1, wherein the binder resin has different minimum filming temperatures for a surface portion and an interior portion.

35 3. The printing method according to claim 2, wherein the minimum filming temperature of the binder resin is lower in the surface portion than in the interior portion.

40 4. The printing method according to any one of claims 1 to 3,  
 wherein the solvent is at least one of water and a hydrophilic solvent, and  
 wherein the ink contains the solvent in 50 weight% or more of the total weight of the ink.

45 5. The printing method according to any one of claims 1 to 4, wherein the heating means and the preliminary heating means are controlled to heat the recording medium at different temperatures.

6. The printing method according to claim 5,  
 wherein the preliminary heating means heats the inked surface of the recording medium to a surface temperature of 30°C or more and 50°C or less, and  
 wherein the heating means heats the surface temperature of the inked surface of the recording medium to 40°C or more and 60°C or less.

50 7. The printing method according to any one of claims 1 to 4, wherein the heating means and the preliminary heating means are controlled to heat the recording medium at the same temperature.

55 8. The printing method according to any one of claims 1 to 7, wherein the recording medium is one selected from the group consisting of a vinyl chloride sheet, a PET sheet, a tarpaulin sheet, and coated paper neither of which is coated with coating material, and uncoated polypropylene resin, uncoated glass, uncoated metal, and molded products thereof.

