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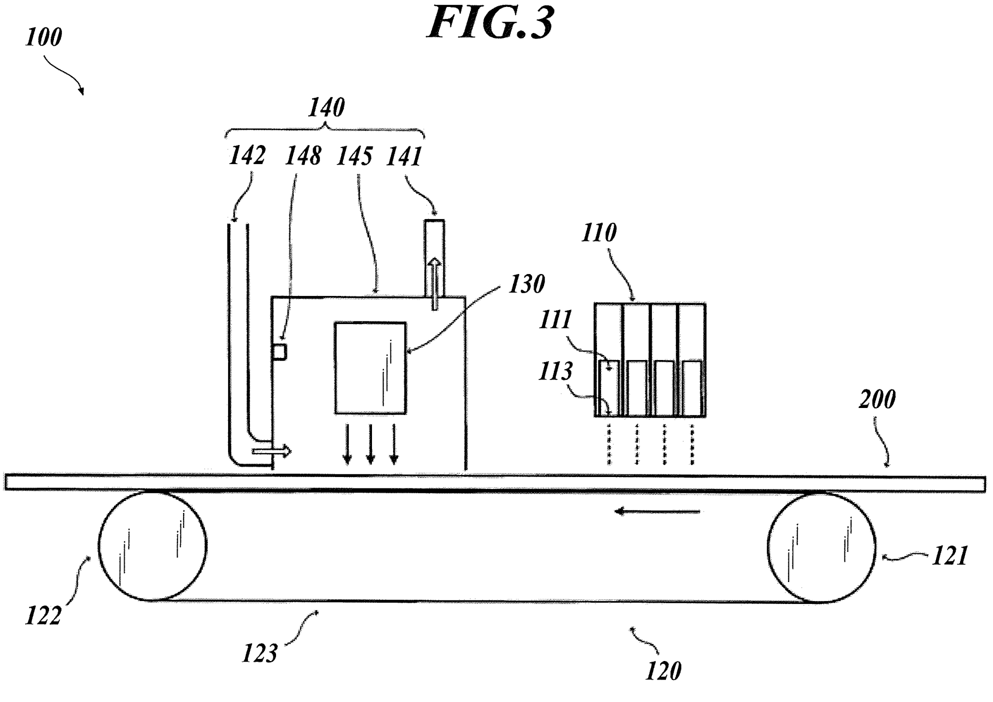
(54) INK-JET RECORDING METHOD AND ACTINIC RAY CURABLE INK-JET INK SET

(57) Provided is an ink-jet recording method using an actinic ray curable ink-jet ink set having a first ink-jet ink containing at least titanium oxide and a gelling agent, and a second ink-jet ink containing a colorant other than titanium oxide, the ink-jet recording method containing the steps of: forming a lower print layer by printing the first ink-jet ink; forming an upper print layer on the lower print layer by printing the second ink-jet ink; and curing the lower print layer and the upper print layer by irradiating the lower print layer and the upper print layer with actinic rays, wherein an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

FIG.3



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Description

[0001] Japanese Patent Application No. 2018-132833, filed on July 13, 2018 with Japan Patent Office, is incorporated herein by reference in its entirety.

Technological Field

[0002] The present invention relates to an ink-jet recording method and an actinic ray curable ink-jet ink set. More particularly, the present invention relates to an ink-jet recording method in which the adhesion between the upper layer and the colored ink is excellent even when a white ink or a clear ink is used for undercoating.

Background

[0003] Ink-jet printing techniques have been used in various fields of printing since images may be formed easily at low cost. In the ink-jet image recording method, a suitable combination of inks is selected from yellow ink, magenta ink, cyan ink and black ink according to the color to be formed, and a full color image may be obtained by overprinting the selected inks.

[0004] At present, in the case of recording an image using a transparent film or vapor-deposited paper widely used as a soft packaging material in the field of packaging materials currently using an ink-jet ink, since the recording medium does not have an ink absorbing layer, there is a problem that the image quality is lowered due to liquid deviation or color bleeding.

[0005] An actinic ray curable ink-jet ink is used as one of the measures against the above problems. In this method, after ink droplets are landed on a recording medium, an actinic ray, for example, an ultraviolet ray is irradiated and cured to form an image. The actinic ray curable ink-jet image forming method has been attracting attention in recent years because an image having high abrasion resistance and adhesiveness may be formed even on a recording medium having no ink absorbability.

[0006] On the other hand, when an image is recorded on a non-absorptive recording medium such as a transparent film or vapor-deposited paper using an actinic ray curable ink-jet ink as described above, generally, a white ink having a shielding property is used. After priming with a white image, a method of forming a color image (colored image) and enhancing the visibility of the color image is adopted. In such a method, titanium oxide having high hiding power is widely used as a white pigment used for a white ink (see, for example, Patent Document 1: WO 2015/156267 and Patent Document 2: WO 2016/098678). Furthermore, instead of the white ink, a clear ink may be used to make the surface of the non-absorptive recording medium uniform.

[0007] Thus, when using a white ink or a clear ink for undercoating, a gelling agent may be added to the white ink and the clear ink in order to suppress the coalescence of the droplets or to impart a certain texture formed by the gelling agent. In this case, when the amount of the gelling agent is too small, the coalescence of the droplets is not prevented, and when the amount of the gelling agent is too large, the gelling agent is excessively deposited on the surface, and the droplets does not sufficiently level. However, titanium oxide is more polar than pigments in colored ink, and is less likely to interact with the gelling agent, and the gelling agent is likely to precipitate on the surface. Therefore, it is less susceptible to oxygen inhibition and has good curing properties, so it cures and shrinks compared to colored ink, and when white ink is used as a base, there is a problem that adhesion between the upper layer and colored ink is poor.

Summary

[0008] The present invention has been made in view of the above problems and circumstances. An object of the present invention is to provide an ink-jet recording method and an actinic ray curable ink-jet ink set which achieve excellent adhesion between the upper layer and the colored ink even when a white ink or a clear ink is used for undercoating.

[0009] In order to solve the above-mentioned problems the present inventor examined the cause of the above-mentioned problem and achieved the method of the present invention. This method contains: forming a lower print layer with a white ink or a clear ink; forming an upper print layer with a colored ink containing a colorant; and controlling an oxygen concentration when curing the lower print layer and the upper print layer by collectively irradiating with actinic rays. By this method, even when white ink or clear ink is used for undercoating, adhesion between the upper layer and colored ink becomes excellent. That is, the above-mentioned object concerning the present invention is solved by the following means.

[0010] An ink-jet recording method reflecting an aspect of the present invention is an ink-jet recording method using an actinic ray curable ink-jet ink set having a first ink-jet ink containing at least titanium oxide and a gelling agent, and a second ink-jet ink containing a colorant other than titanium oxide, the ink-jet recording method comprising the steps of:

forming a lower print layer by printing the first ink-jet ink;
forming an upper print layer on the lower print layer by printing the second ink-jet ink; and
curing the lower print layer and the upper print layer by irradiating the lower print layer and the upper print layer with actinic rays,
wherein an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

[0011] An ink-jet recording method using reflecting another aspect of the present invention is an ink-jet recording method using an actinic ray curable ink-jet ink set having a third ink-jet ink containing a gelling agent without containing a colorant, and a second ink-jet ink containing a colorant other than titanium oxide, the ink-jet recording method comprising the steps of:

forming a lower print layer by printing the third ink-jet ink;
forming an upper print layer on the lower print layer by printing the second ink-jet ink; and
curing the lower print layer and the upper print layer by irradiating the lower print layer and the upper print layer with actinic rays,
wherein an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

Brief Description of the Drawings

[0012] The advantages and features provided by one or more embodiments of the invention will become more fully understood from the detailed description given hereinbelow and the appended drawings which are given by way of illustration only, and thus are not intended as a definition of the limits of the present invention.

FIG. 1 is a schematic side view which illustrates an example of an ink-jet recording apparatus provided with an oxygen concentration adjustment part applicable to an ink-jet recording method of the present invention.
FIG. 2 is a schematic side view which illustrates an example of an ink-jet recording apparatus provided with an oxygen concentration adjustment part applicable to an ink-jet recording method of the present invention.
FIG. 3 is a schematic side view which illustrates an example of an ink-jet recording apparatus provided with an oxygen concentration adjustment part applicable to an ink-jet recording method of the present invention.
FIG. 4 is a schematic side view which illustrates an example of an ink-jet recording apparatus applicable to an ink-jet recording method of the present invention.
FIG. 5 is a schematic top view which illustrates an example of an ink-jet recording apparatus applicable to an ink-jet recording method of the present invention.
FIG. 6 is a schematic cross-sectional view illustrating an example of a configuration of an ink-jet recording image formed by an ink-jet recording method of the present invention.

Detailed Description of the Embodiments

[0013] Hereinafter, one or more embodiments of the present invention will be described with reference to the drawings. However, the scope of the invention is not limited to the disclosed embodiments.

[0014] By the above means of the present invention, it is possible to provide an ink-jet recording method and an actinic ray curable ink-jet ink set which achieve excellent adhesion between the upper layer and the colored ink even when a white ink or a clear ink is used for undercoating. Although an appearing mechanism or an action mechanism of the effect of the present invention is not clarified, it is presumed as follows.

In this method, a lower print layer is formed by printing a first ink-jet ink containing titanium oxide and a gelling agent, that is, a white ink; thereafter, un upper print layer is formed on the lower print layer by printing a second ink-jet ink containing a colorant other than titanium oxide, i.e., a colored ink; and the lower print layer and the upper print layer are simultaneously irradiated with oxygen at a concentration of 10% or less. By reducing the oxygen concentration, the curability of the colored ink is improved, and the curing shrinkage degree of the colored ink and the curing shrinkage degree of the white ink may be made equal. As a result, the adhesion between the lower print layer containing a white ink and the upper print layer containing a colored ink may be improved.

[0015] An ink-jet recording method reflecting an aspect of the present invention is an ink-jet recording method using an actinic ray curable ink-jet ink set, wherein the actinic ray curable ink-jet ink set have a first ink-jet ink containing at least titanium oxide and a gelling agent (hereinafter it may be called simply as "a first ink"), and a second ink-jet ink containing a colorant other than titanium oxide (hereinafter it may be called simply as "a second ink"). The ink-jet recording method comprises the steps of: forming a lower print layer by printing the first ink-jet ink; forming an upper print layer on the lower print layer by printing the second ink-jet ink; and curing the lower print layer and the upper print layer by irradiating them by with actinic rays with controlling an oxygen concentration in an atmosphere to which the actinic rays are irradiated to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

[0016] An ink-jet recording method reflecting another aspect of the present invention is an ink-jet recording method using an actinic ray curable ink-jet ink set, wherein the actinic ray curable ink-jet ink set have a third ink-jet ink containing a gelling agent without containing a colorant (hereinafter it may be called simply as "a third ink"), and a second ink-jet ink containing a colorant other than titanium oxide. The ink-jet recording method comprises the steps of: forming a lower print layer by printing the third ink-jet ink; forming an upper print layer on the lower print layer by printing the second ink-jet ink; and curing the lower print layer and the upper print layer by irradiating them with actinic rays with controlling an oxygen concentration in an atmosphere to which the actinic rays are irradiated to be 10 volume% or less in the step of curing the lower print layer and the upper print layer. That is, in the other ink-jet recording method of the present invention, the adhesion between the upper layer and the colored ink becomes excellent even when the clear ink is used for the undercoating.

[0017] These features are a technical feature common or corresponding to the following embodiments.

[0018] In the embodiment of the present invention, it is preferable that the second ink-jet ink further contains a gelling agent from the viewpoint that the coalescence of droplets may be suppressed.

[0019] It is preferable that the gelling agent in the first inkjet ink or the gelling agent in the third inkjet ink is in the range of 50 to 90 mass% with respect to the gelling agent of the second inkjet ink. By this the curing and shrinkage of the lower print layer and the upper print layer may be made comparable, and the adhesion between the lower print layer and the upper print layer becomes better.

[0020] It is preferable that the gelling agent in the first ink-jet ink is contained in the range of 0.4 to 2.4 mass% with respect to the total mass of the first ink-jet ink, or the gelling agent in the third ink-jet ink is contained in the range of 0.4 to 2.4 mass% with respect to the total mass of the third ink-jet ink. By this, the pinning property of the first ink or the third ink may be sufficiently enhanced to form a higher definition image, and the deposition of the gelling agent from the surface of the formed image may be suppressed, and adhesion may be improved.

[0021] It is preferable that the first or the third ink-jet ink and the second ink-jet ink contain monomer A having an acrylic equivalent (molecular weight / number of acrylic groups) of less than 170, and that the addition amount of the component derived from the monomer A in the first ink-jet ink or the third ink-jet ink is 60 to 90 mass% with respect to the component derived from the monomer A in the second ink-jet ink. By this, the degree of curing and shrinkage of the lower print layer and the upper print layer may be made comparable, and the adhesion between the lower print layer and the upper print layer becomes better.

[0022] It is preferable that the first or the third ink-jet ink and the second ink-jet ink contain monomer B having an acrylic equivalent (molecular weight / number of acrylic groups) of 170 or more, and that the addition amount of the component derived from the monomer B in the second ink-jet ink is in the range of 60 to 90 mass% with respect to the component derived from the monomer B in the first or the third ink-jet ink. By this, the degree of curing and shrinkage of the lower print layer and the upper print layer may be made comparable, and the adhesion between the lower print layer and the upper print layer becomes better.

[0023] It is preferable that the titanium oxide is surface-modified with alumina, and the amount of the alumina surface-modified to the titanium oxide is in the range of 0.3 to 0.8 mass% with respect to the titanium oxide before surface modification (or untreated). By this, the film deterioration with time due to the photocatalytic effect of titanium oxide may be suppressed, and the adhesion between the lower print layer and the upper print layer may be maintained for a long time.

[0024] The first ink-jet ink preferably contains 200 mass ppm or less of sodium (Na) ion with respect to the titanium oxide. The sodium ion may combine with the residual fatty acid in the gelling agent to form a metal soap to cause gelation failure or to precipitate in an inkjet head to cause a failure. By setting the sodium ion content to less than 200 mass ppm, poor gelation may be suppressed, and deposition in an ink-jet head may also be prevented.

[0025] It is preferable that the gelling agent contains a compound having a structure represented by at least Formula (G1) or Formula (G2) (described later) from the viewpoint of better adhesion between the lower print layer and the upper print layer.

[0026] An actinic ray curable ink-jet ink set used in the ink-jet recording method of the present invention comprises: a first ink-jet ink containing titanium oxide and a gelling agent; and a second ink-jet ink containing a colorant other than titanium oxide. An actinic ray curable ink-jet ink set used in another ink-jet recording method of the present invention contains: a third ink-jet ink containing a gelling agent and containing no colorant; and a second colorant containing a colorant other than titanium oxide.

[0027] The present invention and the constitution elements thereof, as well as configurations and embodiments to carry out the present invention, will be detailed in the following. In the present description, when two figures are used to indicate a range of value before and after "to", these figures are included in the range as a lowest limit value and an upper limit value.

