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(54) Ink-jet recording sheet

(57) The present invention provides an ink-jet recording sheet comprising a support and an image-receiving layer which contains fine particles of inorganic pigment and a cationic polymer having at the end there-

of a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group.

Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

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[0001] The present invention relates to a recording material suitable for ink-jet recording, using a liquid ink such as a water based ink and an oil based ink, a solid ink in a solid state at an ordinary temperature, which is provided for printing after melting, or the like. More specifically, the present invention relates to an ink-jet recording sheet having excellent ink accepting capability.

Description of the Related Art

[0002] Recently, with the rapid growth of the information technology industry, various information processing systems have been developed. Thus recording methods and apparatuses suitable for recording systems have also been developed and put into practical use.

[0003] Among the above-mentioned recording methods, the ink-jet recording method is widely used not only in offices but also in home. This is due to many factors, such as its capability of recording on various kinds of recording materials, the relative inexpensiveness of the hardware (apparatus), its compactness, and its superior quietness.

[0004] Moreover, with the recent trend toward high resolution in ink-jet printers, a recording material that provides high quality photograph-like images can be obtained. Furthermore, with the development of hardware (apparatuses), various kinds of recording sheets for ink-jet recording have also been developed.

[0005] In general, the above-mentioned recording sheets for ink-jet recording require several characteristics. They are (1) a quick-drying property (quick ink absorbancy); (2) appropriate and even ink dot size (absence of blurring); (3) good graininess; (4) excellent dot roundness; (5) high color density; (6) high saturation (absence of dullness); (7) good light and water resistance in the printing portion; (8) a high degree of whiteness; (9) good storage stability (absence of yellowish coloring even after long term storage); (10) good stability without deformation (sufficiently minor curling); and (11) good running property in hardware. Furthermore, when glossy photo paper is used as a recording material for obtaining photograph-like high image quality, in addition to the above-mentioned characteristics, the recording material must possess qualities such as glossiness, surface smoothness, and printing paper-like feeling similar to silver salt photography.

[0006] In order to improve these characteristics, an ink-jet recording sheet having a porous structure in its image-receiving layer with excellent ink absorbancy (i.e., quick drying) and high glossiness has been developed and put into practical use.

[0007] Japanese Patent Application Laid-open (JP-A) No. 62-178384 and Japanese Patent Application Publication (JP-B) No. 3-24905 propose a recording material having an image-receiving layer containing silica particles whose surfaces are treated with a silane coupling agent. However, although the weather resistance is improved with the decline of the surface activity of the silica particles, since the cohesive force between the silica particles is lowered as well, the film strength of the image-receiving layer is weakened.

[0008] Moreover, since the silica dispersion aggregates when mixed with a binder such as PVA, the viscosity increases to the point where it deteriorates the stability of the dispersion. Therefore, the size of the silica particles in the dispersion become large and adversely affect glossiness, coating film strength, speed of ink absorbancy, water resistance, printing density, and the like. Among those characteristics adversely affected, the printing density is particularly influenced so as to deteriorate drastically.

[0009] JP-A No. 2001-10209 proposes an ink-jet recording paper containing fine particles of inorganic pigment, a silane coupling agent having an ammonium structure, and a cationic resin. However, because such an ink-jet recording sheet is coated with inorganic fine particles and cationic resin in one solution on the surface of a support, aggregation is generated between the cationic resin and the inorganic fine particles that have an anionic charge, and thus desired properties of the ink-jet recording paper cannot be fully realized.

[0010] JP-A Nos. 8-39927, 2000-309159 and 2000-313164 disclose an ink-jet recording sheet using a chain transfer agent at the time of cationic polymerization. However, these use a chain transfer agent for adjusting the degree of polymerization, and not for improving the dispersion property of the fine particles of inorganic pigment

[0011] JP-A Nos. 10-181190, 10-181191, 11-321079 and 11-348409 disclose dispersion of inorganic fine particles in the presence of a cationic resin. However, these references do not mention terminals of the polymer.

[0012] JP-A No. 63-260477 discloses a recording material including a polyamine compound having surface activity due to introduction of an alkyl group having 6 to 18 carbon atoms into the end of the compound. The polyamine compound is similar to the polymer used in the present invention but is used as a mordant. In addition, silica is not an essential component in the recording material.

[0013] As mentioned above, at present, an ink-jet recording sheet having a firm image-receiving layer having no cracking or the like and good ink absorbancy and providing a high resolution image that is highly water resistant, and further resistant to blurring with time, while possessing excellent printing density, sharpness and glossiness, has yet to be proposed so far.

SUMMARY OF THE INVENTION

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[0014] The purpose of the present invention is to solve the above-mentioned conventional problems and achieve the following objects.

[0015] A first object of the invention is to provide an ink-jet recording sheet having a high image printing density.

[0016] A second object of the invention is to provide a firm ink-jet recording sheet having no cracking or the like, having good ink absorbancy, providing a high resolution image, and having excellent glossiness, water resistance and resistance to blurring after printing, and excellent light resistance even under the light irradiation of the sunlight, the fluorescent light, or the like.

[0017] The invention provides an ink-jet recording sheet comprising a support and an image-receiving layer which contains fine particles of inorganic pigment and a cationic polymer having at the end thereof a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

<Ink-jet recording sheet>

[0018] An ink-jet recording sheet of the invention comprises an image-receiving layer containing fine particles of inorganic pigment, and a cationic polymer having at the end thereof a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group (hereinafter also referred to as a "cationic polymer of the invention"). When the cationic polymer of the invention is added to a dispersion of inorganic pigment at the time of dispersing the inorganic pigment in the formation of the image-receiving layer, the aggregation of the inorganic pigment, for example, the aggregation of the pigment at the time of mixing it with a water-soluble resin such as a polyvinyl alcohol, or the like can be prevented and then a coating solution with a low viscosity and a small dispersion particle size can be prepared. In the case of a dispersion with a low viscosity and a small particle size, the properties of the ink-jet recording sheet using the same, such as glossiness, prevention of cracking of the image-receiving layer, speed of ink absorbancy, water resistance and resistance to blurring with time can be improved and an ink-jet recording sheet with a extremely high printing density can be provided.

[0019] Moreover, in the case where a cationic polymer of the invention is used in dispersion of the fine particles of inorganic pigment, compared with the case of merely dispersing the fine particles of inorganic pigment using a known cationic polymer, printing density can be improved by addition of a small amount of the polymer. Therefore, coloring of the image-receiving layer which occurs in the case of using a large amount of the known cationic polymer can be prevented, and deterioration of light resistance and film strength of the image-receiving layer, and generation of blurring with time can be prevented.

Image-receiving layer

[0020] First, the materials contained in the image-receiving layer will be explained. The image-receiving layer in the invention contains at least a cationic polymer of the invention and fine particles of inorganic pigment, and preferably contains a water soluble resin, a cross-linking agent capable of cross-linking the water soluble resin, and an organic mordant. Furthermore, as needed, various additives may be included.

Cationic polymer of the invention

[0021] The cationic polymer of the invention has, at the end thereof, a group selected from the group consisting of an alkyl group having 4 to 36 carbon atoms, an aryl group and an aralkyl group. The cationic polymer of the invention may have any of these groups at at least one end. It may have the groups at the both ends, but from the viewpoint of improvement of the dispersion property and the flowability of the fine particles of inorganic pigment, it is preferable to have the group at only one end. Moreover, the alkyl group, aryl group and aralkyl group may have a branched structure or a cyclic structure.

[0022] The total number of the carbon atoms of the alkyl group is 4 to 36, and preferably 8 to 18. In the case where the number of the carbon atoms thereof is less than 4, aggregation of the fine particles of inorganic pigment may not be prevented. In the case where it is more than 36, the dissolubility of the cationic polymer in water or alcohol is lowered

and such a cationic polymer may not be suitable for production. Examples of the alkyl group include 1-butyl group, 1-pentyl group, 1-hexyl group, 1-hetyl group, 1-octyl group, 1-nonyl group, 1-decyl group, 1-undecyl group, 1-dodecyl group, 1-triacoryl group, 1-tetradecyl group, 1-pentadecyl group, 1-hexadecyl group, 1-hexatriacortyl group, 1-nonadecyl group, 1-eicosyl group, 1-docosyl group, 1-hexacosyl group, 1-triacontyl group, 1-hexatriacontyl group, sec-butyl group, isobutyl group, tert-butyl group, neopentyl group, 2-methyl-1-butyl group, 3-methyl-1-butyl group, 3-methyl-1-butyl group, 3-methyl-1-pentyl group, 2-methyl-1-pentyl group, 3-methyl-1-pentyl group, 4-methyl-1-pentyl group, 2-propyl-1-pentyl group, 2-pentyl group, 3-pentyl group, 2-hexyl group, 3-hexyl group, 3-hexyl group, 2-heptyl group, 2-octyl group, 3-octyl group, 2-nonyl group, 2-decyl group, 4-decyl group, 2-undecyl group, 2-dodecyl group, 2-tetradecyl group, 2-hexadecyl group, 3-methyl-2-butyl group, 3-methyl-2-pentyl group, 4-methyl-2-pentyl group, 2-dimethyl-3-pentyl group, 2,4-dimethyl-3-pentyl group, 3-methyl-2-hexyl group, 3-methyl-3-hexyl group, 6-methyl-2-heptyl group, 4-methyl-3-heptyl group, 2,6-dimethyl-4-heptyl group, 2,3-dimethyl-3-pentyl group, 3-methyl-2-butyl group, 3-methyl-2-butyl group, 3-methyl-2-butyl group, 3-methyl-2-hexyl group, 3-methyl-3-pentyl group, 3-methyl-3-pentyl group, 3-ethyl-3-pentyl group, 3-

Compound (A)

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[0023] The number of the carbon atoms of the aryl group is preferably 6 to 14, and more preferably 6 to 10. Examples of the aryl group include phenyl group, tolyl group, xylyl group, naphthyl group, biphenyl group and an alkylphenyl. [0024] The number of the carbon atoms of the aralkyl group is preferably 7 to 15, and more preferably 7 to 11. Examples of the aralkyl group include benzyl group, phenethyl group, diphenylmethyl group, triphenylmethyl group, and α or β -stylyl group.

[0025] Those represented by the following General formula (1) are particularly preferable as the cationic polymer of the invention.

General formula (1)

 $R \times S \times A \rightarrow M \times B \rightarrow M$

[0026] In General formula (1), X represents a single bond or a divalent connecting group, and R represents a straight,

branched or cyclic alkyl group having 4 to 36 carbon atoms, an aryl group, or an aralkyl group. A represents at least one kind of a repeating unit having a cation, and B represents at least one kind of a repeating unit copolymerizable with A. m and n each represent a molar ratio of the A component and the B component, and $0.2 \le m \le 1.0$, $0 \le n \le 0.8$ (m + n = 1.0).

⁵ **[0027]** The copolymer having A and B units may be any of random, block and graft copolymers.

[0028] In General formula (1), X represents a single bond or a divalent connecting group. The divalent connecting group is not particularly limited, and for example, a divalent connecting group represented by the following General formula (8) is preferable.

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General formula (8)

$$-Y-R^8-$$

[0029] In General formula (8), R⁸ represents a single bond or an alkylene group having 1 to 8 carbon atoms, which may have a side chain, and Y represents a divalent connecting group.

[0030] The number of the carbon atoms of the alkylene group is 1 to 8, and preferably 1 to 4. The alkylene group may have a side chain. Example of the alkylene group include methylene, ethylene, propylene, tetramethylene, hexamethylene and octamethylene. Examplesof the side chain include methyl group, ethyl group, propyl group, butyl group, phenyl group, methoxy group, ethoxy group, and phenoxy group, and methyl group, ethyl group, and methoxy group are preferable.

