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(54) RESIN COMPOSITION FOR INK-JET RECORDING SHEET AND RECORDING SHEET MADE WITH THE SAME

(57) The present invention Nos. I-VII are a resin composition for an ink-jet recording sheet for constructing an image-receiving layer which is formed on at least one surface of a base material for an ink-jet recording sheet.

The present invention No. I relates to a resin composition for an ink-jet recording sheet which comprises (1) 2-80% by mass of a cationic acrylic copolymer (A) having a crosslinkable group, (2) 5-80% by mass of a saponified product (B) of a vinyl acetate-based copolymer having a polymerization degree of 200-1000, and (3) 0-80% by mass of a modifier (R), the present invention No. II relates to a resin composition for an ink-jet recording sheet which contains (1) 2-80 wt% of a cationic acrylic copolymer (A) having a crosslinkable group, (2) 5-80 wt% of a saponified product (B) of a vinyl acetate-based copolymer, (3) (n_1 -80) wt% of a water-based polyurethane resin (C), (4) (n_2 -60) wt% of a polyurethane-based graft polymer mixture (D), and (5) (n_3 -60) wt% of a polyester-based graft polymer mixture (E) in a solid content-based ratio, and total is 100 wt%, in which there are satisfied conditions that

a minimum value in n_1 , n_2 , and n_3 is 0, and ($n_1+n_2+n_3$) is ≥ 5 ,

the present invention No. III relates to a resin composition for an ink-jet recording sheet which comprises, [1] 2-80% by weight of a cationic acrylic copolymer (A) having a crosslinkable group,

[2] 5-60% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and

[3] 0-80% by weight of a water-based polyurethane resin (C) {total of the (A), (B), and (C) is 100% by weight}, and

[4] 0.05-10 parts by weight of a block isocyanate compound (F) based on 100 parts by weight of the saponified product (B) of a vinyl acetate-based copolymer,

the present invention No. IV relates to a resin composition for an ink-jet recording sheet which comprises the use of 2-100% by weight of a cationic acrylic copolymer (A) composed of a monomer having an alkylene oxide group, a monomer having a hydrophilic group, a monomer having a crosslinkable group, a monomer contain-

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ing cationic group, 0-90% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and 5-60% by weight of a modifier (R), and an image-receiving layer is formed over at least one surface, the present invention No. V relates to a resin composition for an ink-jet recording sheet which comprises formulating 70-100% by weight of a cationic (meth)acrylic polymer (A) in which there are copolymerized a cationic (meth)acrylate monomer having a polyalkylene oxide group, a monomer having a hydrophilic group, a monomer having a crosslinkable group, a monomer containing cationic group, and a cationic monomer, 0-30% by weight of a saponified product (B) of a vinyl acetate-based copolymer (total thereof is 100% by weight), and 0-15 parts by weight of a modifier (R) based on 100 parts by weight of the (A) and the (B), the present invention No. VI relates to an ink-jet recording sheet which comprises being constructed by a composition containing a (meth)acrylic-based copolymer having a hydrolyzable silyl group in which a polymerizable unsaturated monomer having a hydrolyzable silyl group is copolymerized with monomers containing a (meth)acrylate-based polymerizable unsaturated monomer, and inorganic compound fine particles, the present invention No. VII relates to a resin composition for an ink-jet recording sheet characterized by

containing 100 parts by weight of a resin composition composed of (1) 1-30% by weight of a cellulose derivative (A) and (2) 70-99% by weight of a good solvent (B) for the cellulose derivative (total is 100% by weight), (3) 0.1-20 parts by weight of an organic acid (C) which can dissolve in the good solvent (B) or a weak solvent (D) for the cellulose derivative, and optionally, (4) 0-150 parts by weight of a weak solvent (D) for the cellulose derivative, and relates to a recording sheet in which an image-receiving layer is formed on a body to be recorded composed of the resin composition.

the present invention No. VIII is to provide a heat transfer sheet which is excellent in an ink-absorbing ability, an ink-fixing ability, and a printing ability in the case of molding into the heat transfer sheet, and which is high in a water resistance, durability, particularly, micro cracks resistance of a recorded picture, and in which an ink-receiving layer is formed on an elastic material, and micro cracks are not caused even though the recorded picture is expanded and shrunk, and a resin composition for constructing thereof, a resin composition containing a polymer (A) containing a monomer unit shown by a specified formula (1) and a hot-melt adhesive resin (B), a heat transfer sheet comprised the resin composition, and a method for the preparation thereof.