[Ink-jet recording method]

[0028] The ink-jet recording method according to the first embodiment of the present invention is an ink-jet recording method using an actinic ray curable ink-jet ink set. The actinic ray curable ink-jet ink set has a first ink containing titanium oxide and a gelling agent, and a second ink containing a colorant other than titanium oxide. This ink-jet recording method comprises the steps of: forming a lower print layer by printing the first ink-jet ink; forming an upper print layer on the lower print layer by printing the second ink-jet ink; and curing the lower print layer and the upper print layer by irradiating them with actinic rays. And an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

[0029] The ink-jet recording method according to the second embodiment of the present invention uses an actinic ray curable inkjet ink set having a third ink-jet ink containing a gelling agent without containing a colorant, and a second ink-jet ink containing a colorant other than titanium oxide. The ink-jet recording method comprising the steps of: forming a lower print layer by printing the third ink-jet ink; forming an upper print layer on the lower print layer by printing the second ink-jet ink; and curing the lower print layer and the upper print layer by irradiating them with actinic rays. And an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

[0030] That is, in the ink-jet recording method according to the first embodiment, the first ink, which is a white ink containing titanium oxide, is used as the lower print layer. The ink-jet recording method according to the second embodiment is a method using a third ink which is a clear ink containing no colorant, instead of the aforesaid first ink as the lower print layer. Others are basically the same as the ink-jet recording method according to the first embodiment. Also in the ink-jet recording method according to the second embodiment, in the step of curing the lower print layer and the upper print layer, by setting the oxygen concentration at the time of actinic ray irradiation to be 10% or less, the oxygen inhibition of the second ink is less likely to occur, and the curability of the second ink is improved. As a result, the degree of cure and expansion of the second ink may be made equal to that of the third ink, and the adhesion between the upper print layer and the lower print layer may be improved. Further, by lowering the oxygen concentration, the second and third inks may be sufficiently cured even with a smaller amount of light.

[0031] Each step will be described below. The configuration of the actinic ray curable ink-jet ink set (the first to the third ink-jet inks) will be described later.

<Step of forming Lower print layer>

[0032] In the step of forming the lower print layer, the first or the third ink is printed (landed) on the recording medium to form the lower print layer. At this time, it is essential that the first or the third ink droplet lands on a position on the recording medium corresponding to the image to be formed.

[0033] The ejection stability may be enhanced by discharging the first or the third ink droplet from the ink-jet head in a heated state. The temperature of the first or the third ink at the time of ejection is preferably in the range of 35 to 100 °C, and from the viewpoint of further enhancing the ejection stability, it is more preferably in the range of 35 to 80 °C. From the viewpoint of further enhancing the ejection stability, ejection is performed at an ink temperature such that the viscosity of the first or the third ink is preferably in the range of 3 to 20 mPa·s, more preferably in the range of 8 to 13 mPa·s.

[0034] An example of a method of heating the first or the third ink to a predetermined temperature include a method to heat to a predetermined temperature at least one of an ink tank constituting the head carriage, an ink supply system such as a supply pipe and an ink chamber in the front chamber immediately before the head, a pipe with a filter, and a piezo head.

[0035] From the viewpoint of increasing the recording speed and enhancing the image quality, an amount of the droplet of the first or the third ink when ejected is preferably in the range of 2 to 20 pL.

[0036] The discharge system from the ink-jet head may be either an on-demand system or a continuous system. Examples of the on-demand system include: electro-mechanical conversion systems including single cavity type, double cavity type, bender type, piston type, shear mode type and shared wall type; electro-thermal conversion systems including thermal ink-jet type and bubble jet (registered trademark).

<Step of forming Upper print layer>

[0037] In the step of forming the upper print layer, the second ink is printed (landed) on the lower print layer to form the upper print layer.

[0038] At this time, it is essential that the second ink droplet lands on the lower print layer at a position corresponding to the image to be formed.

[0039] The temperature and viscosity of the second ink at the time of ejection, the method of heating the second ink, the amount of droplets, and the ejection method are the same as the case described for the first or the third ink in the step of forming the lower print layer described above.

<Step of curing Lower print layer and Upper print layer>

[0040] In the step of curing the lower print layer and the upper print layer, the lower print layer and the upper print layer are irradiated with actinic rays to cure the lower print layer and the upper print layer. And the oxygen concentration in the atmosphere to which irradiates actinic rays are irradiated is made to be 10 volume% or less.

[0041] In this step, the first and the second inks or the second and the third inks landed in the previous step are irradiated with actinic rays to form a cured film constituting an image. By irradiating the first and the second inks or the second and the third inks with actinic rays, the first and the second inks or the second and the third inks are cured to form a cured film.

[0042] The oxygen concentration in the atmosphere to which actinic rays are applied is preferably 10 volume% or less, more preferably 5% by volume% or less. By setting the oxygen concentration at the time of actinic ray irradiation to a low concentration of 10% or less, it is possible to make the second ink less susceptible to oxygen inhibition and to improve the curability of the second ink. As a result, the degree of curing and expansion of the second ink may be made equal to that of the first ink or the third ink, and the adhesion between the upper print layer and the lower print layer may be improved. In addition, by reducing the oxygen concentration, the first and the second inks or the second and the third inks may be sufficiently cured even with a smaller amount of light.

[0043] Examples of means for setting the oxygen concentration to 10% or less include gas replacement using a nitrogen gas.

[0044] An example of an apparatus used as a means for reducing the oxygen concentration to 10% or less will be described below. As illustrated in FIG. 1, an ink-jet recording apparatus 100 is equipped with a transport unit 120 for transporting the recording medium 200, an ink-jet head 110 for discharging the ink onto a transported recording medium 200, and an irradiation unit 130 for irradiating the ink with actinic rays, and an oxygen concentration adjustment unit 140 for adjusting the oxygen concentration of the atmosphere surrounding the surface of the recording medium 200 on which the ink has landed when the irradiation unit 130 emits the actinic rays.

[0045] The configuration of the oxygen concentration adjustment unit 140 is not particularly limited as long as the oxygen concentration of the atmosphere may be set to 0.1 volume% or more and 10.0 volume% or less. The oxygen concentration adjustment unit 140 is connected to an external exhaust device. It is equipped with an exhaust pipe 141 capable of sucking and exhausting the gas near the surface of the recording medium and a supply pipe 142 that generates a gas with a low oxygen concentration such as a nitrogen gas generator and located in the downstream of the exhaust pipe 141. At this time, the exhaust gas amount from the exhaust pipe 141 and the gas supply amount from the supply pipe 142 may be adjusted to make the oxygen concentration of the atmosphere in the range of 0.1 to 10.0 volume%. Although the exhaust pipe 141 and the supply pipe 142 are continuous in FIG. 1, they may be separated from each other as long as the adjustment to the oxygen concentration is possible. Moreover, the supply pipe 142 is preferably in the vicinity of the irradiation unit 130, and may be provided continuously with the irradiation unit 130, for example. Also, the exhaust pipe 141 and the supply pipe 142 are not essential components, and for example, only the supply pipe 142 may be used as illustrated in FIG. 2.

[0046] Further, as illustrated in FIG. 3, the oxygen concentration adjustment unit 140 may be configured to include a partition wall 145 surrounding the irradiating unit 130 and the transporting unit 120. At this time, by adjusting the exhaust amount from the exhaust pipe 141 and the supply amount of gas from the supply pipe 142, the oxygen concentration in the space partitioned by the partition wall 145 and the transport unit 120 may be made in the range of 0.1 to 10.0 volumes%. At this time, an oxygen concentration measuring device 148 may be provided in the space (for example, on the partition wall 145) to adjust the exhaust amount and the supply amount while measuring the oxygen concentration in the space.

[0047] Examples of actinic rays that may be applied to the first and the second inks or the second and the third inks include electron beams, ultraviolet rays, α-rays, γ-rays, and X rays. Among these, from the viewpoint of ease of handling and less influence on the human body, it is preferable to irradiate ultraviolet rays. The light source is preferably a light emitting diode (LED) from the viewpoint of suppressing the occurrence of curing failure of the ink due to melting of the first and the second inks or the second and the third inks by radiant heat of the light source. Examples of the LED light sources that enables to irradiate ultraviolet light to form a cured film include water-cooled LED, 395 nm, manufactured by Phoseon Technology.

[0048] From the viewpoint of further suppressing irradiation of radiant heat to the first and the second inks or the second and the third inks, it is preferable that the LED light source is configured to emit ultraviolet light in the range of 370 to 410 nm at a peak illuminance of 0.5 to 10 W/cm^2 on the image surface. It is more preferable to be configured to set in the range of 1 to 5 W/cm^2. Alternatively, it is preferable that the light amount irradiated to the image is set to be less than 350 mJ/cm^2.

[0049] The transport speed of the recording medium is preferably in the range of 30 to 120 m/min from the viewpoint of high speed recording.

(Recoding medium)

[0050] The recording medium used in the ink jet recording method according to the first and the second embodiments of the present invention may be any as long as an image may be formed by the first, the second and the third inks according to the present invention. Examples of the recording medium include non-absorptive recording media composed of plastics such as polyester, polyvinyl chloride, polyethylene, polyurethane, polypropylene, acrylic resin, polycarbonate, polystyrene, acrylonitrile-butadiene-styrene copolymer, polyethylene terephthalate and polybutadiene terephthalate; non-absorptive inorganic recording media composed of metals and glasses; and papers (for example, coated paper for printing, and coated paper B for printing). Among them, it is preferably used for an OK top coat paper and a Mali coat paper for which coating with overcoat liquid is required.

[0051] Ink droplets are deposited on the recording medium by discharging the ink droplets from the ink-jet recording head. It is preferable that the temperature of the recording medium is set in the range of 20 to 50 °C when the ink droplets land in order to form a high quality image with good repeatability.

[Actinic ray curable ink-jet ink set]

[0052] An actinic ray curable ink-jet ink set according to the first embodiment of the present invention (hereinafter, also simply referred to as an ink set) is an actinic ray curable ink-jet ink set used in the ink-jet recording method according to the first embodiment. It includes a first ink containing titanium oxide and a gelling agent, and a second ink containing a colorant other than titanium oxide.

[0053] In addition, an actinic ray curable ink-jet ink set according to the second embodiment of the present invention (hereinafter, also simply referred to as an ink set) is an actinic ray curable ink-jet ink used in the ink-jet recording method according to the second embodiment. It includes a third ink containing a gelling agent and containing no colorant, and a second ink containing a colorant other than titanium oxide.

[0054] That is, the ink set according to the first embodiment includes the first ink which is a white ink containing titanium oxide. The ink set according to the second embodiment is an ink set provided with a third ink containing a gelling agent without containing a colorant (namely, a clear ink) instead of the first ink in the ink set according to the first embodiment. The other configuration of the second ink is the same as that of the ink set according to the first embodiment.

[0055] The first ink contains titanium oxide and a gelling agent. The second ink contains a colorant other than titanium oxide. The third ink contains a gelling agent and does not contain a colorant. The first to the third inks preferably contain a photopolymerizable compound and a photopolymerization initiator. Further, it is preferable that at least the first ink and the third ink contain a gelling agent, and it is preferable that all of the first to the third inks contain a gelling agent.

<Titanium oxide>

[0056] The first ink preferably contains titanium oxide as a white pigment, and 50 mass% or more of the titanium oxide is preferably rutile titanium dioxide. The titanium oxide applied to the present invention is preferably surface-modified (surface-treated) with alumina, silica, zinc, zirconia, or an organic substance, and particularly preferably surface-modified with alumina.

[0057] Specific methods for surface-modifying titanium oxide with alumina include, for example, the following methods. First, titanium oxide is dispersed in water to form a slurry. At this time, a dispersant may be added. Further, separately from the titanium oxide slurry, dilute sulfuric acid aqueous solution is dropped to an aqueous solution of sodium aluminate (sodium aluminate ($Na[Al(OH)_4]$)) to adjust the pH to 10.5 to 11.8; thus an aluminum compound solution is prepared. Next, addition and mixing of the titanium oxide slurry obtained above to the aluminum compound solution is started. At the time of mixing, stirring is performed using a stirrer, and stirring is continued after addition of the titanium oxide slurry to deposit aluminum oxide hydrate on the titanium dioxide surface. After this, neutralization treatment is performed using a dilute aqueous sulfuric acid solution to adjust the pH of the slurry to 8.15. The slurry after surface treatment is filtered with a membrane filter followed by washing, the collected cake (filtered matter) is dried, and crushed using a commercially available automatic mortar to obtain a surface-modified titanium oxide pigment powder.

[0058] The surface modification amount of the alumina surface-modified to titanium oxide is preferably in the range of 0.3 to 0.8 mass% with respect to the titanium oxide before (or untreated) the surface modification. By this, it is possible to suppress the film deterioration over time due to the photocatalytic effect of titanium oxide, and maintain the adhesion between the lower print layer and the upper print layer for a long time. The surface modification amount of the surface modified alumina to titanium oxide may be determined from the value of the ratio of the amount of alumina to titanium oxide (Al_2O_3/TiO_2) based on the analysis result of aluminum element by inductively coupled plasma atomic emission spectrometry (I. C. P.).

[0059] When the surface modification of titanium oxide is carried out, it is preferable to carry out sufficient washing treatment. When the washing treatment is insufficient, a large amount of sodium (Na) ions of the sodium aluminate may remain on the surface of the titanium oxide, and when the amount of sodium ions is large, the sodium acid is associated with the residual fatty acid in the gelling agent, and may form metal soaps. This metal soap is a factor that causes gelation failure of the gelling agent. Or, it may be deposited and cause problems in the ink jet head and cause problem. Therefore, it is preferable to set the sodium ion in the first ink to 200 mass ppm or less with respect to titanium oxide. That is, in other words, the amount of alumina surface-modified to titanium oxide is preferably in the range of 0.3 to 0.8 mass% with respect to titanium oxide before surface modification.

[0060] The sodium ion content in the first ink may be measured using ICP-AES (SPS 3520 UV, manufactured by SII Nano Technology Inc.). Details will be described below.

(1) Methanol is added to the first ink, and the resulting solution is placed in a centrifuge tube and separated into a solid and a solution in a centrifuge at 20000 rpm for 1 hour.
(2) The dried solid is decomposed in a closed microwave decomposition apparatus with a mixed acid of concentrated nitric acid / concentrated hydrochloric acid (molar ratio 1/10) to form a solution.
(3) The amount of sodium ions in the concentrated nitric acid / concentrated hydrochloric acid solution obtained in (2) is measured by ICP-AES (SPS 3520 UV, manufactured by SII Nano Technology Inc.) to determine the amount of sodium ions in the solid component.
(4) Similarly, the sodium ion content of the solution obtained in (1) is measured by the above-mentioned ICP-AES to determine the sodium ion content of the solution component.
(5) The amount of sodium ions of the solid component obtained in (3) and the amount of sodium ions of the solution component obtained in (4) are added together to obtain "the amount of sodium ions in the first ink".