[0031] Y represents a divalent connecting group. Examples thereof include an ether, a thioether, an amino, an ester, an amide, a thioester, an ester carbonate, a urea, a thioester carbonate, a dithioester carbonate, an aromatic ring, and a heterocycle.

[0032] A combination in which X is a single bond or a divalent connecting group represented by General formula (8) and Y is an ether, a thioether, an ester, or an amide is preferable. A single bond or a divalent connecting group represented by General formula (8) and having an ether or an ester as Y is particularly preferable.

[0033] Specific examples of the divalent connecting groups represented by X will be presented below, but the invention is not limited thereto.

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$$-O(CH_{2})_{2}-O(CH_{2})_{3}-CH_{3}$$

$$-OCH_{2}CH-$$

$$-S(CH_{2})_{2}-O(CH_{2})_{6}-$$

$$-NH(CH_{2})_{2}-O(CH_{2})_{2}-$$

$$-N(CH_{2})_{2}-O(CH_{2})_{2}-$$

$$-O-C-CH_{2}-O(CH_{2})_{2}-$$

$$-O-C-CH_{2}-O(CH_{2})_{2}-$$

$$-N-C-CH_{2}-O(CH_{2})_{2}-$$

$$+O-C-CH_{2}-O(CH_{2})_{2}-$$

$$+O-C-CH_{2}-O(CH_{2})_{2}-$$

$$+O-C-CH_{2}-O(CH_{2})_{2}-$$

$$+O-C-CH_{2}-O(CH_{2})_{2}-$$

$$+O-C-CH_{2}-O(CH_{2})_{2}-$$

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[0034] In General formula (1), R represents a straight, branched or cyclic alkyl group having a total of 4 to 36 carbon atoms, an aryl group or an aralkyl group.

[0035] The total number of the carbon atoms of the alkyl group is 4 to 36, and preferably 8 to 18. In the case where the number of the carbon atoms thereof is less than 4, aggregation of the fine particles of inorganic pigment may not be prevented. In the case where it is more than 18, the dissolubility of the cationic polymer in water or alcohol is lowered and such a cationic polymer may not be suitable for production. Examples of the alkyl group include 1-butyl group, 1-pentyl group, 1-hexyl group, 1-heptyl group, 1-octyl group, 1-nonyl group, 1-decyl group, 1-undecyl group, 1-dodecyl group, 1-tridecyl group, 1-tetradecyl group, 1-pentadecyl group, 1-hexadecyl group, 1-hexadecyl group, 1-octadecyl group, 1-nonadecyl group, 1-eicosyl group, 1-docosyl group, 1-hexacosyl group, 1-triacontyl group, 1-hexatriacontyl group, sec-butyl group, isobutyl group, tert-butyl group, neopentyl group, 2-methyl-1-butyl group, 3-methyl-1-butyl group, 2-ethyl-1-butyl group, 3,3-dimethyl-1-butyl group, 2-methyl-1-pentyl group, 3-methyl-1-pentyl group, 4-methyl-1-pentyl group, 2-propyl-1-pentyl group, 2,4,4-trimethyl-1-pentyl group, 2-ethyl-1-hexyl group, 3,5,5-trimethyl-1-hexyl group, 3,7-dimethyl-1-octyl group, 2-pentyl group, 3-pentyl group, 2-hexyl group, 3-hexyl group, 2-heptyl group, 2-octyl group, 3-octyl group, 2-nonyl group, 2-decyl group, 4-decyl group, 2-undecyl group, 2-dodecyl group, 2-tetradecyl group, 2-hexadecyl group, 3-methyl-2-butyl group, 3,3-dimethyl-2-butyl group, 3-methyl-2-pentyl group, 4-methyl-2-pentyl group, 2-methyl-3-pentyl group, 4,4-dimethyl-2-pentyl group, 4,4-dimethyl-2-methyl-2-pentyl group, 2,2-dimethyl-3-pentyl group, 2,4-dimethyl-3-pentyl group, 5-methyl-2-hexyl group, 2-methyl-3-hexyl group, 6-methyl-2-heptyl group, 4-methyl-3-heptyl group, 2,6-dimethyl-4-heptyl group, tert-amyl group, 2,3-dimethyl-2-butyl group, 2-methyl-2-pentyl group, 3-methyl-3-pentyl group, 3-ethyl-3-pentyl group, 2,3-dimethyl-3-pentyl group, 3-ethyl-2,2-dimethyl-3-pentyl group, 2-methyl-2-hexyl group, 3,7-dimethyl-3-octyl group, cyclohexyl group, and the above-described compound (A).

[0036] The number of the carbon atoms of the aryl group is preferably 6 to 14, and more preferably 6 to 10. Examples of the aryl group include phenyl group, tolyl group, xylyl group, naphthyl group, biphenyl group and an alkylphenyl group. [0037] The number of the carbon atoms of the aralkyl group is preferably 7 to 15, and more preferably 7 to 11. Examples of the aralkyl group include benzyl group, phenethyl group, diphenylmethyl group, triphenylmethyl group, and α or β -stylyl group.

[0038] Specific examples of R in General formula (1) include 1-butyl group, 1-pentyl group, 1-hexyl group, 1-hexyl group, 1-octyl group, 1-nonyl group, 1-decyl group, 1-undecyl group, 1-dodecyl group, 1-tridecyl group, 1-tetradecyl group, 1-pentadecyl group, 1-hexadecyl group, 2-ethyl-1-butyl group, 2-methyl-1-butyl group, 2-methyl-1-butyl group, 2-methyl-1-pentyl group, 2-methyl-1-pentyl group, 2-methyl-1-pentyl group, 2-methyl-1-pentyl group, 2-pentyl group, 3-fentyl group, 3-fentyl group, 3-fentyl group, 3-fentyl group, 2-hexadecyl group, 2-hexadecyl group, 2-hexadecyl group, 2-methyl-2-pentyl group, 3-methyl-2-pentyl group, 3-methyl-2-pentyl group, 2-methyl-3-pentyl group, 2-methyl-3-pentyl group, 2-methyl-3-pentyl group, 3-methyl-2-hexyl group, 2-methyl-3-hexyl group, 2-methyl-3-pentyl group, 3-methyl-3-pentyl group, 3-methyl-3-pentyl group, 2-methyl-3-pentyl group, 3-methyl-3-pentyl group, 3

group, 3,7-dimethyl-3-octyl group, cyclohexyl group, phenyl group, naphthyl group, tolyl group, benzyl group, phenethyl group, and the above-described compound (A).

[0039] In General formula (1), A represents at least one kind of a repeating unit having a cation. A is not particularly limited, and is preferably a repeating unit represented by the following (I) to (IV).

(I) Repeating unit represented by the following General formula (2)

[0040]

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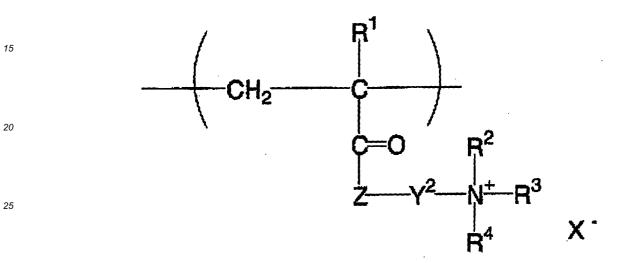
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General formula (2)



[0041] In General formula (2), R¹ represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each of R², R³, R⁴ independently represents a hydrogen atom, or an alkyl group having 1 to 18 carbon atoms, which may have a substituent or bond to each other to form a saturated or unsaturated ring, an aryl group or an aralkyl group. Z represents -O- or -NH-, and Y² represents a divalent connecting group having a total of 1 to 8 carbon atoms, which may have a hetero atom. X⁻ represents an anion.

[0042] In General formula (2), R¹ represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms. In the case where the number of the carbons thereof is more than 4, it may be difficult to obtain a polymer. The number of the carbon atoms of the alkyl group is preferably 1 to 2. Examples of the alkyl group include methyl group, ethyl group, propyl group, isobutyl group, and n-butyl group. R¹ is preferably a hydrogen atom, or methyl group.

[0043] In General formula (2), each of R², R³, R⁴ independently represents a hydrogen atom, or an alkyl group having 1 to 18 carbon atoms, an aryl group or an aralkyl group. The alkyl group, the aryl group and the aralkyl group may have a substituent. Examples of the substituent include a halogen atom, a hydroxyl group, an amino group, an ester group, an ether group, and an amide group.

[0044] The number of the carbon atoms of the alkyl group is 1 to 18, and preferably 1 to 8. In the case where the number of the carbon atoms thereof is more than 18, the dissolubility of the cationic polymer in water or alcohol is lowered and a desired properties may not be obtained. Examples of the alkyl group include methyl group, ethyl group, propyl group, butyl group, hexyl group, cyclohexyl group, octyl group, decyl group, dodecyl group, tetradecyl group, and octadecyl group, and methyl group, ethyl group, butyl group, hexyl group and cyclohexyl group are preferable.

[0045] The number of the carbon atoms of the aryl group is preferably 6 to 14, and more preferably 6 to 10. Examples of the aryl group include phenyl group, tolyl group, xylyl group, and naphthyl group, and phenyl group and tolyl group are preferable.

[0046] The number of the carbon atoms of the aralkyl group is preferably 7 to 15, and more preferably 7 to 11. Examples of the aralkyl group include benzyl group, phenethyl group, diphenylmethyl group, triphenylmethyl group, and α or β -stylyl group, and benzyl group is preferable.

[0047] In General formula (2), Z represents -O- or -NH-.

[0048] In General formula (2), y² represents a divalent connecting group having a total of 1 to 8 carbon atoms, which may have a hetero atom. Examples of the hetero atom include an oxygen atom, a nitrogen atom, a sulfur atom, a silicon atom and a phosphorus atom, and an oxygen atom, a nitrogen atom and a sulfur atom are preferable. The total number of the carbons of Y² is preferably 2 to 6. Examples of the divalent connecting group include methylene group,

ethylene group, propylene group, tetramethylene group, hexamethylene group, xylylene group, and 3-oxapentamethylene.

[0049] In General formula (2), X⁻ represents an anion. The anion is not particularly limited, and examples thereof include F⁻, Cl⁻, Br⁻, l⁻, AcO⁻, NO₃⁻, SO₄²-, HSO₄⁻, MeSO₄⁻, PO₄³-, HPO₄²-, H₂PO₄⁻, TsO⁻, CH₃SO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, CH₃CH₂CO₂⁻, Ph-CO₂⁻, (CO₂)₂²-, and a (meth)acrylate anion.

[0050] Specific examples of the repeating unit represented by General formula (2) will be presented below, but the invention is not limited thereto.

(II) Repeating unit represented by the following Genera formula (3)

[0051]

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General formula (3)

 $\begin{array}{c} & & \\$

[0052] In General formula (3), R⁵ represents a hydrogen atom of methyl group, and hydrogen atom is preferable. R², R³, R⁴ and X⁻ are the same as in General formula (2).

[0053] Specific examples of the repeating unit represented by General formula (3) will be presented below, but the invention is not limited thereto.

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(CH₂ CH)

$$\Pi - 1$$

(CH₂ CH)

 $N(C_2H_2)_3$ CI

(CH₂ CH)

 $N(C_2H_3)_3$ CI

(CH₂ CH)

 $N(R - C_4H_2)_3$ CI

 $R - 4$

35 (III) Repeating unit represented by the following General formula (4) or General formula (5)

[0054]

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[0055] In General formula (4) and (5), R², R³, and X⁻ are the same as in General formula (2).

[0056] Specific examples of the repeating unit represented by General formula (4) or (5) will be presented below, but the invention is not limited thereto.

