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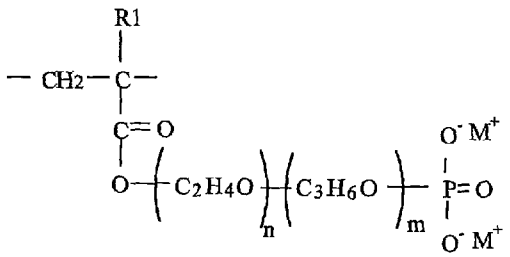
(54) Title: INKJET RECORDING INK, INK CARTRIDGE, INKJET RECORDING METHOD, INKJET RECORDING DEVICE AND INK RECORDED MATTER



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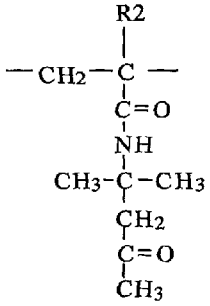

(2)

(57) Abstract: An inkjet recording ink, including: water; a water-soluble organic solvent; a pigment; and a phosphate group-containing copolymer, wherein the phosphate group-containing copolymer contains a structural unit represented by the following General Formula (1) and a structural unit represented by the following General Formula (2): where R1 denotes a hydrogen atom or a methyl group; M^+ denotes an alkali metal ion, an organic amine ion, or a hydrogen ion; half or more of M^+ in the copolymer is the alkali metal ion or the organic amine ion, the remainder of M^+ is the hydrogen ion; n and m each denote an integer of 0 to 6, provided that both of n and m are not 0; and a block of (C_2H_4O) and a block of (C_3H_6O) may be exchanged with each other, where R2 denotes a hydrogen atom or a methyl group.

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DESCRIPTION

Title of Invention

INKJET RECORDING INK, INK CARTRIDGE, INKJET RECORDING METHOD, INKJET RECORDING DEVICE AND INK RECORDED MATTER

Technical Field

The present invention relates to an inkjet recording ink, an ink cartridge, an inkjet recording method, an inkjet recording device, and an ink recorded matter.

Background Art

In recent years, as an image formation method, an inkjet recording method has become popular because the inkjet recording method provides a simpler process and is easier to make a full-color image than other recording methods, and can provide a high-resolution image even with a simple device.

According to the inkjet recording method, a small amount of ink is jetted by foam generated by heat, or by pressure that is generated with the use of a piezoelectric or electrostatic force. The jetted ink is allowed to be adhered to a recording medium such as paper and then promptly dried or penetrated into the recording medium. In this manner, an image is formed. An application of the inkjet recording method has become widespread in various fields such as personal and industrial printers or printing.

For an inkjet recording device, an aqueous ink containing a water-soluble dye as a color material (a dye ink) is mainly used. However, the dye ink is disadvantageously poor in weather resistance and water resistance. Therefore, in recent years, a pigment ink containing a pigment instead of the water-soluble dye has been researched.

However, the pigment ink is poorer in color-developability, ink ejection stability, and storage stability than the dye ink. As the high-quality image technology for OA printers has advanced, higher image density is increasingly required even when recording is performed on plain paper with the pigment ink. However, in the case where the plain paper is used, there has been a problem that the pigment ink penetrates into the paper, resulting in a decrease in the pigment concentration on the paper surface and a drop in image density.

In recent years, in particular, a demand for industrial applications has been growing, and high-speed printing has been desired. For the high-speed printing, an inkjet printer equipped with a line head has been proposed. In the case of the high-speed printing, in order to accelerate the drying speed of the ink which has adhered to the recording medium, a penetrating agent is added to the ink to thereby allow water to penetrate into the recording medium. However, in this case, in addition to water, the pigment also penetrates into the recording medium in a high degree. As a result, the image density further decreases, which is problematic.

In the case of the plain paper, immediately after printing, water

serving as an ink solvent makes a surface of the plain paper to swell, so that a difference between extension rates on a front surface and a back surface is increased to cause curling. This curling phenomenon has not been problematic in low-speed printing because it is eliminated as water is gradually dried. However, in the high-speed printing, the recording medium must be conveyed after printing in a state in which curling still remains thereon, which causes paper jam. An increase of an amount of a water-soluble organic solvent contained in the ink is effective for the curling, but, as a result, the ink is allowed to be more hydrophobic, making it difficult to ensure storage stability of the ink.

PTL 1 describes an ink containing an aqueous solvent, a pigment, a water-insoluble polymer dispersing agent, and a self-dispersing polymer which is excellent in ink ejection property and blocking resistance of an image. In addition, as a monomer of the water-insoluble polymer, a phosphate group-containing monomer is described. However, neither a copolymer containing a monomer represented by General Formula (5) of the present invention, nor its effects of improving dispersibility of the self-dispersing polymer and image density has been described.

PTL 2 describes a UV-curable white ink composition for inkjet recording which contains a while pigment, and a vinyl polymer containing a terminal substituent of an acid or salt thereof and a sulfonyl group or a phosphonyl group in molecule thereof. A terminal ammonium phosphate of a polymethacrylic acid derivative is exemplified as the polymer dispersing agent. However, neither a copolymer

containing a monomer represented by the General Formula (5) of the present invention, nor its effect of improving image density in the case of using the polymer dispersing agent has been described.

PTL 3 describes improvement of fixability and image density by use of a combination of printing paper containing a polyvalent water-soluble metal salt, with an ink containing a pigment and a certain phosphate group having no surface activating ability. However, an effect of improving dispersibility of the ink and image density has not been described.

Citation List

Patent Literature

PTL 1 Japanese Patent Application Laid-Open (JP-A) No. 2010-189478

PTL 2 JP-A No. 2007-270089

PTL 3 JP-A No. 2011-122072

Summary of Invention

Technical Problem

An object of the present invention is to provide an inkjet recording ink which achieves high image density and has excellent storage stability.

Solution to Problem

A means for solving the above problems is as follows:

An inkjet recording ink, including:

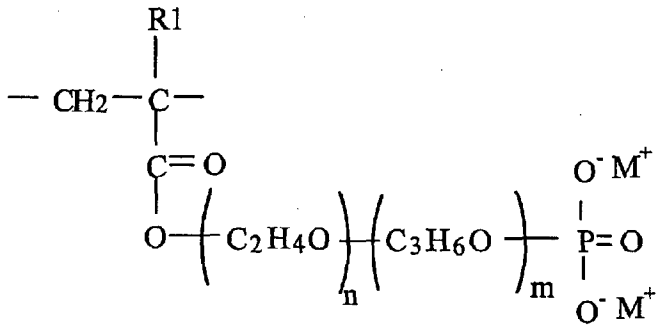
water;

a water-soluble organic solvent;

a pigment; and

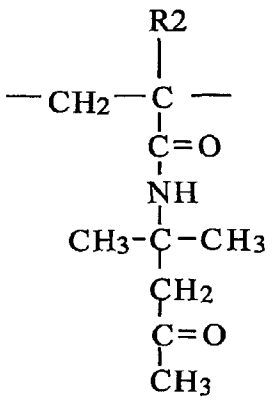
a phosphate group-containing copolymer,

wherein the phosphate group-containing copolymer contains a structural unit represented by the following General Formula (1) and a structural unit represented by the following General Formula (2):



(Formula 1)

where R1 denotes a hydrogen atom or a methyl group; M^+ denotes an alkali metal ion, an organic amine ion, or a hydrogen ion; half or more of M^+ in the copolymer is the alkali metal ion or the organic amine ion, the remainder of M^+ is the hydrogen ion; n and m each denote an integer of 0 to 6, provided that both of n and m are not 0; and a block of (C_2H_4O) and a block of (C_3H_6O) may be exchanged with each other,



(Formula 2)

where R2 denotes a hydrogen atom or a methyl group.

Advantageous Effects of Invention

The present invention can solve the above existing problems, and achieve the above object. That is, the present invention can provide an inkjet recording ink which achieves high image density and has excellent storage stability.

Brief Description of Drawings

FIG. 1 is a schematic diagram illustrating one example of an ink cartridge.

FIG. 2 is a schematic diagram illustrating the ink cartridge illustrated in FIG. 1 and a case thereof.

FIG. 3 is a perspective diagram illustrating one example of an inkjet recording device.

FIG. 4 is a diagram illustrating one example of the inkjet recording device illustrated in FIG. 3.

FIG. 5 is a schematic enlarged diagram illustrating one example of an inkjet head of the inkjet recording device illustrated in FIG. 3.

Description of Embodiments

(Inkjet recording ink)

An inkjet recording ink (hereinafter may be referred to as "ink") of the present invention contains water, a water-soluble solvent, a pigment, and a phosphate group-containing copolymer; and, if necessary,

other ingredients.

A mechanism of pigment aggregation in the case of using an ink of the present invention has not been known exactly, but is thought as follows:

A phosphate group or a salt of the phosphate group in a structural unit represented by the General Formula (1) has high affinity with a polyvalent metal ion, so that it is rapidly coordinated with a polyvalent metal ion eluted from a recording medium.

In the case where a copolymer containing a salt of a phosphate group used in the present invention is used as a dispersing agent, most of the copolymer is adsorbed onto a pigment in an ink. In this state, when the phosphate group or the salt of the phosphate group in a structural unit represented by the General Formula (1) is coordinated with the polyvalent metal ion eluted from the recording medium, the pigment in the ink is decreased in dispersion stability due to at least one cause of the following (1) to (3), leading to the pigment aggregation.

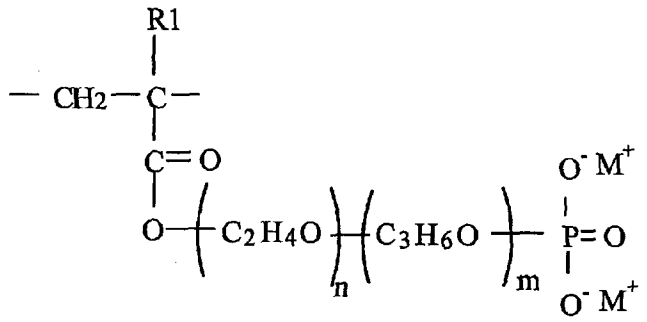
(1) A valence of a counter ion is increased, so that electrostatic repulsive force between pigments is decreased.

(2) The copolymer containing the salt of the phosphate group is decreased in solubility into the ink, so that a polymer adsorbing layer is decreased to thereby decrease steric repulsive force between pigments.

(3) The copolymer containing the salt of the phosphate group is decreased in solubility into the ink, so that a pigment onto which the copolymer containing the salt of the phosphate group is adsorbed is decreased in hydration stability.

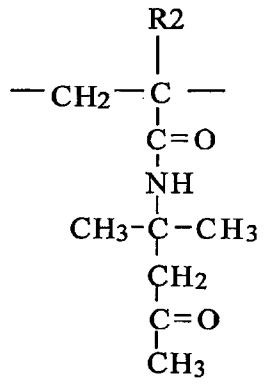
In the case where the copolymer containing the salt of the phosphate group is used as an additive, the copolymer itself is coordinated with the polyvalent metal ion eluted from the recording medium to form an insoluble matter which, in turn, acts as a core of an aggregate to cause the pigment aggregation.

In an inkjet recording ink of the present invention, the phosphate group-containing copolymer contains a structural unit represented by the following General Formula (1) and a structural unit represented by the following General Formula (2); preferably further contains a structural unit represented by the following General Formula (3), a structural unit represented by the following General Formula (4), or both thereof; and, if necessary, further contains other structural units.



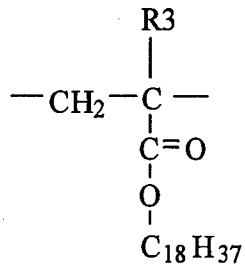
(Formula 1)

In the General Formula (1), R1 denotes a hydrogen atom or a methyl group; M^+ denotes an alkali metal ion, an organic amine ion, or a hydrogen ion; half or more of M^+ in the copolymer is the alkali metal ion or the organic amine ion, the remainder of M^+ is the hydrogen ion; n and m each denote an integer of 0 to 6, provided that both of n and m are not 0; and a block of (C_2H_4O) and a block of (C_3H_6O) may be exchanged with each other.



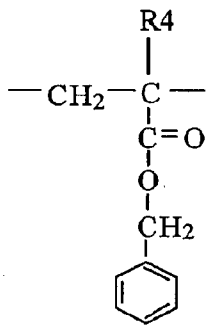
(Formula 2)

In the General Formula (2), R2 denotes a hydrogen atom or a methyl group.



(Formula 3)

In the General Formula (3), R3 denotes a hydrogen atom or a methyl group.



(Formula 4)

In the General Formula (4), R4 denotes a hydrogen atom or a methyl group.

The structural unit represented by the General Formula (1) is characterized by exhibiting hydrophilicity, but exhibiting hydrophobicity in a state of being bound to a polyvalent metal ion (in particular, a calcium ion). Accordingly, in the case where an ink which contains a

copolymer having a structural unit represented by the General Formula (1) is used to form an image on printing paper containing a water-soluble polyvalent metal salt, the structural unit represented by the General Formula (1) is hydrophobized by the action of a polyvalent metal ion eluted from the paper to the ink to thereby form an aggregate with a pigment. As a result, the pigment remains on a surface of the paper, leading to an improved image density.

However, in the case of plain paper, a polyvalent metal salt contained in the paper is generally a water-insoluble calcium carbonate, so that only a small amount of calcium ion is eluted into an ink. Therefore, the structural unit represented by the General Formula (1) is not enough to achieve satisfactory image density.

As a means for solving the problem, there has been proposed that a percentage of the structural unit represented by the General Formula (1) is increased in the phosphate group-containing copolymer. However, when the percentage of the structural unit represented by the General Formula (1) is increased, the copolymer is formed into a gel, leading to a deteriorated storage stability of the ink. This is probably because an interaction between phosphate groups is enhanced. Therefore, conventionally, in the case where a phosphate group-containing copolymer is used, a percentage of a phosphate group-containing structural unit had to be less than 20% by mass.

In contrast, in the present invention, the structural unit represented by the General Formula (1) is used in combination with the structural unit represented by the General Formula (2), and preferably

with the structural unit represented by the General Formula (3), the structural unit represented by the General Formula (4), or both thereof. Therefore, the affinity with the pigment and an effect of forming the aggregation with the pigment are improved. Storage stability is also improved even in an ink containing a large amount of a water-soluble organic solvent. Additionally, a copolymer is less likely to be formed into a gel. As a result, a percentage of the structural unit represented by the General Formula (1) can be increased, and reactivity with the polyvalent metal ion (in particular, calcium ion) can be improved.

The structural unit represented by the General Formula (3), the structural unit represented by the General Formula (4), or both thereof has particularly high affinity with the pigment. Combined use of the structural unit represented by the General Formula (2) therewith improves the affinity with the pigment, and prevents the copolymer from being formed into a gel.

Thus, an inkjet recording ink of the present invention can achieve high image density even in common plain paper which contains a small amount of a polyvalent water-soluble metal salt and be improved in storage stability and ejection stability by using the phosphate group-containing copolymer which contains the structural unit represented by the General Formula (1), the structural unit represented by the General Formula (2), and, preferably, the structural unit represented by the General Formula (3), the structural unit represented by the General Formula (4), or both thereof.

An ink of the present invention contains water, a water-soluble

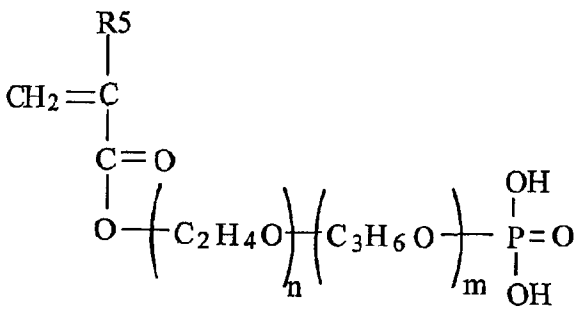
organic solvent, a pigment, and a phosphate group-containing copolymer; and, if necessary, other ingredients. Each of these ingredients will be described hereinafter.

<Phosphate group-containing copolymer>

The phosphate group-containing copolymer at least the structural unit represented by the General Formula (1) and the structural unit represented by the General Formula (2); preferably further contains the structural unit represented by the General Formula (3), the structural unit represented by the General Formula (4), or both thereof; and, if necessary, further contains other structural units.

The phosphate group-containing copolymer can be obtained by allowing a monomer represented by the following General Formula (5) to polymerize with a monomer represented by the following General Formula (6). The copolymer is preferably allowed to further polymerize with a monomer represented by the following General Formula (7), a monomer represented by the following General Formula (8), or both thereof, and, if necessary, with other monomers.

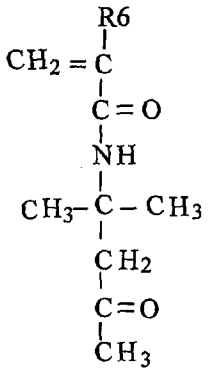
Then, the resultant copolymer is neutralized with an alkali metal base or an organic amine base.



(Formula 5)

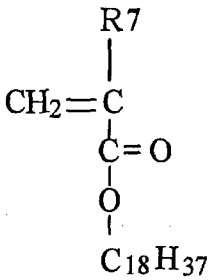
In the General Formula (5), R5 denotes a hydrogen atom or a

methyl group, and n and m each denote an integer of 0 to 6, provided that both of n and m are not 0.



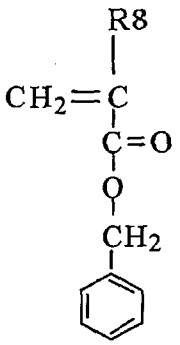
(Formula 6)

In the General Formula (6), R6 denotes a hydrogen atom or a methyl group.



(Formula 7)

In the General Formula (7), R7 denotes a hydrogen atom or a methyl group.



(Formula 8)

In the General Formula (8), R8 denotes a hydrogen atom or a methyl group.