[0061] The average particle diameter of the titanium oxide particles according to the present invention is preferably in the range of 50 to 500 nm, and more preferably in the range of 100 to 300 nm. By adjusting the average particle diameter of the titanium oxide particles in the range defined above, the effects of the present invention are remarkably exhibited. In addition, suppression of nozzle clogging in the ink-jet head, storage stability of the first ink (in particular, suppression of sedimentation), and hiding power to the print substrate may be sufficiently exhibited.

[0062] The titanium oxide particles applicable to the present invention are also commercially available. Examples thereof are CR-50, CR-57, CR-58, CR-67, CR-Super-70, CR-80, CR-90, CR-90-2, CR-93, CR-95, CR-EL, R- 550, R-580, R-630, R-670, R-680, R-780, R-820, R-830, R-850, R-930, R-980, PF-736, PF-737, and PF-742 (made by Ishihara Sangyo Kaisha, Ltd); and SR-41, R-5N, R-7E, R-11P, R-21, R-25, R-32, R-42, R-44, R-45M, R-62N, R-310, R- 650, TCR-52, GTR-100, D-918, and FTR-700 (made by Sakai Chemical Industry Co., Ltd.).

[0063] The addition amount of titanium oxide in the first ink according to the present invention is preferably in the range of 5.0 to 35 mass%, more preferably 10 to 20 mass%, with respect to the total mass of the first ink. By adjusting the addition amount of titanium oxide in the first ink according to the present invention to the range defined above, it is possible to achieve both the storage stability of the first ink (particularly the suppression of sedimentation) and the shielding property to the print substrate.

[0064] In the first ink according to the present invention, known white pigments other than the titanium oxide according to the present invention may be used in combination as needed. As other white pigments applicable to the present invention, for example, inorganic white pigments, organic white pigments, and white hollow polymer fine particles may be used.

[0065] Examples of the inorganic white pigment include, sulfates of alkaline earth metals such as barium sulfate, carbonates of alkaline earth metals such as calcium carbonate, silica such as fine powder silicic acid and synthetic silicates, calcium silicate, alumina, alumina hydrates, zinc oxide, talc, and clay.

<Colorant other than titanium oxide>

[0066] The second ink according to the present invention further includes a colorant other than titanium oxide. The colorant other than titanium oxide may be a dye or a pigment without limitation, but from the viewpoint of having satisfactory dispersibility in the constituent components of the ink and having excellent weather resistance, a pigment is preferred. There are no particular limitations on the pigment; examples thereof include organic pigments or inorganic pigments assigned the numbers that are described in the Color Index.

[0067] Examples of red or magenta pigments include: Pigment Red 3, 5, 19, 22, 31, 38, 43, 48:1, 48:2, 48:3, 48:4, 48:5, 49:1, 53:1, 57:1, 57:2, 58:4, 63:1, 81, 81:1, 81:2, 81:3, 81:4, 88, 104, 108, 112, 122, 123, 144, 146, 149, 166, 168, 169, 170, 177, 178, 179, 184, 185, 208, 216, 226, and 257; Pigment Violet 3, 19, 23, 29, 30, 37, 50, and 88; and Pigment Orange 13, 16, 20, and 36 and the mixture thereof.

[0068] Examples of blue or cyan pigments include Pigment Blue 1, 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 17-1, 22, 27, 28, 29, 36, and 60 and the mixture thereof.

[0069] Examples of green pigments include Pigment Green 7, 26, 36, and 50 and the mixture thereof.

[0070] Examples of yellow pigments include Pigment Yellow 1, 3, 12, 13, 14, 17, 34, 35, 37, 55, 74, 81, 83, 93, 94, 95, 97, 108, 109, 110, 137, 138, 139, 153, 154, 155, 157, 166, 167, 168, 180, 185, and 193 and the mixture thereof.

[0071] Examples of black pigments include Pigment Black 7, 28, and 26 and the mixture thereof.

[0072] Examples of commercially available pigment products include CHROMOFINE YELLOW 2080, 5900, 5930, AF-1300, and 2700L; CHROMOFINE ORANGE 3700L and 6730; CHROMOFINE SCARLET 6750; CHROMOFINE MAGENTA 6880, 6886, 6891N, 6790, and 6887; CHROMOFINE VIOLET RE; CHROMOFINE RED 6820 and 6830; CHROMOFINE BLUE HS-3, 5187, 5108, 5197, 5085N, SR-5020, 5026, 5050,4920, 4927, 4937, 4824, 4933GN-EP, 4940, 4973, 5205, 5208, 5214, 5221, and 5000P; CHROMOFINE GREEN 2GN, 2GO, 2G-550D, 5310, 5370, and 6830; CHROMOFINE BLACK A-1103; SEIKA FAST YELLOW 10 GH, A-3, 2035, 2054, 2200, 2270, 2300, 2400(B), 2500, 2600, ZAY-260, 2700(B), and 2770; SEIKA FAST RED 8040, C405(F), CA120, LR-116, 1531B, 8060R, 1547, ZAW-262, 1537B, GY, 4R-4016, 3820, 3891, and ZA-215; SEIKA FAST CARMINE 6B1476T-7, 1483LT, 3840, and 3870; SEIKA FAST BORDEAUX 10B-430; SEIKA LIGHT ROSE R40; SEIKA LIGHT VIOLET B800 and 7805; SEIKA FAST MAROON 460N; SEIKA FAST ORANGE 900 and 2900; SEIKA LIGHT BLUE C718 and A612; Cyanine Blue 4933M, 4933GN-EP, 4940, and 4973 (manufactured by Dainichiseika Color & Chemicals Manufacturing Co., Ltd.); KET Yellow 401, 402, 403, 404, 405, 406, 416, and 424; KET Orange 501; KET Red 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 336, 337, 338, and 346; KET Blue 101, 102, 103, 104, 105, 106, 111, 118, and 124; KET Green 201 (manufactured by Dainippon Ink & Chemicals, Inc.); COLORTEX Yellow 301, 314, 315, 316, P-624, 314, U10GN, U3GN, UNN, UA-414, and U263; FINECOL Yellow T-13 and T-05; Pigment Yellow 1705; COLORTEX Orange 202; COLORTEX Red 101, 103, 115, 116, D3B, P-625, 102, H-1024, 105C, UFN, UCN, UBN, U3BN, URN, UGN, UG276, U456, U457, 105C, and USN; COLORTEX Maroon 601; COLORTEX Brown B610N; COLORTEX Violet 600; Pigment Red 122; COLORTEX Blue 516, 517, 518, 519, A818, P-908, and 510; COLORTEX Green 402 and 403; COLORTEX Black 702; U905 (manufactured by Sanyo Color Works, Ltd.); LIONOL Yellow 1405G; LIONOL Blue FG7330, FG7350, FG7400G, FG7405G, ES, and ESP-S (manufactured by Toyo Ink Group); Toner Magenta E02; Permanent Rubin F6B; Toner Yellow HG; Permanent Yellow GG-02; HOSTAPEAM Blue B2G (manufactured by Hoechst Industry, Ltd.); NOVOPERM P-HG; HOSTAPERM Pink E; HOSTAPERM Blue B2G (manufactured by Clariant International, Ltd.); carbon black #2600, #2400, #2350, #2200, #1000, #990, #980, #970, #960, #950, #850, MCF88, #750, #650, MA600, MA7, MA8, MA11, MA100, MA100R, MA77, #52, #50, #47, #45, #45L, #40, #33, #32, #30, #25, #20, #10, #5, #44, and CF9 (manufactured by Mitsubishi Chemical Corp.).

[0073] In addition, as dyes, conventionally known yellow dyes, magenta dyes, cyan dyes, and black dyes may be applied.

<Dispersion method of Pigment>

[0074] When titanium oxide is used for the pigment of the first ink, and when the pigment is sued for a colorant of the second ink, dispersion methods used to prepare the first and second inks are as follows. Dispersion of titanium oxide and the pigment are made by ball mill, sand mill, attritor, roll mill, agitator, HENSCHEL mixer, colloid mill, ultrasonic homogenizer, pearl mill, wet jet mill, or paint shaker.

[0075] As the dispersion conditions of the pigment, it is preferable that the dispersion is performed so that the volume average particle diameter of pigment particles becomes in the range of 0.08 to 0.5 μm, and the maximum particle diameter becomes in the range of 0.3 to 10 μm, more preferably in the range of 0.3 to 3 μm.

[0076] The dispersion of the pigment may be adjusted by the selection of the pigment, the dispersing agent and the dispersing medium, the dispersing conditions, and the filtering conditions to obtain a pigment dispersion having a desired particle size.

<Pigment dispersant>

[0077] The first and the second ink according to the present invention may further include a dispersant in order to increase dispersibility of the pigment. Examples of the dispersant include hydroxyl group-containing carboxylic acid esters, salts of long-chain polyaminoamides and high-molecular weight acid esters, salts of high-molecular weight polycarboxylic acids, salts of long-chain polyaminoamides and polar acid esters, high molecular weight unsaturated acid esters, polymer copolymerization products, modified polyurethanes, modified polyacrylates, polyether ester type-anionic active agents, naphthalenesulfonic acid-formalin condensate salts, aromatic sulfonic acid-formalin condensate salts, polyoxyethylene alkyl phosphoric acid esters, polyoxyethylene nonyl phenyl ethers, and stearyl amine acetates. Examples of commercially available dispersant products include SOLSPERSE series of Avecia Biotechnology, Inc., and PB series of Ajinomoto Fine-Techno Co., Inc.

<Gelling agent>

[0078] The first ink according to the present invention contains a gelling agent, and the gelling agent in the first ink is contained in the range of 50 to 90 mass% with respect to the gelling agent in the second ink. It is preferable in view of the fact that the curing and shrinkage of the lower print layer and the upper print layer may be made comparable and the adhesion between the lower print layer and the upper print layer becomes better. Further, the third ink according to the present invention contains a gelling agent, and the gelling agent in the third ink is in the range of 50 to 90 mass% with respect to the gelling agent in the second ink. It is preferable that the lower printing layer and the upper printing layer have the same curing and shrinkage degree, and the adhesion between the lower printing layer and the upper printing layer is further improved. Also, the gelling agent in the first ink is preferably in the range of 0.4 to 2.4 mass% with respect to the total mass of the first ink. And the gelling agent in the third ink is also preferably in the range of 0.4 to 2.4 mass% with respect to the total mass of the third ink. When the content of the gelling agent is 0.4 mass% or more, the pinning property of the first ink or the third ink may be sufficiently enhanced, and a higher definition image may be formed. When the content of the gelling agent is 2.4 mass% or less, precipitation of the gelling agent from the surface of the formed image may be suppressed, and the adhesiveness of the formed image may be improved.

[0079] In the ink set according to the first and second embodiments of the present invention, at least the first and third inks contain a gelling agent from the viewpoint of suppressing excessive wetting and spreading of the ink droplets landed on the recording medium and making it easy to obtain a high-definition image.

[0080] The gelling agent is an organic substance which becomes solid at normal temperature and becomes a liquid when heated, and is an additive having a function of causing the ink to reversibly undergo a sol-gel phase transition depending on the temperature.

[0081] When the gelling agent crystallizes in the ink, crystals which are crystallization products of the gelling agent form a space surrounded three-dimensionally. The structure thus formed may be referred to as a "card-house structure". The card-house structure can retain the unreacted radically polymerizable compound and the unreacted photopolymerization initiator, thereby enhancing the pinning property of the ink droplet. As a result, the unity of adjacent ink droplets may be suppressed.

[0082] Furthermore, at room temperature, the actinic ray curable ink-jet ink containing the gelling agent is crystallized and has a high viscosity, so that the molecular motion of the photopolymerization initiator is easily suppressed. As a result, storage stability is less likely to be lost even when the ink is stored for a long time at room temperature.

[0083] In order to stably eject ink droplets from the ink-jet recording apparatus, it is required that compatibility between the radically polymerizable compound and the gelling agent is good in a sol-state ink (at high temperature, for example, about 80 °C).

[0084] Examples of a gelling agent suitable for forming a card-house structure are: aliphatic ketone compounds; aliphatic ester compounds; petroleum-based waxes such as paraffin wax, microcrystalline wax, and petrolatum; plant waxes such as candelilla wax, carnauba wax, rice wax, wood wax, jojoba oil, jojoba solid wax, and jojoba esters; animal waxes such as beeswax, lanolin and whale wax; mineral waxes such as montan wax and hydrogenated waxes; hardened castor oil or hardened castor oil derivatives; modified waxes such as montan wax derivatives, paraffin wax derivatives, microcrystalline wax derivatives, and polyethylene wax derivatives; higher fatty acids such as behenic acid, arachidic acid, stearic acid, palmitic acid, myristic acid, lauric acid, oleic acid, and erucic acid; higher alcohols such as stearyl alcohol and behenyl alcohol; hydroxystearic acid such as 12-hydroxystearic acid; 12-hydroxystearic acid derivatives; fatty acid amides such as lauric acid amide, stearic acid amide, behenic acid amide, oleic acid amide, erucic acid amide, ricinolic acid amide, and 12-hydroxystearic acid amide (for example, NIKKAMIDE series manufactured by Nippon Kasei Chemical Co., Ltd.; ITOHWAX series manufactured by Itoh Oil Chemicals Co., Ltd., and FATTYAMID series manufactured by Kao Corp.); N-substituted fatty acid amides such as N-stearylstearic acid amide and N-oleylpalmitic acid amide; specific fatty acid amides such as N,N'-ethylenebis(stearylamide), N,N'-ethylenebis(12-hydroxystearylamide), and N,N'-xylenebisstearyl amide; higher amines such as dodecylamine, tetradecylamine, and octadecyl amine; fatty acid ester compounds such as a stearylstearic acid, an oleylpalmitic acid, glycerin fatty acid esters, sorbitan fatty acid esters, propylene glycol fatty acid esters, ethylene glycol fatty acid esters, and polyoxyethylene fatty acid esters (for example, EMALLEX series produced by Nippon Emulsion Co., Ltd., RIKEMAL series produced by Riken Vitamin Co., Ltd., and POEM series produced by Riken Vitamin Co., Ltd); sucrose fatty acid esters such as sucrose stearate and sucrose palmitate (e.g., RYOTO Sugar Ester series, manufactured by Mitsubishi Kagaku Foods Corp.); synthetic waxes such as polyethylene wax and α-olefin-maleic anhydride copolymer wax (e.g., UNILIN series, manufactured by Baker Petrolite Corp.); dimer acids; and dimer diols (e.g., PRIPOR series, manufactured by Croda International PLC); fatty acid inulin such as stearic acid inulin; dextrin fatty acid esters such as dextrin palmitate and dextrin myristate (e.g., RHEOPEARL series, manufactured by Chiba Flour Milling Co., Ltd.); glyceryl behenate eicosanedioate and polyglyceryl eicosane behenate (e.g., NOMCORT series, manufactured by Nisshin Oillio Group, Ltd.); amide compounds such as N-lauroyl-L-glutamic acid dibutylamide and N-(2-ethylhexanoyl)-L-glutamic acid dibutylamide (available from Ajinomoto Fine-Techno Co., Inc.); dibenzylidene sorbitols such as 1,3:2,4-bis-O-benzylidene-D-glusitol (GEL ALL D, available from New

Japan Chemical Co., Ltd.); and low-molecular weight oil gelling agents described in JP-A Nos. 2005-126507, 2005-255821 and 2010-111790.