Description

TECHNICAL FIELD

5 **[0001]** The present invention Nos. I-VII relate to a resin composition to be employed for an image-receiving layer in an ink jet recording sheet and an ink jet recording sheet having an image-receiving layer in which the resin composition is employed and, in more detail, relate to a resin composition employed for an image-receiving layer in an ink jet recording sheet which is excellent in an ink-absorbing ability, water resistance, and clearness of a recorded image, and relate to an ink jet recording sheet having an image-receiving layer which is formed by the use of the resin composition.

10 **[0002]** The present invention No. I relates to a resin composition to be employed for an ink jet recording sheet which comprises a cationic acrylic copolymer containing a crosslinkable group, a saponified product of a vinyl acetate-based copolymer having a polymerization degree of 200-1000, and an improving material, and a recording sheet in which it is employed is high in an image quality of printing, and a characteristics that beading is not caused even in an ink jet printer having a quick printing speed, water resistance is highly improved in addition to clearness and an ink absorbability such as image uniformity, and water resistance and an ink absorbing ability can be coexisted which are of a contrary property in each other.

15 **[0003]** The present invention No. II particularly relates to a resin composition for an ink jet recording sheet which comprises a cationic acrylic copolymer containing a crosslinkable group, a saponified product of a vinyl acetate-based copolymer, a water-based polyurethane resin and a polyester-based graft polymer mixture, and a recording sheet in which it is employed has a high clearness, high printing quality, and an ink absorbing ability, in which water resistance is highly improved, and which has a characteristics being capable of coexisting water resistance and an ink absorbing ability which are of a contrary property in each other.

20 **[0004]** The present invention No. III relates to a resin composition for an ink jet recording sheet which comprises a cationic acrylic copolymer containing a crosslinkable group, a saponified product of a vinyl acetate-based copolymer, a water-based polyurethane resin composition, and a block isocyanate compound and a recording sheet in which it is employed has a characteristics being capable of highly improving water resistance while maintaining an ink absorbing ability and a printing ability.

25 **[0005]** The present invention No. IV relates to a resin composition for an ink jet recording sheet which comprises a cationic copolymer obtained by copolymerization of a monomer having a polyalkylene oxide group, a monomer containing a hydrophilic group, a monomer containing a crosslinkable group, and a cationic monomer, a saponified product of a vinyl acetate-based copolymer and a modifier, and in a recording sheet in which it is employed, there is obtained a printing quality which is excellent in uniformity and blur resistance, and even in a circumstance in which a shift of high resolution and high speed is required, there are highly-improved water resistance, an ink absorbing ability, and a printing image quality, it has a characteristics that water resistance and an ink absorbing ability can be coexisted which are a contrary property each other while improving a printing quality such as a photographic picture image.

30 **[0006]** The present invention No. V relates to a resin composition for an ink jet recording sheet which comprises a cationic (meth)acrylic copolymer obtained by copolymerization of a (meth)acrylic monomer containing a polyalkylene oxide group, a monomer containing a hydrophilic group, a monomer containing a crosslinkable group, and a cationic monomer, a saponified product of a vinyl acetate-based copolymer and a modifier, and a recording sheet in which it is employed has an image-receiving layer having an excellent roll-adhering resistance, an excellent high glossiness, and no-occurrence of worse in an image such as beading.