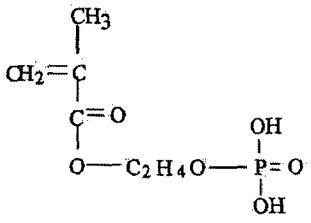
Conventional general copolymerization methods may be used. For example, the following method can be used. To a solvent contained

in a flask equipped with a stirrer, a thermometer, and a nitrogen-inducing pipe, are added the monomer represented by the General Formula (5) and the monomer represented by the General Formula (6), and preferably further the monomer represented by the General Formula (7), the monomer represented by the General Formula (8), or both thereof, followed by allowing to react together in the presence of a polymerization initiator, under reflux in a nitrogen gas, at a temperature of about 60°C to about 150°C.

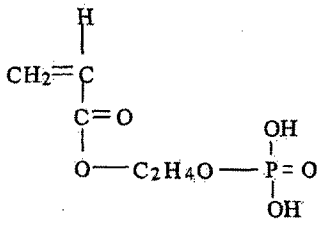
A molecular weight of the copolymer can be controlled by adjusting a concentration of the monomer upon polymerization and/or an amount of the polymerization initiator. Copolymerization aspect of the copolymer is not particularly limited. For example, the copolymer may be a block copolymer or a random copolymer.

Examples of monomers represented by the General Formulae (5) to (8) include monomers represented by the General Formulae (5-1) to (5-5), (6-1), (6-2), (7-1), (7-2), (8-1), and (8-2).

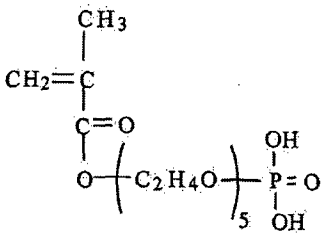
(Formula 5-1)



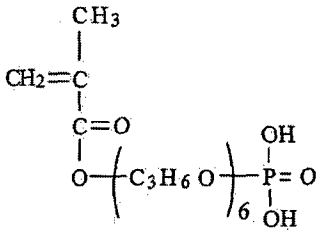
(Formula 5-2)



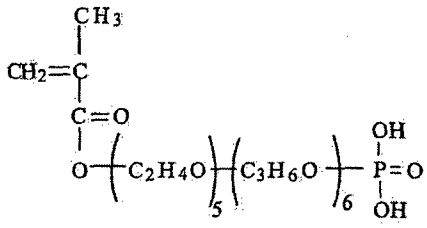
(Formula 5-3)



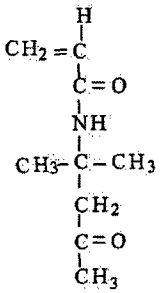
(Formula 5-4)



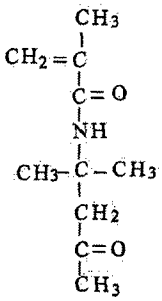
(Formula 5-5)



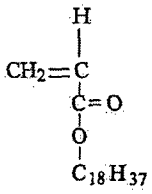
(Formula 6-1)



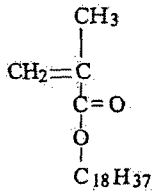
(Formula 6-2)



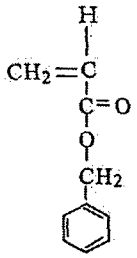
(Formula 7-1)



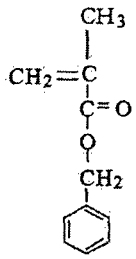
(Formula 7-2)



(Formula 8-1)



(Formula 8-2)



A percentage of the structural unit represented by the General Formula (1) in the phosphate group-containing copolymer is preferably 10% by mass to 80% by mass, more preferably 10% by mass to 60% by mass, further preferably 20% by mass to 40% by mass, relative to a mass

of the copolymer. When the structural unit is contained in a percentage falling within the above range, the most excellent image density, dispersibility, and storage stability can be achieved.

A mass average molecular weight of the phosphate group-containing copolymer is preferably 3,000 to 60,000, more preferably 5,000 to 50,000, further preferably 6,000 to 30,000.

An amount of the phosphate group-containing copolymer is preferably 0.05% by mass to 10.0% by mass, more preferably 0.5% by mass to 5% by mass, further preferably 1% by mass to 3% by mass, on a solid basis, relative to a total mass of an ink.

An effect of improving image density begins to be developed over 0.5% by mass. Meanwhile, use of 10.0% by mass or less of the phosphate group-containing copolymer enables a viscosity of an ink to fall within a range suitable for being ejected from an ink head.

Use of the phosphate group-containing copolymer as a pigment-dispersing agent is preferable because image density in plain paper and storage stability of an ink containing 10% by mass to 60% by mass of a water-soluble organic solvent are further improved. An amount of the water-soluble organic solvent is more preferably 20% by mass to 50% by mass.

In the case where the phosphate group-containing copolymer is used as the pigment-dispersing agent, an amount of the phosphate group-containing copolymer is 1% by mass to 100% by mass, preferably 5% by mass to 80% by mass, further preferably 10% by mass to 50% by mass, relative to 100% by mass of a pigment. When the amount of

phosphate group-containing copolymer falls within the above range, a particle diameter of the pigment is the most suitable, leading to excellent image density, dispersibility, and storage stability.

Phosphate groups in the phosphate group-containing copolymer are preferably partially or wholly neutralized with bases to thereby be ionized. Examples of the bases to be used for neutralization include alkali metals such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; ammonium; mono-, di-, or tri-methylamine; mono-, di-, or tri-ethylamine; monoethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, dimethylethanolamine, choline, aminoethane propanediol, monopropanolamine, dipropanolamine, tripropanolamine, isopropanolamine, trishydroxymethylaminomethane, aminoethylpropanediol; organic ammoniums such as tetramethylammonium, tetraethylammonium, and tetrabutylammonium; cyclic amines such as morpholine, N-methyl morpholine, N-methyl-2pyrrolidone, and 2-pyrrolidone.

The M in the General Formula (1) constituting the phosphate group-containing copolymer is preferably a hydrogen atom, a potassium atom, or a sodium atom. When the M is any of these atoms, image density is improved. This is probably because a pigment is more likely to aggregate when a counter ion of a phosphate group is any of the above-described atoms upon moisture evaporation from an ink.

As for the M in the General Formula (1) constituting the phosphate group-containing copolymer, a percentage of the number of a

hydrogen atom is preferably 40% or less relative to the total number of the M in the copolymer. When the percentage is 40% or less, a pigment dispersion and an ink are improved in storage stability. A pigment is kept in a dispersion state in a dispersion and in an ink due to repulsion between negative charges of the phosphate group. Accordingly, in the case where the M is a metal atom or an organic amine, repulsive force between pigments is enhanced, leading to stable dispersion.

Note that, the percentage of the number of a hydrogen atom relative to the total number of the M in the copolymer can be determined according to the following expression: 100% – neutralization rate (%) where the neutralization rate (%) is defined below.

In the present invention, the neutralization rate of a phosphate group in the copolymer obtained through neutralization is defined as a value determined according to the below-described method. Actually, the neutralization rate herein is different from a percentage of a proton substituted with a metal ion or an organic ammonium ion in the copolymer.

When the compound represented by the General Formula (5) is assumed to be Monomer 1, the following equation is satisfied:

Neutralization rate X (%) = (Number of moles of Base to be added × Valence of positive ion of Base) / (Number of moles of Monomer 1 contained in copolymer × 2) × 100

where Number of moles of Base to be added = Amount of Base to be added Yg / Molecular weight of Base, and

Number of moles of Monomer 1 contained in copolymer =

Amount of Monomer 1 to be charged Zg / Molecular weight of Monomer 1.

Accordingly, an amount of a base which is required to achieve the neutralization rate X (%) is expressed as the following equation:

Amount of Base to be added Yg = Neutralization rate X (%) × (Amount of Monomer 1 to be charged × 2) × Molecular weight of Base / (Valence of positive ion of Base × 100 × Molecular weight of Monomer 1).

<Water>

An ink of the present invention uses water as a liquid medium. Examples of the water include pure water such as ion-exchanged water, ultrafiltrated water, Milli-Q water, and distilled water.

<Water-soluble organic solvent>

An ink of the present invention contains a water-soluble organic solvent for the purpose of preventing the ink from drying as a wetting agent, improving dispersing stability, and preventing curling in plain paper. The water-soluble organic solvent may be used in combination.

Specific examples of the water-soluble organic solvent include:

polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, polypropylene glycol, dipropylene glycol, tripropylene glycol, poly polypropylene glycol, 1,3-butanediol, 3-methyl-1,3-butanediol, 1,5-pentanediol, 1,6-hexane diol, glycerin, isopropylidene glycerol, trimethylolethane, trimethylolpropane, 1,2,3-butanetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, and petriol;

polyhydric alcohol alkyl ethers, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl

ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, and propylene glycol monoethyl ether;

polyhydric alcohol aryl ethers, such as ethylene glycol monophenyl ether, and ethylene glycol monobenzyl ether;

nitrogen-containing heterocyclic compounds, such as 2-pyrrolidone, N-methyl-2-pyrrolidone, N-hydroxyethyl-2-pyrrolidone, 1,3-dimethylimidazolidinone, ε-caprolactam, and γ-butyrolactone;

amides, such as formamide, N-methylformamide, N,N-dimethylformamide, N,N-dimethyl-β-methoxypropionamide, and N,N-dimethyl-β-butoxy propionamide;

amines, such as monoethanolamine, diethanolamine, triethanolamine, monoethylamine, diethylamine, and triethylamine;

sulfur-containing compounds, such as dimethyl sulfoxide, sulfolane, and thiodiethanol; and

3-ethyl-3-hydroxymethyloxetane, propylene carbonate and ethylene carbonate.

Among these water-soluble organic solvents, particularly preferable are 3-ethyl-3-hydroxymethyloxetane, isopropylidene glycerol, N,N-dimethyl-β-methoxypropionamide, and N,N-dimethyl-β-butoxy propionamide, which are excellent in preventing curling in plain paper.

In addition, 1,3-butanediol, diethyleneglycol, 2,2,4-trimethyl-1,3-pentanediol, triethylene glycol, and/or glycerol are excellent in preventing ejection failure due to moisture evaporation.

Additionally, saccharides may be contained as a wetting agent.

Examples of the saccharides include monosaccharides, disaccharides, oligosaccharides (including trisaccharides, and tetrasaccharides), and polysaccharides. Preferable examples thereof include glucose, mannose, fructose, ribose, xylose, arabinose, galactose, maltose, cellobiose, lactose, sucrose, trehalose, and maltotriose. As used herein, the polysaccharides mean saccharides in a broad sense, which may include materials existing widely in nature, such as α-cyclodextrin and cellulose.

Moreover, examples of derivatives of the saccharides include reducing sugars, oxidized sugars, amino acids, and thio acids of the saccharides. Sugar alcohol is particularly preferable. Specific examples of the sugar alcohol include maltitol and sorbitol.

A ratio of the pigment to the water-soluble organic solvent greatly affects ejection stability of the ink from an ink head. When a solid content of the pigment is large, but an amount of the water-soluble organic solvent is small, moisture evaporation proceeds in proximity to an ink meniscus of a nozzle, leading to ejection failure.

An amount of the water-soluble organic solvent is preferably 10% by mass to 60% by mass, more preferably 20% by mass to 50% by mass, relative to a total amount of an ink. An ink containing the water-soluble organic solvent in an amount falling within the above range has highly excellent drying property and ejection reliability.

<Pigment>

An amount of a pigment to be used in the present invention contained in an ink is preferably 0.1% by mass to 20.0% by mass.

When the amount is 0.1% by mass or more, low image density

and unclear printing can be prevented. When the amount is 20.0% by mass or less, excessively high viscosity of the ink and a clogged nozzle can be prevented.

A 50% volume average particle diameter of the pigment is preferably 150 nm or less. The 50% volume average particle diameter of the pigment is a value of D50 measured by means of MICROTRAC UPA (manufactured by Nikkiso Co., Ltd.) through a dynamic light scattering method in an environment of 23°C and 55%RH.

A type of the pigment is not particularly limited and may be appropriately selected depending on the intended purpose. For example, the pigment may be an inorganic pigment or an organic pigment. The pigment may be used alone or in combination.

Examples of the inorganic pigment include titanium oxide, iron oxide, calcium carbonate, barium sulfate, aluminum hydroxide, barium yellow, navy blue, cadmium red, chrome yellow, metal powder, and carbon black. Among them, carbon black is preferable.

Examples of the organic pigment include an azo pigment, an azomethine pigment, a polycyclic pigment, a dye chelate, a nitro pigment, a nitroso pigment, and aniline black. Among them, the azo pigment and the polycyclic pigment are preferable.

Examples of the azo pigment include azo lake, an insoluble azo pigment, a condensed azo pigment, and a chelate azo pigment.

Examples of the polycyclic pigment include a phthalocyanine pigment, a perylene pigment, a perinone pigment, an anthraquinone pigment, a quinacridone pigment, a dioxazine pigment, an indigo

pigment, a thioindigo pigment, an isoindolinone pigment, a quinophthalone pigment, and a rhodamine B lake pigment.

Examples of the dye chelate include a basic dye-type chelate and an acidic dye-type chelate.

Examples of a pigment for a black ink include carbon blacks (C.I. Pigment Black 7) such as furnace black, lampblack, acetylene black, and channel black; metals such as copper and iron (C.I. Pigment Black 11); metal compound such as titanium oxide; organic pigments such as aniline black (C.I. Pigment Black 1).

Preferable example of the carbon black include carbon blacks produced by a furnace method or a channel method, with a primary particle diameter of 15 nm to 40 nm, a specific surface area as measured by a BET method of 50 m^2/g to 300 m^2/g, a DBP oil absorption amount of 40 mL/100 g to 150 mL/100 g, a volatile matter content of 0.5% to 10%, and a pH of 2 to 9.

Commercially available products of the carbon black include No. 2300, No. 900, MCF-88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100, and No. 2200B (all manufactured by Mitsubishi Chemical Corporation); RAVEN 700, RAVEN 5750, RAVEN 5250, RAVEN 5000, RAVEN 3500, and RAVEN 1255 (all manufactured by Columbia Corp); REGAL 400R, REGAL 330R, REGAL 660R, MOGUL L, MONARCH 700, MONARCH 800, MONARCH 880, MONARCH 900, MONARCH 1000, MONARCH 1100, MONARCH 1300, and MONARCH 1400 (all manufactured by Cabot Corporation); and COLOR BLACK FW1, COLOR BLACK FW2, COLOR BLACK FW2V, COLOR BLACK FW18, COLOR

BLACK FW200, COLOR BLACK S150, COLOR BLACK S160, COLOR BLACK S170, PRINTEX 35, PRINTEX U, PRINTEX V, PRINTEX 140U, PRINTEX 140V, SPECIAL BLACK 6, SPECIAL BLACK 5, SPECIAL BLACK 4A, and SPECIAL BLACK 4 (all manufactured by Degussa AG).

A pigment for a yellow ink is not particularly limited and may be appropriately selected depending on the intended purpose. Examples thereof include C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 16, C.I. Pigment Yellow 17, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 75, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 98, C.I. Pigment Yellow 114, C.I. Pigment Yellow 120, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 138, C.I. Pigment Yellow 150, C.I. Pigment Yellow 151, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 174, and C.I. Pigment Yellow 180.

A pigment for a magenta ink is not particularly limited and may be appropriately selected depending on the intended purpose. Examples thereof include C.I. Pigment Red 5, C.I. Pigment Red 7, C.I. Pigment Red 12, C.I. Pigment Red 48 (Ca), C.I. Pigment Red 48 (Mn), C.I. Pigment Red 57 (Ca), C.I. Pigment Red 57:1, C.I. Pigment Red 112, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 146, C.I. Pigment Red 168, C.I. Pigment Red 176, C.I. Pigment Red 184, C.I. Pigment Red 185, C.I. Pigment Red 202, and Pigment Violet 19.

A pigment for a cyan ink is not particularly limited and may be

appropriately selected depending on the intended purpose. Examples thereof include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 15, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:34, C.I. Pigment Blue 16, C.I. Pigment Blue 22, C.I. Pigment Blue 60, C.I. Pigment Blue 63, and C.I. Pigment Blue 66; and C.I. Bat Blue 4 and C.I. Bat Blue 60.

Novel pigments produced for the present invention may be used in an ink of the present invention.

Note that, use of Pigment Yellow 74 as a yellow pigment, Pigment Red 122 and Pigment Violet 19 as a magenta pigment, and Pigment Blue 15:3 as a cyan pigment makes it possible to obtain a balanced ink which is excellent in color tone and light resistance.

<Other ingredients>

The other ingredients are not particularly limited and may be appropriately selected depending on the intended purpose. Examples thereof include a dispersing agent, a penetrating agent, a pH adjusters, a water-dispersible resin, a antiseptic and antifungal agent, a chelating reagent, a rust preventive agent, an antioxidant, a ultraviolet absorber, an oxygen absorber, and a light stabilizer.

-Dispersing agent-

The dispersing agent is preferably the phosphate group-containing copolymer. However, various surfactants such as an anionic surfactant, a cationic surfactant, an amphoteric surfactant, and a nonionic surfactant; and polymer dispersing agents may also be used. These may be used alone or in combination.

Examples of the anionic surfactant include alkyl sulfocarboxylate, α-olefin sulfonate, polyoxyethylene alkyl ether acetate, N-acylamino acid and salts thereof, N-acyl methyl taurine salt, polyoxyalkyl ether sulfate, polyoxyethylene alkyl ether phosphate, rosin acid soap, castor-oil sulfate ester salt, lauryl alcohol sulfate ester salt, alkylphenol type phosphate ester, naphthalenesulfonate formalin condensate, alkyl-type phosphate ester, alkyl aryl sulfonate, diethyl sulfosuccinate, diethyl hexyl sulfosuccinate, and dioctyl sulfosuccinate.

Examples of the cationic surfactant include 2-vinylpyridine derivative and poly-4-vinylpyridine derivative.

Examples of the amphoteric surfactant include lauryl dimethylamino acetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, coconut oil fatty acid amide propyl dimethylamino acetic acid betaine, polyoctyl polyaminoethyl glycine, and imidazoline derivative.