[0085] The gelling agent preferably contains a linear or branched hydrocarbon group having a carbon number of 9 to 25 from the viewpoint of easily forming the above-mentioned "card-house structure".

[0086] Among them, aliphatic ketones having a structure represented by Formula (G1) and aliphatic esters having a structure represented by Formula (G2) are particularly preferable.

Formula (G1): R_1-CO-R_2

Formula (G2): R_3-COO-R_4

In Formula (G1) or (G2), R_1 to R_4 each independently represent a linear or branched hydrocarbon group having a carbon number in the range of 9 to 25. The hydrocarbon group is preferably an alkyl group.

[0087] The hydrocarbon group represented by R_1 and R_2 in the Formula (G1) is not particularly limited, but is preferably a linear or branched hydrocarbon group having 12 to 25 carbon atoms. More preferably, it is an alkyl group having 12 to 25 carbon atoms containing a linear or a branched moiety.

[0088] Examples of the aliphatic ketone compound represented by Formula (G2) include 18-pentatriacontanone (C17-C17), Diglyceryl ketone (C24-C24), dibehenyl ketone (C22-C22), distearyl ketone (C18-C18), dieicosyl ketone (C20-C20), dipalmityl ketone (C16-C16), dimyristyl Ketone (C14-C14), dilauryl ketone (C12-C12), lauryl myristyl ketone (C12-C14), lauryl palmityl ketone (C12-C16), myristyl palmityl ketone (C14-C16), myristyl stearyl ketone (C14 -C18), myristyl behenyl ketone (C14-C22), palmityl stearyl ketone (C16-C18), palmityl behenyl ketone (C16-C22), and stearyl behenyl ketone (C18-C22). The numbers in the parentheses indicate the number of carbon atoms, and the number of carbon atoms indicates the number of carbon atoms of each of two hydrocarbon groups separated by a carbonyl group.

[0089] Examples of commercially available products of the compound represented by Formula (G1) include 18-Pentatriacontanon (manufactured by Alfa Aeser Co., Ltd.), Hentriacontan-16-on (manufactured by Alfa Aeser Co., Ltd.), and KAO-WAX T1 (manufactured by Kao Corp.). The aliphatic ketone contained in the ink may be one kind or a mixture of two or more kinds.

[0090] The hydrocarbon group represented by R_3 and R_4 in Formula (G2) is not particularly limited, but is preferably a linear or branched hydrocarbon group having 12 to 25 carbon atoms. More preferably, it is an alkyl group having 12 to 25 carbon atoms containing a linear or branched moiety.

[0091] Examples of the aliphatic ester compound represented by Formula (G2) include behenyl behenate (C21-C22), icosyl icosanoate (C19-C20), stearyl stearate (C17-C18), palmityl stearate (C17-C16), lauryl stearate (C17-C12), cetyl palmitate (C15-C16), stearyl palmitate (C15-C18), myristyl myristate (C13-C14), cetyl myristate (C13-C16), octyl dodecyl myristate (C13-C20), lauryl laurate (C11-C12), cetyl caprate (C9-C16), stearyl oleate (C17-C18), stearyl erucate (C21-C18), stearyl linolate (C17-C18), behenyl oleate (C18-C22), myricyl cerotate (C25-C16), stearyl montanate (C27-C18), behenyl montanate (C27-C22), and arachidyl linolate (C17-C20). The figures in the parentheses indicate carbon atom numbers. In addition, the numbers in the parentheses indicate the number of carbon atoms, and the number of carbon atoms indicates the number of carbon atoms of each of two hydrocarbon groups separated by a carbonyloxy group.

[0092] Examples of commercially available products of the compound represented by General Formula 2 include UNISTAR M-2222SL (manufactured by NOF Corp.), EXCEPARL SS (manufactured by Kao Corp., melting point: 60° C), EMALEX CC-18 (manufactured by Nihon-Emulsion Co., Ltd.), AMREPS PC (manufactured by Kokyu Alcohol Kogyo Co., Ltd.), EXCEPARL MY-M (manufactured by Kao Corp.), SPERMACETI (manufactured by NOF Corp.), and EMALEX CC-10 (manufactured by Nihon Emulsion Co., Ltd.). Since many of these commercially available products are mixtures of two or more kinds, the commercially available products may also be used after being subjected to separation and purification as necessary.

[0093] The gelling agent contained in the first to the third inks may one kind or a mixture of two or more kinds.

<Photopolymerizable compound>

[0094] The photopolymerizable compound according to the present invention has a function of polymerizing by actinic ray and curing the ink. The photopolymerizable compound may be any of a monomer, a polymerizable oligomer, a prepolymer or a mixture thereof. In the ink according to the present invention, only one type of photopolymerizable compound may be contained, or two or more types may be contained.

[0095] The actinic rays mentioned here are, for example, energy rays such as electron beams, ultraviolet rays, α-rays, γ-rays, and X rays, and preferably ultraviolet rays and electron beams. The actinic ray curable compound is a radical polymerizable compound or a cationic polymerizable compound, and is preferably a radical polymerizable compound.

[0096] The content of the photopolymerizable compound is, for example, preferably in the range of 1 to 97 mass% with respect to the total mass of the ink according to the present invention from the viewpoint of film properties such as curability and flexibility. More preferably, it is in the range of 95 mass%.

(Radically polymerizable compound)

[0097] As a radically polymerizable compound applicable to the present invention, an unsaturated carboxylic acid ester is preferable, and (meth) acrylate is more preferable.

[0098] In the present invention, the term "(meth) acrylate" means acrylate or methacrylate, the term "(meth) acryloyl group" means acryloyl group or methacryloyl group, and the term "(meth) acryl" is acryl or methacryl.

[0099] Examples of the (meth)acrylate compound include monofunctional monomers such as isoamyl (meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, octyl (meth)acrylate, decyl (meth)acrylate, isomyristyl (meth)acrylate, isostearyl (meth)acrylate, 2-ethylhexyl diglycol (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-(meth)acryloyloxyethylhexahydrophthalic acid, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, phenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 2-(meth)acryloyloxyethylsuccinic acid, 2-(meth)acryloyloxyethylphthalic acid, 2-(meth)acryloyloxyethyl-2-hydroxyethylphthalic acid, and t-butylcyclohexyl (meth)acrylate; bifunctional monomers such as triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, dimethyloltricyclodecane di(meth)acrylate, PO adduct di(meth)acrylate of bisphenol A, hydroxypivalic acid neopentyl glycol di(meth)acrylate, and polytetramethylene glycol di(meth)acrylate; polyfunctional monomers of trifunctionality or higher functionality, such as trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, glycerin propoxytri(meth)acrylate, and pentaerythritol ethoxytetra(meth)acrylate; and oligomers having a meth(acryloyl) group including polyester acrylate oligomer, and modified compounds of these compounds.

[0100] Examples of the modified product include ethylene oxide modified (EO modified) acrylate having an ethylene oxide group inserted, and propylene oxide modified (PO modified) acrylate having a propylene oxide inserted.

[0101] The photopolymerizable compound preferably has a molecular weight in the range of 280 to 1,500.

[0102] In particular, the first to the third inks according to the present invention preferably contain a monomer A having an acrylic equivalent (molecular weight / number of acrylic groups) of less than 170. Further, the first ink to the third inks preferably contain a monomer B having an acrylic equivalent (molecular weight / number of acrylic groups) of 170 or more. Furthermore, the addition amount of the component derived from the monomer A in the first ink is preferably in the range of 60 to 90 mass% with respect to the component derived from the monomer A in the second ink. The third ink also contains a monomer A having an acrylic equivalent (molecular weight / number of acrylic groups) less than 170, and the addition amount of the component derived from the monomer A in the third ink is preferably in the range of 60 to 90 mass% with respect to the component derived from the monomer A in the second ink. Furthermore, the addition amount of the component derived from the monomer B in the second ink is preferably in the range of 60 to 90 mass% with respect to the component derived from the monomer B in the first ink or the third ink. Thus, the addition amount of the component derived from the monomer A in the first ink or the third ink and the addition amount of the component derived from the monomer B in the second ink are made to fall within the above range. Thereby the curing shrinkage of the lower print layer and the upper print layer may be made comparable, and the adhesion between the lower print layer and the upper print layer becomes better.

[0103] Examples of the monomer A include tripropylene glycol (TPG) diacrylate, dipropylene glycol (DPG) diacrylate, neopentyl glycol hydroxypivalate (NPG) diacrylate, polyethylene glycol (PEG) # 200 dimethacrylate, 1,6-hexanediol (HD) diacrylate acrylate dimer acid esterification, 1,6-hexanediol diacrylate, 1,10-decanediol diacrylate, acrylate ester (dioxane glycol diacrylate), tricyclodecane dimethanol diacrylate, EO modified (3) trimethylpropane (TMP) triacrylate, PO modified (3) trimethylpropane (TMP) triacrylate, EO modified (4) pentaerythritol tetraacrylate, glycerinpropoxy acrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tetramethylolmethane triacrylate, di-methyl propane (TMP) tetraacrylate, dipentaerythritol polyacrylate, and caprolactone-modified dipentaerythritol hexaacrylate.

[0104] Commercially available products of such monomer A include 3PO-modified trimethylolpropane triacrylate (EM2381, manufactured by Choko Chemical Co., Ltd., acrylic equivalent: 156.8667), and tripropylene glycol diacrylate (APG-200, manufactured by Shin-Nakamura Chemical Co., Ltd., acrylic equivalent: 150.2000). Among these, 3PO-modified trimethylolpropane triacrylate and tripropylene glycol diacrylate are preferable.

[0105] Examples of the monomer B include polyethylene glycol (PEG) #400 dimethacrylate, polyethylene glycol (PEG) #600 dimethacrylate, polyethylene glycol (PEG) #400 diacrylate, polyethylene glycol (PEG) #600 diacrylate, alkoxylated neopentyl glycol (NPG) diacrylate, EO modified (4) 1,6-hexanediol (HD) diacrylate, EO modified (6) trimethylpropane (TMP) triacrylate, and EO modified (9) trimethylpropane (TMP) triacrylate. Commercially available products of such monomer B include polyethylene glycol #400 diacrylate (A-400, manufactured by Shin-Nakamura Chemical Co., Ltd., acrylic equivalent 254.0000), among which polyethylene glycol #400 diacrylate is preferable.

(Cationic polymerizable compound)

[0106] Examples of the cationic polymerizable compound include epoxy compounds, vinyl ether compounds, and oxetane compounds.

[0107] The cationic polymerizable compound may be included alone in the ink, or two or more kinds thereof may be included in the ink.

[0108] Examples of the epoxy compounds include aromatic epoxides, alicyclic epoxides, and aliphatic epoxides, and in order to increase curability, aromatic epoxides and alicyclic epoxides are preferred.

[0109] The aromatic epoxide may be a di- or poly-glycidyl ether obtainable by reacting a polyhydric phenol or an alkylene oxide adduct thereof with epichlorohydrin.

[0110] Examples of the polyhydric phenol or an alkylene oxide adduct thereof to be reacted include bisphenol A or an alkylene oxide adduct thereof.

[0111] The alkylene oxide in the alkylene oxide adduct may be ethylene oxide or propylene oxide.

[0112] The alicyclic epoxide may be a cycloalkane oxide-containing compound obtainable by epoxidizing a cycloalkane-containing compound with an oxidizing agent such as hydrogen peroxide or a peracid. The cycloalkane in the cycloalkane oxide-containing compound may be cyclohexene or cyclopentene.

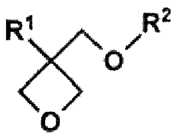
[0113] The aliphatic epoxide may be a di- or poly-glycidyl ether obtainable by allowing an aliphatic polyhydric alcohol or an alkylene oxide adduct thereof to react with epichlorohydrin.

[0114] Examples of the aliphatic polyhydric alcohol include alkylene glycols such as ethylene glycol, propylene glycol, and 1,6-hexanediol. The alkylene oxide in the alkylene oxide adduct may be ethylene oxide or propylene oxide.

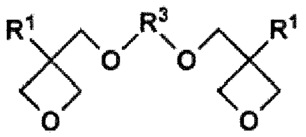
[0115] Examples of the vinyl ether compound include monovinyl ethers such as ethyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxybutyl vinyl ether, 2-ethylhexyl vinyl ether, cyclohexanedimethanol monovinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, isopropenyl ether-o-propylene carbonate, dodecyl vinyl ether, diethylene glycol monovinyl ether, and octadecyl vinyl ether; and di- or tri-vinyl ether compounds such as ethylene glycol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, propylene glycol divinyl ether, dipropylene glycol divinyl ether, butanediol divinyl ether, hexanediol divinyl ether, cyclohexanedimethanol divinyl ether, and trimethylolpropane trivinyl ether. Among these vinyl ether compounds, di- or tri-vinyl ether compounds are preferred in view of curability, and adhesiveness.

[0116] The oxetane compound is a compound having an oxetane ring, and examples thereof include the oxetane compounds described in Japanese Patent Application Publication (JP-A) Nos. 2001-220526, 2001-310937, and 2005-255821. Among the foregoing, cited are the compound represented by Formula (1) given in paragraph No. (0089) of JP-A No. 2005-255821, the compound represented by Formula (2) given in paragraph No. (0092), the compound represented by Formula (7) in paragraph No. (0107), the compound represented by Formula (8) in paragraph No. (0109), and the compound represented by Formula (9) in paragraph No. (0116) of the same Patent Literature. Formulas (1), (2) and (7) to (9) described in JP-A No. 2005-255821 are presented below.

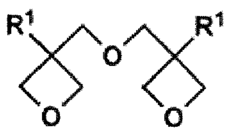
Formula (1)



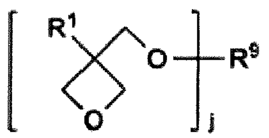
Formula (2)



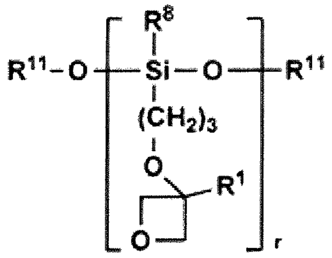
Formula (7)



Formula (8)



Formula (9)



[0117] The details of R^1, R^2, R^3, R^8, R^9 and R^{11} in Formulas (1), (2) and (7) to (9) are identical with the description described in JP-A 2005-255821. The description will be omitted here.