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$$H_{3}C H_{3} = III - 15A H_{4}C H_{3} = III - 15A$$

$$H_{3}C H_{3} = III - 17A H_{3}C H_{3} = III - 17A$$

$$H_{3}C H_{3} = III - 17A H_{3}C H_{3} = III - 18A$$

$$H_{3}C H_{3} = III - 18A H_{3}C H_{3} = III - 18A$$

$$H_{3}C H_{3} = III - 18A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

$$H_{3}C H_{3} = III - 19A H_{3}C H_{3} = III - 19A$$

(IV) Repeating unit represented by the following General formula (6) or General formula (7)

[0057]

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General formula (6)

General formula (7)

15 (CH₂)_n-N

$$(CH_2)_{\overline{n}} \stackrel{N^+}{N^+} R^3 \times X$$

[0058] In General formula (6) and (7), n represents 0 or 1 and is preferably 1, and R^2 , R^3 , R^4 and X^- are the same as in General formula (2).

[0059] Specific examples of the repeating unit represented by General formula (6) or (7) will be presented below, but the invention is not limited thereto.

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$$H_{3}C$$
 CI
 $IV-23$
 $IV-24$
 $IV-24$
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 $IV-30$
 $IV-31$
 $IV-31$

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[0060] In General formula (1), B represents at least one kind of a repeating unit copolymerizable with A. B is not particularly limited, and examples thereof include an aromatic vinyl compound (such as styrene, α -methylstyrene, phydroxystyrene, chloromethylstyrene and vinyltoluene), an alkyl (meth)acrylate (such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate and 2-ethylhexyl (meth)acrylate), an alkylaryl (meth) acrylate (such as benzyl (meth)acrylate), a substituted alkyl (meth)acryliate (such as glycidyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate and dimethylaminopropyl (meth)acrylate), an alkyl (meth) acrylic amide (such as (meth)acrylic amide, dimethyl (meth) acrylic amide, N-isopropyl (meth) acrylic amide, n-butyl (meth)acrylic amide, tert-butyl (meth)acrylic amide and tert-octyl (meth)acrylic amide), a substituted alkyl (meth)acrylic amide (such as dimethylaminoethyl (meth)acrylic amide and dimethylaminopropyl (meth)acrylic amide), a vinyl cyanide (such as (meth)acrylonitrile and α -chloroacrylonitrile), a vinyl carboxylate (such as vinyl acetate, vinyl benzoate and vinyl formate), an aliphatic conjugate diene (such as 1,3-butadiene and isoprene), and a polymerizable oligomer (such as polymethyl methacrylate oligomer having a methacryloyl group at one end thereof, polystyrene oligomer having a methacryloyl group at one end thereof).

[0061] In General formula (1), m and n each represent a molar ratio of the A component and the B component, and $0.2 \le m \le 1.0$, and $0 \le n \le 0.8$, wherein m + n = 1.0. The ratio of m:n is preferably 0.4:0.6 to 1.0:0, and more preferably 0.5:0.5 to 1.0:0.

[0062] The number-average molecular weight of the cationic polymer of the invention is preferably 1,000 to 20,000, more preferably 1,000 to 10,000, and particularly preferably 1,500 to 10,000. In the case where the molecular weight thererof is less than 1,000 or more than 20,000, aggregation of the fine particles of inorganic pigment may not be prevented.

[0063] The mass ratio of the fine particles of inorganic pigment and the cationic polymer of the invention in the image-receiving layer is preferably 1:0.001 to 1:0.2, more preferably 1:0.1, and particularly preferably 1:0.005 to 0.05. In the case where the amount of the cationic polymer of the invention is less than 0.001% by mass based on the amount of the fine particles of inorganic pigment, aggregation of the fine particles of inorganic pigment may not be prevented. In the case where it is more than 0.2% by mass, aggregation of the fine particles of inorganic pigment may not be prevented or a thick coating solution which is not suitable for coating may be obtained.

[0064] The cationic polymer of the invention can be obtained by radical (co)polymerization of a monomer containing a cationic group and a monomer copolymerizable therewith in the presence of a chain transfer agent having an alkyl group having a total of 4 to 36 carbon atoms and a mercapto group. Examples of the chain transfer agent include

1-butylmercaptan, 1-pentylmercaptan, 1-hexylmercaptan, 1-heptylmercaptan, 1-octylmercaptan, 1-nonylmercaptan, 1-decylmercaptan, 1-undecylmercaptan, 1-dodecylmercaptan, 1-tridecylmercaptan, 1-tetradecylmercaptan, 1-pentadecylmercaptan, 1-hexadecylmercaptan, 1-heptadecylmercaptan, 1-octadecylmercaptan, 1-nonadecylmercaptan, 1-eicosylmercaptan, 1-docosylmercaptan, 1-hexacosylmercaptan, 1-triacontylmercaptan, 1-hexatriacontylmercaptan, sec-butylmercaptan, isobutylmercaptan, tert-butylmercaptan, neopentylmercaptan, 2-methyl-1-butylmercaptan, 3-methyl-1-butylmercaptan, 2-ethyl-1-butylmercaptan, 3,3-dimethyl-1-butylmercaptan, 2-methyl-1-pentylmercaptan, 3-methyl-1-pentylmercaptan, 4-methyl-1-pentylmercaptan, 2-propyl-1-pentylmercaptan, 2,4,4-trimethyl-1-pentylmercaptan, 2-ethyl-1-hexylmercaptan, 3,5,5-trimethyl-1-hexylmercaptan, 3,7-dimethyl-1-octylmercaptan, 2-pentylmercaptan, 3-pentylmercaptan, 2-hexylmercaptan, 3-hexylmercaptan, 2-heptylmercaptan, 2-octylmercaptan, 3-octylmercaptan, 3captan, 2-nonylmercaptan, 2-decylmercaptan, 4-decylmercaptan, 2-undecylmercaptan, 2-dodecylmercaptan, 2-tetradecylmercaptan, 2-hexadecylmercaptan, 3-methyl-2-butylmercaptan, 3,3-dimethyl-2-butylmercaptan, 3-methyl-2-pentylmercaptan, 4-methyl-2-pentylmercaptan, 2-methyl-3-pentylmercaptan, 4,4-dimethyl-2-pentylmercaptan, 4,4-dimethyl-2-methyl-2-pentylmercaptan, 2,2-dimethyl-3-pentylmercaptan, 2,4-dimethyl-3-pentylmercaptan, 5-methyl-2-hexylmercaptan, 2-methyl-3-hexylmercaptan, 6-methyl-2-heptylmercaptan, 4-methyl-3-heptylmercaptan, 2,6-dimethyl-4-heptylmercaptan, tert-amylmercaptan, 2,3-dimethyl-2-butylmercaptan, 2-methyl-2-pentylmercaptan, 3-methyl-3-pentylmercaptan, 3-ethyl-3-pentylmercaptan, 2,3-dimethyl-3-pentylmercaptan, 3-ethyl-2,2-dimethyl-3-pentylmercaptan, 2-methyl-2-hexylmercaptan, 3,7-dimethyl-3-octylmercaptan, cyclohexylmercaptan, phenylmercaptan, naphtylmercaptan, tolylmercaptan, benzylmercaptan, phenethylmercaptan, 1-octyl thioglycolate, 1-decyl thioglycolate, 1-octadecyl thioglycolate, 2-ethylhexyl thioglycolate, isooctyl thioglycolate, 1-octyl mercaptopropionate, 1-decyl mercaptopropionate, 1-octadecyl mercaptopropionate, 2-ethylhexyl mercaptopropionate, isooctyl mercaptopropionate, octyloxyethylmercaptan, octyloxyethyl thioglycolate, octyloxyethyl mercaptopropionate, and the following compounds (B) to (D).

[0065] Specific examples of the cationic polymers (cationic polymers 1 to 45) will be presented below, but the invention is not limited thereto.

Cationic polymer 1

 $nC_4H_9-S-\left(CH_2-C\right)_{m}$ C=O $O \longrightarrow {}^{+}N(CH_3)_3 CI$

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Cationic polymer 2

 $nC_8H_{17}-S+CH_2-C-M_m$ C=O $^+N(CH_3)_3$ CI

Cationic polymer 3

 $nC_{12}H_{25}-S-CH_{2}-CH_{3}$ C=O $^{+}N(CH_{3})_{3}$ CI^{-}

Cationic polymer 4

Cationic polymer 7

Cationic polymer 8

Cationic polymer 9

Cationic polymer 10

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Cationic polymer 11

Cationic polymer 12

$$nC_{12}H_{25}-O$$
 S
 CH_{2}
 CH_{3}
 $C=O$
 CH_{3}
 $C=O$
 CH_{3}
 $C=O$
 CH_{3}
 $C=O$

Cationic polymer 13

Cationic polymer 14

5 CH₂ CH₃

CH₂ CH₃

Thick is

Cationic polymer 15

Cationic polymer 16

$$\begin{array}{c|c} & & & \\ &$$

Cationic polymer 17

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$$\begin{array}{c} & & & \\ & &$$

Cationic polymer 19

Cationic polymer 20

$$CH_{2} - CH_{3}$$

$$CH_{2} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3}$$

Cationic polymer 23

Cationic polymer 24

nC₈H₁₇-O S (CH₂-C) m

Cationic polymer 27

5 CH_2 CH_2 $N(C_2H_5)_3$ CI

Cationic polymer 30

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Cationic polymer 31

 $CH_{2} \xrightarrow{H} CH_{2} \xrightarrow{H} n$

Cationic polymer 32

55 H₂C CH₂ Cl⁻

Cationic polymer 33

Cationic polymer 34

Cationic polymer 35

Cationic polymer 36

Cationic polymer 37

Cationic polymer 38

Cationic polymer 40

Cationic polymer 42

$$nC_{12}H_{25}-O$$
 S CH_{2} CH_{3} CH_{3} CH_{2} CH_{3} CH_{3}

Cationic polymer 43

Fine particles of inorganic pigment

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[0066] Examples of the fine particles of inorganic pigment include silica fine particles, colloidal silica, titanium dioxide, barium sulfate, calcium silicate, zeolite, kaolinite, halloysite, mica, talc, calcium carbonate, magnesium carbonate, calcium sulfate, boehmite, and quasi boehmite. Among these compounds, silica fine particles and a quasi boehmite are particularly preferable.

[0067] The silica fine particles have high ink absorbancy and retaining efficiency because of their particularly large specific surface area. In addition, since they have a low refractive index, they can provide transparency to the image-receiving layer by dispersing them to an appropriate particle size, and thereby a high color density and a good color forming property can be obtained. Transparency of the image-receiving layer is important from the viewpoint of obtainment of a high color density and a good color forming property not only in the application requiring the transparency such as the OHP, but also in a recording sheet such as a photo glossy paper.

[0068] The average primary particle size of the fine particles of inorganic pigment is preferably 20 nm or less, more preferably 10 nm, and particularly preferably 3 to 10 nm.

[0069] Since the silica fine particles have a silanol group on the surface thereof and the particles can easily adhere to each other by the hydrogen bond of the silanol group, they can provide a structure with a high void ratio when the average primary particle size thereof is 10 mm or less. Thereby, the ink absorbing characteristic of the sheet can be improved effectively.

[0070] Moreover, the silica fine particles can be geerally classified into particles produced by a wet method and particles produced by a dry method according to the production method.

[0071] A method of obtaining a silica hydrate by producing an active silica by the acid decomposition of a silicate, appropriately polymerizing the active silica, aggregating and precipitating the resultant product is widely used as the wet method. In contrast, a method of high temperature gas phase hydrolysis of a silica halide (flame hydrolysis method), and a method of producing a silica anhydride by heating, reducing and gasificating silica sand and coke by arc in an electric furnace, and acidifing the same by the air (arc method) are the widely used as the dry method,.