Examples of the nonionic surfactant include:

ether-based surfactants, such as polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene dodecyl phenyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleyl ether, polyoxyethylene alkyl ether, and polyoxyaralkyl alkyl ether;

ester-based surfactants, such as polyoxyethylene oleate, polyoxyethylene oleate ester, polyoxyethylene distearate ester, sorbitan laurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, polyoxyethylene monooleate, and polyoxyethylene stearate; and

acetylene glycol-based surfactants, such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol, and 3,5-dimethyl-1-hexyne-3-ol.

-Penetrating agent-

Unlike the water-soluble organic agent used as the wetting agent, the penetrating agent to be used is those having relatively low wettability, i.e., non-wetting penetrating agent. That is, preferable are those having a solubility of 0.2% by mass to 5.0% by mass in water at 25°C.

Specifically, a polyol compound having 8 to 11 carbon atoms or a glycol ether compound having 8 to 11 carbon atoms is preferably contained. Among them, particularly preferable are 2-ethyl-1,3-hexane diol [solubility: 4.2% by mass (25°C)], and 2,2,4-trimethyl-1,3-pentanediol [solubility: 2.0% by mass (25°C)].

Examples of other aliphatic diols include 2-ethyl-2-methyl-1,3-propanediol, 3,3-dimethyl-1,2-butanediol, 2,2-diethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2,4-dimethyl-2,4-pentanediol, 2,5-dimethyl-2,5-hexane diol, and 5-hexene-1,2-diol.

Other penetrating agents capable of being used in combination therewith are not particularly limited and may be appropriately selected depending on the intended purpose, so long as they can be dissolved in an ink and adjusted to desired physical properties. Examples thereof include alkyl and aryl ethers of polyhydric alcohols, such as diethylene glycol monophenyl ether, ethylene glycol monophenyl ether, ethylene

glycol monoallyl ether, diethylene glycol monophenyl ether, diethylene glycol monobutyl ether, propylene glycol monobutyl ether, and tetraethylene glycol chlorophenyl ether; and lower alcohols such as ethanol.

An amount of the penetrating agent contained in an ink is preferably 0.1% by mass to 4.0% by mass. When the amount is less than 0.1% by mass, satisfactory quick-drying property can not achieved, potentially leading to a blurred image. When the amount is greater than 4.0% by mass, the pigment is deteriorated in dispersion stability, making it likely to cause a clogged nozzle. Alternatively, the resultant ink excessively penetrates into a recording medium, potentially leading to a deterioration in the image density or occurrence of set-off.

-pH Adjuster-

The pH adjuster is not particularly limited and may be appropriately selected depending on the intended purpose, so long as it can adjust the pH to 8.5 to 11, preferably 9 to 11, without adversely affecting the resultant ink. When the pH is less than 8.5 or greater than 11, a large amount of an inkjet head or an ink supply unit is dissolved out, potentially leading to a defect such as deterioration, leakage, or ejection failure of the resultant ink. When the pH is less than 8.5, the resultant ink is decreased in the pH during storage, so that polymer particles may be increased in particle diameter to aggregate together. For example, the pH can be measured by a pH meter HM-30R (manufactured by DKK-TOA Corporation).

Examples of the pH adjuster include alcohol amines, hydroxides

of alkali metal elements, hydroxides of ammonium, hydroxides of phosphonium and carbonates of alkali metals.

Examples of the alcohol amines include diethanolamine, triethanolamine, and 2-amino-2-ethyl-1,3 propanediol.

Examples of the hydroxides of alkali metal elements include lithium hydroxide, sodium hydroxide, and potassium hydroxide.

Examples of the hydroxides of ammonium include ammonium hydroxide, and quaternary ammonium hydroxide.

Examples of the hydroxides of phosphonium include quaternary phosphonium hydroxide.

Examples of the carbonates of alkali metals include lithium carbonate, sodium carbonate, and potassium carbonate.

-Water-dispersible resin-

The water-dispersible resin is excellent in film formation performance (image formation performance), and has high water repellency, water resistance, and weather resistance. Accordingly, it is useful for recording an image which is water resistant and has high image density (high color-developability). Examples thereof include condensation-type synthetic resins, addition-type synthetic resins, and natural polymer compounds.

Examples of the condensation-type synthetic resin include a polyester resin, a polyurethane resin, a polyepoxy resin, a polyamide resin, a polyether resin, a poly(meth)acrylic resin, an acryl-silicone resin, and a fluorine-based resin.

Examples of the addition-type synthetic resin include a polyolefin

resin, a polystyrene-based resin, a polyvinyl alcohol-based resin, a polyvinyl ester-based resin, a polyacrylic acid-based resin, and an unsaturated carboxylic acid-based resin.

Examples of the natural polymer compounds include celluloses, rosins, and natural rubber.

Among them, preferable are polyurethane resin particles, acryl-silicone resin particles, and fluorine-based resin particles.

An average particle diameter of the water-dispersible resin correlates with the viscosity of a dispersion. In the case of water-dispersible resins which are the same in composition as each other, but different in the average particle diameter from each other, as the particle diameter becomes smaller, the viscosity increases with the same solid contents. In order to prevent the ink from having excessively high viscosity, the water-dispersible resin preferably has the volume average particle diameter of 50 nm or more. When the volume average particle diameter is several ten micrometers, the resultant ink cannot be used because the particle diameter is larger than a nozzle opening of an inkjet head. Even when the particle diameter is smaller than the nozzle opening, the presence of large particles in the ink deteriorates ejection stability. In order to prevent the ejection stability from being impaired, the volume average particle diameter is preferably 200 nm or less.

The water-dispersible resin preferably has a function to fix a water-dispersible pigment onto a paper surface, and forms a film at a normal temperature to improve fixability of the pigment. Therefore, the minimum film forming temperature (MFT) of the water-dispersible resin

is preferably 30°C or less.

When the glass transition temperature of the water-dispersible resin is −40°C or lower, a resin coating is increased in consistency, leading to tack in printed matter. Therefore, the glass transition temperature of the water-dispersible resin is preferably −30°C or higher.

An amount of the water-dispersible resin contained in the ink is preferably 1% by mass to 15% by mass, more preferably 2% by mass to 7% by mass on a solid basis.

-Antiseptic and antifungal agent-

Examples of the antiseptic and antifungal agent include sodium dehydroacetate, sodium sorbate, 2-pyridinethiol-1-oxide sodium, sodium benzoate, and pentachlorophenol sodium.

-Chelating reagent-

Examples of the chelating reagent include sodium ethylenediamine tetraacetate, sodium nitrilotriacetate, sodium hydroxyethyl ethylenediamine triacetate, sodium diethylenetriamine pentaacetate, and sodium uramil diacetate.

-Rust preventive agent-

Examples of the rust preventive agent include acidic sulfite, sodium thiosulfate, ammonium thiodiglycolate, diisopropyl ammonium nitrite, pentaerythritol tetranitrate, and dicyclohexyl ammonium nitrite.

-Antioxidant-

Examples of the antioxidant include phenolic antioxidants (including hindered phenolic antioxidants), amine-based antioxidants, sulfur-based antioxidants, and phosphorus-based antioxidants.

-Ultraviolet absorber-

Examples of the ultraviolet absorber include benzophenone-based ultraviolet absorbers, benzotriazole-based ultraviolet absorbers, salicylate-based ultraviolet absorbers, cyanoacrylate-based ultraviolet absorber, and nickel complex salt-based ultraviolet absorbers.

<Production method of inkjet recording ink>

An inkjet recording ink of the present invention is produced by dispersing or dissolving water, a water-soluble organic solvent, a pigment, a phosphate group-containing copolymer, and, if necessary, other ingredients into an aqueous medium, followed by appropriately stirring and mixing.

The pigment is contained in an ink as a pigment dispersion prepared by mixing water, a pigment, and, if necessary, a dispersing agent and other materials, followed by dispersing with known dispersers to adjust its particle diameter.

For example, the dispersing can be performed with a sand mill, a homogenizer, a ball mill, a paint shaker, or an ultrasonic disperser. The stirring and mixing can be performed with a stirrer with a typical stirring blade, a magnetic stirrer, or a high speed disperser.

A concentration of the pigment to be used for producing the pigment dispersion is preferably 0.1% by mass to 50% by mass, particularly preferably 0.1% by mass to 30% by mass.

If necessary, the pigment dispersion and the resultant ink are preferably filtered through a filter or subjected to centrifugation to thereby remove coarse particles, followed by degassing.

Physical properties of an ink of the present invention are not particularly limited and may be appropriately selected depending on the intended purpose.

For example, the viscosity of the ink is preferably 3 mPa·s to 20 mPa·s at 25°C. When the viscosity is 3 mPa·s or more, an effect of improving printing density and character quality can be attained. When the viscosity is 20 mPa·s or less, ejection property can be ensured.

For example, the viscosity can be measured at 25°C by means of a viscometer (RL-550, manufactured by Toki Sangyo Co., Ltd.).

A surface tension of the ink is preferably 40 mN/m or less at 25°C. When the surface tension is 40 mN/m or less, leveling of the ink is prevented on a recording medium, and the ink does not take a long time to be dried.

(Ink cartridge)

An ink cartridge of the present invention includes a container and an ink of the present invention stored in the container. The ink cartridge may further include other members, which are appropriately selected as needed.

The shape, structure, size, and material of the container are not particularly limited and may be appropriately selected depending on the intended purpose. For example, those having an ink bag made of aluminum laminated film or resin film may be used.

One example of the ink cartridge of the present invention will be described with reference to FIGs. 1 and 2.

FIG. 1 is a diagram illustrating one example of an ink cartridge

of the present invention. FIG. 2 is a diagram illustrating the ink cartridge 200 illustrated in FIG. 1 and a case (exterior) thereof. As shown in FIG. 1, in an ink cartridge 200, an ink bag 241 is filled with ink via an ink inlet 242. After the air is discharged therefrom, the ink inlet 242 is sealed by welding. When using, a needle provided in a device body is stuck into an ink outlet 243, which is made of a rubber member, to thereby supply the ink to the device. The ink bag 241 is made from a packaging material such as an aluminum laminated film with no air permeability. As shown in FIG. 2, the ink bag 241 is usually stored in a cartridge case 244 which is made of plastics, and is configured to be detachably mounted on various inkjet recording devices.

(Inkjet recording device and inkjet recording method)

An inkjet recording device of the present invention includes at least an ink jetting unit; and, if necessary, further includes appropriately selected other units such as a stimulus generating unit and a controlling unit.

An inkjet recording method of the present invention includes at least an ink jetting step; and, if necessary, further includes appropriately selected other steps such as a stimulus generating step and a controlling step.

The inkjet recording method of the present invention can be suitably performed by means of the inkjet recording device of the present invention, and the ink jetting step can be suitably performed by means of the ink jetting unit. Moreover, the other steps can be suitably performed by means of the other units.

The ink jetting step is a step of applying a stimulus to an ink to allow the ink to jet, to thereby form an image.

The ink jetting unit is a unit configured to apply a stimulus to an ink to allow the ink to jet, to thereby form an image. The ink jetting unit is not particularly limited. Examples thereof include various nozzles used for ejecting inks.

The stimulus can be generated, for example, by a stimulus generating unit. The stimulus is not particularly limited and may be appropriately selected depending on the intended purpose. Examples thereof include heat (temperature), pressure, vibration, and light. These may be used alone or in combination. Among them, heat and pressure are suitable.

The stimulus generating unit may be a heating device, a pressurizing device, a piezoelectric element, a vibration generator, an ultrasonic wave oscillator, and a light. Specific examples of the stimulus generating unit include a piezoelectric actuator such as a piezoelectric element; a thermal actuator utilizing a phase change due to film boiling of liquid caused by using an electric-heat transducer such as a heat element; a shape memory alloy actuator utilizing a metal phase change due to a temperature change; and an electrostatic actuator utilizing electrostatic force.

An embodiment of the jetting of the ink is not particularly limited, and varies depending on the stimulus. In the case where the stimulus is "heat", for example, there is a method in which a thermal energy corresponding to a recording signal is applied to the ink in a recording

head, for example, by a thermal head, to thereby generate bubbles in the ink by the action of the thermal energy, and then, by the action of pressure of the bubbles, droplets of the ink are allowed to be ejected from a nozzle hole of the recording head.

Meanwhile, in the case where the stimulus is "pressure", there is a method in which voltage is applied to a piezoelectric element adhered to a pressure chamber in an ink flow channel within a recording head, to thereby bend the piezoelectric element, and reduce a volume of the pressure chamber, so that droplets of the ink are allowed to be ejected from a nozzle hole of the recording head.

The controlling unit is not particularly limited and may be appropriately selected depending on the intended purpose, as long as it can control operation of each of the units. Examples thereof include a device such as a sequencer and a computer.

One embodiment for performing an inkjet recording method of the present invention by an inkjet recording device of the present invention will be described hereinafter with reference to figures.

FIG. 3 is a schematic diagram illustrating one example of a serial type inkjet recording device of the present invention. This inkjet recording device contains a device main body 101, a paper feeding tray 102 provided in the device main body 101 and configured to feed a sheet of paper, a paper discharging tray 103 provided in the device main body 101 and configured to store a sheet of paper on which an image has been recorded (formed), and an ink cartridge loading section 104.

On an upper surface of the ink cartridge loading section 104, a

control section 105 such as operation keys and a display is provided. The ink cartridge loading section 104 has a front cover 115 that can be opened and closed for attaching or detaching the ink cartridge 200.

In the device main body 101, as illustrated in FIGs. 4 and 5, a carriage 133 is slidably held in a main-scanning direction by a guide rod 131, which is a guide member horizontally bridged between left and right side plates, and a stay 132; and is moved for scanning in an arrow direction in FIG. 5 by a main scanning motor.

A recording head 134 composed of four inkjet recording heads configured to eject ink droplets of yellow (Y), cyan (C), magenta (M) and black (Bk) is installed in the carriage 133 such that a plurality of ink ejection outlets are aligned in the direction intersecting the main-scanning direction and that the ink droplet ejection direction faces downward.

For each of the inkjet recording heads constituting the recording head 134, it is possible to use, for example, a head provided with any of the following energy-generating units for ejecting ink: a piezoelectric actuator such as a piezoelectric element; a thermal actuator utilizing a phase change due to film boiling of liquid caused by using an electric-heat transducer such as a heat element; a shape memory alloy actuator utilizing a metal phase change due to a temperature change; and an electrostatic actuator utilizing electrostatic force.

Also, the carriage 133 is provided with sub-tanks 135 for each color configured to supply each color ink to the recording head 134. Each sub-tank 135 is supplied and replenished with the ink from the ink

cartridge 200 loaded into the ink cartridge loading section 104, via a ink supply tube.

Meanwhile, as a paper feeding section configured to feed sheets of paper 142 loaded on a paper loading section (pressurizing plate) 141 of the paper feed tray 103, there are provided a half-moon roller (paper feeding roller 143) which feeds sheets of paper 142 one by one from the paper loading section 141, and a separation pad 144 which faces the paper feeding roller 143 and is formed of a material with a large friction coefficient. This separation pad 144 is biased toward the paper feeding roller 143 side.

As a conveyance section configured to convey the sheet of paper 142, which has been fed from this paper feeding section, underneath the recording head 134, there are provided a conveyance belt 151 configured to convey the sheet of paper 142 by means of electrostatic adsorption; a counter roller 152 configured to convey the sheet of paper 142, which is fed from the paper feeding section via a guide 145, while the sheet of paper is sandwiched between the counter roller and the conveyance belt 151; a conveyance guide 153 configured to make the sheet of paper 142, which is fed upward in the substantially vertical direction, change its direction by approximately 90° and thusly run along the conveyance belt 151; and an end pressurizing roller 155 biased toward the conveyance belt 151 side by a pressing member 154.

Also, there is provided a charging roller 156 as a charging unit configured to charge a surface of the conveyance belt 151. The conveyance belt 151 is an endless belt; and is capable of rotating around

in a belt conveyance direction by stretching between a conveyance roller 157 and a tension roller 158. The conveyance belt 151 includes, for example, a surface layer serving as a paper adsorbing surface, which is formed of a resinous material such as an ethylene-tetrafluoroethylene copolymer (ETFE) having a thickness of approximately 40 μm for which resistance control has not been conducted; and a back layer (intermediate resistance layer, ground layer) which is formed of the same material as the surface layer, and for which resistance control has been conducted using carbon. On the back of the conveyance belt 151, a guide member 161 is placed correspondingly to a region where printing is carried out by the recording head 134.

Additionally, as a paper discharge section configured to discharge the sheet of paper 142 on which an image has been recorded by the recording head 134, there are provided a separation claw 171 configured to separate the sheet of paper 142 from the conveyance belt 151, a paper discharge roller 172, and a paper discharge roller 173, with the paper discharge tray 103 being placed below the paper discharge roller 172.

A double-sided paper feeding unit 181 is detachably mounted on a rear surface portion of the device main body 101. The double-sided paper feeding unit 181 takes in the sheet of paper 142 returned by rotation of the conveyance belt 151 in the opposite direction and reverses it, then refeeds it between the counter roller 152 and the conveyance belt 151. Additionally, a manual paper feeding section 182 is provided on an upper surface of the double-sided paper feeding unit 181.

In the inkjet recording device, the sheets of paper 142 are fed one

by one from the paper feeding section, and the sheets of paper 142 fed upward in the substantially vertical direction is guided by the guide 145 and conveyed with being sandwiched between the conveyance belt 151 and the counter roller 152. Further, an end of the sheet of paper is guided by the conveyance guide 153 and pressed onto the conveyance belt 151 by the end pressurizing roller 155, so that the conveyance direction of the sheet of paper is changed by approximately 90°. On this occasion, the conveyance belt 151 is charged by the charging roller 156, and the sheet of paper 142 is electrostatically adsorbed onto the conveyance belt 151 and thusly conveyed. Here, by driving the recording head 134 according to an image signal while moving the carriage 133, ink droplets are ejected onto the sheet of paper 142 having stopped so as to perform recording for one line. Thereafter, the sheet of paper 142 is conveyed by a predetermined distance, and then recording for the next line is carried out.

On receipt of a recording completion signal or a signal indicating that a rear end of the sheet of paper 142 has reached a recording region, recording operation is finished, and the sheet of paper 142 is discharged onto the paper discharge tray 103. Once an amount of the ink remaining in the sub-tanks 135 has been detected as too small, a required amount of the ink is supplied from the ink cartridge 200 into the sub-tanks 135.