<Photopolymerization initiator>

[0118] As the photopolymerization initiator according to the present invention, when the first to the third inks according to the present invention contain a radical polymerizable compound as a photopolymerizable compound, it is preferable to apply a photo radical polymerization initiator, and when the first to the third inks contain a cationic polymerizable compound as the photo polymerizable compound, it is preferable to apply a photo cationic polymerization initiator.

(Photo-radical polymerization initiator)

[0119] Radical photopolymerization initiators include intramolecular bond cleavage type initiators and intramolecular hydrogen abstraction type initiators.

[0120] Examples of the intramolecular bond cleavage type photopolymerization initiators include acetophenone compounds such as diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl (2-hydroxy-2-propyl)ketone, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-2-morpholino(4-thiomethylphenyl)propan-1-one, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanone; benzoins such as benzoin, benzoin methyl ether, and benzoin isopropyl ether; and acylphosphine oxide compounds such as 2,4,6-trimethylbenzoin diphenylphosphine oxide; benzil; and methyl phenyl glyoxy esters.

[0121] Examples of the intramolecular hydrogen abstraction type photopolymerization initiators include benzophenone compounds such as benzophenone, o-benzoylbenzoic acid methyl-4-phenyl benzophenone, 4,4'-dichlorobenzophenone, hydroxybenzophenone, 4-benzoyl-4'-methyldiphenyl sulfide, acrylated benzophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, and 3,3'-dimethyl-4-methoxybenzophenone; thioxanthone compounds such as 2-isopropylthioxanthone, 2,4-dimethyl thioxanthone, 2,4-diethylthioxanthone, and 2,4-dichlorothioxanthone; aminobenzophenone compounds such as Michler's ketone and 4,4'-diethylaminobenzophenone; 10-butyl-2-chloroacridone, 2-ethylanthraquinone, 9,10-phenanthrenequinone, and camphor-quinone.

[0122] Among them, acyl phosphine oxide and acyl phosphonate are preferably used in view of reactivity.

[0123] Specific examples are: bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentyl phosphine oxide.

(Photo-cationic polymerization initiator)

[0124] In the present invention, it is preferable to apply a photoacid generator as a photocationic polymerization initiator.

[0125] Examples of the photoacid generator that may be used include the compounds used in chemically amplified photoresists or photocationic polymerization (see Japanese Research Association for Organic Electronics Materials, Ed. "Imejingu yo Yuki Zairyo (Organic Materials for Imaging)", Bunshin Publishing Company (1993), pp. 187-192). The suitable compounds for the present invention are describd in the following.

[0126] First, $B(C_6F_5)_4^-$, PF_6^-, AsF_6^-, SbF_6^-, $CF_3SO_3^-$ salts of aromatic onium compounds such as diazonium, ammonium, iodonium, sulfonium, and phosphonium may be cited.

[0127] As specific examples of the onium compounds that may be used in the present invention, the compounds described in paragraph No. (0132) of JP-A 2005-255821 may be mentioned.

[0128] As specific compounds of the sulfonated compound that generates a sulfonic acid, which is mentioned as a second example, the compounds described in paragraph No. (0136) of JP-A 2005-255821 may be mentioned.

[0129] Third, a halide which photo-generates a hydrogen halide may also be used. As specific compounds thereof, the compounds described in paragraph No. (0138) of JP-A2005-255821 may be mentioned.

[0130] Fourth, iron-allene complexes described in paragraph No. (0140) of JP-A 2005-255821 may be mentioned.

(Addition amount of photopolymerization initiator)

[0131] In the ink set of the present invention, the content of the photopolymerization initiator in the first to the third inks is preferably in the range of 0.01 to 10 mass%, although it depends on the type of the actinic ray and the photopolymerizable.

(Photopolymerization initiator aid and Polymerization inhibitor)

[0132] The ink set of the present invention may further include a photopolymerization initiator aid and a polymerization inhibitor according to necessary. The photopolymerization initiator aid may be a tertiary amine compound, and is preferably an aromatic tertiary amine compound. Examples of the aromatic tertiary amine compound include N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethyl-p-toluidine, N,N-dimethylamino-p-benzoic acid ethyl ester, N,N-dimethylamino-p-benzoic acid isoamyl ethyl ester, N,N-dihydroxyethylaniline, triethylamine, and N,N-dimethylhexylamine. Among the foregoing, N,N-dimethylamino-p-benzoic acid ethyl ester and N,N-dimethylamino-p-benzoic acid isoamyl ethyl ester are preferred. These compounds may be used singly, or two or more kinds may be used in combination.

[0133] Examples of the polymerization inhibitor include (alkyl)phenol, hydroquinone, catechol, resorcin, p-methoxyphenol, t-butylcatechol, t-butylhydroquinone, pyrogallol, 1,1-picrylhydrazyl, phenothiazine, p-benzoquinone, nitrosobenzene, 2,5-di-tert-butyl-p-benzoquinone, dithiobenzoyl disulfide, picric acid, cupferron, aluminum N-nitrosophenylhydroxylamine, tri-p-nitrophenylmethyl, N-(3-oxyanilino-1,3-dimethylbutylidene)aniline oxide, dibutylcresol, cyclohexanone oxime cresol, guaiacol, o-isopropylphenol, butyraldoxime, methyl ethyl ketoxime, and cyclohexanone oxime.

<Other constituting components in ink set (ink)>

[0134] The first to the third inks that constitute the ink set of the present invention may further contain other components as necessary. The other components may be various additives or other resins. Examples of the additives include surfactants, leveling agents, matting agents, ultraviolet absorbers, infrared absorbers, antibacterial agents, and basic compounds for enhancing the storage to stability of ink. Examples of the basic compounds include basic alkali metal compounds, basic alkaline earth metal compounds, and basic organic compounds such as amines. Examples of the other resins include resins for regulating the properties of a cured film, and examples thereof include polyester resins, polyurethane resins, vinyl resins, acrylic resins, and rubber resins.

<Physical properties of ink>

[0135] From the viewpoint of further enhancing the ejection ability from the ink-jet head, the viscosity at 80 °C of each ink according to the present invention is preferably in the range of 3 to 20 mPa·s, and more preferably in the range of 8 to 13 mPa·s. In addition, from the viewpoint of causing the ink to gel sufficiently when it lands and is cooled to normal temperature, the viscosity at 25 °C of the ink according to the present invention is preferably 1000 mPa·s or more.

[0136] Moreover, in the ink containing the gelling agent, degelling and regelling in the range of 40 to 90 °C is preferable from the viewpoint of durability of the ink-jet head and in that it may be prevented from becoming mixed and bleeding due to the gel state at the time of landing.

[0137] That is, in the ink according to the present invention, the ink containing the gelling agent can undergo a sol-gel phase transition reversibly with temperature. Sol-gel phase transition type actinic ray curable ink is a sol at a high temperature (for example, about 80 °C), so it may be ejected from an ink ejection recording head, but after being landed on a recording medium, it is naturally cooled to become a gel state. Thereby, the unity of adjacent ink droplets may be suppressed, and the image quality may be enhanced.

[0138] Viscosity of the ink at 80 °C, and viscosity and gelling temperature of the ink at 25 °C may be determined by measuring a change in dynamic viscoelasticity of the ink with temperature using a rheometer.

[Ink-jet recording apparatus]

[0139] An actinic ray curable ink-jet recording apparatus using the ink set according to the first and the second embodiments of the present invention will be described.

[0140] There exist a line recording system (single pass recording system, line head system) and a serial recording system for an ink-jet recording apparatus of an actinic ray curable ink-jet system. It may be selected according to the resolution of the image to be obtained and the recording speed, but from the viewpoint of high speed recording, the line recording method (single pass recording method, line head method) is preferable.

[0141] The ink-jet recording method according to the first embodiment of the present invention is a method of using a first ink containing a gelling agent and a second ink. In this method, first, the first ink is discharged onto the recording medium to form the lower printing layer, and then the second ink is discharged onto the lower printing layer to form the upper printing layer. The ink-jet recording method according to the second embodiment of the present invention is a method of using a third ink containing a gelling agent and containing no colorant, and a second ink. In this method, first, the third ink is ejected onto the recording medium to form the lower printing layer, and then the second ink is ejected onto the lower printing layer to form the upper printing layer. In both methods, in the step of curing the lower print layer and the upper print layer, the oxygen concentration in the atmosphere to which the actinic radiation is applied is made to be 10 volume% or less. By this, deterioration in image quality due to liquid deviation, color bleeding, and color mixing of the formed ink image are prevented, and the abrasion resistance, and the adhesion between the upper print layer and the lower print layer are improved.

[0142] FIG. 4 and Fig. 5 illustrate a whole configuration diagram indicating an example of the configuration of the main part of a line recording type ink-jet recording apparatus applicable to the ink-jet recording method according to the first embodiment of the present invention. In FIG. 4 and FIG. 5, illustration of the oxygen concentration adjustment unit described in FIG. 1 to FIG. 3 is omitted.

[0143] FIG. 4 is a schematic side view of the ink-jet recording apparatus (20), and FIG. 5 is a top view thereof.

[0144] As indicated in FIG. 4 and FIG. 5, the following inks are arranged from the upstream side with respect to the transport direction (arrow) of the recording medium (1): a white head carriage (2W) which discharges a first ink (W) containing a gelling agent from an ink head (5); a yellow head carriage (2Y) which discharges a yellow ink (Y) from an ink head (5); a magenta head carriage (2M) which discharges a magenta ink (M) from an ink head (5); a cyan head carriage (2C) which discharges a cyan ink (C) from an ink head (5); and a black head carriage (2K) which discharges a black ink (K) from an ink head (5). At the most downstream side, an actinic ray irradiation light source (4) is disposed to perform photocuring. As indicated in FIG. 6, an ink-jet recording image (60) in which a lower print layer (52) containing a gelling agent and an upper print layer (54) are laminated on a recording medium (51) is formed.

[0145] In the ink-jet recording method according to the first embodiment of the present invention, from the viewpoint of enhancing the curability of the ink, the irradiation with actinic radiation is preferably performed within 10 seconds, preferably within 0.001 to 5 seconds, and more preferably within 0.01 to 2 seconds after all the ink droplets have been deposited on the recording medium. The irradiation of the actinic light is preferably performed after the ink is ejected from all the ink heads accommodated in the head carriage.

[0146] In the ink-jet recording method according to the first embodiment of the present invention, after a lower print layer (52) is formed using the first ink containing a gelling agent and titanium oxide, un upper print is performed using a second ink containing a colorant (for example, a colored pigment) other than titanium oxide to form an upper print layer (54). Therefore, as illustrated in FIG. 6, in the upper print layer (54) having the colored pigment located on the surface, the interaction between the colored pigment particles (55) and the gelling agent (G) is strong, and the gelling agent (G) is formed on the surface of the colored pigment particles (55). And the crystallized regions (54A, 54B) rich in gelling agent in the surface region are a thin configuration.

[0147] On the other hand, titanium oxide (53), which constitutes a white ink, has a more hydrophilic particle surface compared to other colored pigments (yellow pigment, magenta pigment, cyan pigment, and black pigment). Therefore, the interaction with the coexisting gelling agent is weak. Therefore, the gelling agent is more easily deposited on the surface area (52A, 52B) of the lower print layer (52) compared to the upper print layer (54).

[0148] As a result, when the adhesion is evaluated by the abrasion resistance test and the tape peeling method, in the lower print layer (52) disposed between the recording medium (51) and the upper print layer (54), peeling tends to occur at the interface between the recording medium (51) located at the lower part or the upper print layer (54) located at the upper part.

[0149] In view of the situation as described above, in the ink set used for an ink-jet recording method according to the first embodiment of the present invention, after printing a first ink containing titanium oxide and a gelling agent, and then printing a second ink containing a coloring material other than titanium oxide, the image recording is performed by irradiating them with the actinic rays all together. In this method, the oxygen concentration is reduced to 10 volume% or less when the actinic ray irradiation is performed, thereby reducing the oxygen concentration to obtain improvement of curability of the second ink. The degree of cure shrinkage of the second ink may be made equal to the degree of cure shrinkage of the first ink. As a result, the adhesion between the lower print layer containing the first ink and the upper print layer containing the second ink may be improved.

[0150] The ink-jet recording apparatus illustrated in FIG. 4 and FIG. 5 may be applied to the ink-jet recording method according to the second embodiment of the present invention as well as the ink-jet recording method according to the first embodiment. In the ink-jet recording apparatus, a clear color head carriage that discharges the third ink from the ink head may be provided.

<Image recording conditions of first to third inks>

[0151] The temperature of the ink in the ink head at the time of ejecting the ink from the ink head is preferably set to a temperature in the range of 10 to 30 °C higher than the gelation temperature of the ink in order to enhance the ink ejection property.

[0152] An amount of droplet ejected from each nozzle of the ink head is preferably in the range of 0.5 to 10 pL, although it depends on the viscosity of the ink. In order to discharge only to a desired region, it is more preferably in the range of 0.5 to 4.0 pL, and still more preferably in the range of 1.5 to 4.0 pL. Even when such an amount of ink is applied, since the sol-gel phase transition is performed in the ink according to the present invention, the ink does not spread excessively and may be ejected only to a desired location.

[0153] The ink droplets deposited on the recording medium are cooled and gelled rapidly due to the sol-gel phase transition. Thus, the ink droplets may be pinned without being excessively spread. Furthermore, since the droplets gelate rapidly and the viscosity increases, oxygen is less likely to enter the ink surface deposited on the recording medium, and the curing of the ink surface is less likely to be inhibited by oxygen.

[0154] Here, by discharging ink droplets from the ink head, the ink droplets adhere to the recording medium. It is preferable that the temperature of the recording medium when the ink droplets adhere is set to a temperature lower than the gelation temperature of the ink by a range of 10 to 20 °C.

[0155] When the actinic ray is an electron beam, the acceleration voltage for electron beam irradiation is preferably in the range of 30 to 250 kV, and more preferably in the range of 30 to 100 kV, in order to achieve sufficient curing. When the accelerating voltage is in the range of 100 to 250 kV, the electron beam irradiation dose is preferably in the range of 30 to 100 kGy, and more preferably in the range of 30 to 60 kGy.

[0156] The total ink film thickness after curing is preferably in the range of 2 to 25 μm. The "total ink film thickness" is the maximum value of the ink film thickness drawn on the recording medium.

[0157] Although the line recording type ink-jet recording apparatus has been described as the ink-jet recording apparatus described above, a serial recording type ink-jet recording apparatus may be applied as long as the conditions defined in the present invention are satisfied. In the present invention, the description of the serial recording type ink-jet recording apparatus is omitted.

[0158] Although the embodiments of the present invention have been described and illustrated in detail, the disclosed embodiments are made for purpose of illustration and example only and not limitation. The scope of the present invention should be interpreted by terms of the appended claims.

Examples

[0159] Hereinafter, the present invention will be specifically described by way of examples, but the present invention is not limited thereto. In addition, although the term "part" or "%" is used in examples, unless otherwise indicated, it represents "mass part" or "mass%." Also, unless otherwise stated, each operation was performed at room temperature (25 °C).