35 **[0007]** The present invention No. VI relates to an ink jet recording sheet in which there is employed a composition (P) composed of a (meth)acrylic-based copolymer containing a hydrolyzable silyl group obtained by copolymerization of monomers containing a polymerizable unsaturated monomer having a hydrolyzable silyl group and a (meth)acrylic-based polymerizable unsaturated monomer and inorganic compound-based fine particles, and it has an image-receiving layer which is excellent in glossiness, etc. regardless of using a composition containing the inorganic compound-based fine particles.

40 **[0008]** The present invention No. VII relates to a resin composition for recording which contains a resin composition composed of a cellulose derivative and a good solvent for the cellulose derivative, an organic acid which can dissolve in the good solvent or a weak solvent of the cellulose derivative, and a recording sheet in which it is employed is excellent in a blocking resistance, and it can form an image-receiving layer in which there can be improved surface glossiness of the picture image-receiving layer, clearness of a recorded image, and reproducibility of colors.

45 **[0009]** The present invention No. VIII relates to a resin composition containing a polymer having a monomer unit shown by formula (14) described below and a hot-melt adhesive resin, and a heat-transfer sheet in which it is employed is excellent in an ink absorbing ability, an ink-fixing ability, printing ability, a water resistance of a recorded image, micro crack resistance, durability, and washing resistance.

BACKGROUND TECHNOLOGY

[0010] An ink jet recording method in which is low in cost, and in which full-coloration can be readily attained, and since it is low in noise and excellent in a printing ability, it is recently being rapidly spread, and it has been widely employed as a printer in an office and usual home use and a printer for a sign display.

[0011] In the ink jet recording method, a water-based ink is mainly employed from a viewpoint of safeness and applicability to recording, recording is conducted by spraying small droplets of an ink from a fine nozzle toward a recording sheet. For that reason, in the recording sheet, a quick absorbable ink is desired. That is, in a recording sheet having a low ink absorbing ability, an ink remains on the surface of the recording sheet for a long time of period after completion of recording, whereby, it is anxious that a recording portion becomes dirty by contact with a portion of an apparatus and handling person, and by overlapping of the sheets.

[0012] Further, there is a problem that in a portion of high density image, a large amount-supplied ink mixedly flows out without being absorbed, and an image becomes unclear.

[0013] In order to solve such the problems and to show a functional property, a variety of properties are required in an ink jet recording sheet, and a most important property is capability of quickly absorbing an ink sprayed from a nozzle and having a water resistance to a water-based ink.

[0014] In order to solve the above-described various problems, a variety of proposes are made. For example, JP-A-57036692 Official Gazette discloses a technology concerning an ink jet recording sheet in which there is coated a basic latex polymer together with a water-soluble polymer and pigments in order to improve water resistance and dissolution. Further, JP-A-63115780 Official Gazette discloses an ink jet recording sheet in which a polymer containing a quaternary ammonia salt is coated on a base material for a recording sheet, and it also states that a synthesized silica is employed together and a polyvinyl alcohol, etc. is employed together as a binder.

[0015] Still further, JP-A-07061113 Official Gazette discloses an ink jet recording medium in which an ink-receiving layer is constructed by a polyvinyl alcohol resin and a cationic compound.

[0016] Besides, JP-A-06227114 Official Gazette discloses an ink jet recording medium in which an ink receiving-layer which is constructed by pigments such as finely-powdered silica and an amphoteric ion latex.

[0017] The Official Gazettes teach that there can be fairly improved a fixing-ability and water resistance by a modification to non-flowing of an ink in the ink jet recording sheet. However, since there is a contrary relationship between the ink-fixing ability, water resistance, and an ink absorbing ability, if the water resistance and the ink-fixing ability are elevated, the ink absorbing ability lowers. Accordingly, both of the water resistance and the ink absorbing ability cannot be maintained in a high level by conventional technologies.

[0018] Also, there is a problem that glossiness of the recording sheet unavoidably lowers by the use of the synthesized silica and finely-powdered silica, etc.

[0019] And also, JP-A-01174484 Official Gazette discloses an ink jet recording sheet in which a covering layer containing a copolymer of a fatty acid vinyl ester such as vinyl acetate with a cationic monomer and pigments is formed on the surface of a base material for the recording sheet, and the cationic copolymer may be a copolymer with a cationic monomer and a graft copolymer with a polyvinyl alcohol, and it may further contain even a water-soluble polymer binder.