[0072] Since the silica hydrate and the silica anhydride obtained by these methods are different in terms of the concentration of the surface silanol group, existence or absence of holes, or the like, each of them has different natures. In particular, since the silica anhydride (silic acid anhydride) can easily form a three-dimensional structure with a high void ratio, it is preferable. Although the reason is not apparent, in the case of a silica hydrate, the silanol group concentration on the fine particle surface is as large as 5 to 8 groups/nm² so that the silica fine particles can easily aggregate densely. In contrast, in the case of a silica anhydride, since the silanol group concentration on the fine particle surface is as small as 2 to 3 groups/nm², it provides non-dense flocculation. It is presumed that a silica anhydride provides a structure with a high void ratio as a result.

[0073] Therefore, in the invention, it is preferable to use a silica (silica fine particles) having a 2 to 3 silanol groups per nm² of the fine particle surface.

[0074] A quasi boehmite is also preferable as the fine particles of inorganic pigment. The quasi boehmite is a crystal colloidal agglomerate of boehmite (composition thereof is AlOOH) and contains preferably a binder. As for the pore characteristic thereof, the average pore radius is preferably 1 to 10 nm, and more preferably 3 to 10 nm, and the pore volume is preferably 0.5 to 1.0 ml/g.

[0075] The coating amount of the quasi boehmite is preferably 5 to 30 g/m². In the case where the coating amount thereof is less than 5 g/m², the ink absorbancy is lowered or the glossiness may be deteriorated due to the influence of the ruggedness of the support. In the case where the coating amount thereof is more than 30 g/m², not only the quasi boehmite is consumed wastefully but also the strength of the quasi boehmite may be deteriorated.

[0076] As to the composition of the quasi boehmite coating solution, one preferably containing 5 to 50 parts by mass of a binder with respect to 100 parts by mass of the quasi boehmite solid component, with a total solid content thereof being 5 to 30% by mass can be used preferably. The solvent of the coating solution is preferable a water-based one from the viewpoint of the handling property. An organic binder, a starch or a modified product thereof, a polyvinyl alcohol

or a modified product thereof, a polymer compound such as an SBR latex, an NBR latex, a carboxymethyl cellulose, a hydroxymethyl cellulose, and a polyvinyl pyrrolidone, or the like can be preferably used as the binder.

Water soluble resin

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[0077] It is preferable that the image-receiving layer is formed by coating a dispersion containing fine particles of inorganic pigment and a water soluble resin on a support. Examples of the water soluble resin include a resin having a hydroxyl group as a hydrophilic structure unit, such as a polyvinyl alcohol (PVA), a cation modified polyvinyl alcohol, an anion modified polyvinyl alcohol, a silanol modified polyvinyl alcohol, a polyvinyl acetal, a cellulose resin [such as a methyl cellulose (MC), an ethyl cellulose (EC), a hydroxyethyl cellulose (HEC), and a carboxymethyl cellulose (CMC)], chitins, chitosans, and a starch; a resin having an ether bond, such as a polyethylene oxide (PEO), a polypropylene oxide (PPO), a polyethylene glycol (PEG), and a polyvinyl ether (PVE); and a resin having an amide group or a amide bond, such as a polyacrylic amide (PAAM) and a polyvinyl pyrrolidone (PVP).

[0078] Moreover, one having a carboxyl group as a dissociating group, such as a polyacrylic acid salt, a maleic acid resin, an alginic acid salt, and gelatins can be used as the water soluble resin.

[0079] Among the above-mentioned examples, polyvinyl alcohols are particularly preferable.

[0080] The content of the water soluble resin is preferably 9 to 40% by mass with respect to the mass of total solid component of the image-receiving layer, and more preferably 16 to 33% by mass.

[0081] In the case where the content of the water soluble resin is less than 9% by mass, the film strength is lowered, so that cracking may easily be generated at the time of drying. In the case where it is more than 40%, pores can easily be choked by the resin, so that the ink absorbancy may be lowered due to reduction of the void ratio.

[0082] Each of the fine particles of inorganic pigment and the water soluble resin mainly composing the image-receiving layer may be provided as a single material or as a mixture of a plurality of materials.

[0083] Furthermore, from the viewpoint of the transparency, the kind of the resin used in a combination with the fine particles of inorganic pigment is important. In the case where the silica anhydride is used, the water soluble resin is preferably a polyvinyl alcohol (PVA), more preferably a PVA having a saponification degree of 70 to 99%, and particularly preferably a PVA having a saponification degree of 70 to 90%.

[0084] The PVA has a hydroxyl group in the structure unit. The hydroxyl group and the silanol group on the surface of the silica fine particles form a hydrogen bond so as to facilitate formation of a three-dimensional mesh structure with a chain unit composed of the secondary particles of the silica fine particles. It is considered that an image-receiving layer having a porous structure with a high void ratio can be formed with the formation of the three-dimensional mesh structure.

[0085] In ink-jet recording, a porous image-receiving layer obtained as mentioned above absorbs an ink rapidly by the capillary phenomenon to form dots with a good roundness without ink blurring.

-Content ratio of the fine particles of inorganic pigment and the water soluble resin-

[0086] The content ratio of the fine particles of inorganic pigment (preferably silica fine particles or a quasi boehmite; i) and the water soluble resin (p) [PB ratio (i:p), the mass of the total fine particles of inorganic pigment with respect to 1 part by mass of the water soluble resin] provides a significant influence to the film structure of the image-receiving layer. That is, with a large PB ratio, the void ratio, the pore volume, and the surface area (per unit mass) become large. [0087] Specifically, the PB ratio (i:p) is preferably 1.5:1 to 10:1. In the case where the PB ratio is more than 10:1, that is, in the case where the PB ratio is too large, the film strength is lowered, so that cracking may easily be generated at the time of drying. In contrast, in the case where it is less than 1.5:1, that is, in the case where the PB ratio is too small, pores can easily be choked by the resin, so that the ink absorbancy may be lowered due to reduction of the void ratio.

[0088] When an ink-jet recording sheet is passing through a conveyance system of an ink-jet printer, a stress may be applied to the recording sheet, and therefore the image-receiving layer should have sufficient film strength. Furthermore, when the recording material is cut into sheets, the image-receiving layer should have sufficient film strength also from the viewpoint of prevention of cracking, peeling off, or the like of the image-receiving layer.

[0089] In this case, the PB ratio is preferably 5:1 or less. From the viewpoint of ensuring the high speed of ink absorbancy in the ink-jet printer, it is preferably 2:1 or more.

[0090] For example, in the case where a coating solution obtained by dispersing fine particles of inorganic pigment having an average primary particle size of 20 nm or less and a water soluble resin in an aqueous solution in a PB ratio of 2:1 to 5:1 is coated on a support and dried, a three-dimensional mesh structure with a chain unit composed of secondary particles of the fine particles of inorganic pigment is formed, so that a light transmittable porous film having an average pore size of 30 nm or less, a void ratio of 50% to 80%, a pore volume of 0.5 ml/g or more and a specific surface area of 100 m²/g or more can easily be formed.

Cross-linking agent

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[0091] It is preferable that an image-receiving layer of an ink-jet recording sheet of the invention is preferably a coating layer (porous layer) containing a cross-linking agent capable of cross-linking a water soluble resin in addition to fine particles of inorganic pigment and the water-soluble resin, and hardened by the cross-linking reaction of the cross-linking agent and the water soluble resin.

[0092] The cross-linking agent is preferably added to the sheet simultaneously with the coating of the coating solution (first coating solution) for forming the porous image-receiving layer, or added to the sheet as a second coating solution before the coating layer formed by coating the first coating solution shows the decreasing rate of drying. According to this operation, generation of cracking during drying of the coating layer can be prevented effectively. That is, the cross-linking agent solution permeates into the coating layer and is reacted quickly with the water soluble resin in the coating layer to cause the water soluble resin to gel (is hardened) upon simultaneous addition thereof with coating of the coating solution, or before the coating layer shows decreasing rate of drying. Thereby, the film strength of the coating layer can instantaneously be improved dramatically. The cross-linking agent may be included in the first and/or second coating solutions, or added to a coating solution other than the first and second coating solutions.

[0093] The cross-linking agent capable of cross-linking the water soluble resin can be selected optionally according to the water soluble resin used in the image-receiving layer. In particular, it is preferably a boron compound for its rapid cross-linking reaction. Examples of the boron compound include a borax, a boric acid, a borate (such as orthoborate, InBO₃, ScBO₃, YBO₃, LaBO₃, Mg₃(BO₃)₂, and Co₃(BO₃)₂), a diborate (such as Mg₂B₂O₅ and Co₂B₂O₅), a metaborate (such as LiBO₂, Ca(BO₂)₂, NaBO₂, and KBO₂), a tetraborate (such as Na₂B₄O₇·10H₂O), and a pentaborate (such as KB₅O₈·4H₂O, Ca₂B₆O₁₁·7H₂O, and CsB₅O₅). Furthermore, a glyoxal, a melamine-formaldehyde (such as a methylolmalemine, and an alkylated methylolmelamine), a methylolurea, a resol resin, a polyisocyanate, an epoxy resin, or the like can be used as the cross-linking agent. In particular, a borax, a boric acid, and a borate are preferable for its quick cross-linking reaction. Furthermore, they are preferably used in combination with a polyvinyl alcohol as the water soluble resin.

[0094] In the case where a gelatin is used as the water soluble resin, the following compounds known as a film hardener for a gelatin can be used as the cross-linking agent. Specifically, examples thereof include an aldehyde compound such as formaldehyde, glyoxal, and glutaraldehyde; a ketone compound such as diacetyl and cyclopentanedione; an active halogen compound such as bis(2-chloroethylurea)-2-hydroxy-4,6-dichloro-1,3,5-triazine, and sodium salt of 2,4-dichloro-6-S-triazine; an active vinyl compound such as divinylsulfonic acid, 1,3-vinylsulfonyl-2-propanol, N,N'-ethylenebis(vinylsulfonylacetamide), and 1,3,5-triacryloylhexahydro-S-triazine; an N-methylol compound such as dimethylolurea, and methylol dimethyl hydantoin; an isocyanate compound such as 1,6-hexamethylene diisocyanate; an aziridine compound disclosed in U.S. Patent Nos. 3,017,280 and 2,983,611; a carboxyimide compound disclosed in U.S. Patent No. 3,100,704; an epoxy compound such as glycerol triglycidyl ether; an ethyleneimino compound such as 1,6-hexamethylene-N,N'-bisethyleneurea; a halogenated carboxyaldehyde compound such as mucochloric acid and mucophenoxy chloric acid; a dioxane compound such as 2,3-dihydroxydioxane; and a chrome alum, a potash alum, a zirconium sulfate, and a chromium acetate.

[0095] The cross-linking agents may be used alone or in a combination of two or more kinds.

[0096] The cross-linking agent solution can be prepared by dissolving a cross-linking agent in water and/or an organic solvent. The concentration of the cross-linking agent in the cross-linking agent solution is preferably 0.05 to 10% by mass with respect to the mass of the cross-linking agent solution, and more preferably 0.1 to 7% by mass.

[0097] The solvent of the cross-linking solution is generally water, and a mixture containing water and an organic solvent which is miscible with water may be also used.

[0098] Any organic solvent can be used optionally so long as it can dissolve the cross-linking agent. Examples thereof include an alcohol such as methanol, ethanol, isopropyl alcohol, and glycerol; a ketone such as acetone, and methyl ethyl ketone; an ester such as methyl acetate and ethyl acetate; an aromatic solvent such as toluene; an ether such as tetrahydrofuran, and a halogenated carbon solvent such as dichloromethane.

Organic mordant

[0099] In the invention, in order to further improve the water resistance of the formed image and the resistance to blurring with time, it is preferable to include an organic mordant (hereinafter also referred to simply as the "mordant") in the image-receiving layer.

[0100] The mordant is preferably a cationic polymer (cationic mordant). The mordant added to the image-receiving layer can interact with a liquid ink having an anionic dye as a colorant, stabilize the colorant and improve the water resistance and the resistance to blurring with time.