As for the inkjet recording device, when the ink in the ink cartridge 200 has been used up, it is possible to replace only the ink bag inside the ink cartridge by dismantling a housing of the ink cartridge 200.

Also, even when the ink cartridge 200 is vertically mounted and employs a front-loading configuration, the ink can be supplied stably.

Therefore, even when the device main body 101 is installed with little space over it, for example when it is stored in a rack or when an object is placed over the device main body 101, the ink cartridge 200 can be easily replaced.

Note that, a serial (shuttle) type inkjet recording device in which the carriage is used for scanning and to which the present invention is applied is described above, but the present invention can be also applied to a line type inkjet recording device equipped with a line-type head.

The inkjet recording device of the present invention can be applied in various recording by the inkjet recording system, and can be particularly suitably applied to an inkjet recording printer, a facsimile, a photocopier, and a multifunction printer (printer-fax-copier).

(Ink recorded matter)

An ink recorded matter of the present invention includes an image recorded on a recording medium with an ink of the present invention. The ink recorded matter of the present invention has high image quality, is excellent in stability over time, and can be suitably used in various applications, for example, as material on which characters or images are recorded.

The recording medium is not particularly limited as long as it is a recording medium on which an ink of the present invention is impacted to thereby form an image. However, preferable is plain paper defined as follows.

That is, an ink of the present invention is preferably used for paper from which a Ca ion is eluted in an amount of 1.0×10^{-4} [g/g] to 5.0×10^{-4} [g/g]. When the amount is 1.0×10^{-4} [g/g] or more, an effect of increasing image density is improved due to aggregation reaction with a pigment dispersing agent. When the amount is 5.0×10^{-4} [g/g] or less, the ink is not prevented from being penetrated into paper, so that drying property of the ink, scratch resistance, and marker resistance are improved.

The amount of the Ca ion eluted from paper can be calculated according to, for example, the following method.

Specifically, a sheet of paper is cut into pieces of paper of 2.5 cm (±0.5 cm) × 3.5 cm (±0.5 cm). The resultant pieces of paper are filtered through a 0.8 μm cellulose acetate filter (manufactured by Toyo Roshi Kaisha, Ltd.) with highly pure water to thereby remove a contaminant such as paper powder. Then, the pieces of paper are immersed in highly pure water to produce an immersion liquid, and quantified for a Ca ion contained in the immersion liquid with an ICP emission spectrophotometer to thereby obtain a Ca ion concentration [ppm]. The resultant Ca ion concentration [ppm] is multiplied by 200 g, which is a weight of the highly pure water, and divided by 16 g, which is a weight of the pieces of paper to be immersed, to thereby calculate the amount of the Ca ion [g/g].

Examples of the plain paper include MYPAPER (manufactured by Ricoh Company, Ltd., amount of Ca ion: 4.3×10^{-4} [g/g]) and XEROX 4024 (manufactured by Fuji Xerox Co., Ltd., amount of Ca ion: 1.7×10^{-4}

[g/gl]).

In addition to the plain paper, for example, coated paper for printing, glossy paper, and special paper may be used. These papers contain calcium carbonate, talc, kaolin, or aluminium sulfate (sulfate band). Accordingly, at a time when an ink of the present invention is impacted onto these papers, polyvalent metal ions, in particular, divalent or trivalent metal ions are eluted such as calcium, magnesium, or aluminium. That is, an ink of the present invention is reacted with the polyvalent metal ions to thereby cause aggregation of a pigment, which achieves high image density.

Many of loading materials, sizing agents, or fixing agents contained in the plain paper are water-insoluble metal salts. Only a small amount of water-soluble metal salt is contained, if any. Therefore, a smaller amount of polyvalent metal ion is eluted than paper of which surface is processed with a water-soluble polyvalent metal salt. This is why the effect of increasing image density could not be achieved in conventional technology.

In contrast, in the present invention, high image density can be achieved even in paper from which only a small amount of polyvalent metal ion is eluted (e.g., plain paper) as well as in the above-described processed paper.

Examples

The present invention will be described hereinafter in more detail with reference to Examples and Comparative Examples, but the present

invention is not limited to Examples. Note that, "part(s)" and "%" in Examples are on a mass basis.

<Synthesis of Copolymers 1 to 25>

Copolymers 1 to 25 were synthesized as follows according to materials and contents described in lines of Synthetic Examples 1 to 25 in Table 1-1. Numerical values described in a column of content in Table 1-1 denote "parts by mass". Note that, styrene and methacrylic acid described in columns of Formulae (5) and (6) in Synthetic Examples 23 to 25 are different from monomers represented by Formulae (5) and (6). Additionally, numerical values described in parentheses in a column of content of Formula (5) denote content of styrene.

Abbreviations of materials have the following meanings.

PHOSMER M: Acid phosphooxyethyl methacrylate (manufactured by Uni-Chemical Co., Ltd.) = a compound represented by (Formula 5-1)

DAAM: Diacetone acrylamide = a compound represented by (Formula 6-1)

P-1A: Acid phosphooxyethyl acrylate (manufactured by Kyoeisha Chemical Co.,Ltd.)

PHOSMER PE: Acid phosphooxypolyoxy ethylene glycol monomethacrylate (manufactured by Uni-Chemical Co., Ltd.)

PHOSMER PP: Acid phosphooxypolyoxy propylene glycol monomethacrylate (manufactured by Uni-Chemical Co., Ltd.)

DMEA: Dimethyl ethanolamine

Note that, mass average molecular weights of Copolymers 1 to 25

described in Table were measured as follows.

The mass average molecular weights were measured by GPC method by means of a thermostat bath for column (CTO-20A, manufactured by Shimadzu Corporation), a detector (RID-10A, manufactured by Shimadzu Corporation), a pump for eluent flow channel (LC-20AD, manufactured by Shimadzu Corporation), a degasser (DGU-20A, manufactured by Shimadzu Corporation), and an autosampler (SIL-20A, manufactured by Shimadzu Corporation). As for the column, the following were connected with each other: Aqueous SEC column TSKgelG3000PWXL (exclusion limit molecular weight: 2×10^5); TSKgelG5000PWXL (exclusion limit molecular weight: 2.5×10^6); and TSKgelG6000PWXL (exclusion limit molecular weight: 5×10^7) (all manufactured by Tosoh Corporation). A measurement sample was adjusted to a concentration of 2 g/100 mL with the use of an eluent. As for the eluent, an aqueous solution containing 0.5 mol/L of acetic acid and 0.5 mol/L of sodium acetate was used. A temperature of the column was 40°C, and the flow rate was 1.0 mL/min. A calibration curve was generated using, as standard samples, 9 polyethylene glycols having molecular weights of 1,065, 5,050, 24,000, 50,000, 107,000, 140,000, 250,000, 540,000, and 920,000. Based on the calibration curve, the mass average molecular weights were calculated.

(Synthetic Example 1)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was

charged with a mixed solution produced by dissolving 15 parts of PHOSMER M and 85 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 1.

(Synthetic Example 2)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 5 parts of PHOSMER M and 95 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 2.

(Synthetic Example 3)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of PHOSMER M, 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 3.

(Synthetic Example 4)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 55 parts of PHOSMER M and 45 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 4.

(Synthetic Example 5)

A 1 L five-necked flask equipped with a reflux condenser, a

thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 250 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 65 parts of PHOSMER M and 35 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 5.

(Synthetic Example 6)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 55 parts of PHOSMER M and 45 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the

neutralization rate of 100%, to thereby obtain Copolymer 6.

(Synthetic Example 7)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 55 parts of PHOSMER M, 45 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 7.

(Synthetic Example 8)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 65 parts of PHOSMER M, 35 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 8.

(Synthetic Example 9)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 55 parts of PHOSMER M, 45 parts of DAAM, and 200 parts of ethanol.

The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 9.

(Synthetic Example 10)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 15 parts of PHOSMER M, 85 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 10.

(Synthetic Example 11)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 5 parts of PHOSMER M, 95 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization

rate of 100%, to thereby obtain Copolymer 11.

(Synthetic Example 12)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 15 parts of PHOSMER M, 85 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 12.

(Synthetic Example 13)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 20 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M and 85 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with sodium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 13.

(Synthetic Example 14)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M and 85 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with lithium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 14.

(Synthetic Example 15)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 5 parts of PHOSMER M and 95 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 3 hours while keeping a temperature at

70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 15.

(Synthetic Example 16)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 65 parts of PHOSMER M, 35 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 16.

(Synthetic Example 17)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of P-1A, 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 17.

(Synthetic Example 18)

A 1 L four-necked flask equipped with a reflux condenser, a

thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of PHOSMER PE, 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 18.

(Synthetic Example 19)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of PHOSMER PP, 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 19.

(Synthetic Example 20)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of the monomer represented by (Formula 3-5), 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours

while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 20.

(Synthetic Example 21)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 30 parts of PHOSMER M, 70 parts of DAAM, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give 50% of the neutralization rate, to thereby obtain Copolymer 21.

(Synthetic Example 22)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M and 85 parts of DAAM into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at

70°C. After termination of the reaction, the resultant reaction product was neutralized with dimethylethanolamine so as to give the neutralization rate of 100%, to thereby obtain Copolymer 22.

(Synthetic Example 23) Comparative Synthetic Example 1

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 15 parts of styrene, 85 parts of DAAM, and 100 parts of ethanol. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 23.

(Synthetic Example 24) Comparative Synthetic Example 2

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Then, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M and 85 parts of methacrylic acid into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product

was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 24.

(Synthetic Example 25) Comparative Synthetic Example 3

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 15 parts of styrene, 85 parts of methacrylic acid, and 100 parts of ethanol. The flask was heated under a nitrogen stream, and 0.2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer 25.

Tables 1-1

		Monomer		Content
		(Formula 5)	(Formula 6)	(Formula 5)
Syn. Ex. 1	Copolymer 1	PHOSMER M	DAAM	15
Syn. Ex. 2	Copolymer 2	PHOSMER M	DAAM	5
Syn. Ex. 3	Copolymer 3	PHOSMER M	DAAM	30
Syn. Ex. 4	Copolymer 4	PHOSMER M	DAAM	55
Syn. Ex. 5	Copolymer 5	PHOSMER M	DAAM	65
Syn. Ex. 6	Copolymer 6	PHOSMER M	DAAM	55
Syn. Ex. 7	Copolymer 7	PHOSMER M	DAAM	55
Syn. Ex. 8	Copolymer 8	PHOSMER M	DAAM	65
Syn. Ex. 9	Copolymer 9	PHOSMER M	DAAM	55
Syn. Ex. 10	Copolymer 10	PHOSMER M	DAAM	15
Syn. Ex. 11	Copolymer 11	PHOSMER M	DAAM	5
Syn. Ex. 12	Copolymer 12	PHOSMER M	DAAM	15
Syn. Ex. 13	Copolymer 13	PHOSMER M	DAAM	15
Syn. Ex. 14	Copolymer 14	PHOSMER M	DAAM	15
Syn. Ex. 15	Copolymer 15	PHOSMER M	DAAM	5
Syn. Ex. 16	Copolymer 16	PHOSMER M	DAAM	65
Syn. Ex. 17	Copolymer 17	P-1A	DAAM	30
Syn. Ex. 18	Copolymer 18	PHOSMER PE	DAAM	30
Syn. Ex. 19	Copolymer 19	PHOSMER PP	DAAM	30
Syn. Ex. 20	Copolymer 20	(Formula 5-5)	DAAM	30
Syn. Ex. 21	Copolymer 21	PHOSMER M	DAAM	30
Syn. Ex. 22	Copolymer 22	PHOSMER M	DAAM	15
Syn. Ex. 23	Copolymer 23	Styrene	DAAM	(15)
Syn. Ex. 24	Copolymer 24	PHOSMER M	Methacrylic acid	15
Syn. Ex. 25	Copolymer 25	Styrene	Methacrylic acid	(15)

* In Table 1-1, (Formula 5) and (Formula 6) denote monomers represented by the General Formulae (5) and (6), respectively.

Table 1-2

	Mass average molecular weight	Counter ion	Neutralization rate (%)
Syn. Ex. 1	3,000	K	100
Syn. Ex. 2	7,000	K	100
Syn. Ex. 3	30,000	K	100
Syn. Ex. 4	3,000	K	100
Syn. Ex. 5	7,000	K	100
Syn. Ex. 6	7,000	K	100
Syn. Ex. 7	60,000	K	100
Syn. Ex. 8	45,000	K	100
Syn. Ex. 9	45,000	K	100
Syn. Ex. 10	60,000	K	100
Syn. Ex. 11	45,000	K	100
Syn. Ex. 12	45,000	K	100
Syn. Ex. 13	7,000	Na	100
Syn. Ex. 14	7,000	Li	100
Syn. Ex. 15	3,000	K	100
Syn. Ex. 16	60,000	K	100
Syn. Ex. 17	30,000	K	100
Syn. Ex. 18	30,000	K	100
Syn. Ex. 19	30,000	K	100
Syn. Ex. 20	30,000	K	100
Syn. Ex. 21	30,000	K/H	50
Syn. Ex. 22	7,000	DMEA	100
Syn. Ex. 23	7,000	K	100
Syn. Ex. 24	7,000	K	100
Syn. Ex. 25	10,000	K	100

<Preparation of Pigment dispersions 1 to 30>

Firstly, each of Copolymers, a pigment, and pure water were pre-mixed together using materials described in each of columns of Pigment dispersions 1 to 30 in Tables 2-1 to 3-2, to thereby produce mixed slurry. Then, the mixed slurry was subjected to circulation dispersion with a disc-type media mill (MODEL DMR, manufactured by Ashizawa Finetech Ltd.) and 0.05 mm zirconia beads (packing rate: 55%) at a circumferential speed of 10 m/s and a liquid temperature of 10°C for 3 min, followed by centrifugation with a centrifuge (MODEL-7700, manufactured by KUBOTA CORPORATION) to remove coarse particles,

to thereby obtain Pigment dispersion. Numerical values described in Tables 2-1 to 3-2 denote blending ratios (parts by weight).

Note that, each of Copolymers 1 to 25 was dried to remove a solvent therein, and then, the resultant solid matter was dissolved into water so as to give a 20% aqueous solution, which was used as Copolymer. Materials other than Copolymers will be described in detail.

Carbon black (NIPEX160, manufactured by Degussa AG, BET specific surface area: 150 m^2/g, average primary particle diameter: 20 nm, pH 4.0, DBP oil absorption amount: 620 g/100 g)

Pigment Blue 15:3 (CHROMOFINE BLUE-A-220JC, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

Pigment Red 122 (TONER MAGENTA EO02, manufactured by Clariant International Ltd.)

Pigment Yellow 74 (FAST YELLOW 531, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

Table 2-1

	Pigment dispersion									
	1	2	3	4	5	6	7	8	9	10
Copolymer 1							20			
Copolymer 2								20		
Copolymer 3	10	20	80	20	20	20				
Copolymer 4									20	
Copolymer 5										20
Copolymer 6										
Copolymer 7										
Copolymer 8										
Copolymer 9										
Carbon black	16	16	16				16	16	16	16
Pigment Blue 15:3				16						
Pigment Red 122					16					
Pigment Yellow 74						16				
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100

Table 2-2

	Pigment dispersion			
	11	12	13	14
Copolymer 1				
Copolymer 2				
Copolymer 3				
Copolymer 4				
Copolymer 5				
Copolymer 6	20			
Copolymer 7		20		
Copolymer 8			20	
Copolymer 9				20
Carbon black	16	16	16	16
Pigment Blue 15:3				
Pigment Red 122				
Pigment Yellow 74				
Pure water	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100

Table 3-1

	Pigment dispersion									
	15	16	17	18	19	20	21	22	23	24
Copolymer 10	20									
Copolymer 11		20								
Copolymer 12			20							
Copolymer 13				20						
Copolymer 14					20					
Copolymer 15						20				
Copolymer 16							20			
Copolymer 17								20		
Copolymer 18									20	
Copolymer 19										20
Copolymer 20										
Copolymer 21										
Copolymer 22										
Copolymer 23										
Copolymer 24										
Copolymer 25										
Carbon black	16	16	16	16	16	16	16	16	16	16
Pigment Blue 15:3										
Pigment Red 122										
Pigment Yellow 74										
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100

Table 3-2

	Pigment dispersion					
	25	26	27	28	29	30
Copolymer 10						
Copolymer 11						
Copolymer 12						
Copolymer 13						
Copolymer 14						
Copolymer 15						
Copolymer 16						
Copolymer 17						
Copolymer 18						
Copolymer 19						
Copolymer 20	20					
Copolymer 21		20				
Copolymer 22			20			
Copolymer 23				20		
Copolymer 24					20	
Copolymer 25						20
Carbon black	16	16	16	16	16	16
Pigment Blue 15:3						
Pigment Red 122						
Pigment Yellow 74						
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100

[Examples 1 to 29 and Comparative Examples 1 to 3]

<Production of ink>

Materials described in each of columns of Examples 1 to 29 and Comparative Examples 1 to 3 in Tables 4-1 to 5-2 were mixed and stirred for 1 hour to thereby produce a uniform dispersion. The resultant dispersion was subjected to pressure filtration with a polyvinylidene fluoride membrane filter having an average pore diameter of 5.0 μm to remove coarse particles and contaminants, to thereby obtain an ink.

Note that, numerical values described in Tables denote % by mass.