[0020] Furthermore, JP-A-62083178 Official Gazette proposes an ink jet recording sheet having a coating layer containing a finely-powdered silicate and a cationic polymer emulsion, and it also states that it is preferred to employ together a self-crosslinkable acrylic emulsion having a glass transition temperature of not more than 0°C as an adhesive.

[0021] Although it was confirmed that the water resistance can be passably improved in the above-described ink jet recording sheet, the improvement is a low level, and water resistance is low, accordingly, a recording portion is flown out by water droplets, and blots are caused at a printing portion and an image portion, in the case that the blots are remarkable, the portions dissolve out and disappear. Accordingly, it cannot help being said that a quality concerning a recording property is still insufficient. As described hereinabove, conventional technologies cannot attain to a high level of improvement of water resistance and an ink absorbing ability while maintaining a printing quality.

[0022] Further, in a recent printer, a recording sheet has become severely and severely employed at a high dissolution printing such as not less than 1000 dpi, multiple-printing by a light-colored ink at a high speed printing such as several times compared to. conventional speed in order to actualize a printing by a photographic image quality, and it is difficult to improve a problem of a worse image quality such as beading caused by a highest photographic image quality mode in a printer, and a high glossiness such as a print for silver chloride photograph becomes also desired in an outer appearance, there is a new problem of a mark of an embossed roll (a pressurized mark by a paper-discharging roll having a gear shape) which is printed on the surface of a high gloss recording sheet.

[0023] On the other hand, JP-A-57014091 and JP-A-61019389 Official Gazettes disclose an ink jet recording sheet which is constructed by a colloidal silica and a water-soluble resin. However, there is a problem that sufficient water resistance cannot be obtained because of the use of a water-soluble polymer as a binder.

[0024] Still further, JP-A-02276670 and JP-A-03281385 Official Gazettes disclose an ink jet recording sheet formed

from a pseudo boehmite fine particles. Although the recording sheet shows a high ink absorbing ability and water resistance, an ink-receiving layer does not show a sufficient gloss.

[0025] Furthermore, JP-A-59174381 and JP-A-60224578 Official Gazettes propose the use of a hydrophilic polymer such as starches, a water-soluble cellulose derivative, and a polyvinyl alcohol as an ink-receiving layer on a base material. However, although it satisfies an ink absorbing ability, it is poor in water resistance and an ink-receiving layer is dissolved out, and blocking is caused by sticking of surface when recording sheets are overlaid, resulting in that it is practically problematic.

[0026] Also, JP-B-91072460 Official Gazette proposes a method in which an ink is absorbed at an under-layer and a blocking resistance is improved at a surface layer, which comprises a combination of an ink-permeable surface layer with an ink-absorbing under layer. However, since an ink is absorbed in the ink-absorbing under-layer passing through the surface layer, it looks like a recording sheet in which an ink deeply penetrates, and there is a drawback that color concentration does not readily come out and, there are also a problem of layer-separation between a surface layer and an under-layer and a problem of low water resistance of the under-layer.

[0027] Further, there is proposed a recording sheet in which a porous layer is formed as an ink-absorbing layer and, an ink is absorbed by a capillary phenomenon, JP-A-58110287 and JP-A-05051470 Official Gazettes propose recording sheets in which there is formed a porous layer having air cells formed by spaces between particles themselves by coagulating fine particles such as silica on a base material. In the recording sheets, there is a problem that although an ink-absorbing ability is improved, surface gloss is low by light scattering of the particles, and an ink-absorbing capacity is not sufficient.

[0028] Although JP-A-61085251 proposes a recording sheet in which a porous plastic thin layer is laminated with an ink-absorbing layer, since the porous plastic thin layer is formed by a hydrophobic plastics such as a polyethylene and polypropylene, an ink permeability is not sufficient in ink jet recording in which a water-based ink is mainly employed, and since the porous plastic thin layer is laminated by a thermally-compressurizing method, pores are crushed and deformed.