<Preparation of Black dispersion>

[0160] In a stainless steel beaker were placed 71 mass parts of tripropylene glycol diacrylate and 9 mass parts of Ajisper PB 824 (Ajinomoto Fine Techno Co., Ltd.) as a dispersant, and the mixture was stirred for 1 hour while heating on a hot plate at 65 °C to dissolve dispersant. Subsequently, after cooling the obtained dispersant solution to room temperature, 20 mass parts of Pigment Black 7 (# 52; Mitsubishi Chemical Corporation) as a black pigment was added, and the liquid mixture was prepared. Then, the mixed solution was put in a glass bottle together with 200 g of zirconia beads having a diameter of 0.5 mm, and the container was sealed and dispersed for 5 hours with a paint shaker. The zirconia beads were removed from the dispersion to prepare a black (K) dispersion.

<Preparation of White dispersion 1>

[0161] A white (W) dispersion 1 was obtained in the same manner as the preparation of the above black dispersion, except that titanium oxide (TCR-52; Sakai Chemical Industry Co., Ltd.) was used as a white pigment in place of the black pigment and the addition amount is changed to 60 mass parts.

<Preparation of each ink>

[0162] In accordance with the composition (the unit is mass%) described in the following Table I and Table II, a black dispersion, a white dispersion 1, a photopolymerizable compound (monomer A, monomer B), a polymerization initiator, a surfactant, a polymerization inhibitor and a gelling agent were mixed, and the mixture was stirred while heated to 80 °C. Next, in a heated state, the mixture was filtered using a Teflon (registered trademark) 3 μm membrane filter (Advantech Toyo Co., Ltd.) to prepare inks having the configuration described in the following table: black inks K1-1, K1-2, K2-1 to K2-6, white inks W1-1, W1-2, W2-1 to W2-6, W3-1 to W3-8, and clear ink C1-1, C2-1 to C2-6, C3-1 to C3-8.

Table I

(Unit: mass%)

Ink No.	Pigment dispersion		Monomer A		Monomer B	Polymerization initiator		Surfactant	Polymerization inhibitor	Gelling agent		Total
	Black dispersion	White Dispersion1	EM2381	APG-200	A-400	IRGACURE TPO	IRGACURE 819	BYK UV3500	Irgastab UV10	WEP2	EMALEX EG-di-S	
W1-1	-	25.0	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W1-2	-	25.0	20.0	15.7	30.0	3.0	3.0	0.1	0.2	1.5	1.5	100.0
W2-1	-	25.0	4.0	5.3	57.4	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W2-2	-	25.0	8.0	10.7	48.0	3.0	3.0	0.1	0. 2	1.0	1.0	100.0
W2-3	-	25.0	12.0	16.0	38.7	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W2-4	-	25.0	18.0	24.0	24.7	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W2-5	-	25.0	20.0	26.7	20.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W2-6	-	25.0	24.0	32.0	10.7	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K1-1	15.0	-	20.0	26.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K1-2	15.0	-	20.0	25.7	30.0	3.0	3.0	0.1	0.2	1.5	1.5	100.0
K2-1	15.0	-	20.0	50.7	6.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K2-2	15.0	-	20.0	44.7	12.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K2-3	15.0	-	20.0	38.7	18.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K2-4	15.0	-	20.0	29.7	27.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K2-5	15.0	-	20.0	26.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
K2-6	15.0	-	20.0	20.7	36.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W3-1	-	25.0	20.0	18.3	30.0	3.0	3.0	0.1	0.2	0.2	0.2	100.0
W3-2	-	25.0	20.0	17.9	30.0	3.0	3.0	0.1	0.2	0.4	0.4	100.0
W3-3	-	25.0	20.0	17.7	30.0	3.0	3.0	0.1	0.2	0.5	0.5	100.0
W3-4	-	25.0	20.0	16.9	30.0	3.0	3.0	0.1	0.2	0.9	0.9	100.0
W3-5	-	25.0	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W3-6	-	25.0	20.0	16.3	30.0	3.0	3.0	0.1	0.2	1.2	1.2	100.0

(continued)

(Unit: mass%)

Ink No.	Pigment dispersion		Monomer A		Monomer B	Polymerization initiator		Surfactant	Polymerization inhibitor	Gelling agent		Total
	Black dispersion	White Dispersion1	EM2381	APG-200	A-400	IRGACURE TPO	IRGACURE 819	BYK UV3500	Irgastab UV10	WEP2	EMALEX EG-di-S	
W3-7	-	25.0	20.0	18.5	30.0	3.0	3.0	0.1	0.2	0.1	0.1	100.0
W3-8	-	25.0	20.0	15.7	30.0	3.0	3.0	0.1	0.2	1.5	1.5	100.0

[Table II]

(Unit: mass%)

Ink No.	Pigment dispersion		Monomer A		Monomer B	Polymerization initiator			Polymerization inhibitor	Gelling agent		Total
	Black dispersion	White Dispersion1	EM2381	APG-200	A-400	IRGACURE TPO	IRGACURE 819	Surfactant BYK UV3500	Irgastab UV10	WEP2	EMALEX EG-di-S	
C1-1	-	-	20.0	41.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-1	-	-	4.0	5.3	82.4	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-2	-	-	8.0	10.7	73.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-3	-	-	12.0	16.0	63.7	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-4	-	-	18.0	24.0	49.7	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-5	-	-	20.0	26.7	45.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C2-6	-	-	24.0	32.0	35.7	3.0	3.0	0. 1	0.2	1.0	1.0	100.0
C3-1	-	-	20.0	43.3	30.0	3.0	3.0	0.1	0.2	0.2	0.2	100.0
C3-2	-	-	20.0	42.9	30.0	3.0	3.0	0.1	0.2	0.4	0.4	100.0
C3-3	-	-	20.0	42.7	30.0	3.0	3.0	0.1	0.2	0.5	0.5	100.0
C3-4	-	-	20.0	41.9	30.0	3.0	3.0	0.1	0.2	0.9	0.9	100.0
C3-5	-	-	20.0	41.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
C3-6	-	-	20.0	41.3	30.0	3.0	3.0	0.1	0.2	1.2	1.2	100.0
C3-7	-	-	20.0	43.5	30.0	3.0	3.0	0.1	0.2	0.1	0.1	100.0
C3-8	-	-	20.0	40.7	30.0	3.0	3.0	0.1	0.2	1.5	1.5	100.0

[0163] The details of the additives described in the above Tables in an abbreviated form are as follows.

- EM 2381: 3PO-modified trimethylolpropane triacrylate, acrylic equivalent (molecular weight / number of acrylic groups) = 156.8667 (manufactured by Eternal Material Co., Ltd.)
- APG-200: tripropylene glycol diacrylate, acrylic equivalent (molecular weight / number of acrylic groups) = 150.2000 (manufactured by Shin-Nakamura Chemical Co., Ltd.)
- A-400: polyethylene glycol # 400 diacrylate, acrylic equivalent (molecular weight / number of acrylic groups) = 254.0000 (manufactured by Shin-Nakamura Chemical Co., Ltd.)
- IRGACURE TPO (manufactured by BASF)
- IRGACURE 819 (manufactured by BASF)
- BYK UV3500 (manufactured by BYK Japan, KK)
- Irgastab UV10 (manufactured by BASF)
- WEP2 ((manufactured by NOF Corporation)
- EMALEX EG-di-S (manufactured by Nippon Emulsion Co., Ltd.)

<Ink-jet recording apparatus>

[0164] By using black inks K1-1, K1-2, and K2-1 to K2-6, which are colored inks prepared, and white inks W1-1, W1-2, W2-1 to W2-6, W3-1 to W3-8, the respective ink sets configured by combining them were introduced into a Konica Minolta ink-jet head (KM1048). In addition, by combining black inks K1-1, K1-2, K2-1 to K2-6, which are colored inks, and clear inks C1-1, C2-1 to C2-6, C3-1 to C3-8, the respective ink sets were similarly introduced into the Konica Minolta ink-jet head (KM1048).

[Example 1]: Experiment in which oxygen concentration was changed

(Formation of Image 1)

[0165] The white ink W1-1 was printed as a solid image on an OK top coat paper (printing paper) as a printing substrate under the conditions of 100 nm x 100 nm printing width and 720 x 720 dpi resolution. Thereafter, the black ink K1-1 is similarly printed as a solid image, and ultraviolet light is applied to the white ink and the black ink printed under an oxygen concentration of 5% with energy of 350 mJ using an LED lamp manufactured by Kyocera Corporation as a UV irradiation light source. It was simultaneously irradiated and cured to form an Image 1.

(Formation of Images 2 to 4)

[0166] Images 2 to 4 were formed in the same manner as formation of the Image 1, except that the oxygen concentration at the time of ultraviolet irradiation was changed as indicated in the following Table III.

(Formation of Images 5 to 8)

[0167] Images 5 to 8 were formed in the same manner as formation of the Image 1, except that the white ink W1-1 was changed to W1-2, the black ink K1-1 was changed to K1-2, and the oxygen concentration at the time of ultraviolet irradiation was changed as indicated in the following Table III.

(Formation of Images 101 to 104)

[0168] Images 101 to 104 were formed in the same manner as formation of the Image 1, except that the white ink W1-1 was changed to the clear ink C1-1, and the oxygen concentration at the time of ultraviolet irradiation was changed as indicated in the following Table III.

[Example 2-1]: Experiment in which the ratio of monomer A (white or clear ink / black ink) was changed

(Formation of Images 11 to 16)

[0169] Images 11 to 16 were formed in the same manner as formation of the image 1, except that the white ink W1-1 was changed as indicated in the following Table IV, and the oxygen concentration at the time of ultraviolet irradiation was made to be 10%.

(Formation of Images 111 to 116)

[0170] Images 111 to 116 were formed in the same manner as formation of the Image 101, except that the clear ink C1-1 was changed as indicated in the following Table IV, and the oxygen concentration at the time of ultraviolet irradiation was made to be 10%.

[Example 2-2]: Experiment in which the ratio of monomer B (black ink / white or clear ink) was changed

(Formation of images 21 to 26)

[0171] Images 21 to 26 were formed in the same manner as formation of the Image 11, except that the white ink W2-1 was changed to W1-1, and the black ink K1-1 was changed as indicated in the following Table V.

(Formation of Images 121 to 126)

[0172] Images 121 to 126 were formed in the same manner as formation of the Image 111, except that the clear ink C2-1 was changed to C1-1, and the black ink K1-1 was changed as indicated in the following Table VI.

[Example 3-1]: Experiment in which the ratio of the gelling agent (white ink or clear ink / black ink) was changed

(Formation of images 31 to 36)

[0173] Images 31 to 36 were formed in the same manner as formation of the Image 1, except that the white ink W1-1 was changed as indicated in the following Table VI, and the oxygen concentration at the time of ultraviolet irradiation was made to be 10%.

(Formation of Images 131 to 136)

[0174] Images 131 to 136 were formed in the same manner as formation of the Image 101, except that the clear ink C1-1 was changed as indicated in the following Table VI, and the oxygen concentration at the time of ultraviolet irradiation was made to be 10%.

[Example 3-2]: Experiment in which the amount (mass%) of gelling agent in white ink or clear ink was changed

(Formation of Images 41 to 45)

[0175] Images 41 to 45 were formed in the same manner as formation of the Image 31, except that the white ink W3-1 was changed as indicated in the following Table VII.

(Formation of Images 141 to 145)

[0176] Images 141 to 145 were formed in the same manner as formation of the Image 131, except that the clear ink C3-1 was changed as indicated in the following Table VII.

[Evaluation]

<Tape peeling test: Adhesion>

[0177] For each of the images obtained above, 1 cm x 2 cm cellophane tape was attached to the image of 3 cm x 3 cm, and rubbed with a finger from the top to sufficiently adhere the cellophane tape to the image surface. Thereafter, the cellophane tape was peeled off so as to be 90° with respect to the image surface, and the image surface condition thereafter was visually confirmed. In the following evaluation criteria, Δ, ○ and ◎ were judged to be practically preferred ranks.

(Evaluation criteria)

[0178] ◎: There is no change at all.
○ : A trace remains slightly.
Δ : A part of the black part is peeled off and a slightly white part is exposed.
×: Most of the image is peeled off, and the white ink on the white background or the lower layer of the substrate is clearly visible.

Table III

Image No.	Ink No.		Oxygen Concentration (volume%)	Adhesion	Remarks
1	W1-1	K1-1	5	◎	Present invention
2	W1-1	K1-1	10	○	Present invention
3	W1-1	K1-1	15	x	Comparative example
4	W1-1	K1-1	Under the atmosphere	×	Comparative example
5	W1-2	K1-2	5	○	Present invention
6	W1-2	K1-2	10	Δ	Present invention
7	W1-2	K1-2	15	×	Comparative example
8	W1-2	K1-2	Under the atmosphere	×	Comparative example
101	C1-1	K1-1	5	◎	Present invention
102	C1-1	K1-1	10	○	Present invention
103	C1-1	K1-1	15	×	Comparative example
104	C1-1	K1-1	Under the atmosphere	×	Comparative example

Table IV

Image No.	Ink No.		Ratio of Monomer A (White or Clear ink /Black ink)	Adhesion	Remarks
11	W2-1	K1-1	0.2	Δ	Present invention
12	W2-2	K1-1	0.4	○	Present invention
13	W2-3	K1-1	0.6	◎	Present invention
14	W2-4	K1-1	0.9	◎	Present invention
15	W2-5	K1-1	1.0	○	Present invention
16	W2-6	K1-1	1.2	○	Present invention
111	C2-1	K1-1	0.2	Δ	Present invention
112	C2-2	K1-1	0.4	○	Present invention
113	C2-3	K1-1	0.6	◎	Present invention
114	C2-4	K1-1	0.9	◎	Present invention
115	C2-5	K1-1	1.0	○	Present invention
116	C2-6	K1-1	1.2	○	Present invention

Table V

Image No.	Ink No.		Ratio of Monomer B (Black ink / White or Clear ink)	Adhesion	Remarks
21	W1-1	K2-1	0.2	Δ	Present invention
22	W1-1	K2-2	0.4	○	Present invention
23	W1-1	K2-3	0.6	◎	Present invention
24	W1-1	K2-4	0.9	◎	Present invention
25	W1-1	K2-5	1.0	○	Present invention
26	W1-1	K2-6	1.2	○	Present invention
121	C1-1	K2-1	0.2	Δ	Present invention
122	C1-1	K2-2	0.4	○	Present invention
123	C1-1	K2-3	0.6	◎	Present invention
124	C1-1	K2-4	0.9	◎	Present invention
125	C1-1	K2-5	1.0	○	Present invention
126	C1-1	K2-6	1.2	○	Present invention

Table VI

Image No.	Ink No.		Ratio of Gelling agent (White or Clear ink / Black ink)	Adhesion	Remarks
31	W3-1	K1-1	0.2	○	Present invention
32	W3-2	K1-1	0.4	○	Present invention
33	W3-3	K1-1	0.5	◎	Present invention
34	W3-4	K1-1	0.9	◎	Present invention
35	W3-5	K1-1	1.0	○	Present invention
36	W3-6	K1-1	1.2	○	Present invention
131	C3-1	K1-1	0.2	○	Present invention
132	C3-2	K1-1	0.4	○	Present invention
133	C3-3	K1-1	0.5	◎	Present invention
134	C3-4	K1-1	0.9	◎	Present invention
135	C3-5	K1-1	1.0	○	Present invention
136	C3-6	K1-1	1.2	○	Present invention

Table VII

Image No.	Ink No.		Amount of gelling agent (mass%)	Adhesion	Remarks
41	W3-7	K1-1	0.2	Δ	Present invention
42	W3-1	1-1	0.4	○	Present invention
43	W3-4	K1-1	1.8	◎	Present invention
44	W3-6	K1-1	2.4	○	Present invention
45	W3-8	K1-1	3.0	Δ	Present invention
141	C3-7	K1-1	0.2	Δ	Present invention
142	C3-1	K1-1	0.4	○	Present invention

(continued)

Image No.	Ink No.		Amount of gelling agent (mass%)	Adhesion	Remarks
143	C3-4	K1-1	1.8	◎	Present invention
144	C3-6	K1-1	2.4	○	Present invention
145	C3-8	K1-1	3.0	Δ	Present invention

[Example 4]: Experiment in which the amount of aluminum required for surface modification of titanium oxide was changed

<Surface modification method of titanium oxide>

[0179] Titanium oxide (TCR-52; Sakai Chemical Industry Co., Ltd.), which is a white pigment, was surface-modified according to the following method.