Table 4-1

	Material name	Copolymer	Example							
			1	2	3	4	5	6	7	8
Pigment dispersion	Pigment dispersion 1	Copolymer 3	50							
	Pigment dispersion 2	Copolymer 3		50	50	50				
	Pigment dispersion 3	Copolymer 3					50			
	Pigment dispersion 4	Copolymer 3						30		
	Pigment dispersion 5	Copolymer 3							30	
	Pigment dispersion 6	Copolymer 3								50
	Pigment dispersion 7	Copolymer 1								
	Pigment dispersion 8	Copolymer 2								
	Pigment dispersion 9	Copolymer 4								
	Pigment dispersion 10	Copolymer 5								
	Pigment dispersion 11	Copolymer 6								
	Pigment dispersion 12	Copolymer 7								
	Pigment dispersion 13	Copolymer 8								
Water-soluble Organic solvent	Glycerin		10	10		20	10	10	10	10
	1,3-Butanediol		20	20	30		20	20	20	20
	Trimethylol propane					5				
	2-Pyrroridone					5				
Pure water			Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total			100	100	100	100	100	100	100	100

Table 4-2

	Material name	Copolymer	Example						
			9	10	11	12	13	14	15
Pigment dispersion	Pigment dispersion 1	Copolymer 3							
	Pigment dispersion 2	Copolymer 3							
	Pigment dispersion 3	Copolymer 3							
	Pigment dispersion 4	Copolymer 3							
	Pigment dispersion 5	Copolymer 3							
	Pigment dispersion 6	Copolymer 3							
	Pigment dispersion 7	Copolymer 1	50						
	Pigment dispersion 8	Copolymer 2		50					
	Pigment dispersion 9	Copolymer 4			50				
	Pigment dispersion 10	Copolymer 5				50			
	Pigment dispersion 11	Copolymer 6					50		
	Pigment dispersion 12	Copolymer 7						50	
	Pigment dispersion 13	Copolymer 8							50
Water-soluble Organic solvent	Glycerin		10	10	10	10	10	10	10
	1,3-Butanediol		20	20	20	20	20	20	20
	Trimethylol propane								
	2-Pyrroridone								
Pure water			Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total			100	100	100	100	100	100	100

Table 5-1

	Material name	Copolymer	Example								
			16	17	18	19	20	21	22	23	24
Pigment dispersion	Pigment dispersion 14	Copolymer 9	50								
	Pigment dispersion 15	Copolymer 10		50							
	Pigment dispersion 16	Copolymer 11			50						
	Pigment dispersion 17	Copolymer 12				50					
	Pigment dispersion 18	Copolymer 13					50				
	Pigment dispersion 19	Copolymer 14						50			
	Pigment dispersion 20	Copolymer 15							50		
	Pigment dispersion 21	Copolymer 16								50	
	Pigment dispersion 22	Copolymer 17									50
	Pigment dispersion 23	Copolymer 18									
	Pigment dispersion 24	Copolymer 19									
	Pigment dispersion 25	Copolymer 20									
	Pigment dispersion 26	Copolymer 21									
	Pigment dispersion 27	Copolymer 22									
	Pigment dispersion 28	Copolymer 23									
	Pigment dispersion 29	Copolymer 24									
	Pigment dispersion 30	Copolymer 25									
Water-soluble Organic solvent	Glycerin		10	10	10	10	10	10	10	10	10
	1,3-Butanediol		20	20	20	20	20	20	20	20	20
	Trimethylol propane										
	2-Pyrroridone										
Pure water			Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total			100	100	100	100	100	100	100	100	100

Table 5-2

	Material name	Copolymer	Example					Comp. Ex.		
			25	26	27	28	29	1	2	3
Pigment dispersion	Pigment dispersion 14	Copolymer 9								
	Pigment dispersion 15	Copolymer 10								
	Pigment dispersion 16	Copolymer 11								
	Pigment dispersion 17	Copolymer 12								
	Pigment dispersion 18	Copolymer 13								
	Pigment dispersion 19	Copolymer 14								
	Pigment dispersion 20	Copolymer 15								
	Pigment dispersion 21	Copolymer 16								
	Pigment dispersion 22	Copolymer 17								
	Pigment dispersion 23	Copolymer 18	50							
	Pigment dispersion 24	Copolymer 19		50						
	Pigment dispersion 25	Copolymer 20			50					
	Pigment dispersion 26	Copolymer 21				50				
	Pigment dispersion 27	Copolymer 22					50			
	Pigment dispersion 28	Copolymer 23						50		
	Pigment dispersion 29	Copolymer 24							50	
	Pigment dispersion 30	Copolymer 25								50
Water-soluble Organic solvent	Glycerin		10	10	10	10	10	10	10	10
	1,3-Butanediol		20	20	20	20	20	20	20	20
	Trimethylol propane									
	2-Pyrroridone									
Pure water			Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total			100	100	100	100	100	100	100	100

The Pigment dispersions 1 to 30, and inks of Examples 1 to 29, and Comparative Examples 1 to 3 were evaluated for viscosity and

storage stability. Additionally, the inks also evaluated for image density.

<Storage stability>

The Pigment dispersions and inks were measured for viscosity. Storage stability was evaluated by using the viscosity as an index.

The viscosity was measured at 25°C by means of a viscometer (RE500L, manufactured by Toki Sangyo Co., Ltd.) equipped with a rotor of which rotation speed had been adjusted in accordance with a sample. Results are shown in Tables 6-1 and 6-2.

Initial viscosities after production of the Pigment dispersions and inks also were measured, which was evaluated according to the following criteria. Then, the Pigment dispersions and inks were sealed into polyethylene containers and stored at 70°C for 1 week. Thereafter, the viscosities of the Pigment dispersions and inks were measured again. Storage stability was evaluated according to the following criteria based on a rate of change in viscosity after storage relative to the initial viscosity. Evaluation results are shown in Tables 6-1 and 6-2.

[Evaluation criteria of pigment dispersion]

Initial viscosity

A: Initial viscosity was less than 7 mPa·s.

B: Initial viscosity was 7 mPa·s or more but less than 20 mPa·s.

C: Initial viscosity was 20 mPa·s or more.

Storage stability

A: Rate of change in viscosity after storage was less than 2%.

B: Rate of change in viscosity after storage was 2% or more but less

than 5%.

C: Rate of change in viscosity after storage was 5% or more but less than 10%.

D: Rate of change in viscosity after storage was 10% or more but less than 50%.

E: Rate of change in viscosity after storage was 50% or more.

[Evaluation criteria of ink]

A: Initial viscosity was less than 9 mPa·s.

B: Initial viscosity was 9 mPa·s or more but less than 20 mPa·s.

C: Initial viscosity was 20 mPa·s or more.

Storage stability

A: Rate of change in viscosity after storage was less than 2%.

B: Rate of change in viscosity after storage was 2% or more but less than 5%.

C: Rate of change in viscosity after storage was 5% or more but less than 10%.

D: Rate of change in viscosity after storage was 10% or more but less than 50%.

E: Rate of change in viscosity after storage was 50% or more.

<Image density>

An inkjet printer (IPSIO GX3000, manufactured by Ricoh Company, Ltd.) was set by varying a driving voltage of a piezo element to unify an amount of an ink to be ejected, so that the same amount of the ink would be deposited on each recording medium.

A chart including a 64-point general symbol according to JIS X

0208 (1997), 2223 of black and each color produced using Microsoft Word 2003 was printed on a sheet of paper (MYPAPER, manufactured by Ricoh Company, Ltd., wood free paper having a basis weight of 69.6 g/m^2, a sizing degree of 23.2 second, and an air permeability of 21.0 second).

Then, the color in the general symbol according to JIS X 0208 (1997), 2223 was measured by X-Rite 938 (manufactured by X-Rite Inc.), and the image density of each of the measured colors was evaluated based on the following evaluation criteria. Here, a printing mode of the inkjet printer was set to "Plain Paper-High Speed." Note that, the general symbol according to JIS X 0208 (1997), 2223 is a square shaped symbol inside of which is painted out with an ink. Evaluation results are shown in Tables 6-1 and 6-2.

[Evaluation criteria]

A:	OD value	Black: 1.30 or more
		Yellow: 0.75 or more
		Magenta: 0.90 or more
		Cyan: 1.00 or more
B:	OD value	Black: 1.20 or more but less than 1.30
		Yellow: 0.70 or more but less than 0.75
		Magenta: 0.85 or more but less than 0.90
		Cyan: 0.90 or more but less than 1.00
C:	OD value	Black: 1.10 or more but less than 1.20
		Yellow: 0.65 or more but less than 0.70
		Magenta: 0.70 or more but less than 0.85
		Cyan: 0.80 or more but less than 0.90

D: OD value Black: 1.00 or more but less than 1.10

Yellow: 0.60 or more but less than 0.65

Magenta: 0.65 or more but less than 0.70

Cyan: 0.70 or more but less than 0.80

E: OD value Black: less than 1.00

Yellow: less than 0.60

Magenta: less than 0.65

Cyan: less than 0.70

Table 6-1

	Copolymer	*1	Mw	Pigment dispersion		Ink		Image density
				Initial viscosity	Storage stability	Initial viscosity	Storage stability	
Ex. 1	Copolymer 3	30	30,000	A	C	B	C	B
Ex. 2	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 3	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 4	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 5	Copolymer 3	30	30,000	B	B	B	C	B
Ex. 6	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 7	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 8	Copolymer 3	30	30,000	A	B	B	C	B
Ex. 9	Copolymer 1	15	3,000	A	B	B	C	C
Ex. 10	Copolymer 2	5	7,000	A	B	B	C	C
Ex. 11	Copolymer 4	55	3,000	A	B	B	C	C
Ex. 12	Copolymer 5	65	7,000	B	B	B	C	B
Ex. 13	Copolymer 6	55	7,000	A	B	B	C	B
Ex. 14	Copolymer 7	55	60,000	B	B	B	C	B
Ex. 15	Copolymer 8	65	45,000	A	C	B	C	B
Ex. 16	Copolymer 9	55	45,000	A	B	B	C	B
Ex. 17	Copolymer 10	15	60,000	A	C	B	C	B
Ex. 18	Copolymer 11	5	45,000	A	B	B	C	C
Ex. 19	Copolymer 12	15	45,000	A	B	B	C	B
Ex. 20	Copolymer 13	15	7,000	B	B	A	B	B
Ex. 21	Copolymer 14	15	7,000	B	B	A	B	B
Ex. 22	Copolymer 15	5	3,000	B	C	B	C	C
Ex. 23	Copolymer 16	65	60,000	A	B	B	C	B

Table 6-2

	Copolymer	*1	Mw	Pigment dispersion		Ink		Image density
				Initial viscosity	Storage stability	Initial viscosity	Storage stability	
Ex. 24	Copolymer 17	30	30,000	A	B	B	C	B
Ex. 25	Copolymer 18	30	30,000	A	B	B	C	B
Ex. 26	Copolymer 19	30	30,000	A	B	B	C	B
Ex. 27	Copolymer 20	30	30,000	A	B	B	C	B
Ex. 28	Copolymer 21	30	30,000	A	B	B	C	B
Ex. 29	Copolymer 22	30	30,000	B	B	A	B	B
Comp. Ex. 1	Copolymer 23	(15)	7,000	B	C	B	C	E
Comp. Ex. 2	Copolymer 24	15	7,000	C	E	C	E	C
Comp. Ex. 3	Copolymer 25	(15)	10,000	B	E	B	E	E

In Tables 6-1 and 6-2, *1 denotes "(Formula 1) structural unit content (%)" which means a percentage of the structural unit represented by the General Formula (1) in the phosphate group-containing copolymer, and Mw denotes the mass average molecular weight.

As can be seen from Tables 6-1 and 6-2, when comparing Examples 1 to 29 with Comparative Examples 1 to 3, inks which contain a phosphate group-containing copolymer of the present invention are more excellent in both of image density and storage stability.

Additionally, it can be seen that Examples in which the structural unit represented by the General Formula (1) is contained in a percentage of 10% by mass to 60% by mass are more excellent in both of image density and storage stability than other Examples.

It can be seen that Examples in which the copolymer has a

molecular weight of 5,000 to 50,000 are more excellent in both of image density and storage stability than other Examples.

<Synthesis of Copolymers A1 to A45>

Copolymers A1 to A45 were synthesized as follows according to materials and contents described in lines of Synthetic Examples A1 to A45 in Tables A1-1 and A1-2. Numerical values described in columns of content in Table A1-2 denote "parts by mass". Additionally, numerical values described in parentheses in columns of content of F (5) or F (6) in Synthetic Examples A40 to A42 denote content of styrene or methacrylic acid. Abbreviations of materials have the following meanings.

PHOSMER M: Acid phosphooxyethyl methacrylate (manufactured by Uni-Chemical Co., Ltd.) = a compound represented by (Formula 5-1)

DAAM: Diacetone acrylamide = a compound represented by (Formula 6-1)

DAMAM: Diacetone methacrylamide = a compound represented by (Formula 6-2)

StA: Stearyl acrylate = a compound represented by (Formula 7-1)

StMA: Stearyl methacrylate = a compound represented by (Formula 7-2)

BzA: Benzyl acrylate = a compound represented by (Formula 8-1)

BzMA: Benzyl methacrylate = a compound represented by (Formula 8-2)

P-1A: Acid phosphooxyethyl acrylate (manufactured by Kyoeisha Chemical Co.,Ltd.)

PHOSMER PE: Acid phosphooxypolyoxy ethylene glycol monomethacrylate (manufactured by Uni-Chemical Co., Ltd.)

PHOSMER PP: Acid phosphooxypolyoxy propylene glycol monomethacrylate (manufactured by Uni-Chemical Co., Ltd.)

DMEA: Dimethyl ethanolamine

Note that, mass average molecular weights of Copolymers A1 to A45 described in Tables A1-1 and A1-2 were measured as follows.

The mass average molecular weights were measured by GPC method by means of a thermostat bath for column (CTO-20A, manufactured by Shimadzu Corporation), a detector (RID-10A, manufactured by Shimadzu Corporation), a pump for eluent flow channel (LC-20AD, manufactured by Shimadzu Corporation), a degasser (DGU-20A, manufactured by Shimadzu Corporation), and an autosampler (SIL-20A, manufactured by Shimadzu Corporation). As for the column, the following were connected with each other: Aqueous SEC column TSKgelG3000PWXL (exclusion limit molecular weight: 2×10^5); TSKgelG5000PWXL (exclusion limit molecular weight: 2.5×10^6); and TSKgelG6000PWXL (exclusion limit molecular weight: 5×10^7) (all manufactured by Tosoh Corporation). A measurement sample was adjusted to a concentration of 2 g/100 mL with the use of an eluent. As for the eluent, an aqueous solution containing 0.5 mol/L of acetic acid and 0.5 mol/L of sodium acetate was used. A temperature of the column was 40°C, and the flow rate was 1.0 mL/min. A calibration curve was generated using, as standard samples, 9 polyethylene glycols having molecular weights of 1,065, 5,050, 24,000, 50,000, 107,000, 140,000,

250,000, 540,000, and 920,000. Based on the calibration curve, the mass average molecular weights were calculated.

(Synthetic Example A1)

A 1 L four-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, and a stirrer was charged with 15 parts of PHOSMER M, 35 parts of DAAM, 50 parts of StA, and 500 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A1.

(Synthetic Example A2)

A 1 L five-necked flask equipped with a reflux condenser, a thermometer, a pipe for nitrogen purge, a dropping funnel, and a stirrer was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 5 parts of PHOSMER M, 35 parts of DAAM, and 60 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar

amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A2.

(Synthetic Example A3)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER M, 10 parts of DAAM, 60 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A3.

(Synthetic Example A4)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 55 parts of PHOSMER M, 35 parts of DAAM, 10 parts of StA and 500 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A4.

(Synthetic Example A5)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the

dropping funnel was charged with a mixed solution produced by dissolving 65 parts of PHOSMER M, 20 parts of DAAM, and 15 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A5.

(Synthetic Example A6)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 30 parts of PHOSMER M, 5 parts of DAAM, and 65 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer

so as to give the neutralization rate of 100%, to thereby obtain Copolymer A6.

(Synthetic Example A7)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 55 parts of PHOSMER M, 35 parts of DAAM, 10 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A7.

(Synthetic Example A8)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 65 parts of PHOSMER M, 20 parts of DAAM, 15 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A8.

(Synthetic Example A9)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 55 parts of PHOSMER M, 35 parts of

DAAM, 10 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A9.

(Synthetic Example A10)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of PHOSMER M, 35 parts of DAAM, 50 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A10.

(Synthetic Example A11)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 5 parts of PHOSMER M, 35 parts of DAAM, 60 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was

neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A11.

(Synthetic Example A12)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of PHOSMER M, 35 parts of DAAM, 50 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A12.

(Synthetic Example A13)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with sodium hydroxide in a molar amount equivalent to an acid monomer so as to give

the neutralization rate of 100%, to thereby obtain Copolymer A13.

(Synthetic Example A14)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with lithium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A14.

(Synthetic Example A15)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 5 parts of PHOSMER M, 35 parts of DAAM, 60 parts of StA and 500 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A15.

(Synthetic Example A16)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 65 parts of PHOSMER M, 20 parts of DAAM, 15 parts of StA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A16.

(Synthetic Example A17)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of P-1A, 35 parts of DAAM, and 50 parts of StA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A17.

(Synthetic Example A18)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A18.

(Synthetic Example A19)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 5 parts of PHOSMER M, 35 parts of DAAM, and 60 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.2 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours

while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A19.

(Synthetic Example A20)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A20.

(Synthetic Example A21)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 55 parts of PHOSMER M, 35 parts of DAAM, and 10 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask

was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A21.

(Synthetic Example A22)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 65 parts of PHOSMER M, 20 parts of DAAM, and 15 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A22.

(Synthetic Example A23)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 55 parts of PHOSMER M, 35 parts of DAAM, and 10 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A23.

(Synthetic Example A24)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 55 parts of PHOSMER M, 35 parts of DAAM, 10 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A24.

(Synthetic Example A25)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 65 parts of PHOSMER M, 20 parts of DAAM, 15 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A25.

(Synthetic Example A26)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 55 parts of PHOSMER M, 35 parts of DAAM, 10 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A26.

(Synthetic Example A27)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of PHOSMER M, 35 parts of DAAM, 50 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6

hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A27.

(Synthetic Example A28)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 5 parts of PHOSMER M, 35 parts of DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A28.

(Synthetic Example A29)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of PHOSMER M, 35 parts of DAAM, 50 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A29.

(Synthetic Example A30)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with sodium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A30.

(Synthetic Example A31)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with lithium

hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A31.

(Synthetic Example A32)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 5 parts of PHOSMER M, 35 parts of DAAM, and 60 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A32.