[0029] As described hereinabove, although there are made a variety of proposes concerning an ink-receiving layer in an ink jet recording sheet and an ink absorbing ability, water resistance, and glossiness are passably improved in the above-described ink jet recording sheets, it cannot help saying that a level of improvement is still small, and quality concerning recording ability and glossiness is still insufficient.

[0030] Further, in the recording sheets, an ink-fixing ability and water resistance cannot be elevated to a high level. Particularly, it is difficult to thermally-transfer an image to be recorded to a body to be transferred. Still further, even though an image can be transferred to the body to be transferred, washing resistance and durability are poor.

[0031] JP-A-63060784 Official Gazette discloses an ink jet recording sheet in which there is formed an ink-absorbing layer containing organic polymer fine particles which are dissolved or swelled in solvents in an ink (particularly, an oily ink) on surface of a substrate.

[0032] JP-A-07025133 Official Gazette discloses an ink jet recording sheet in which an ink-receiving layer is formed on at least one surface of a substrate which is formed by a polyolefine resin-coated paper or a polyester film, and the ink-receiving layer contains spherical fine particle polymers having an average particle diameter of 5-15 μm in a proportion of 5-30 g/m² by dry weight and thickness thinner than the average particle diameter of the spherical fine particle polymers.

[0033] JP-A-08324106 Official Gazette discloses an ink jet recording sheet in which an ink-receiving layer having a porous structure is formed on one surface of a base material, and the layer is constructed by a hot-melt resin (an ethylene-vinyl acetate-based resin, a polyester-based resin, and a rubber-based resin, etc.).

[0034] JP-A-08207425 Official Gazette discloses an ink jet recording sheet in which an ink-receiving layer is formed on one surface of a base material, and the layer contains a hot-melt resin (a polyamide-based resin, a polyester-based resin, and a water-soluble hot-melt resin such as an unsaturated polyester resin) and a hydrophilic resin (a polyacrylic amide, a polyvinyl alcohol, and polyvinyl pyrrolidone, etc.). The recording sheet can be thermallylaminated with a film, etc.

[0035] However, in the ink-receiving layers, an ink-fixing ability and water resistance are not sufficient.

[0036] Particularly, since washing resistance and durability (a micro crack resistance, etc.) are not sufficient, even though an image to be recorded is thermally-transferred to clothes, etc., a clear image transferred cannot become maintained for a long time of period.

[0037] Accordingly, the purpose of the present invention Nos. I-III is to provide a resin composition for an ink-jet recording sheet by which an ink-absorbing ability and water resistance can be improved in a high level.

[0038] Further, the purpose of the present invention No. IV is to provide an ink-jet recording sheet in which there is not caused worse of an image such as beading even in a printer having a high printing speed by which a letter-printing quality is improved, and water resistance and an ink-absorbing ability are simultaneously satisfied.

[0039] Still further, the purpose of the present invention No. V is to provide an ink-jet recording sheet having a photographic tone which is preferred in an ink jet recording type method by which an excellent letter-printing quality, water

resistance, and high glossiness can be attained, in which an outer appearance of a printed image is not deteriorated by transferring to a recording paper of an embossed roll mark in the printer when the printer discharges the recording paper.

[0040] Besides, the purpose of the present invention No. VI is to provide an ink-jet recording sheet which is excellent in a glossy property and, in which there are obtained an excellent ink-absorbing ability and water resistance.

[0041] Furthermore, the purpose of the present invention No. VII is to provide a resin composition for recording and a recording sheet in which there is formed an image-receiving layer composed thereof.

[0042] The image-receiving layer can be formed by the resin composition for recording, and which is excellent in an ink-absorbing ability and a blocking resistance and, in which there can be improved surface gloss of the image-receiving layer, clearness of the recorded image, water resistance, weatherability, and reproducibility of colors, etc.