[0101] In the case where the mordant is added directly to the first coating solution for forming the image-receiving layer, aggregation may be generated between the mordant and the fine particles of inorganic pigment having the anion

charge, however, in the case where it is added as a solution other than the first coating solution, such an aggregation does not occur.

Therefore, in the invention, the mordant is included and used in the second coating solution not including the fine particles of inorganic pigment.

[0102] The cationic mordant is preferably a polymer mordant having a primary to tertiary amino group, or a quaternary ammonium salt as the cationic group, but a cationic non-polymer mordant can also be used.

[0103] The polymer mordant is preferably a homopolymer of a monomer (mordant monomer) having a primary to tertiary amino group or a salt thereof, or a quaternary ammonium salt, or a copolymer or a condensation polymer of the mordant monomer and another monomer (hereinafter referred to as the "non-mordant monomer"). Moreover, these polymer mordants can be used in a form of either a water soluble polymer or latex particles that can be dispersed in water

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[0104] Examples of the monomer (mordant monomer) include trimethyl-p-vinylbenzylammonium chloride, trimethylm-vinylbenzylammonium chloride, triethyl-p-vinylbenzylammonium chloride, triethyl-m-vinylbenzylammonium chloride, ride, N,N-dimethyl-N-ethyl-N-p-vinylbenzylammonium chloride, N,N-diethyl-N-methyl-N-p-vinylbenzylammonium chloride, N,N-diethyl-N-meth ride, N,N-dimethyl-N-n-propyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-n-octyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-benzyl-N-p-vinylbenzylammonium chloride, N,N-diethyl-N-benzyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-(4-methyl)benzyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-phenyl-N-p-vinylbenzylammonium chloride, trimethyl-p-vinylbenzylammonium bromide, trimethyl-m-vinylbenzylammonium bromide, trimethyl-p-vinyl benzylammonium sulfonate, trimethyl-m-vinylbenzylammonium sulfonate, trimethyl-p-vinylbenzylammonium acetate, trimethyl-m-vinylbenzylammonium acetate, N,N,N-triethyl-N-2-(4-vinylphenyl)ethylammonium chloride, N,N,N-triethyl-N-2-(3-vinylphenyl)ethylammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinylphenyl)ethylammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinyl phenyl)ethylammonium acetate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth) acrylate; a guaternary product of N,N-dimethylaminoethyl (meth)acrylic amide, N,N-diethylaminoethyl (meth)acrylic amide, N,N-dimethylaminopropyl (meth)acrylic amide, and N,N-diethylaminopropyl (meth)acrylic amide, due to methyl chloride, ethyl chloride, methyl bromide, ethyl bromide, methyl iodide or ethyl iodide; and a sulfonate, an alkyl sulfonate, an acetate and an alkyl carboxylate with the anion thereof substituted.

[0105] Specifically, for example, monomethyl diallyl ammonium chloride, trimethyl-2-(methacryloyloxy)ethylammonium chloride, triethyl-2-(acryloyloxy)ethylammonium chloride, trimethyl-2-(acryloyloxy)ethylammonium chloride, trimethyl-3-(methacryloyloxy)propylammonium chloride, triethyl-3-(methacryloyloxy)propylammonium chloride, trimethyl-2-(methacryloylamino)ethylammonium chloride, trimethyl-2-(acryloylamino)ethylammonium chloride, trimethyl-3-(acryloylamino)propylammonium chloride, trimethyl-3-(methacryloylamino)propylammonium chloride, trimethyl-3-(acryloylamino)propylammonium chloride, trimethyl-3-(acryloylamino)propylammonium chloride, triethyl-3-(acryloylamino)propylammonium chloride, N,N-dimethyl-N-ethyl-2-(methacryloyloxy)ethylammonium chloride, trimethyl-3-(acryloylamino)propylammonium chloride, trimethyl-2-(methacryloyloxy)ethylammonium bromide, trimethyl-3-(acryloylamino)propylammonium bromide, trimethyl-2-(methacryloyloxy)ethylammonium bromide, trimethyl-3-(acryloylamino)propylammonium bromide, trimethyl-2-(methacryloyloxy)ethylammonium sulfonate, trimethyl-3-(acryloylamino)propylammonium acetate, and the like can be used as the mordant monomer.

[0106] In addition thereto, N-vinylimidazol, N-vinyl-2-methylimidazol, and the like can be used as a copolymerizable monomer.

[0107] The non-mordant monomer denotes a monomer not including a basic or cationic portion such as a primary to tertiary amino group and a salt thereof, and a quaternary ammonium salt, and the like, and not interacting with a dye in an ink-jet ink, or having a substantially small interaction therewith.

[0108] Examples of the non-mordant monomer include an alkyl (meth)acrylate; a cycloalkyl (meth)acrylate such as cyclohexyl (meth)acrylate; an aryl (meth)acrylate such as phenyl (meth) acrylate; an aralkyl ester such as benzyl (meth) acrylate; aromatic vinyls such as styrene, vinyltoluene, and α-methylstyrene; vinyl esters such as vinyl acetate, vinyl propionate, and vinyl barsatate; ally esters such as allyl acetate; a halogen-containing monomer such as vinylidene chloride and vinyl chloride; a vinyl cyanide such as (meth)acrylonitrile; and olefins such as ethylene and propylene.

[0109] The alkyl (meth)acrylate preferably has 1 to 18 carbon atoms in the alkyl group. Examples thereof include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, and stearyl (meth)acrylate.

[0110] Among these compounds, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, and hydroxylethyl methacrylate are preferable.

[0111] The non-mordant monomers can be used alone or in a combination of two or more kinds.

[0112] Furthermore, preferable examples of the polymer mordant include polydiallyl dimethyl ammonium chloride, polymethacryloyloxyethyl-β-hydroxyethyl dimethyl ammonium chloride, a polyethyleneimine, a polyallylamine and a

modified product thereof, a polyallylamine hydrochloride, a polyamide-polyamine resin, a cationated starch, a condensed product of dicyan diamide formalin, a polymer of dimethyl-2-hydroxy propyl ammonium salt, a polyamidine, and a polyvinylamine. A polyallylamine and a derivative thereof are particularly preferable.

[0113] The polyallylamine derivative is a product obtained by adding acrylonitrile, chloromethylstyrene, TEMPO, epoxyhexane, sorbic acid, or the like to a polyallylamine in an amount of 2 to 50 mol%. It is preferably an adduct in which 5 to 10 mol% of acrylonitrile or chloromethylstyrene is added to a polyallylamine. In particular, an adduct of a polyallylamine and 5 to 10 mol% of acrylonitrile is preferable from the viewpoint of preventing discoloration due to ozone. **[0114]** The weight-average molecular weight of the mordant is preferably 5,000 to 200,000. In the case where the molecular weight is 5,000 to 200,000, the water resistance and the resistance to blurring with time can be improved.

Other components

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[0115] The image-receiving layer may include the following components as needed.

[0116] For the purpose of restraining the colorant deterioration, various kinds of discoloration preventing agent such as an ultraviolet ray absorbent, an antioxidant, and a singlet oxygen quencher may be included.

[0117] Exmples of the ultraviolet ray absorbent include a cinnamic acid derivative, a benzophenone derivative, and the like. Concrete examples thereof include butyl α -cyano-phenylcinnamate, obenzotriazolphenol, o-benzotriazol-p-chlorophenol, o-benzotriazol-2,4-di-t-butylphenol, o-benzotriazol-2,4-di-t-octylphenol. A hindered phenol compound can be used as an ultraviolet ray absorbent. Specifically, a phenol derivative with at least one of the second position and the sixth position thereof substituted by a branched alkyl group is preferable. [0118] Moreover, a benzotriazol ultraviolet ray absorbent, a salicylic acid ultraviolet ray absorbent, a cyanoacrylate ultraviolet ray absorbent, an oxalic acid anilide ultraviolet ray absorbent, and the like can be used as well. These are disclosed in for example, JP-A Nos. 47-10537, 58-111942, 58-212844, 59-19945, 59-46646, 59-109055, 63-53544, JP-B Nos. 36-10466, 42-26187, 48-30492, 48-31255, 48-41572, 48-54965, 50-10726, U.S. Patent Nos. 2,719,086, 3,707,375, 3,754,919, 4,220,711, and the like.

[0119] A fluorescent brightener can also be used as the ultraviolet ray absorbent. Examples thereof include a coumarin brightener. Specifically, this compound is disclosed in JP-B Nos. 45-4699, 54-5324, and the like.

[0120] Examples of the antioxidant include those disclosed in EU Patent Publication Nos. 223,739, 309,401, 309,402, 310,551, 310,552, 459,416, German Patent Publication No. 3,435,443, JP-A Nos. 54-48535, 60-107384, 60-107383, 60-125470, 60-125471, 60-125472, 60-287485, 60-287486, 60-287487, 60-287488, 61-160287, 61-185483, 61-211079, 62-146678, 62-146680, 62-146679, 62-282885, 62-262047, 63-051174, 63-89877, 63-88380, 66-88381, 63-113536, 63-163351, 63-203372, 63-224989, 63-251282, 63-267594, 63-182484, 1-239282, 2-262654, 2-71262, 3-121449, 4-291685, 4-291684, 5-61166, 5-119449, 5-188687, 5-188686, 5-110490, 5-1108437, 5-170361, JP-B Nos. 48-43295, 48-33212, and U.S. Patent Nos. 4,814,262, and 4,980,275.

[0121] Specifically, concrete examples thereof include 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2,3,4,-tetrahydroquinoline, nickel cyclohexanoate, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-2-ethylhexane, 2-methyl-4-methoxy-diphenylamine, and 1-methyl-2-phenylindole.

[0122] The discoloration preventing agents may be used alone or in a combination of two or more kinds. The discoloration preventing agents may be used as a water soluble product, a dispersion or an emulsion, or it may be contained in microcapsules.

[0123] The amount of the discoloration preventing agent is preferably 0.01 to 10% by mass with respect to the image-receiving layer coating solution.

[0124] Moreover, for the purpose of improving the dispersing property of the fine particles of inorganic pigment, an inorganic salt and, as a pH adjusting agent, an acid, an alkaline, or the like may be included.

[0125] Furthermore, for the purpose of restraining the friction charge or the peeling charge of the surface, fine particles of metal oxide having electron conductivity may be included, and for the purpose of reducing the friction characteristic of the surface, any matting agent may be included.

50 Method for forming the image-receiving layer

[0126] Next, a method for forming an image-receiving layer will be described. It is preferable that an image-receiving layer in the invention is formed by coating a first coating solution (coating solution for an image-receiving layer) containing at least fine particles of inorganic pigment and a cationic polymer of the invention, and applying a second coating solution containing at least a cross-linking agent and an organic mordant on the coating layer (1) simultaneously with the coating of the first coating solution, (2) during the drying of the coating layer formed by the first coating solution and before the coating layer showing the decreasing rate of drying, or (3) after drying the coating layer, so as to harden the coating layer.

[0127] As mentioned above, the water resistance of the image-receiving layer can be improved by adding the mordant to the second coating solution together with the cross-linking agent and applying the second coating solution simultaneously with the coating. That is, in the case where the mordant is added to the first coating solution, aggregation may be generated between the mordant that is cationic and the fine particles of inorganic pigment having the anion charge on the surface. However, by adopting a method of preparing the second coating solution containing the mordant and the first coating solution independently, and coating the same separately, the selection range of the mordant can be widened without having to consider the aggregation of fine particles of inorganic pigment.

[0128] In the invention, the first coating solution for an image-receiving layer containing at least fine particles of inorganic pigment (such as silica fine particles), a cationic polymer of the invention, and a water soluble resin (such as PVA) can be prepared for example as follows.