(Synthetic Example A33)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 65 parts of PHOSMER M, 20 parts of DAAM, 15 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 1 part of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium

hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A33.

(Synthetic Example A34)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of P-1A, 10 parts of DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A34.

(Synthetic Example A35)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER PE, 10 parts of DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A35.

(Synthetic Example A36)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER PP, 10 parts of

DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A36.

(Synthetic Example A37)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of (Formula 5-5), 10 parts of DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A37.

(Synthetic Example A38)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER M, 10 parts of DAAM, 60 parts of BzA and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium

hydroxide so as to give 50% of the neutralization rate, to thereby obtain Copolymer A38.

(Synthetic Example A39)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 35 parts of DAAM, and 50 parts of BzA into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. Then, the mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with dimethyl ethanolamine in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A39.

(Synthetic Example A40)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of styrene, 85 parts of DAAM, and 100 parts of ethanol. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give

the neutralization rate of 100%, to thereby obtain Copolymer A40.

(Synthetic Example A41)

A five-necked flask being the same as described in Synthetic Example A2 was charged with 200 parts of ethanol. Additionally, the dropping funnel was charged with a mixed solution produced by dissolving 15 parts of PHOSMER M, 85 parts of methacrylic acid into 50 parts of ethanol and uniformly mixing together. The flask was heated under a nitrogen stream, and 0.5 parts of a radical polymerization initiator was added thereto at 70°C. The mixed solution which had been charged in the dropping funnel was added dropwise to the flask for 2 hours, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide in a molar amount equivalent to an acid monomer so as to give the neutralization rate of 100%, to thereby obtain Copolymer A41.

(Synthetic Example A42)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 15 parts of styrene, 85 parts of methacrylic acid, and 100 parts of ethanol. The flask was heated under a nitrogen stream, and 0.2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A42.

(Synthetic Example A43)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER M, 10 parts of DAMAM, 60 parts of StA, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A43.

(Synthetic Example A44)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER M, 10 parts of DAAM, 60 parts of StA, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A44.

(Synthetic Example A45)

A four-necked flask being the same as described in Synthetic Example A1 was charged with 30 parts of PHOSMER M, 10 parts of DAAM, 60 parts of BzMA, and 200 parts of ethanol. The flask was heated under a nitrogen stream, and 2 parts of a radical polymerization

initiator was added thereto at 70°C, followed by allowing to react together for 6 hours while keeping a temperature at 70°C. After termination of the reaction, the resultant reaction product was neutralized with potassium hydroxide so as to give the neutralization rate of 100%, to thereby obtain Copolymer A45.

Table A1-1

		Monomer			
		(F 5)	(F 6)	(F 7)	(F 8)
Syn. Ex. A1	Copolymer A1	PHOSMER M	DAAM	StA	–
Syn. Ex. A2	Copolymer A2	PHOSMER M	DAAM	StA	–
Syn. Ex. A3	Copolymer A3	PHOSMER M	DAAM	StA	–
Syn. Ex. A4	Copolymer A4	PHOSMER M	DAAM	StA	–
Syn. Ex. A5	Copolymer A5	PHOSMER M	DAAM	StA	–
Syn. Ex. A6	Copolymer A6	PHOSMER M	DAAM	StA	–
Syn. Ex. A7	Copolymer A7	PHOSMER M	DAAM	StA	–
Syn. Ex. A8	Copolymer A8	PHOSMER M	DAAM	StA	–
Syn. Ex. A9	Copolymer A9	PHOSMER M	DAAM	StA	–
Syn. Ex. A10	Copolymer A10	PHOSMER M	DAAM	StA	–
Syn. Ex. A11	Copolymer A11	PHOSMER M	DAAM	StA	–
Syn. Ex. A12	Copolymer A12	PHOSMER M	DAAM	StA	–
Syn. Ex. A13	Copolymer A13	PHOSMER M	DAAM	StA	–
Syn. Ex. A14	Copolymer A14	PHOSMER M	DAAM	StA	–
Syn. Ex. A15	Copolymer A15	PHOSMER M	DAAM	StA	–
Syn. Ex. A16	Copolymer A16	PHOSMER M	DAAM	StA	–
Syn. Ex. A17	Copolymer A17	P-1A	DAAM	StA	–
Syn. Ex. A18	Copolymer A18	PHOSMER M	DAAM	–	BzA
Syn. Ex. A19	Copolymer A19	PHOSMER M	DAAM	–	BzA
Syn. Ex. A20	Copolymer A20	PHOSMER M	DAAM	–	BzA
Syn. Ex. A21	Copolymer A21	PHOSMER M	DAAM	–	BzA
Syn. Ex. A22	Copolymer A22	PHOSMER M	DAAM	–	BzA
Syn. Ex. A23	Copolymer A23	PHOSMER M	DAAM	–	BzA
Syn. Ex. A24	Copolymer A24	PHOSMER M	DAAM	–	BzA
Syn. Ex. A25	Copolymer A25	PHOSMER M	DAAM	–	BzA
Syn. Ex. A26	Copolymer A26	PHOSMER M	DAAM	–	BzA
Syn. Ex. A27	Copolymer A27	PHOSMER M	DAAM	–	BzA
Syn. Ex. A28	Copolymer A28	PHOSMER M	DAAM	–	BzA
Syn. Ex. A29	Copolymer A29	PHOSMER M	DAAM	–	BzA
Syn. Ex. A30	Copolymer A30	PHOSMER M	DAAM	–	BzA
Syn. Ex. A31	Copolymer A31	PHOSMER M	DAAM	–	BzA
Syn. Ex. A32	Copolymer A32	PHOSMER M	DAAM	–	BzA
Syn. Ex. A33	Copolymer A33	PHOSMER M	DAAM	–	BzA
Syn. Ex. A34	Copolymer A34	P-1A	DAAM	–	BzA
Syn. Ex. A35	Copolymer A35	PHOSMER PE	DAAM	–	BzA
Syn. Ex. A36	Copolymer A36	PHOSMER PP	DAAM	–	BzA
Syn. Ex. A37	Copolymer A37	(Formula 5-5)	DAAM	–	BzA
Syn. Ex. A38	Copolymer A38	PHOSMER M	DAAM	–	BzA
Syn. Ex. A39	Copolymer A39	PHOSMER M	DAAM	–	BzA
Syn. Ex. A40	Copolymer A40	Styrene	DAAM	–	–
Syn. Ex. A41	Copolymer A41	PHOSMER M	Methacrylic acid	–	–
Syn. Ex. A42	Copolymer A42	Styrene	Methacrylic acid	–	–
Syn. Ex. A43	Copolymer A43	PHOSMER M	DAMAM	StA	–
Syn. Ex. A44	Copolymer A44	PHOSMER M	DAAM	StMA	–
Syn. Ex. A45	Copolymer A45	PHOSMER M	DAAM	–	BzMA

Table A1-2

	Content				Mass average molecular weight	Counter ion	Neutralization rate (%)
	(F 5)	(F 6)	(F 7)	(F 8)			
Syn. Ex. A1	15	35	50	–	3,000	K	100
Syn. Ex. A2	5	35	60	–	7,000	K	100
Syn. Ex. A3	30	10	60	–	30,000	K	100
Syn. Ex. A4	55	35	10	–	3,000	K	100
Syn. Ex. A5	65	20	15	–	7,000	K	100
Syn. Ex. A6	30	5	65	–	7,000	K	100
Syn. Ex. A7	55	35	10	–	60,000	K	100
Syn. Ex. A8	65	20	15	–	45,000	K	100
Syn. Ex. A9	55	35	10	–	45,000	K	100
Syn. Ex. A10	15	35	50	–	60,000	K	100
Syn. Ex. A11	5	35	60	–	45,000	K	100
Syn. Ex. A12	15	35	50	–	45,000	K	100
Syn. Ex. A13	15	35	50	–	7,000	Na	100
Syn. Ex. A14	15	35	50	–	7,000	Li	100
Syn. Ex. A15	5	35	60	–	3,000	K	100
Syn. Ex. A16	65	20	15	–	60,000	K	100
Syn. Ex. A17	15	35	50	–	7,000	K	100
Syn. Ex. A18	15	35	–	50	3,000	K	100
Syn. Ex. A19	5	35	–	60	7,000	K	100
Syn. Ex. A20	15	35	–	50	7,000	K	100
Syn. Ex. A21	55	35	–	10	3,000	K	100
Syn. Ex. A22	65	20	–	15	7,000	K	100
Syn. Ex. A23	55	35	–	10	7,000	K	100
Syn. Ex. A24	55	35	–	10	60,000	K	100
Syn. Ex. A25	65	20	–	15	45,000	K	100
Syn. Ex. A26	55	35	–	10	45,000	K	100
Syn. Ex. A27	15	35	–	50	60,000	K	100
Syn. Ex. A28	5	35	–	60	45,000	K	100
Syn. Ex. A29	15	35	–	50	45,000	K	100
Syn. Ex. A30	15	35	–	50	7,000	Na	100
Syn. Ex. A31	15	35	–	50	7,000	Li	100
Syn. Ex. A32	5	35	–	60	3,000	K	100
Syn. Ex. A33	65	20	–	15	60,000	K	100
Syn. Ex. A34	30	10	–	60	30,000	K	100
Syn. Ex. A35	30	10	–	60	30,000	K	100
Syn. Ex. A36	30	10	–	60	30,000	K	100
Syn. Ex. A37	30	10	–	60	30,000	K	100
Syn. Ex. A38	30	10	–	60	30,000	K/H	50
Syn. Ex. A39	15	35	–	50	7,000	DMEA	100
Syn. Ex. A40	(15)	85	–	–	7,000	K	100
Syn. Ex. A41	15	(85)	–	–	7,000	K	100
Syn. Ex. A42	(15)	(85)	–	–	10,000	K	100
Syn. Ex. A43	30	10	60	–	30,000	K	100
Syn. Ex. A44	30	10	60	–	30,000	K	100
Syn. Ex. A45	30	10	–	60	30,000	K	100

In Tables A1-1 and A1-2, (F 5) to (F 8) denote monomers

represented by the General Formulae (5) to (8), respectively.

<Preparation of Pigment dispersions A1 to A55>

Firstly, each of Copolymers, a pigment, and pure water were pre-mixed together using materials described in each of columns of Pigment dispersions A1 to A55 in Tables A2-1 to A4-2, to thereby produce mixed slurry. Then, the mixed slurry was subjected to circulation dispersion with a disc-type media mill (MODEL DMR, manufactured by Ashizawa Finetech Ltd.) and 0.05 mm zirconia beads (packing rate: 55%) at a circumferential speed of 10 m/s and a liquid temperature of 10°C for 3 min, followed by centrifugation with a centrifuge (MODEL-7700, manufactured by KUBOTA CORPORATION) to remove coarse particles, to thereby obtain Pigment dispersion. Numerical values described in Tables A2-1 to A4-2 denote blending ratios (parts by weight).

Note that, each of Copolymers A1 to A45 was dried to remove a solvent therein, and then, the resultant solid matter was dissolved into water so as to give a 20% aqueous solution, which was used as Copolymer. Materials other than Copolymers will be described in detail.

Carbon black (NIPEX160, manufactured by Degussa AG, BET specific surface area: 150 m^2/g, average primary particle diameter: 20 nm, pH 4.0, DBP oil absorption amount: 620 g/100 g)

Pigment Blue 15:3 (CHROMOFINE BLUE-A-220JC, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

Pigment Red 122 (TONER MAGENTA EO02, manufactured by

Clariant International Ltd.)

Pigment Yellow 74 (FAST YELLOW 531, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

Table A2-1

	Pigment dispersion									
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Copolymer A1							20			
Copolymer A2								20		
Copolymer A3	10	20	80	20	20	20				
Copolymer A4									20	
Copolymer A5										20
Copolymer A6										
Copolymer A7										
Copolymer A8										
Copolymer A9										
Copolymer A10										
Copolymer A11										
Copolymer A12										
Carbon black	16	16	16				16	16	16	16
Pigment Blue 15:3				16						
Pigment Red 122					16					
Pigment Yellow 74						16				
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100

Table A2-2

	Pigment dispersion						
	A11	A12	A13	A14	A15	A16	A17
Copolymer A1							
Copolymer A2							
Copolymer A3							
Copolymer A4							
Copolymer A5							
Copolymer A6	20						
Copolymer A7		20					
Copolymer A8			20				
Copolymer A9				20			
Copolymer A10					20		
Copolymer A11						20	
Copolymer A12							20
Carbon black	16	16	16	16	16	16	16
Pigment Blue 15:3							
Pigment Red 122							
Pigment Yellow 74							
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100

Table A3-1

	Pigment dispersion									
	A18	A19	A20	A21	A22	A23	A24	A25	A26	A27
Copolymer A13	20									
Copolymer A14		20								
Copolymer A15			20							
Copolymer A16				20						
Copolymer A17					20					
Copolymer A18										
Copolymer A19										
Copolymer A20						10	20	80	20	20
Copolymer A21										
Copolymer A22										
Copolymer A23										
Copolymer A24										
Carbon black	16	16	16	16	16	16	16	16	16	
Pigment Blue 15:3										16
Pigment Red 122										
Pigment Yellow 74										
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100

Table A3-2

	Pigment dispersion						
	A28	A29	A30	A31	A32	A33	A34
Copolymer A13							
Copolymer A14							
Copolymer A15							
Copolymer A16							
Copolymer A17							
Copolymer A18		20					
Copolymer A19			20				
Copolymer A20	20						
Copolymer A21				20			
Copolymer A22					20		
Copolymer A23						20	
Copolymer A24							20
Carbon black			16	16	16	16	16
Pigment Blue 15:3							
Pigment Red 122	16						
Pigment Yellow 74		16					
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100

Table A4-1

	Pigment dispersion										
	A35	A36	A37	A38	A39	A40	A41	A42	A43	A44	A45
Copolymer A25	20										
Copolymer A26		20									
Copolymer A27			20								
Copolymer A28				20							
Copolymer A29					20						
Copolymer A30						20					
Copolymer A31							20				
Copolymer A32								20			
Copolymer A33									20		
Copolymer A34										20	
Copolymer A35											20
Copolymer A36											
Copolymer A37											
Copolymer A38											
Copolymer A39											
Copolymer A40											
Copolymer A41											
Copolymer A42											
Copolymer A43											
Copolymer A44											
Copolymer A45											
Carbon black	16	16	16	16	16	16	16	16	16	16	16
Pigment Blue 15:3											
Pigment Red 122											
Pigment Yellow 74											
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100	100

Table A4-2

	Pigment dispersion									
	A46	A47	A48	A49	A50	A51	A52	A53	A54	A55
Copolymer A25										
Copolymer A26										
Copolymer A27										
Copolymer A28										
Copolymer A29										
Copolymer A30										
Copolymer A31										
Copolymer A32										
Copolymer A33										
Copolymer A34										
Copolymer A35										
Copolymer A36	20									
Copolymer A37		20								
Copolymer A38			20							
Copolymer A39				20						
Copolymer A40					20					
Copolymer A41						20				
Copolymer A42							20			
Copolymer A43								20		
Copolymer A44									20	
Copolymer A45										20
Carbon black	16	16	16	16	16	16	16	16	16	16
Pigment Blue 15:3										
Pigment Red 122										
Pigment Yellow 74										
Pure water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100	100	100	100	100

[Examples A1 to A56 and Comparative Examples A1 to A3]

<Production of ink>

Materials described in each of columns of Examples A1 to A56 and Comparative Examples A1 to A3 in Tables A5-1 to A6-4 were mixed and stirred for 1 hour to thereby produce a uniform dispersion. The resultant dispersion was subjected to pressure filtration with a polyvinylidene fluoride membrane filter having an average pore diameter of 5.0 μm to remove coarse particles and contaminants, to thereby obtain an ink.

Note that, numerical values in Tables denote % by mass.