[0043] Further, the purpose of the present invention No. VIII is to provide a resin composition for a heat transfer sheet and a heat transfer sheet. The resin composition is excellent in an ink-absorbing ability, an ink-fixing ability, a printing ability, water resistance of a recorded image, micro crack resistance, durability, and washing resistance, and which is useful for a heat transfer sheet.

DISCLOSURE OF THE INVENTION

[0044] The present inventors, as a result of an intensive investigation for attaining the above-mentioned purposes, have found out that a recording sheet can be prepared by the combination of a cationic acrylic copolymer having a crosslinkable group and a saponified product of a vinyl acetate-based copolymer having a specified polymerization degree with a modifier, or by further combination of a water-based polyurethane resin, a polyurethane-based graft polymer mixture and a polyester-based graft polymer mixture, or a water-based polyurethane resin composition with a block isocyanate, in which water resistance, an ink-absorbing ability, and a printing image quality are remarkably improved and an excellent image quality can be obtained even in a high speed printer, and the present invention Nos. I-III were completed.

[0045] Further, the present inventors have obtained a finding that water resistance, an ink-absorbing ability, and a printing image quality can be remarkably improved even in a high speed printer having a high dissolution by a resin composition composed of a cationic acrylic copolymer (A-IV and A-V) obtained by copolymerization of a monomer having an alkylene oxide group, a monomer having a hydrophilic group, a monomer having a crosslinkable group, and a cationic acrylic monomer and a saponified product (B) of a vinyl acetate-based copolymer, particularly, a saponified product of a vinyl acetate-based copolymer having a specified polymerization degree, and a modifier (R), and there can be solved a various problems in adherence of an embossed roll mark and a high glossiness, etc., and the present invention Nos. IV and V were completed.

[0046] Still further, the present inventors have found that an excellent glossiness, excellent ink absorbing ability, and water resistance can be obtained through constructing an image-receiving layer by a specified copolymer and fine particles of an inorganic compound, and the present invention No. VI was completed.

[0047] Also, the present inventors have found that surface glossiness of an image-receiving layer in a body to be recorded and clearness in a recorded image can be largely improved by the use of a resin composition for recording containing a cellulose derivative, a good solvent for the cellulose derivative, an organic acid which can dissolve in the good solvent or a weak solvent for the cellulose derivative and, optionally, the weak solvent for the cellulose derivative in a specified proportion, and the present invention No. VII was completed.

[0048] And also, the present inventors have found that there can be largely improved durability in a transferred image, particularly, micro crack resistance by forming an ink-absorbing layer which can be stripped from a base material using a resin composition of a polymer containing a specified polymerizable monomer unit and a hot-melt adhesive resin, and there can be further improved an ink absorbing ability, an ink-fixing ability, a letter-printing ability, and durability and washing ability in a picture image by copolymerization of the specified polymerizable monomer with a monomer having a cationic functional group, and the present invention No. VIII was completed.

[0049] That is, subject matters of the present invention are as follows.

[0050] That is, the present invention 1 provides a resin composition for an ink jet recording sheet having an image-receiving layer which is formed on at least one surface of a base material for an ink jet recording sheet, and which is constructed by,

- (1) 2-80% by weight of a cationic (meth)acrylic copolymer (A) having a crosslinkable group,
- (2) 5-80% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and
- (3) 0-80% by weight of a modifier (R).

[0051] The present invention 2 provides a resin composition for an ink jet recording sheet as described in the present invention 1, in which the modifier (R) satisfies conditions that (n₁-80)% by weight of a water-based polyurethane resin

(C), (n_2-60)% by weight of a polyurethane-based graft polymer mixture (D) [the mixture (D) is a graft polymer mixture obtained through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (d_3) and other radical polymerizable vinyl monomer (d_4) to a mixed aqueous solution or a dispersed liquid of a water-based polyurethane (d_1) with a saponified product (d_2) of a vinyl acetate-based copolymer in a proportion of 100-60% by weight: 0-40% by weight], and (n_3-60)% by weight of a polyester-based graft polymer mixture (E) [the mixture (E) is a graft polymer mixture obtained from a graft polymerization through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (e_3) and other radical polymerizable vinyl monomer (e_4) to a mixed aqueous solution or a dispersed liquid of a water-based polyester resin (e_1) with a saponified product (e_2) of a vinyl acetate-based copolymer in a proportion of 100-60% by weight: 0-40% by weight], and total of the resin composition for an ink jet recording sheet is 100% by weight based on the solid content ratio, a minimum value of n_1 , n_2 , and n_3 is 0%, respectively, and ($n_1+n_2+n_3$) \geq 5% by weight.