(1) Titanium dioxide was dispersed in water to form a slurry.
(2) Separately from the above slurry, a dilute aqueous solution of sulfuric acid was dropped into an aqueous solution of sodium aluminate (sodium aluminate) to adjust the pH to 10.5 to 11.8 to prepare an aluminum compound solution.
(3) Addition mixing of the titanium dioxide slurry obtained above to the aluminum compound solution was started. At this time, the amount of aluminum required for surface modification of titanium dioxide was made to be 0.2, 0.4, 0.6, 0.8, and 1.0 mass% respectively with respect to the titanium dioxide before surface modification (untreated). During mixing, stirring was performed using a stirrer, and stirring was continued after addition of the titanium dioxide slurry to deposit aluminum oxide hydrate on the titanium dioxide surface. After this, neutralization treatment was performed using a dilute aqueous sulfuric acid solution to adjust the pH of the slurry to 8.15.
(4) The slurry after surface treatment was filtered and washed with a membrane filter, the collected cake (filtered matter) was dried, crushed using a commercially available automatic mortar, and a surface-modified titanium dioxide pigment powder was prepared.

[0180] With regard to titanium oxide after surface modification, the surface modification amount of alumina surface-modified to titanium oxide was determined from the value of the ratio (Al_2O_3/TiO_2) of the quantity of the alumina to a titanium oxide based on the analysis of elemental aluminum by inductively coupled plasma atomic emission spectrometry (I. C. P.). In addition, the content of sodium (Na) ion in the white ink was measured by ICP-AES (SPS 3520 UV, manufactured by SII Nano Technology Inc.).

<Preparation of White dispersions 2 to 7>

[0181] White dispersions 2 to 7 were prepared in the same manner as preparation of the White dispersion 1, except that surface-modified titanium oxide was used as titanium oxide. The amounts (mass%) of aluminum required for the surface modification to titanium oxide before (or untreated) the surface modification in each of the White dispersions 2 to 7 are as indicated in the following Table VIII.

<Preparation of White ink>

[0182] White dispersion 2, photopolymerizable compound (monomer A, monomer B), polymerization initiator, surfactant, polymerization inhibitor and gelling agent were mixed with the composition (unit: mass%) described in the following Table VIII. The mixture was stirred in the state heated at 80 °C. Next, in a heated state, the mixture is filtered using a Teflon (registered trademark) 3 μm membrane filter (Advantec Toyo Co., Ltd.), and the white ink W4-1 to W4-6 having the configuration described in Table VIII were prepared.

(Formation of Images 51 to 56)

[0183] Images 51 to 56 were formed in the same manner as formation of the Image 11, except that the white ink W2-1 was changed as indicated in the following Table IX.

[Evaluation]

<Tape peeling test: Adhesion>

[0184] To each image obtained above, the same test as the tape peeling test described above was performed and evaluated.

<Weather resistance test>

[0185] Each image obtained above was stored for a total of 600 hours while repeating UV light irradiation with a Xe lamp and humidification assuming wet weather with a low temperature xenon weather meter XL75 manufactured by Gas Tester Co., Ltd. Thereafter, a tape peeling test described above was performed. In the following evaluation criteria, Δ, ○ and ◎ were judged to be practically preferred ranks.

(Evaluation criteria)

[0186] ◎: There is no change at all.
○ : A trace remains slightly.
Δ : A part of the black part is peeled off and a slightly white part is exposed.
×: Most of the image is peeled off, and the white ink on the white background or the lower layer of the substrate is clearly visible.

<Ejection test: Ejection ability>

[0187] Each ink set configured by combining each of the prepared colored inks, black ink K1-1 and white inks W4-1 to W4-6, was introduced into a Konica Minolta ink-jet head (KM1048). The white ink W4-1 was printed as a solid image on an OK top coat paper (printing paper) as a printing substrate under the conditions of printing width 100 nm x 100 nm and resolution 720 x 720 dpi. Thereafter, the black ink K1-1 was similarly printed as a solid image, and 100 sheets of the printing were continuously printed. Then, the number of lacked head nozzles was measured. In the following evaluation criteria, Δ, ○ and ◎: were judged to be practically preferred ranks.
◎ : The number of lacked head nozzles is less than 5.
○ : The number of lacked head nozzles is 5 to 10.
Δ : The number of lacked head nozzles is 11 to 20.
×: The number of lacked head nozzles is 21 or more.

Table VIII

(Unit: mass%)

Ink No.	Pigment dispersion			Monomer A		Monomer B	Polymerization initiator		Surfactant	Polymerization inhibitor	Gelling agent		Total
	Black dispersion	White dispersion											
		No.	Content The figure in parentheses is an amount of aluminum required for surface modification (mass%)	EM2381	APG-200	A-400	IRGACURE TPO	IRGACURE 819	BYK UV3500	Irgastab UV10	WEP2	EMALEX EG-di-S	
W4-1	—	2	25.0 (0.2)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W4-2	—	3	25.0 (0.3)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W4-3	—	4	25.0 (0.4)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W4-4	—	5	25.0 (0.6)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W4-5	—	6	25.0 (0.8)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0
W4-6	—	7	25.0 (1.0)	20.0	16.7	30.0	3.0	3.0	0.1	0.2	1.0	1.0	100.0

Table IX

Image No.	Ink No.		Amount of aluminum required for surface modification (mass%)	Contentof Na ions (mass ppm)	Adhesion	Weather resistance	Ejection ability	Remarks
51	W4-1	K1-1	0.2	50	○	Δ	◎	Present invention
52	W4-2	K1-1	0.3	75	○	○	◎	Present invention
53	W4-3	K1-1	0.4	100	○	○	◎	Present invention
54	W4-4	K1-1	0.6	150	○	○	◎	Present invention
55	W4-5	K1-1	0.8	200	○	◎	○	Present invention
56	W4-6	K1-1	1.0	250	○	◎	Δ	Present invention

[0188] From the results obtained in the above Examples 1 to 4, it is understood that the image using the ink-jet recording method of the present invention is superior in adhesion to the image using the ink-jet recording method of the comparative example. Moreover, it is recognized that the light resistance and the ejection ability are excellent particularly when the alumina surface modification amount of titanium oxide is 0.8 mass% or less.

Claims

1. An ink-jet recording method using an actinic ray curable ink-jet ink set having a first ink-jet ink containing at least titanium oxide and a gelling agent, and a second ink-jet ink containing a colorant other than titanium oxide, the ink-jet recording method comprising the steps of:

forming a lower print layer by printing the first ink-jet ink;
forming an upper print layer on the lower print layer by printing the second ink-jet ink; and
curing the lower print layer and the upper print layer by irradiating the lower print layer and the upper print layer with actinic rays,
wherein an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

2. The ink-jet recording method described in claim 1,
wherein the second ink-jet ink further contains a gelling agent.

3. The ink-jet recording method described in claim 2,
wherein the gelling agent in the first ink-jet ink is contained in the range of 50 to 90 mass% with respect to the gelling agent in the second ink-jet ink.

4. The ink-jet recording method described in any one of claims 1 to 3,
wherein the gelling agent in the first ink-jet ink is contained in the range of 0.4 to 2.4 mass% with respect to the total mass of the first ink-jet ink.

5. The ink-jet recording method described in any one of claims 1 to 4,
wherein the first ink-jet ink and the second ink-jet ink contain a monomer A having an acrylic equivalent (molecular weight / number of acrylic groups) of less than 170, and an addition amount of a component derived from the monomer A in the first ink-jet ink is in the range of 60 to 90 mass% with respect to the component derived from the monomer A in the second ink-jet ink.

6. The ink-jet recording method described in any one of claims 1 to 5,
wherein the first ink-jet ink and the second ink-jet ink contain a monomer B having an acrylic equivalent (molecular weight / number of acrylic groups) of 170 or more, and an addition amount of a component derived from the monomer B in the second ink-jet ink is in the range of 60 to 90 mass% with respect to the component derived from the monomer B in the first ink-jet ink.

7. The ink-jet recording method described in any one of claims 1 to 6,
wherein the titanium oxide is surface-modified with alumina, and an amount of the alumina surface-modified to the titanium oxide is in the range of 0.3 to 0.8 mass% with respect to the titanium oxide before the surface modification.

8. The ink-jet recording method described in any one of claims 1 to 7,
wherein the first ink-jet ink contains 200 mass ppm or less of sodium (Na) ion with respect to the titanium oxide.

9. The ink-jet recording method described in any one of claims 1 to 8,
wherein the gelling agent comprises a compound having a structure represented by Formula (G1) or Formula (G2),

Formula (G1): $R_1\text{-CO-}R_2$

Formula (G2): $R_3\text{-COO-}R_4$

wherein R_1 to R_4 each independently represent a linear or branched hydrocarbon group having a carbon number in the range of 9 to 25.

10. An ink-jet recording method using an actinic ray curable ink-jet ink set having a third ink-jet ink containing a gelling agent without containing a colorant, and a second ink-jet ink containing a colorant other than titanium oxide, the ink-jet recording method comprising the steps of:

forming a lower print layer by printing the third ink-jet ink;
forming an upper print layer on the lower print layer by printing the second ink-jet ink; and
curing the lower print layer and the upper print layer by irradiating the lower print layer and the upper print layer with actinic rays,
wherein an oxygen concentration in an atmosphere to which the actinic rays are irradiated is controlled to be 10 volume% or less in the step of curing the lower print layer and the upper print layer.

11. The ink-jet recording method described in claim 10,
wherein the second ink-jet ink further contains a gelling agent.

12. The ink-jet recording method described in claim 11, wherein the gelling agent in the third ink-jet ink is contained in the range of 50 to 90 mass% with respect to the gelling agent in the second ink-jet ink.

13. The ink-jet recording method described in any one of claims 10 to 12,
wherein the gelling agent in the third ink-jet ink is contained in the range of 0.4 to 2.4 mass% with respect to the total mass of the third ink-jet ink.

14. The ink-jet recording method described in any one of claims 10 to 13,
wherein the second ink-jet ink and the third ink-jet ink contain a monomer A having an acrylic equivalent (molecular weight / number of acrylic groups) of less than 170, and an addition amount of a component derived from the monomer A in the third ink-jet ink is in the range of 60 to 90 mass% with respect to the component derived from the monomer A in the second ink-jet ink.

15. The ink-jet recording method described in any one of claims 10 to 14,
wherein the second ink-jet ink and the third ink-jet ink contain a monomer B having an acrylic equivalent (molecular weight / number of acrylic groups) of 170 or more, and an addition amount of a component derived from the monomer B in the second ink-jet ink is in the range of 60 to 90 mass% with respect to the component derived from the monomer B in the third ink-jet ink.

16. The ink-jet recording method described in any one of claims 10 to 15,
wherein the gelling agent comprises a compound having a structure represented by Formula (G1) or Formula (G2),

Formula (G1): R_1-CO-R_2

Formula (G2): R_3-COO-R_4

wherein R_1 to R_4 each independently represent a linear or branched hydrocarbon group having a carbon number in the range of 9 to 25.

17. The actinic ray curable ink-jet ink set used for the ink-jet recording method described in any one of claims 1 to 9, comprising a first ink-jet ink containing at least titanium oxide and a gelling agent, and a second ink-jet ink containing a colorant other than titanium oxide.

18. The actinic ray curable ink-jet ink set used for the ink-jet recording method described in any one of claims 10 to 16, comprising a third ink-jet ink containing a gelling agent without containing a colorant, and a second ink-jet ink containing a colorant other than titanium oxide.