Table A5-1

	Material name	Example									
		A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Pigment dispersion	Pigment dispersion A1	50									
	Pigment dispersion A2		50	50	50						
	Pigment dispersion A3					50					
	Pigment dispersion A4						30				
	Pigment dispersion A5							50			
	Pigment dispersion A6								30		
	Pigment dispersion A7									50	
	Pigment dispersion A8										50
	Pigment dispersion A9										
	Pigment dispersion A10										
	Pigment dispersion A11										
	Pigment dispersion A12										
	Pigment dispersion A13										
	Pigment dispersion A14										
	Pigment dispersion A15										
	Pigment dispersion A16										
	Pigment dispersion A17										
	Pigment dispersion A18										
	Pigment dispersion A19										
	Pigment dispersion A20										
	Pigment dispersion A21										
	Pigment dispersion A22										
	Pigment dispersion A23										
	Pigment dispersion A24										
Water-soluble Organic solvent	Glycerin	10	10		20	10	10	10	10	10	10
	1,3-Butanediol	20	20	30		20	20	20	20	20	20
	Trimethylol propane				5						
	2-Pyrroridone				5						
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100	100	100

Table A5-2

	Material name	Example									
		A11	A12	A13	A14	A15	A16	A17	A18	A19	A20
Pigment dispersion	Pigment dispersion A1										
	Pigment dispersion A2										
	Pigment dispersion A3										
	Pigment dispersion A4										
	Pigment dispersion A5										
	Pigment dispersion A6										
	Pigment dispersion A7										
	Pigment dispersion A8										
	Pigment dispersion A9	50									
	Pigment dispersion A10		50								
	Pigment dispersion A11			50							
	Pigment dispersion A12				50						
	Pigment dispersion A13					50					
	Pigment dispersion A14						50				
	Pigment dispersion A15							50			
	Pigment dispersion A16								50		
	Pigment dispersion A17									50	
	Pigment dispersion A18										50
	Pigment dispersion A19										
	Pigment dispersion A20										
	Pigment dispersion A21										
	Pigment dispersion A22										
	Pigment dispersion A23										
	Pigment dispersion A24										
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10	10	10	10	10
	1,3-Butanediol	20	20	20	20	20	20	20	20	20	20
	Trimethylol propane										
	2-Pyrroridone										
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100	100	100

Table A5-3

	Material name	Example							
		A21	A22	A23	A24	A25	A26	A27	A28
Pigment dispersion	Pigment dispersion A1								
	Pigment dispersion A2								
	Pigment dispersion A3								
	Pigment dispersion A4								
	Pigment dispersion A5								
	Pigment dispersion A6								
	Pigment dispersion A7								
	Pigment dispersion A8								
	Pigment dispersion A9								
	Pigment dispersion A10								
	Pigment dispersion A11								
	Pigment dispersion A12								
	Pigment dispersion A13								
	Pigment dispersion A14								
	Pigment dispersion A15								
	Pigment dispersion A16								
	Pigment dispersion A17								
	Pigment dispersion A18								
	Pigment dispersion A19	50							
	Pigment dispersion A20		50						
	Pigment dispersion A21			50					
	Pigment dispersion A22				50				
	Pigment dispersion A23					50			
	Pigment dispersion A24						50	50	50
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10		20
	1,3-Butanediol	20	20	20	20	20	20	30	
	Trimethylol propane								5
	2-Pyrroridone								5
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100

Table A6-1

	Material name	Example							
		A29	A30	A31	A32	A33	A34	A35	A36
Pigment dispersion	Pigment dispersion A25	50							
	Pigment dispersion A26		30						
	Pigment dispersion A27			50					
	Pigment dispersion A28				30				
	Pigment dispersion A29					50			
	Pigment dispersion A30						50		
	Pigment dispersion A31							50	
	Pigment dispersion A32								50
	Pigment dispersion A33								
	Pigment dispersion A34								
	Pigment dispersion A35								
	Pigment dispersion A36								
	Pigment dispersion A37								
	Pigment dispersion A38								
	Pigment dispersion A39								
	Pigment dispersion A40								
	Pigment dispersion A41								
	Pigment dispersion A42								
	Pigment dispersion A43								
	Pigment dispersion A44								
	Pigment dispersion A45								
	Pigment dispersion A46								
	Pigment dispersion A47								
	Pigment dispersion A48								
	Pigment dispersion A49								
	Pigment dispersion A50								
	Pigment dispersion A51								
	Pigment dispersion A52								
	Pigment dispersion A53								
	Pigment dispersion A54								
	Pigment dispersion A55								
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10	10	10
	1,3-Butanediol	20	20	20	20	20	20	20	20
	Trimethylol propane								
	2-Pyrroridone								
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100

Table A6-2

	Material name	Example							
		A37	A38	A39	A40	A41	A42	A43	A44
Pigment dispersion	Pigment dispersion A25								
	Pigment dispersion A26								
	Pigment dispersion A27								
	Pigment dispersion A28								
	Pigment dispersion A29								
	Pigment dispersion A30								
	Pigment dispersion A31								
	Pigment dispersion A32								
	Pigment dispersion A33	50							
	Pigment dispersion A34		50						
	Pigment dispersion A35			50					
	Pigment dispersion A36				50				
	Pigment dispersion A37					50			
	Pigment dispersion A38						50		
	Pigment dispersion A39							50	
	Pigment dispersion A40								50
	Pigment dispersion A41								
	Pigment dispersion A42								
	Pigment dispersion A43								
	Pigment dispersion A44								
	Pigment dispersion A45								
	Pigment dispersion A46								
	Pigment dispersion A47								
	Pigment dispersion A48								
	Pigment dispersion A49								
	Pigment dispersion A50								
	Pigment dispersion A51								
	Pigment dispersion A52								
	Pigment dispersion A53								
	Pigment dispersion A54								
	Pigment dispersion A55								
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10	10	10
	1,3-Butanediol	20	20	20	20	20	20	20	20
	Trimethylol propane								
	2-Pyrroridone								
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100

Table A6-3

	Material name	Example							
		A45	A46	A47	A48	A49	A50	A51	A52
Pigment dispersion	Pigment dispersion A25								
	Pigment dispersion A26								
	Pigment dispersion A27								
	Pigment dispersion A28								
	Pigment dispersion A29								
	Pigment dispersion A30								
	Pigment dispersion A31								
	Pigment dispersion A32								
	Pigment dispersion A33								
	Pigment dispersion A34								
	Pigment dispersion A35								
	Pigment dispersion A36								
	Pigment dispersion A37								
	Pigment dispersion A38								
	Pigment dispersion A39								
	Pigment dispersion A40								
	Pigment dispersion A41	50							
	Pigment dispersion A42		50						
	Pigment dispersion A43			50					
	Pigment dispersion A44				50				
	Pigment dispersion A45					50			
	Pigment dispersion A46						50		
	Pigment dispersion A47							50	
	Pigment dispersion A48								50
	Pigment dispersion A49								
	Pigment dispersion A50								
	Pigment dispersion A51								
	Pigment dispersion A52								
	Pigment dispersion A53								
	Pigment dispersion A54								
	Pigment dispersion A55								
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10	10	10
	1,3-Butanediol	20	20	20	20	20	20	20	20
	Trimethylol propane								
	2-Pyrroridone								
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100	100

Table A6-4

	Material name	Example				Comparative Example		
		A53	A54	A55	A56	A1	A2	A3
Pigment dispersion	Pigment dispersion A25							
	Pigment dispersion A26							
	Pigment dispersion A27							
	Pigment dispersion A28							
	Pigment dispersion A29							
	Pigment dispersion A30							
	Pigment dispersion A31							
	Pigment dispersion A32							
	Pigment dispersion A33							
	Pigment dispersion A34							
	Pigment dispersion A35							
	Pigment dispersion A36							
	Pigment dispersion A37							
	Pigment dispersion A38							
	Pigment dispersion A39							
	Pigment dispersion A40							
	Pigment dispersion A41							
	Pigment dispersion A42							
	Pigment dispersion A43							
	Pigment dispersion A44							
	Pigment dispersion A45							
	Pigment dispersion A46							
	Pigment dispersion A47							
	Pigment dispersion A48							
	Pigment dispersion A49	50						
	Pigment dispersion A50					50		
	Pigment dispersion A51						50	
	Pigment dispersion A52							50
	Pigment dispersion A53		50					
	Pigment dispersion A54			50				
	Pigment dispersion A55				50			
Water-soluble Organic solvent	Glycerin	10	10	10	10	10	10	10
	1,3-Butanediol	20	20	20	20	20	20	20
	Trimethylol propane							
	2-Pyrroridone							
Distilled water		Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total		100	100	100	100	100	100	100

The Pigment dispersions A1 to A55, and inks of Examples A1 to A56, and Comparative Examples A1 to A3 were evaluated for viscosity and storage stability in the same manner as in Pigment dispersions 1 to 30, and inks of Examples 1 to 29, and Comparative Examples 1 to 3.

Additionally, the inks also evaluated for image density. Results are shown in Tables A7-1 to A7-3.

Table A7-1

	Copolymer	*1	Mw	Pigment dispersion		Ink		Image density
				Initial viscosity	Storage stability	Initial viscosity	Storage stability	
Ex. A1	Copolymer 3	30	30,000	A	B	B	B	A
Ex. A2	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A3	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A4	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A5	Copolymer 3	30	30,000	B	A	B	B	A
Ex. A6	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A7	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A8	Copolymer 3	30	30,000	A	A	B	B	A
Ex. A9	Copolymer 1	15	3,000	A	A	B	B	B
Ex. A10	Copolymer 2	5	7,000	A	A	B	B	B
Ex. A11	Copolymer 4	55	3,000	A	A	B	B	B
Ex. A12	Copolymer 5	65	7,000	B	A	B	B	A
Ex. A13	Copolymer 6	30	7,000	A	A	B	B	A
Ex. A14	Copolymer 7	55	60,000	B	A	B	B	A
Ex. A15	Copolymer 8	65	45,000	A	B	B	B	A
Ex. A16	Copolymer 9	55	45,000	A	A	B	B	A
Ex. A17	Copolymer 10	15	60,000	A	B	B	B	A
Ex. A18	Copolymer 11	5	45,000	A	A	B	B	B
Ex. A19	Copolymer 12	15	45,000	A	A	B	B	A
Ex. A20	Copolymer 13	15	7,000	B	A	A	A	A
Ex. A21	Copolymer 14	15	7,000	B	A	A	A	A
Ex. A22	Copolymer 15	5	3,000	B	B	B	B	B
Ex. A23	Copolymer 16	65	60,000	B	B	B	B	A
Ex. A24	Copolymer 17	15	7,000	A	A	B	B	A

Table A7-2

	Copolymer	*1	Mw	Pigment dispersion		Ink		Image density
				Initial viscosity	Storage stability	Initial viscosity	Storage stability	
Ex. A25	Copolymer 20	15	7,000	A	B	B	B	A
Ex. A26	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A27	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A28	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A29	Copolymer 20	15	7,000	B	A	B	A	A
Ex. A30	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A31	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A32	Copolymer 20	15	7,000	A	A	B	B	A
Ex. A33	Copolymer 18	15	3,000	A	A	B	B	B
Ex. A34	Copolymer 19	5	7,000	A	A	B	B	B
Ex. A35	Copolymer 21	55	3,000	A	A	B	B	B
Ex. A36	Copolymer 22	65	7,000	B	A	B	B	A
Ex. A37	Copolymer 23	55	7,000	A	A	B	B	A
Ex. A38	Copolymer 24	55	60,000	B	A	B	B	A
Ex. A39	Copolymer 25	65	45,000	A	B	B	B	A
Ex. A40	Copolymer 26	55	45,000	A	A	B	B	A
Ex. A41	Copolymer 27	15	60,000	A	B	B	B	A
Ex. A42	Copolymer 28	5	45,000	A	A	B	B	B
Ex. A43	Copolymer 29	15	45,000	A	A	B	B	A
Ex. A44	Copolymer 30	15	7,000	B	A	A	A	A
Ex. A45	Copolymer 31	15	7,000	B	A	A	A	A
Ex. A46	Copolymer 32	5	3,000	B	B	B	B	B
Ex. A47	Copolymer 33	65	60,000	B	B	B	B	A
Ex. A48	Copolymer 34	30	30,000	A	A	B	B	A

Table A7-3

	Copolymer	*1	Mw	Pigment dispersion		Ink		Image density
				Initial viscosity	Storage stability	Initial viscosity	Storage stability	
Ex. A49	Copolymer 35	30	30,000	A	A	B	B	A
Ex. A50	Copolymer 36	30	30,000	A	A	B	B	A
Ex. A51	Copolymer 37	30	30,000	A	A	B	B	A
Ex. A52	Copolymer 38	30	30,000	A	A	B	B	A
Ex. A53	Copolymer 39	15	7,000	B	A	A	A	A
Ex. A54	Copolymer 43	30	30,000	B	A	B	B	A
Ex. A55	Copolymer 44	30	30,000	B	A	B	B	A
Ex. A56	Copolymer 45	30	30,000	B	A	B	B	A
Comp. Ex. A1	Copolymer 40	(15)	7,000	B	C	B	C	E
Comp. Ex. A2	Copolymer 41	15	7,000	C	E	C	E	B
Comp. Ex. A3	Copolymer 42	(15)	10,000	B	E	B	E	E

In Tables A7-1 and A7-3, *1 denotes "(Formula 1) structural unit content (%)" which means a percentage of the structural unit represented by the General Formula (1) in the phosphate group-containing copolymer, and Mw denotes the mass average molecular weight.

As can be seen from Tables A7-1 and A7-3, when comparing Examples A1 to A56 with Comparative Examples A1 to A3, inks which contain a phosphate group-containing copolymer of the present invention are more excellent in both of image density and storage stability.

Additionally, it can be seen that Examples in which the structural unit represented by the General Formula (1) is contained in a percentage of 10% by mass to 60% by mass are more excellent in both of

image density and storage stability than other Examples.

It can be seen that Examples in which the copolymer has a molecular weight of 5,000 to 50,000 are more excellent in both of image density and storage stability than other Examples.

Embodiments of the present invention are as follows.

<1> An inkjet recording ink, including:

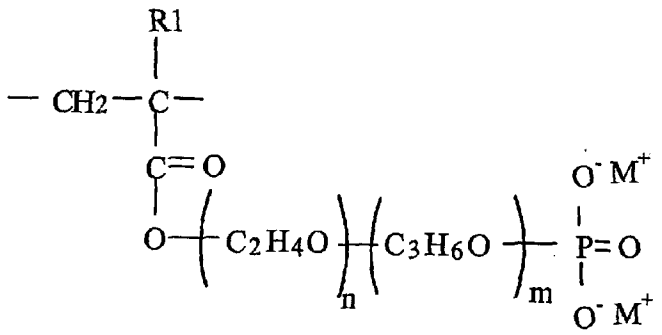
water;

a water-soluble organic solvent;

a pigment; and

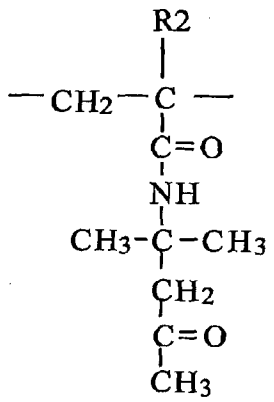
a phosphate group-containing copolymer,

wherein the phosphate group-containing copolymer contains a structural unit represented by the following General Formula (1) and a structural unit represented by the following General Formula (2):



(Formula 1)

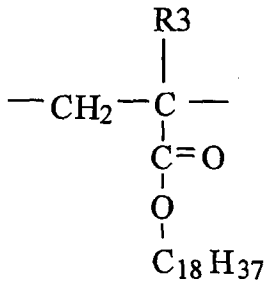
where R1 denotes a hydrogen atom or a methyl group; M^+ denotes an alkali metal ion, an organic amine ion, or a hydrogen ion; half or more of M^+ in the copolymer is the alkali metal ion or the organic amine ion, the remainder of M^+ is the hydrogen ion; n and m each denote an integer of 0 to 6, provided that both of n and m are not 0; and a block of (C_2H_4O) and a block of (C_3H_6O) may be exchanged with each other,



(Formula 2)

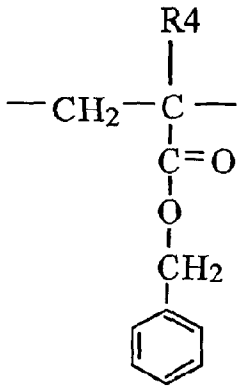
where R2 denotes a hydrogen atom or a methyl group.

<2> The inkjet recording ink according to <1>, wherein the phosphate group-containing copolymer further contains a structural unit represented by the following General Formula (3), a structural unit represented by the following General Formula (4), or both thereof:



(Formula 3)

where R3 denotes a hydrogen atom or a methyl group,



(Formula 4)

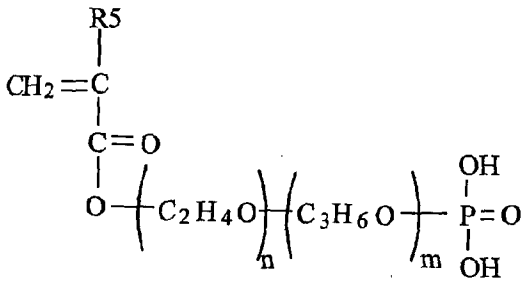
where R4 denotes a hydrogen atom or a methyl group.

<3> The inkjet recording ink according to <1> or <2>, wherein the structural unit represented by the General Formula (1) is contained in

the phosphate group-containing copolymer in a percentage of 10% by mass to 60% by mass.

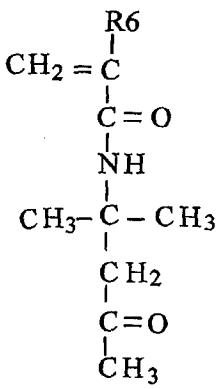
<4> The inkjet recording ink according to any one of <1> to <3>, wherein the phosphate group-containing copolymer has a weight average molecular weight of 5,000 to 50,000.

<5> The inkjet recording ink according to any one of <1> to <4>, wherein the phosphate group-containing copolymer is synthesized by allowing a monomer represented by the following General Formula (5) to polymerize with a monomer represented by the following General Formula (6), followed by neutralizing with an alkali metal salt or an organic amine base:



(Formula 5)

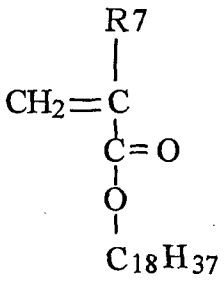
where R5 denotes a hydrogen atom or a methyl group, and n and m each denote an integer of 0 to 6, provided that both of n and m are not 0,



(Formula 6)

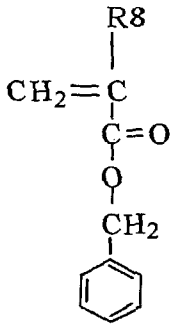
where R6 denotes a hydrogen atom or a methyl group.

<6> The inkjet recording ink according to <5>, wherein the phosphate group-containing copolymer is allowed to further polymerize with a monomer represented by the following General Formula (7), a monomer represented by the following General Formula (8), or both thereof:



(Formula 7)

where R7 denotes a hydrogen atom or a methyl group,



(Formula 8)

where R8 denotes a hydrogen atom or a methyl group.

<7> An ink cartridge, including:

a container; and

the inkjet recording ink according to any one of <1> to <6> contained in the container.

<8> An inkjet recording device, including:

the ink cartridge according to <7>.

<9> An inkjet recording method, including:

applying a stimulus to the inkjet recording ink according to any one of <1> to <6> to allow the inkjet recording ink to jet, to thereby record an image.

<10> An ink recorded matter, including:

a recording medium; and

an image recorded on the recording medium with the inkjet recording ink according to any one of <1> to <6>.