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[0129] That is, it can be prepared by adding silica fine particles to water (for example, in an amount of 10 to 20% by mass), adding to the resultant mixture a solution containing a cationic polymer of the invention (for example, adding a 30% methanol solution so that the amount of the cationic polymer of the invention is 0.005 to 0.05% by mass with respect to the amount of silica produced by a gas phase method), dispersing them for 20 minutes (preferably 10 to 30 minutes) at a high speed rotation condition of 10,000 rpm (preferably 5,000 to 20,000 rpm) using a high speed rotation type and wet type colloid mill (such as Kurea Mix produced by M Technique Co., Ltd.), adding an aqueous solution of polyvinyl alcohol (for example, adding PVA so that the amount thereof is about 1/3 mass of that of the silica), and dispersing them at the above-mentioned rotation condition. The obtained first coating solution is a homogeneous sol, and a porous image-receiving layer having a three-dimensional mesh structure can be formed by coating and drying the same on a support by the following coating method.

[0130] A surfactant, a pH adjusting agent, an antistatic agent, or the like may further be added to the first coating solution, as needed.

[0131] The first coating solution can be coated on the support by a known coating method such as an extrusion die coater, an air doctor coater, a blade coater, a rod coater, a knife coater, squeeze coater, a reverse roll coater and a bar coater.

[0132] The phrase of "before the coating layer showing the decreasing rate of drying" mentioned above in general denotes a time from immediately after application of the first coating solution to several minutes after the completion of the application of the first coating solution. During the time, the coating layer shows the constant rate of drying that means the phenomenon in which the solvent content in the coating layer reduces proportionally with the time. The time in which the coating layer shows the constant rate of drying is disclosed in Chemical Engineering Handbook (p. 707 to 712, published by Maruzen Co., Ltd. October 25, 1980).

[0133] As mentioned above, the coating layer is dried after coating the first coating solution until the coating layer shows the decreasing rate of drying. The drying is carried out in general at 50 to 180°C for 0.5 to 10 minutes (preferably 0.5 to 5 minutes). Although the drying time naturally depends on the coating amount, the above-mentioned range is appropriate.

[0134] Examples of a method for applying a coating solution containing an organic solvent (second coating solution) before the coating layer shows the decreasing rate of drying include (1) a method of coating a second coating solution on the coating layer, (2) a method of spraying the second coating solution, and (3) a method of soaking the support with the coating layer in the second coating solution.

[0135] The method for coating the second coating solution (the above-mentioned method (1)) can be conducted by a known coating method such as a curtain flow coater, an extrusion die coater, an air doctor coater, a blade coater, a rod coater, a knife coater, a squeeze coater, a reverse roll coater, and a bar coater. However, it is preferable to use a method without direct contact of the coater with the coating layer already formed, such as an extrusion die coater, a curtain flow coater and a bar coater. Moreover, in the coating, two or more kinds of coating solutions may be coated simultaneously into superimposed layers.

[0136] The simultaneous coating (formation of superimposed layers) can be conducted by a coating method using, for example, an extrusion die coater and a curtain flow coater. The resultant coating layer is dried after the simultaneous coating. In this case, the drying is usually conducted by heating the coating layer at 40 to 150°C for 0.5 to 10 minutes, and preferably by heating at 40 to 100°C for 0.5 to 5 minutes.

[0137] For example, in the case where a borax and a boric acid is used as the cross-linking agent contained in the second coating solution, it is preferable to heat the superimposed layers at 60 to 100°C for 5 to 20 minutes.

[0138] Moreover, in the case where the second coating solution is applied after drying of the coating layer, the drying of coating layer is conducted by heating it at 40 to 150°C for 0.5 to 10 minutes, and preferably by heating at 40 to 100°C for 0.5 to 5 minutes.

[0139] The cross-linking agent can be added to either of the first and second coating solutions and applied onto the support ,or may be applied by preparing a solution containing it other than the first and second coating solutions and applying the solution at any stage of the coating step.

[0140] Moreover, in each stage of the coating, water, an organic solvent, or a mixture thereof can be used as the

solvent. Examples of the organic solvent used for the coating include alcohols such as methanol, ethanol, n-propanol, isopropanol, and methoxypropanol, ketones such as acetone, and methyl ethyl ketone, tetrahydrofuran, acetonitrile, ethyl acetate, and toluene.

[0141] The surface smoothness, the glossiness degree, the transparency and the coating film strength of the image-receiving layer can be improved by subjecting the thus-obtained image-receiving layer to a calendar process in which the image-receiving layer is made to pass through a roll nip while heated and pressured using, for example, a super calendar, a gloss calendar. However, since the calendar process may cause reduction of the void ratio (that is, the ink absorbancy may be lowered), it should be conducted in conditions which hardly reduces void ratio.

[0142] In the calendar process, the roll temperature is preferably 30 to 150°C, and more preferably 40 to 100°C.

[0143] Moreover, in the calendar process, the linear pressure between the rolls is preferably 50 to 400 kg/cm, and more preferably 100 to 200 kg/cm.

[0144] Since the absorbancy capable of absorbing all the liquid droplets should be provided in the case of an ink-jet recording sheet, the thickness of the image-receiving layer should be determined according to the void ratio of the layer. For example, in the case of an ink amount of 8 nL/mm² and a void ratio of 60%, the thickness of the layer should be about 15 μ m or more.

[0145] In consideration of this point, in the case of ink-jet recording, the thickness of the image-receiving layer is preferably 10 to 50 μ m.

[0146] Moreover, the pore size (median size) of the image-receiving layer is preferably 0.005 to 0.030 μ m, and more preferably 0.01 to 0.025 μ m.

[0147] The void ratio and pore median size can be measured with a mercury porosimeter (product name: pore sizer 9320-PC2, produced by Shimadzu Corporation).

[0148] Furthermore, it is preferable that the image-receiving layer has excellent transparency. As the scale therefor, the haze value of the image-receiving layer formed on the transparent film support is preferably 30% or less, and more preferably 20% or less.

[0149] The haze value can be measured with a haze meter (HGM-2DP: produced by Suga Test Instruments Co., Ltd.).

Support

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[0150] The support can be either of a transparent support comprising a transparent material such as a plastic, or an opaque support comprising an opaque material such as a paper. In order to make use of the transparency of the image-receiving layer, it is preferable to use a transparent support or a highly glossy opaque support.

[0151] The material for the transparent support is preferably a transparent material having a resistance to radiation heat when it is used in an over head projector (OHP) or a backlight display. Examples thereof include a polyester such as polyethylene terephthalate (PET); a polysulfone, a polyphenylene oxide, a polyimide, a polycarbonate, and a polyamide. Among these compounds, a polyester is preferable, and polyethylene terephthalate is more preferable.

[0152] The thickness of the transparent support is not particularly limited, but is preferable 50 to 200 μ m from the viewpoint of easy handling.

[0153] The highly glossy opaque support is preferably those whose glossiness of the surface with the image-receiving layer is 40% or more. The glossiness is a value obtained according to the method disclosed in JIS P-8142 (75 degree mirror surface glossiness testing method for the paper and the cardboard).

[0154] Specifically, examples thereof include highly glossy paper supports such as art paper, coated paper, cast coated paper, and baryta paper used as a support for the silver salt photography; highly glossy opaque films containing a white pigment or the like in a plastic film such as polyesters including polyethylene terephthalate (PET), cellulose polyesters including nitrocellulose, cellulose acetate, and cellulose acetate butylate, a polysulfone, a polyphenylene oxide, a polyimide, a polycarbonate and a polyamide, which highly glossy opaque films may be subjected to a surface calendar process; and a support with a cover layer of polyolefin containing or not containing a white pigment on the surface of the above-mentioned various kinds of the paper supports, the transparent supports or the highly glossy films containing a white pigment.

[0155] Furthermore, a foamed polyester film containing a white pigment (such as a foamed PET with voids formed by containing polyolefin fine particles and orienting) can also be preferably used.

[0156] The thickness of the opaque support is not particularly limited, but is preferably 50 to $300\,\mu m$ from the viewpoint of easy handling.

[0157] Moreover, the supports may be subjected to a corona discharge process, a glow discharge process, a flame process, an ultraviolet ray irradiation process, or the like.

[0158] Next, the base paper used in the paper support will be described in detail.

[0159] The base paper is mainly composed of wood pulp, and can be made from, as needed, a synthetic pulp such as a polypropylene or a synthetic fiber such as a nylon and a polyester in addition to the wood pulp. The wood pulp can be any of LBKP, LBSP, NBKP, NBSP, LDP, NDP, LUKP, and NUKP, and it is preferable to use a large amount of

LBKP, NBSP, LBSP, NDP, and LDP, which have a large amount of short fibers.

[0160] However, the ratio of the LBSP and/or LDP is preferably 10% by mass to 70% by mass.

[0161] A chemical pulp (a sulfate pulp and a sulfite pulp) with little impurity can be used preferably, and a pulp with a whiteness improved by a bleaching process is also useful.

[0162] The base paper can include a sizing agent such as a higher fatty acid and an alkylketene dimmer, a white pigment such as calcium carbonate, talc and titanium oxide, a chemical to enhance the strength of paper such as a starch, a polyacrylic amide, and a polyvinyl alcohol, a fluorescent brightener, a water content retaining agent such as polyethylene glycols, a dispersant, a softening agent such as a quaternary ammonium, if necessary.

[0163] The freeness, measured by CSF standard, of the pulp used for the paper production is preferably 200 to 500 ml. Moreover, as to the fiber length after beating, the sum of mass % of the 24 mesh residual component and the 42 mesh residual component specified in JIS P-8207 is preferably 30 to 70%. The mass% of the 4 mesh residual component is preferably 20% by mass or less.

[0164] The weight of the base paper is preferably 30 to 250 g, and more preferably 50 to 200 g. The thickness of the base paper is preferably 40 to 250 μ m. The base paper can be subjected to a calendar process during or after the paper production to provide it with a high smoothness. The density of base paper is generally 0.7 to 1.2 g/m² (JIS P-8118).

[0165] Furthermore, the rigidity of base paper is preferably 20 to 200 g in conditions specified in JIS P-8143.

[0166] A surface sizing agent may be applied to the base paper surface. The surface sizing agent can be the same as the above-mentioned sizing agents added to the base paper.

[0167] The pH of base paper is preferably 5 to 9 as measured by the hot water extracting method specified in JIS P-8113.

[0168] The polyethylene for covering the front surface and the back surface of the base paper is mainly a low density polyethylene (LDPE) and/or a high density polyethylene (HDPE). a LLDPE, a polypropylene, or the like can be used together with LDPE and/or HDPE.

[0169] The polyethylene layer at the side with the image-receiving layer preferably contains a rutile or anatase type titanium oxide so as to improve its opaqueness and whiteness, similar to a photographic printing paper. The titanium oxide content is preferably about 3 to 20% by mass with respect to the polyethylene, and more preferably 4 to 13% by mass

[0170] The polyethylene covering paper is used as a glossy paper, or one having a matting surface or a silky surface which is obtained by an embossing process at the time of melting-extrusion and coating of the polyethylene onto the base paper surface can be also used, similar to an ordinary photographic printing paper

[0171] As heretofore described, according to the invention, the printing density of the image can be improved without deteriorating the other ink capabilities. Furthermore, since the image-receiving layer containing fine particles of inorganic pigment has a three-dimensional mesh structure with a void ratio of 50 to 80%, a good ink absorbancy can be provided to form a high resolution image, blurring with time under a high temperature and high humidity environment can be restrained, and the excellent ink accepting capability which provides an image having excellent light resistance and water resistance can be also ensured.

EXAMPLES

[0172] Hereinafter, the present invention will be explained with reference to examples, but the invention is not limited to the examples. "Part" and "%" in the examples denote "part by mass" and "% by mass" unless otherwise specified. A number following "WM" denotes a "weight-average molecular weight", and a "polymerization degree" denotes a "weight-average polymerization degree".