FIG.1

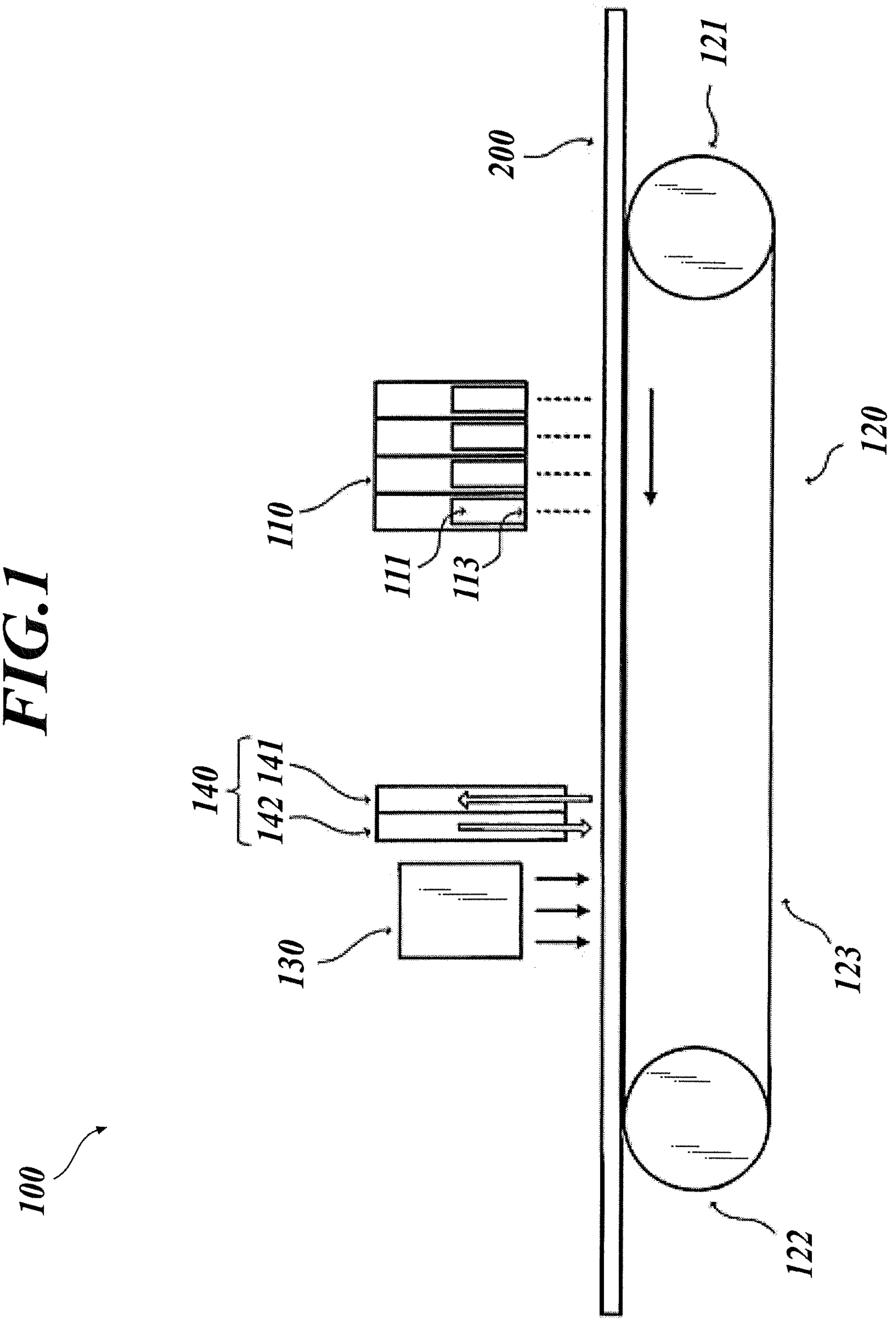


FIG.2

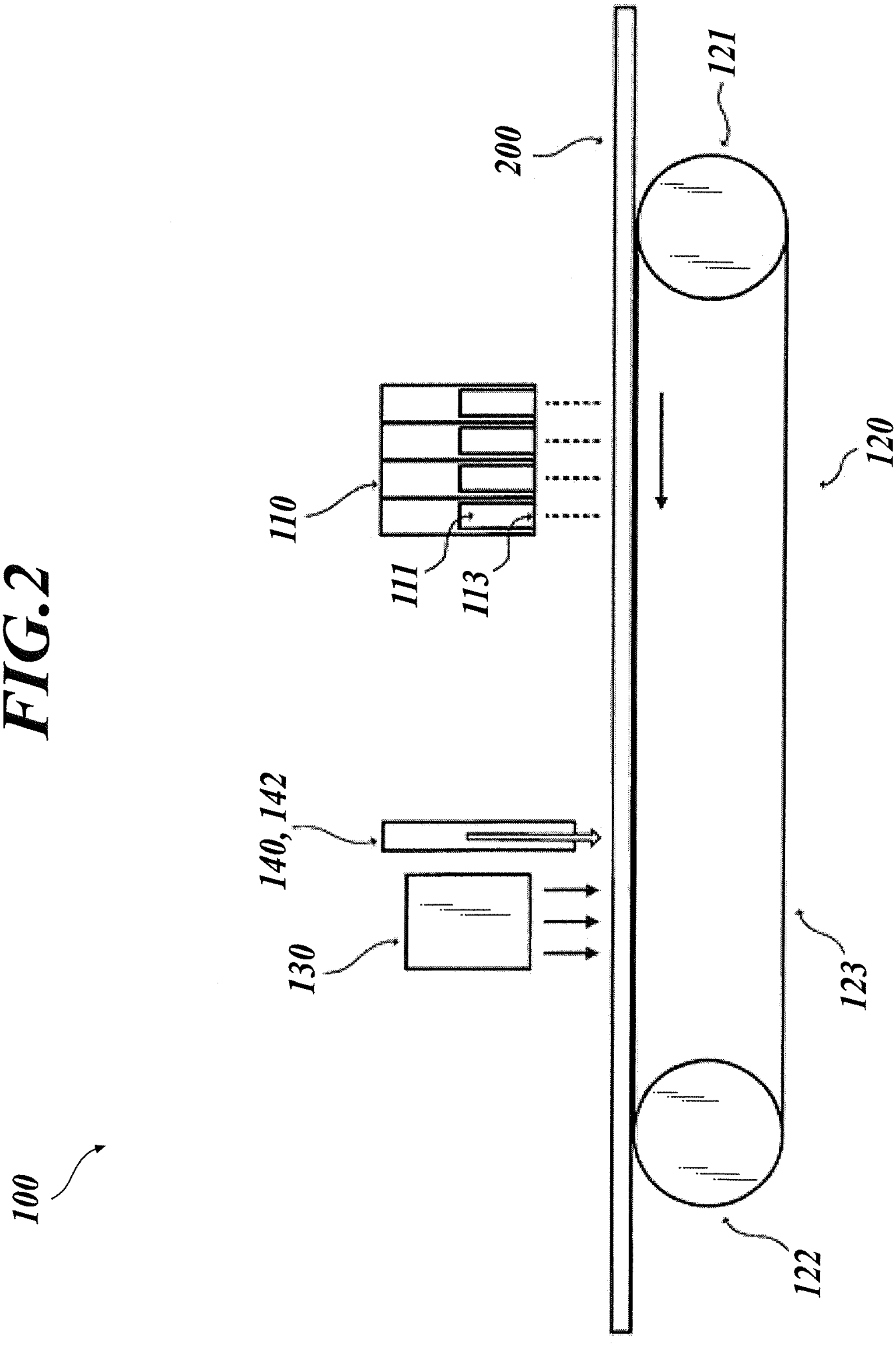


FIG.3

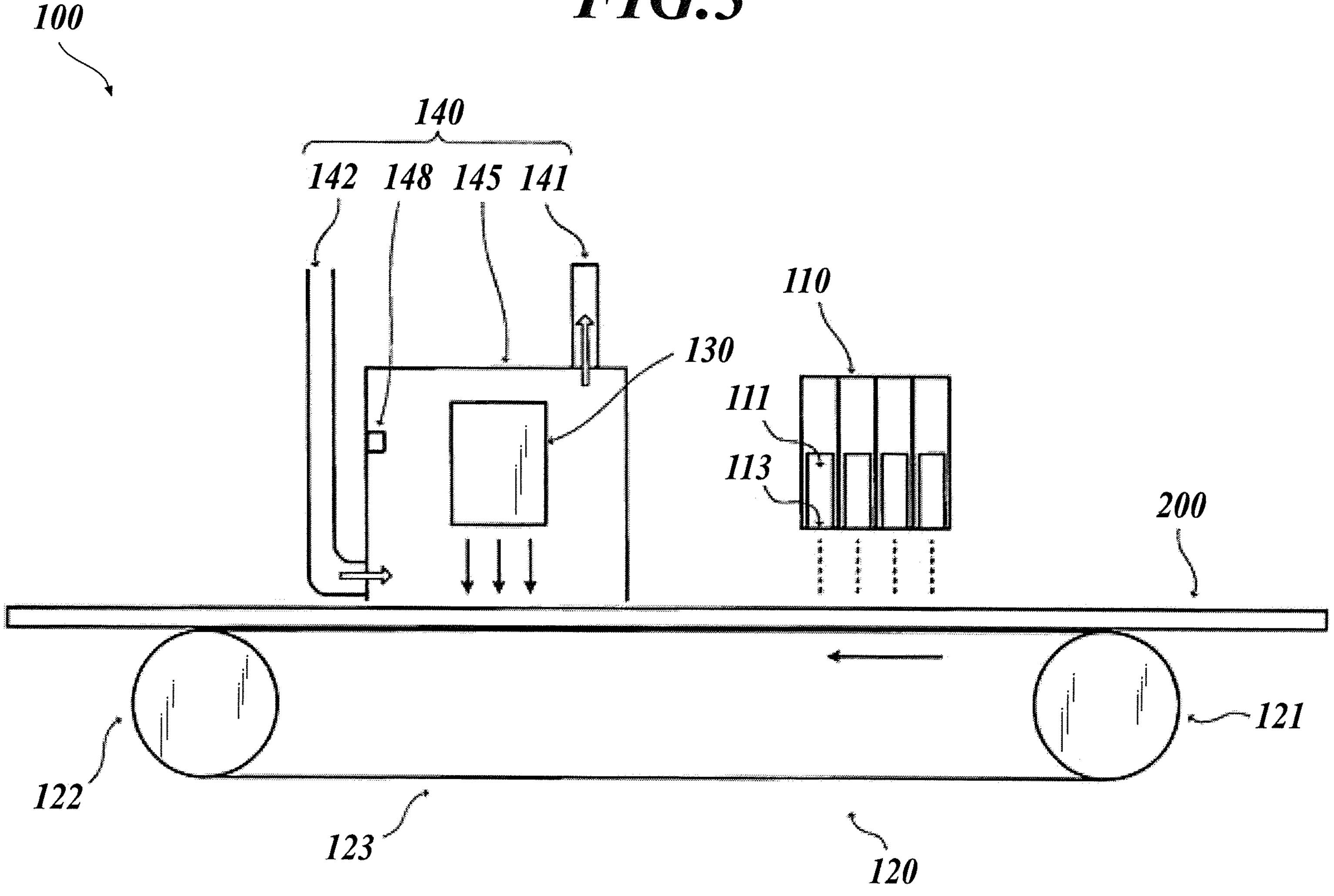


FIG.4

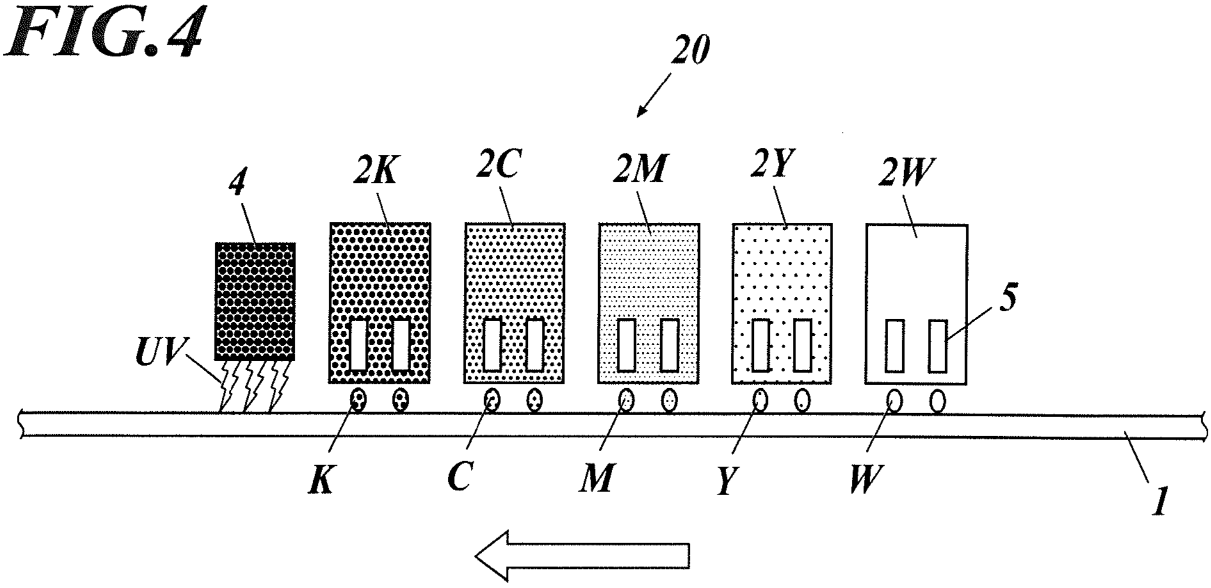


FIG.5

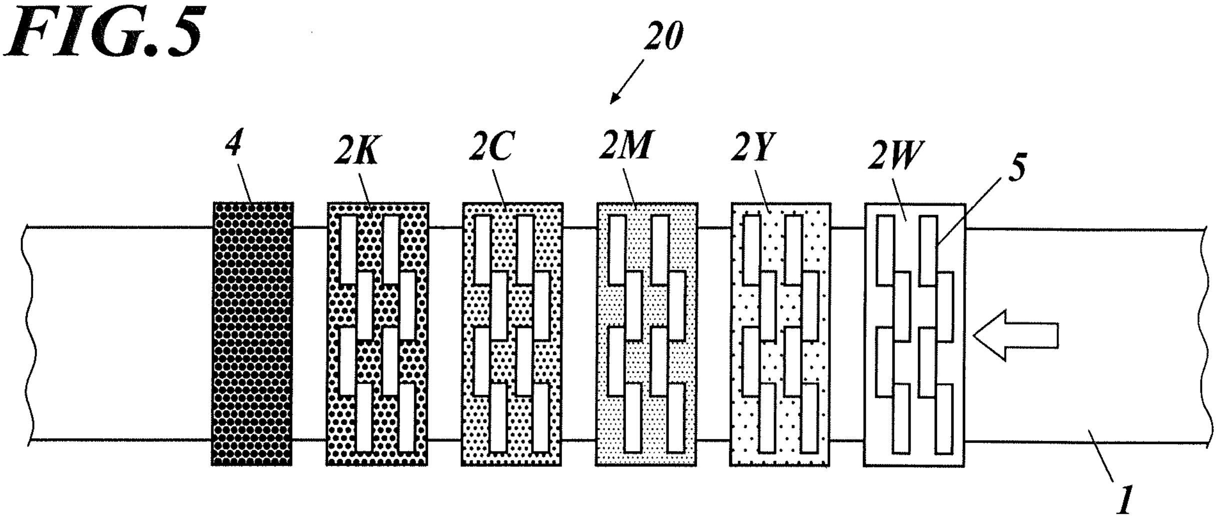
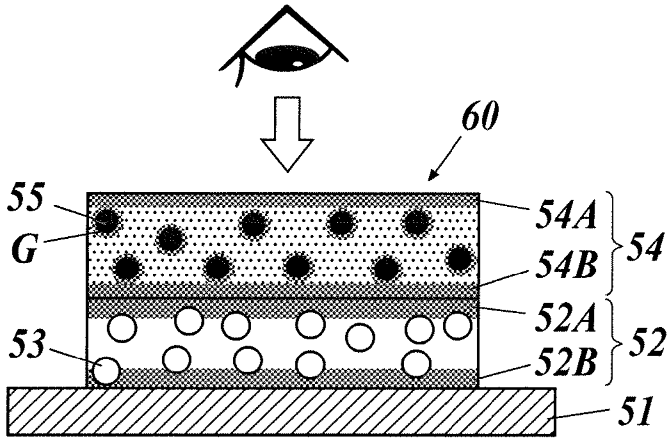


FIG.6



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EUROPEAN SEARCH REPORT

Application Number
EP 19 18 4770

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TECHNICAL FIELDS SEARCHED (IPC)

B41J
B41M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	6 November 2019	Gaubinger, Bernhard

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 19 18 4770

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