Reference Signs List

101 Device Main Body

102 Paper Feeding Tray

103 Paper Discharging Tray

104 Ink Cartridge Loading Section

105 Control Section

111 Head Cover

112 Front Surface of Front Cover

115 Front Cover

131 Guide Rod

132 Stay

133 Carriage

134 Recording Head

135 Sub-Tank

141 Paper Loading Section

142 Sheet of Paper

143 Paper Feeding Roller

144 Separation Pad

145 Guide

151 Conveyance Belt

152 Counter Roller

153 Conveyance Guide

154 Pressing Member

155 Pressurizing Roller

156 Charging Roller

157 Conveyance Roller

158 Tension Roller

161 Guide Member

171 Separation Claw

172 Paper Discharge Roller

173 Paper Discharge Roller

181 Double-Sided Paper Feeding Unit

182 Manual Paper Feeding Section

200 Ink Cartridge

241 Ink Bag

242 Ink Inlet

243 Ink Outlet

244 Cartridge Case

CLAIMS

1. An inkjet recording ink, comprising:

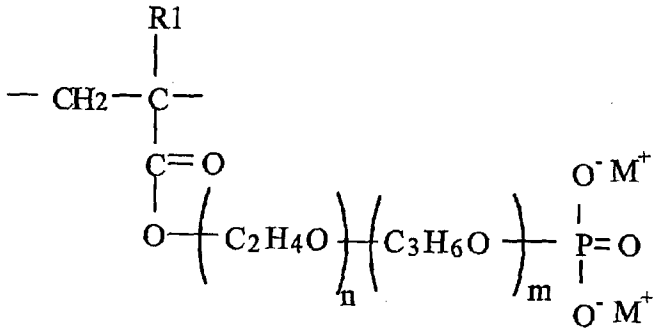
water;

a water-soluble organic solvent;

a pigment; and

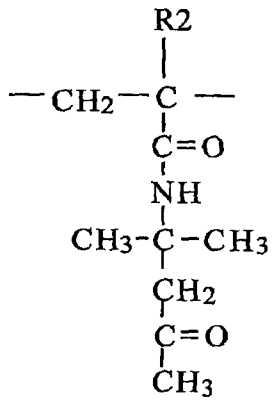
a phosphate group-containing copolymer,

wherein the phosphate group-containing copolymer comprises a structural unit represented by the following General Formula (1) and a structural unit represented by the following General Formula (2):



(Formula 1)

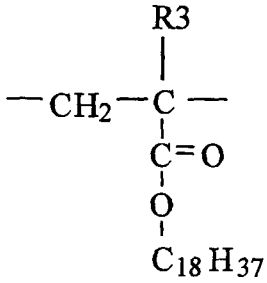
where R1 denotes a hydrogen atom or a methyl group; M^+ denotes an alkali metal ion, an organic amine ion, or a hydrogen ion; half or more of M^+ in the copolymer is the alkali metal ion or the organic amine ion, the remainder of M^+ is the hydrogen ion; n and m each denote an integer of 0 to 6, provided that both of n and m are not 0; and a block of (C_2H_4O) and a block of (C_3H_6O) may be exchanged with each other,



(Formula 2)

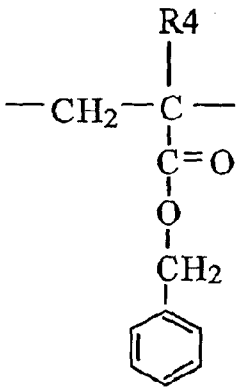
where R2 denotes a hydrogen atom or a methyl group.

2. The inkjet recording ink according to claim 1, wherein the phosphate group-containing copolymer further comprises a structural unit represented by the following General Formula (3), a structural unit represented by the following General Formula (4), or both thereof:



(Formula 3)

where R3 denotes a hydrogen atom or a methyl group,



(Formula 4)

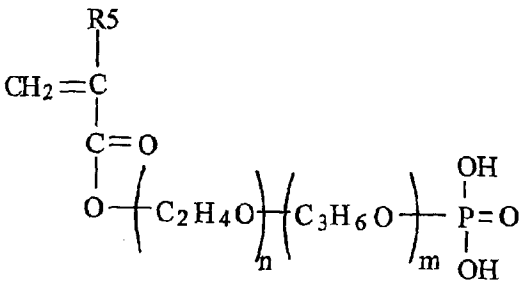
where R4 denotes a hydrogen atom or a methyl group.

3. The inkjet recording ink according to claim 1 or 2, wherein the structural unit represented by the General Formula (1) is contained in

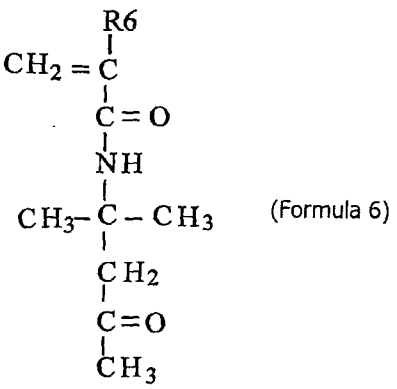
the phosphate group-containing copolymer in a percentage of 10% by mass to 60% by mass.

4. The inkjet recording ink according to any one of claims 1 to 3, wherein the phosphate group-containing copolymer has a weight average molecular weight of 5,000 to 50,000.

5. The inkjet recording ink according to any one of claims 1 to 4, wherein the phosphate group-containing copolymer is synthesized by allowing a monomer represented by the following General Formula (5) to polymerize with a monomer represented by the following General Formula (6), followed by neutralizing with an alkali metal salt or an organic amine base:

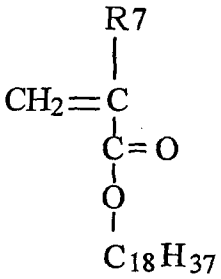

(Formula 5)

where R5 denotes a hydrogen atom or a methyl group, and n and m each denote an integer of 0 to 6, provided that both of n and m are not 0,


(Formula 6)

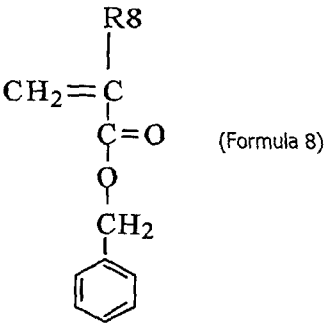
where R6 denotes a hydrogen atom or a methyl group.

6. The inkjet recording ink according to claim 5, wherein the phosphate group-containing copolymer is allowed to further polymerize with a monomer represented by the following General Formula (7), a monomer represented by the following General Formula (8), or both thereof:



(Formula 7)

where R7 denotes a hydrogen atom or a methyl group,



(Formula 8)

where R8 denotes a hydrogen atom or a methyl group.

7. An ink cartridge, comprising:

a container; and

the inkjet recording ink according to any one of claims 1 to 6 contained in the container.

8. An inkjet recording device, comprising:

the ink cartridge according to claim 7.

9. An inkjet recording method, comprising:

applying a stimulus to the inkjet recording ink according to any one of claims 1 to 6 to allow the inkjet recording ink to jet, to thereby

record an image.

10. An ink recorded matter, comprising:

a recording medium; and

an image recorded with the inkjet recording ink according to any one of claims 1 to 6.

FIG. 1

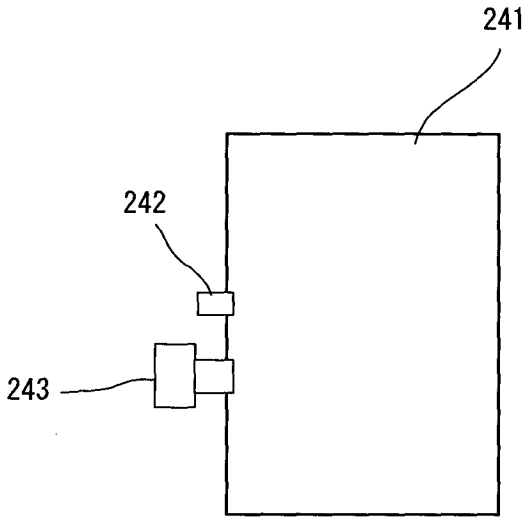


FIG. 2

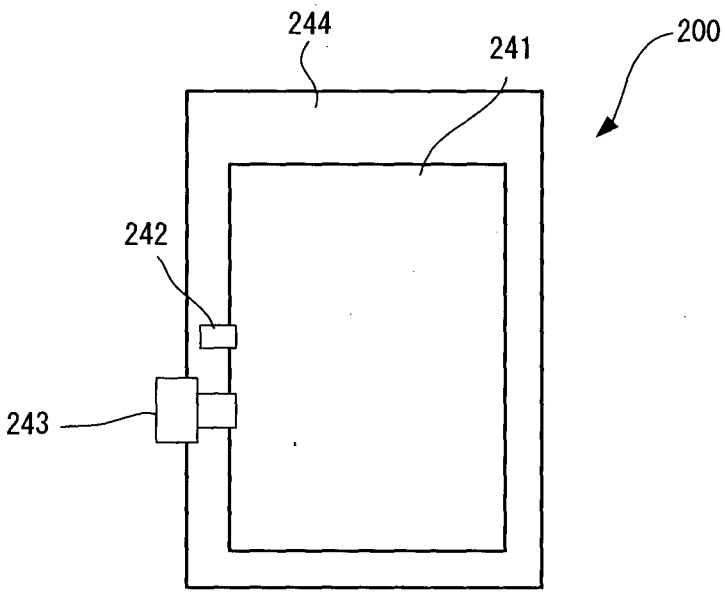


FIG. 3

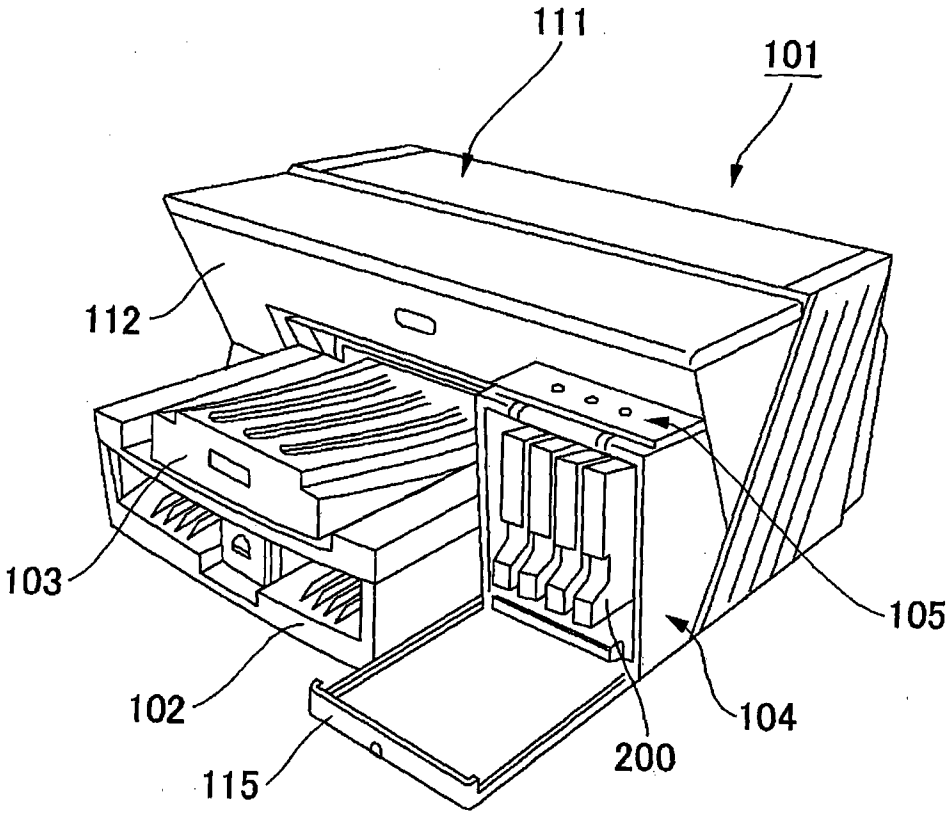


FIG. 4

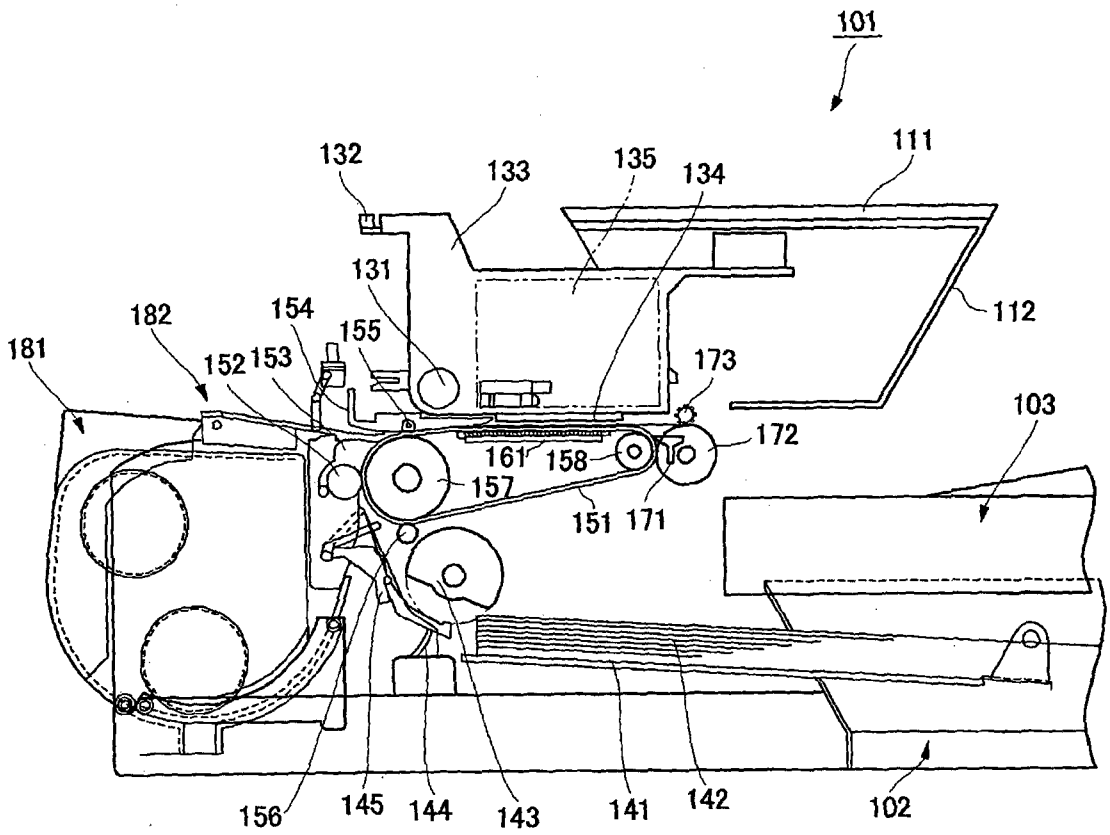

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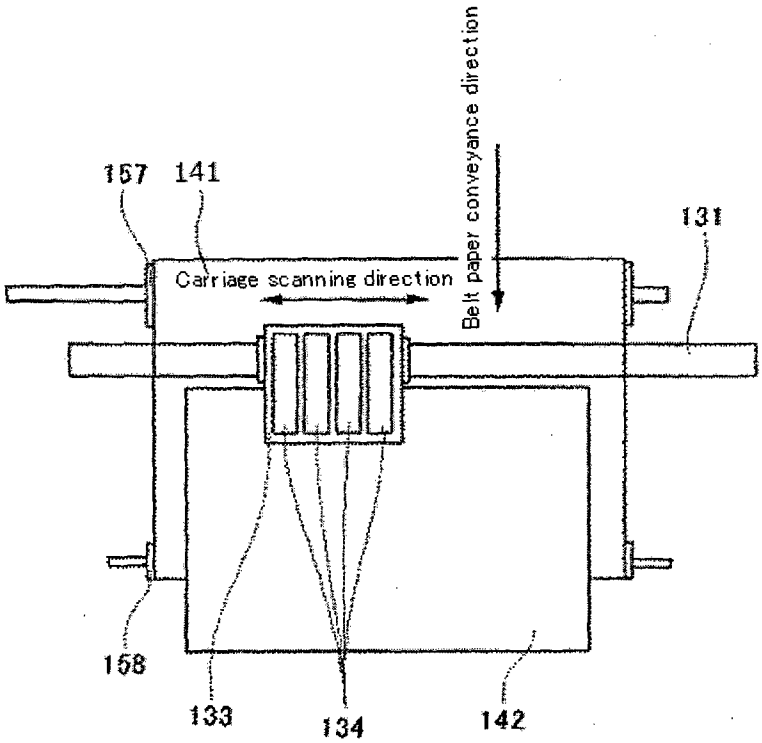
FIG. 5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Carriage scanning direction
Belt paper conveyance direction
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158
133
134
142

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/055882

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C09D11/326(2014.01)i, B41M5/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C09D11/326, B41M5/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2014
Registered utility model specifications of Japan 1996-2014
Published registered utility model applications of Japan 1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2013-28658 A (TOYO INK SC HOLDINGS CO., LTD.) 2013.02.07 claims 1, 5, paragraphs 9, 12, 14, 38, 42	1-2, 7-10 4
Y	JP 2007-99913 A (SEIKO EPSON CORPORATION) 2007.04.19 claim 1, examples 1-10	4
A	JP 61-023652 A (Dainippon Ink and Chemicals, Inc.) 1986.02.01 claim, example 1	1-10

☑ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03.06.2014	17.06.2014

Name and mailing address of the ISA/JP	Authorized officer	
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Masami Sakurada Telephone No. +81-3-3581-1101 Ext. 3480	4Z 3771

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/055882

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-513233 A (FUJIFILM Imaging Colorants Limited) 2007.05.24 claims 10, 11, paragraphs 38, 45	1-10
A	JP 2010-189478 A (Fujifilm Corporation) 2010.09.02 claim 1, paragraphs 40, 57, 119	1-10
A	JP 2007-270089 A (Fujifilm Corporation) 2007.10.18 paragraphs 17, 44, 57	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2014/055882

JP 2013-28658 A	2013.02.07	No Family
JP 2007-99913 A	2007.04.19	US 2007/0263054 A1 EP 1783182 A1 EP 2123722 A1 WO 2006/043700 A1 AT 452947 T CN 101044215 A
JP 61-023652 A	1986.02.01	No Family
JP 2007-513233 A	2007.05.24	US 2007/0263050 A1 GB 328320 D GB 328573 D GB 412831 D GB 328320 D0 EP 1697470 A1 WO 2005/056700 A1 DE 602004017055 D AT 410488 T
JP 2010-189478 A	2010.09.02	No Family
JP 2007-270089 A	2007.10.18	No Family