<Synthesis examples of a cationic polymer of the invention>

Synthesis example 1

[0173] A 30% methanol solution of a cationic polymer 1 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by dissolving 30 parts of N-[2-(methacry-loyloxy)ethyl]-N,N,N-trimethylammonium chloride and 1.6 part of 2-ethylhexyl 3-mercaptopropionate in 70 parts of methanol, heating the resultant mixture to 65°C under a nitrogen air flow, adding 0.16 part of V-50 (polymerization initiator; produced by Wako Pure Chemical Industries, Ltd.) to the mixture and further heating them for 4 hours.

Synthesis example 2

[0174] A 30% methanol solution of a cationic polymer 2 (cationic polymer represented by General formula (1) and

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including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that the adding amount of 2-ethylhexyl 3-mercaptopropionate was changed from 1.6 parts to 3.3 parts.

Synthesis example 3

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[0175] A 30% methanol solution of a cationic polymer 3 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 30 parts of N-[2-(methacryloyloxy)ethyl]-N,N,N-trimethylammonium chloride was changed to 30 parts of N-[3-(methacryloylamino) 2-hydroxypropyl]-N,N,N-trimethylammonium chloride.

Synthesis example 4

[0176] A 30% methanol solution of a cationic polymer 4 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 30 parts of N-[2-(methacryloyloxy)ethyl]-N,N,N-trimethylammonium chloride was changed to 30 parts of N-[2-(methacryloyloxy)ethyl]-N,N-dimethylammonium chloride.

Synthesis example 5

[0177] A 30% methanol solution of a cationic polymer 5 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 30 parts of N-[2-(methacryloyloxy)ethyl]-N,N,N-trimethylammonium chloride was changed to 20 parts of N-[2-(methacryloyloxy)ethyl]-N,N,N-trimethylammonium chloride, and 10 parts of methyl acrylate.

25 Synthesis example 6

[0178] A 30% methanol solution of a cationic polymer 6 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was changed to 1.5 parts of n-dodecanethiol.

Synthesis example 7

[0179] A 30% methanol solution of a cationic polymer 7 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was changed to 2.1 parts of n-octadecanethiol.

Synthesis example 8

[0180] A 30% methanol solution of a cationic polymer 8 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was changed to 0.84 part of cyclohexylmercaptan.

Synthesis example 9

[0181] A 30% methanol solution of a cationic polymer 9 (cationic polymer represented by General formula (1) and including a repeating unit represented by General formula (2)) was obtained by the same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was changed to 2.5 parts of octadecyl thioglycolate.

Comparative synthesis example 1

[0182] A 30% methanol solution of a cationic polymer 10 (cationic polymer for comparison) was obtained by the same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was not added.

Comparative synthesis example 2

[0183] A 30% methanol solution of a cationic polymer 11 (cationic polymer for comparison) was obtained by the

same manner as in synthesis example 1 except that 1.6 parts of 2-ethylhexyl 3-mercaptopropionate was changed to 0.45 part of ethanethiol.

<Production of the ink-jet recording sheet>

Example 1

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-Production of the support-

[0184] Art paper of 186 g/m² as a base paper (OK Kondo; produced by Oji paper Co., Ltd.) was subjected to a corona discharge process, and coated with a high density polyethylene using a melting extruder so that the thickness thereof was 19 μm to form a resin layer having a matting surface (hereinafter the resin layer surface will be referred to as the "rear surface"). Thereafter the resin layer was subjected to a corona discharge process, and then a dispersion in which aluminum oxide (Alumina sol 100, produced by Nissan Chemical Industries, Ltd.) and silicon dioxide (Snow Tex O, produced by Nissan Chemical Industries, Ltd.) were dispersed in water in a mass ratio thereof of 1:2 was coated as an antistatic agent on the resin layer so that the dried mass thereof was 0.2 g/m².

[0185] Furthermore, after applying a corona discharge process to another surface (felt surface) of the base paper without the resin layer, a highly glossy thermoplastic resin layer was formed on this surface (hereinafter, the highly glossy surface will be referred to as the "front surface") by melting and extruding a low density polyethylene having a melt flow rate (MFR) of 3.8 and containing 10% of anatase type titanium dioxide, a slight amount of ultramarine, and 0.01% (with respect to the polyethylene) of a fluorescent brightener with a melting extruder so that the thickness thereof was 24 μ m. A support was thus obtained. A corona discharge process was applied to the front surface of the support before coating a coating solution for an image-receiving layer.

-Preparation of the coating solution for an image-receiving layer (first coating solution)-

[0186] A coating solution A for an image-receiving layer (first coating solution) of the following composition was prepared by mixing (1) silica fine particles produced by a gas phase method with (2) an ion-exchanged water, adding to the resultant mixture (3) the 30% methanol solution of the cationic polymer 1, processing the resultant mixture twice at a 500 kg/m² pressure using a Nanomizer LA31 (produced by Nanomizer Corp.), agitating it for 60 minutes, adding thereto (4) a 8% aqueous solution of a polyvinyl alcohol while agitating, and further adding to the resultant mixture (5) a 10% aqueous solution of Emargen 109P and (6) diethylene glycol monobutyl ether. The mass ratio of the silica fine particles and the water soluble resin (PB ratio/(1):(4)) was 4.5:1.

[Composition of the coating solution A for an image-receiving layer]

[0187]

- (1) Silica fine particles produced by a gas phase method (fine particles of inorganic pigment) 7.7 parts (specific surface area by a BET method: 300 m²/g, average primary particle size: 7 nm, QS-30, produced by Tokuyama Corp.)
 - (2) Ion-exchanged water 72.1 parts
 - (3) 30% methanol solution of the cationic polymer 1 0.51 part
 - (4) 8% aqueous solution of a polyvinyl alcohol 21.3 parts
- (PVA124, produced by Kuraray Co., Ltd., saponification degree: 98.5%, polymerization degree: 2,400)
- (5) Polyoxyethylene lauryl ether 1.0 part
- (Nonionic surfactant; Emargen 109P (10%), produced by Kao Corporation)
- (6) Diethylene glycol monobutyl ether (DEGMBE) 0.6 part
- (High boiling point organic solvent)

-Production of the ink-jet recording sheet-

[0188] The coating solution A for an image-receiving layer obtained as mentioned above was coated on the front surface of the support using an extrusion die coater (coating step) so that the coating amount thereof was 200 ml/m², and the obtained layer was dried at 80°C by a hot air drier (wind velocity 3 to 8 m/sec) until the solid component density thereof became 20%. During the duration, the coating layer showed the constant rate of drying of the coating layer. Immediately thereafter, the support was immersed in a cross-linking agent solution A of the following composition (second coating solution) for 30 seconds, the second coating solution adhered to the coating layer, the amount thereof

was 20 g/m 2 (step of applying the cross-linking agent solution), and the support was dried at 80 $^{\circ}$ C for 10 minutes (drying step). Thereby, an ink-jet recording sheet (1) of the invention provided with an image-receiving layer of a 32 μ m dry film thickness was obtained.

5 [Composition of the cross-linking agent solution A]

[0189]

- Boric acid (cross-linking agent) 2.5 parts
- · Ion-exchanged water 69.5 parts
- · Polyallylamine (10%) aqueous solution (organic mordant; WM: 10,000) 25 parts
- · Polyoxyethylene lauryl ether (nonionic surfactant) 2 parts
- (Emargen 109P (10%), produced by Kao Corporation) Ammonium chloride 1 part
- 15 -Evaluation method-
 - 1. Evaluation of the coating liquid for an image-receiving layer (1-1)

[0190] 300 g of the coating solution A for an image-receiving layer was placed in a 500 ml container. After soaking the container in a constant temperature bath at 30°C for 10 minutes, the viscosity thereof was measured at 60 rpm using a B type viscometer (produced by Tokimec Inc.) and used to evaluate the dispersion state of the coating solution A for an image-receiving layer according to the following standard. Results are shown in the table 1.

[Standard]

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[0191]

- AA: A good dispersion state suitable for coating with a viscosity of less than 100 mPas.
- BB: A dispersion state with a little trouble for coating with a viscosity of 100 to less than 1,000 mPas.
- CC: A dispersion state disabling coating with a viscosity of 1,000 mPa·s or more.
- (1-2) Average particle size

[0192] The volume standard median particle size D50 of the fine particles in the coating solution A for an image-receiving layer was measured using a light scattering diffraction type particle distribution measuring instrument (LA910, produced by Horiba, Ltd.). The value was used as the average particle size and evaluated according to the following standard. Results are shown in the table 1. For the measurement, a 1.10 refractive index was inputted as a parameter.

[Standard]

[0193]

AA: less than 0.2 μm BB: 0.2 to less than 5.0 μm CC: 5.0 μm and over

(1-3) Coarse particles

[0194] This item was evaluated by the ratio of the particles of 5 μ m or more measured by the above item (2) with respect to all the particles. Results are shown in the table 1.

[Standard]

[0195]

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AA: less than 2% BB: 2 to less than 10% CC: 10% or more

- 2. Evaluation of the ink-jet recording sheet
- (2-1) Glossiness
- [0196] The 60° glossiness of the image-receiving layer surface of a recording sheet before printing was measured by a digital variable gloss meter (UGV-50DP, produced by Suga Test Instruments Co., Ltd.), and evaluated according to the following standard. Results are shown in the table 2.

[Standard]

[0197]

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AA: 40 or more

BB: 30 to less than 40 CC: less than 30

(2-2) Ink absorbing speed

[0198] Solid images of Y (yellow), M (magenta), C (cyan), K (black), B (blue), G (green) and R (red) were printed on the ink-jet recording sheet using an ink-jet printer (PM-900C, produced by Seiko Epson Corporation). Immediately thereafter, paper was forced directly against the images and it was evaluated according to the following standard whether or not the ink was transferred onto the paper. Results are shown in the table 2.

[Standard]

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[0199]

- AA: Transfer of the ink onto the paper was not observed at all. It represents a good ink absorbing speed.
- BB: Partial transfer of the ink onto the paper was observed, but to an extent without substantial problem in a practical use.
- CC: Transfer of the ink onto the paper was observed to a significant degree.
- (2-3) Generation of cracking
- ³⁵ **[0200]** Existence or absence of cracking generated on the surface of the ink-jet recording sheet, and size thereof were observed visually and evaluated according to the following standard. Results are shown in the table 2.

[Standard]

40 [0201]

AA: No cracking was observed on the surface.

BB: Cracking of a 1 to 2 mm length was observed.

CC: Cracking of a 3 mm or more length was observed.

(2-4) Water resistance

[0202] The same printing patterns were formed on an ink-jet recording sheet using the same printer as in the above-mentioned (2-2). After leaving the sheet for 3 hours, it was soaked in water for 1 minute. The elution degree of the ink into the water was observed visually and evaluated according to the following standard. Results are shown in the table 2.

[Standard]

[0203]

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- AA: No elution of the dye was observed at all.
- BB: Partial elution of the dye was observed so as to deteriorate the color density.
- CC: The dye was eluted substantially completely into the water.

(2-5) Resistance to blurring with time

[0204] A lattice-like linear pattern (line width 0.28 mm) with a magenta ink and a black ink arranged adjacently was printed on an ink-jet recording paper using the same printer as in the above-mentioned item (2-2) and the visual density thereof was measured by X Rite 310TR (produced by X-Rite). Furthermore, after leaving the printed sheet for 3 hours, it was stored in a constant temperature and humidity vessel at 40° C and a 90% relative humidity for 1 day. Then, the visual density thereof was measured again and the density difference (Δ OD) was calculated and evaluated according to the following standard. A smaller value of the density difference (Δ OD) denotes restraint of generation of blurring. Results are shown in the table 2.