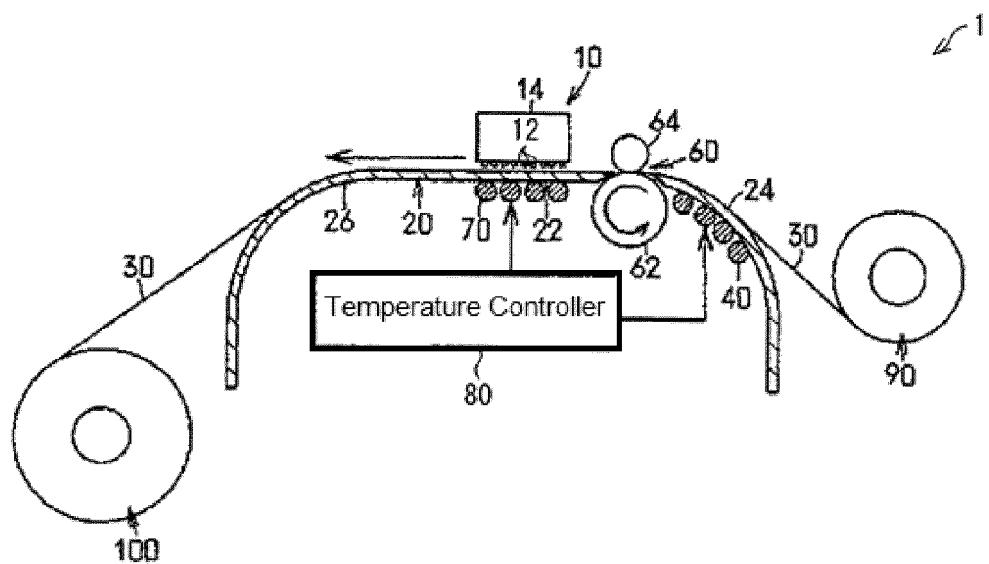


Fig. 1

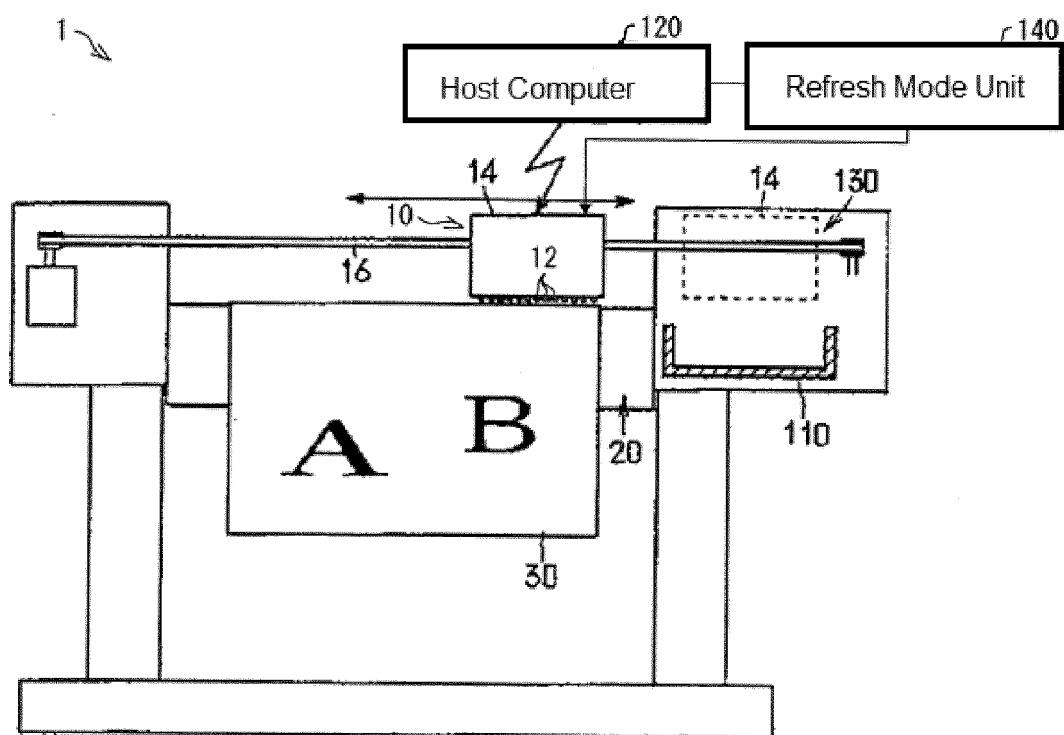


Fig. 2

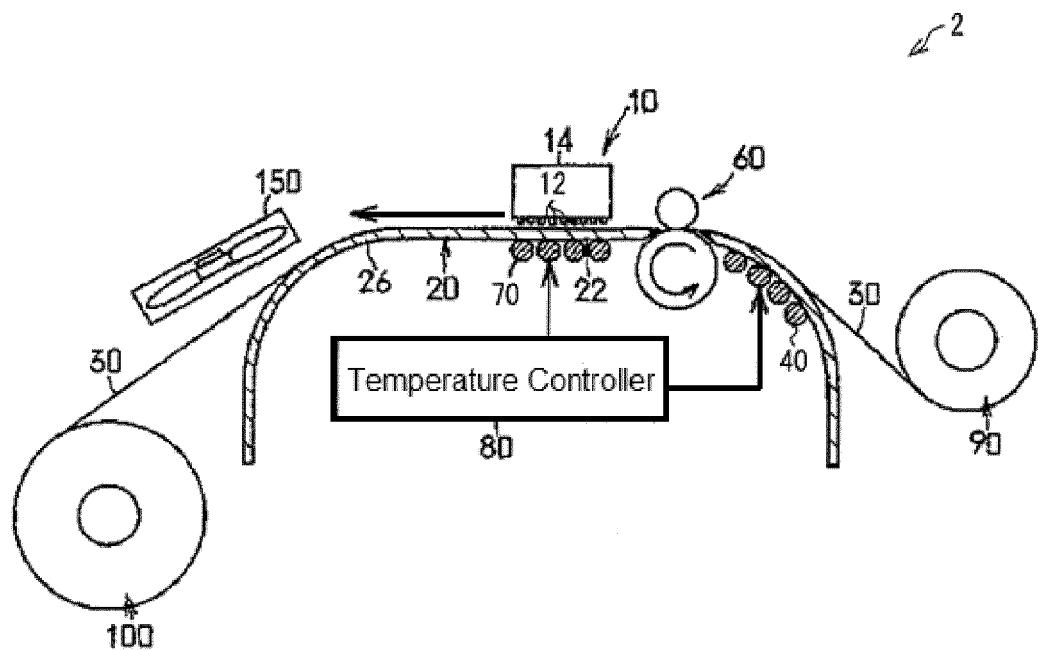


Fig. 3

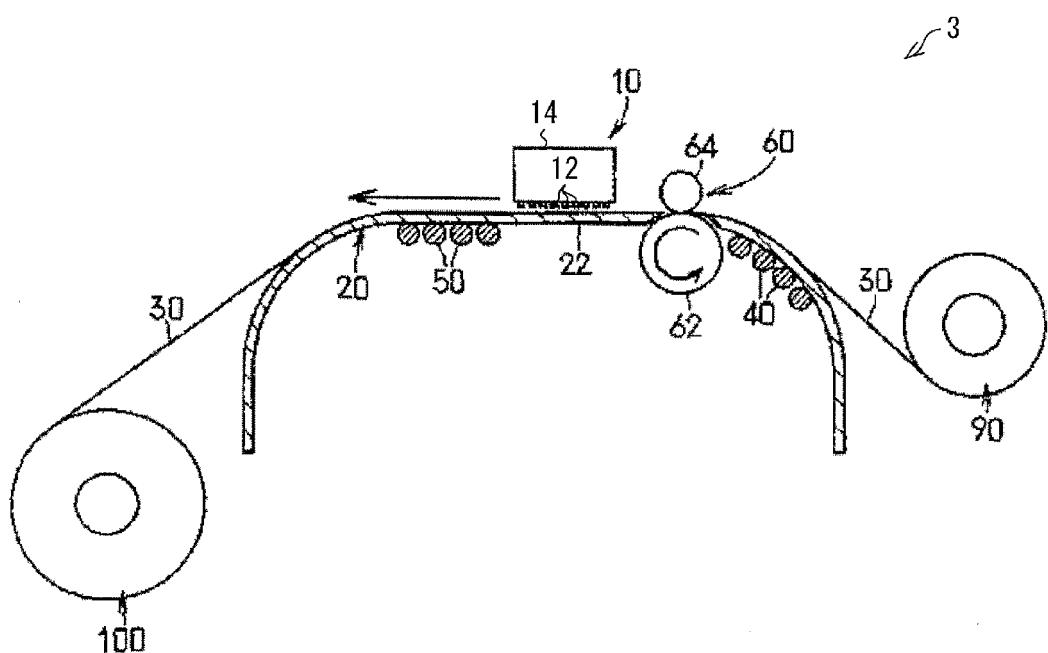


Fig. 4



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Application Number

EP 13 19 1679

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2	Place of search	Date of completion of the search	Examiner
	The Hague	26 February 2014	Wehr, Wolfhard
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
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