[Standard]

[0205]

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15 AA: less than 0.36 BB: 0.36 to less than 0.5

CC: 0.5 or more

(2-6) Light resistance

[0206] Solid images of Y (yellow), M (magenta), C (cyan) and K (black) were printed on an ink-jet recording sheet using the same printer as in the above-mentioned item (2-2) and the visual density of each color was measured by X Rite 310TR (produced by X-Rite). Thereafter, a lamp of Xenon weather-ometer Ci65A (produced by ATLAS Corp.) was turn on for 3.8 hours under a 25°C and a 32% relative humidity environment condition to expose the printed images through a film for cutting an ultraviolet ray whose wavelength region was 365 nm or less to light. Then, the lamp was turned off for 1 hour while the images were left under a 20°C and a 91% relative humidity environment condition. This cycle was repeated for 11 days. Then, the visual density of each color was measured again and the residual ratio (density change ratio before and after the test) as discoloration degree of each color was calculated and evaluated according to the following standard. Results are shown in the table 2.

[Standard]

[0207]

AA: without substantial discoloration

BB: slight discoloration

CC: considerable discoloration

(2-7) Image density (printing density)

[0208] A black solid image was printed on an ink-jet recording sheet using the same printer as in the above-mentioned item (2-2). After leaving the sheet for 3 hours, the reflection density of the printed surface was measured by a Macbeth reflection densitometer and evaluated according to the following standard. Results are shown in the table 2.

AA: 2.0 or more

BB: 1.8 to less than 2.0 CC: less than 1.8

Examples 2 to 9, Comparative examples 1 to 5

[0209] Coating solutions B to N for an image-receiving layer were prepared in the same manner as in example 1 except that the cationic polymer 1 of the coating solution A for an image-receiving layer and the addition amount thereof were changed to the cationic polymers and the addition amounts shown in the table 1, and ink-jet recording sheets of the invention and comparative ink-jet recording sheets were produced and evaluated. Results are shown in the table 2. In comparative examples 1, 2, 4 and 5, a high viscosity of the coating solutions for an image-receiving layer disabled a coating thereof on a support.

Table 1

		Cationic polymer	Addition amount	Viscosity	Particle size	Coarse particles
5	Example 1	1	0.51	AA	AA	AA
	Example 2	2	0.51	AA	AA	AA
	Example 3	3	0.51	AA	AA	AA
	Example 4	4	0.51	AA	AA	AA
10	Example 5	5	0.51	AA	AA	AA
	Example 6	6	0.51	AA	AA	AA
	Example 7	7	0.51	AA	AA	AA
15	Example 8	8	0.51	AA	AA	AA
	Example 9	9	0.51	AA	AA	AA
	Comparative example 1	10	0.51	CC	CC	CC
20	Comparative example 2	11	0.51	CC	CC	CC
25	Comparative example 3	Polymonomethyl diallyl ammonium chloride	1.30	AA	AA	AA
	Comparative example 4	Polyallylamine salt acidic salt	1.30	CC	CC	CC
30	Comparative example 5	None	-	CC	CC	СС

[0210] From table 1, it was found that the coating solutions for an image-receiving layer with the cationic polymers of the invention added can restrain aggregation of the silica fine particles produced by a gas phase method and provide a dispersion with a good flowability.

[0211] In contrast, the coating solutions J, K, M and N for an image-receiving layer using a cationic polymer not having at the end thereof a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group, or including no cationic polymer (aggregation preventing agent) (comparative examples 1, 2, 4 and 5) showed a low result in the evaluation of the viscosity, the average particle size and the coarse particles, and because of its high viscosity, it was impossible to coat them on the support. Moreover, according to the coating solutions L and M for an image-receiving layer not using a cationic polymer of the invention (comparative examples 3 and 4), it was necessary to add a large amount of the cationic polymer.

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5		example 5	Comparative	example 4	Comparative	example 3	Comparative	example 2	Comparative	example 1	Comparative	Evample 9	Example 8	Example 7	Example 6	Example 5	Example 4	Example 3	Example 2	Example 1		I divid V
10 15		2	2	×	3	_		~		C			=	G	F	m	0	C	В	Α	Coating solution for an image-receiving layer	
			-		1		+		+		+			-	-		-	ļ	-	-	¥ 55	
20)	impossible	Evaluation	impossible	Evaluation	≵		impossible	Figuration	impossible	Fundaments 5	ΔΔ	AA	Ą	AA	Ą	A	AA	AA	AA	Glossiness	
25	5	impossible	Evaluation	impossible	Evaluation	\$		impossible	Evoluction	impossible	3	A	AA	A	Ink absorbing speed							
30		impossible	Evaluation	impossible	Evaluation	A	The Colons	impossible	Tiphodicio	imnossible	*	>	AA	Cracking								
35	;	impossible	Evaluation	imnossible	Evaluation	A	III DOGGIGIG	Evaluation	il thooping	Evaluation	A	>	AA	AA	AA	A	AA	AA	AA	AA	Water resistance	
40		impossible	Evaluation	impossible	Evaluation	BB	intocooldic	Evaluation	III DOSOIDIG	impossible	AA	>	AA	ĄĄ	A	AA	ĄĄ	AA	AA	AA	Resistance to blurring with time	
45		impossible	Evaluation	impossible	Evaluation	 	Biologodium	Evaluation	Binecodini	Evaluation	Æ	>	ĄĄ	A	A	AA	AA	A	\$	AA	Light resistance	
50 55		impossible	Evaluation	Lyanauon	Evaluation	۸۵	aldiscodiiii	Evaluation	Hipossipie	Evaluation	A	•	AA	AA	AA	AA	AA	A	A	A	Image density	
	Ĺ				_1_		1		1		1		i	L	1	L	<u>L</u>	i	<u> </u>	1	1	

[0212] From the results shown in the table 2, it was found that the ink-jet recording sheets of the invention in which

the cationic polymers of the invention are added to the coating solutions for an image-receiving layer and which contain inorganic pigment particles are excellent in terms of the glossiness, ink absorbing speed, cracking, water resistance, resistance to blurring with time, light resistance and printing density.

[0213] In contrast, as for the comparative example 3 including no cationic polymer of the invention, blurring was generated with time, and furthermore, the light resistance was low. Moreover, as for the comparative examples 1, 2, 4 and 5, the viscosity of the coating solutions for an image-receiving layer was too high to produce an ink-jet recording sheet, and thus they were not evaluated.

10 Claims

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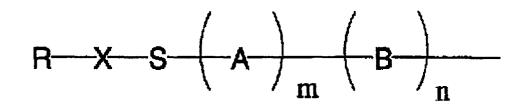
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- 1. An ink-jet recording sheet comprising a support and an image-receiving layer which contains fine particles of inorganic pigment and a cationic polymer having at the end thereof a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group.
- 2. An ink-jet recording sheet according to claim 1, wherein a dispersion in which the fine particles of inorganic pigment is dispersed in the presence of the cationic polymer having at the end thereof a group selected from the group consisting of an alkyl group having a total of 4 to 36 carbon atoms, an aryl group and an aralkyl group is used for the image-receiving layer.
- 3. An ink-jet recording sheet according to claim 1, wherein the cationic polymer is represented by the following General formula (1):

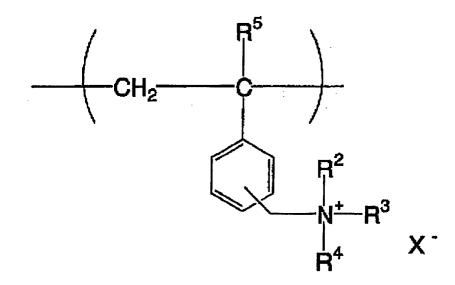


in General formula (1), X represents a single bond or a divalent connecting group, R represents a straight, branched or cyclic alkyl group having a total of 4 to 36 carbon atoms, an aryl group, or an aralkyl group, A represents at least one kind of a repeating unit having a cation, B represents at least one kind of a repeating unit copolymerizable with A, m and n each represents a molar ratio of the A component and the B component, and $0.2 \le m \le 1.0$, $0 \le n \le 0.8$ and m + n = 1.0.

- **4.** An ink-jet recording sheet according to claim 3, wherein R in General formula (1) is selected from the group consisting of a straight, branched or cyclic alkyl group having a total of 8 to 18 carbon atoms, an aryl group, or an aralkyl group.
- 5. An ink-jet recording sheet according to claim 3 or 4, wherein the repeating unit A in General formula (1) is selected from the group consisting of the following (I) to (IV):
- (I) a repeating unit represented by the following General formula (2):

in General formula (2), R^1 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, each of R^2 , R^3 , R^4 independently represents a hydrogen atom, or an alkyl group having 1 to 18 carbon atoms, which may have a substituent or bond to each other to form a saturated or unsaturated ring, an aryl group or an aralkyl group, Z represents -O- or -NH-, Y^2 represents a divalent connecting group having a total of 1 to 8 carbon atoms, which may have a hetero atom, and X^2 represents an anion:

(II) a repeating unit represented by the following General formula (3):



in General formula (3), R^5 represents a hydrogen atom or methyl group, and R^2 , R^3 , R^4 and X^- are the same as in General formula (2):

(III) a repeating unit represented by the following General formula (4) or General formula (5):

General formula (4)

General formula (5)

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N⁺

 R^2 R^3 X

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in General formulae (4) and (5), R^2 , R^3 , and X^- are the same as in General formula (2): (IV) a repeating unit represented by the following General formula (6) or General formula (7):

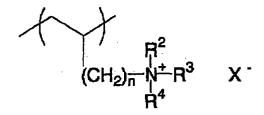
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General formula (6)

General formula (7)

(CH₂)_n-N



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in General formula (6) and (7), n represents 0 or 1, and R², R³, R⁴ and X⁻ are the same as in General formula (2).

6. An ink-jet recording sheet according to any one of claims 1 to 5, wherein the number-average molecular weight of the cationic polymer is 1,000 to 20,000.

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7. An ink-jet recording sheet according to any one of claims 1 to 6, wherein the mass ratio (x:y) of the fine particles of inorganic pigment (x) and the cationic polymer (y) is 1:0.001 to 1:0.2.

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8. An ink-jet recording sheet according to any one of claims 1 to 7, wherein the fine particles of inorganic pigment are silica fine particles having an average primary particle size of 20 nm or less, or a quasi boehmite having an average pore radius of 1 to 10 nm.

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9. An ink-jet recording sheet according to any one of claims 1 to 8, wherein the image-receiving layer is formed by coating a dispersion containing the fine particles of inorganic pigment and a water soluble resin on the support.

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10. An ink-jet recording sheet according to claim 9, wherein the water soluble resin is a polyvinyl alcohol or a derivative thereof.

11. An ink-jet recording sheet according to claim 9 or 10, wherein the image-receiving layer contains a cross-linking agent capable of cross-linking the water soluble resin.

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12. An ink-jet recording sheet according to claim 11, wherein the cross-linking agent is a boron compound.

- **13.** An ink-jet recording sheet according to any one of claims 1 to 12, wherein the image-receiving layer contains an organic mordant.
- 14. An ink-jet recording sheet according to claim 13, wherein the organic mordant is a polyallylamine or a derivative thereof
 - thereof.

- **15.** An ink-jet recording sheet according to any one of claims 9 to 14, wherein the image-receiving layer has a three-dimensional mesh structure with a void ratio of 50 to 80%, and the mass ratio (i:p) of the fine particles of inorganic pigment (i) and the water soluble resin (p) is 1.5:1 to 10:1.
- 16. An ink-jet recording sheet according to any one of claims 13 to 15, wherein the image-receiving layer is obtained by coating a first coating solution containing at least the fine particles of inorganic pigment and the cationic polymer on the support surface, and applying a second coating solution containing at least the organic mordant on the coating layer (1) simultaneously with the coating, (2) during the drying of the coating layer formed by the above-mentioned coating and before the coating layer showing the decreasing rate of drying, or (3) after drying the coating layer, and by hardening and drying the coating layer.

17. An ink-jet recording sheet according to claim 16, wherein the image-receiving layer is obtained by applying the cross-linking agent added to at least one of the first and second coating solutions, or applying a coating solution containing the cross-linking agent independently of the first and second coating solutions.