[0052] The present invention 3 provides a resin composition for an ink jet recording sheet as described in the present invention 2, in which a saponification degree is 75-100% and a polymerization degree is 200-5000, respectively, in the saponified products (d_2) and (e_2) of a vinyl acetate-based copolymer.

[0053] The present invention 4 provides a resin composition for an ink jet recording sheet as described in the present invention 2, in which the water-based polyurethane resin (C) is cationic.

[0054] The present invention 5 provides a resin composition for an ink jet recording sheet as described in the present invention 2, in which the polyurethane-based graft polymer mixture (D) and the polyester-based graft polymer mixture (E) are cationic.

[0055] The present invention 6 provides a resin composition for an ink jet recording sheet having an image-receiving layer formed over at least one surface of a base material for an ink jet recording sheet, which comprises,

[1] 2-80% by weight of a cationic (meth)acrylic copolymer (A) having a crosslinkable group,

[2] 5-60% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and

[3] 0-80% by weight of a water-based polyurethane resin (C) {total of the (A), (B), and (C) is 100% by weight}, and

[4] 0.05-10 parts by weight of a block isocyanate compound (F) based on 100 parts by weight of the saponified product (B) of a vinyl acetate-based copolymer.

[0056] The present invention 7 provides a resin composition for an ink jet recording sheet as described in the present invention 1 or 6, in which the cationic (meth)acrylic copolymer (A) having a crosslinkable group is a copolymer containing monomer units based on a respective monomer (1) or (2) described below,

(1) a cationic monomer (a_4) and a monomer (a_3) having a crosslinkable group

(2) a cationic monomer (a_4) and a monomer (a_3) having a crosslinkable group, and a monomer (a_2) having a hydrophilic group.

[0057] The present invention 8 provides a resin composition for an ink jet recording sheet as described in the present invention 1 or 6, in which the saponification degree is 70-95% in the saponified product (B) of a vinyl acetate-based copolymer.

[0058] The present invention 9 provides a resin composition for an ink jet recording sheet as described in the present invention 7, in which the monomer having a hydrophilic group is a (meth)acrylate containing an ester bond with a polyoxyalkylene.

[0059] The present invention 10 provides a resin composition for an ink jet recording sheet as described in the present invention 1, 6, or 7, in which the cationic (meth)acrylic copolymer (A) having a crosslinkable group is a copolymer containing 0.1-50% by mol of a monomer having a tertiary amino group or a quaternary ammonium salt group and 0.1-25% by mol of a monomer having a crosslinkable group.

[0060] The present invention 11 provides a resin composition for an ink jet recording sheet which is a resin composition which constructs an image-receiving layer which is formed at at least one surface of surface of a base material for an ink jet recording sheet, which comprises 2-100% by weight of a cationic (meth)acrylic copolymer (A-IV) obtained by copolymerizing a (meth)acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), 0-90% by weight of the saponified product (B) of a vinyl acetate copolymer, and 0-80% by weight of the modifier (R) (total thereof is 100% by weight).

[0061] The present invention 12 provides a resin composition for an ink jet recording sheet as described in the present invention 11, which is composed of 5-80% by weight of the cationic (meth)acrylic copolymer (A-IV), 15-80% by weight of the saponified product (B) of a vinyl acetate copolymer, and 5-60% by weight of the modifier (R) (total thereof is 100% by weight).

[0062] The present invention 13 provides a resin composition for an ink jet recording sheet as described in the present

invention 11 or 12, in which the cationic (meth)acrylic copolymer (A-IV) is composed of 0.1-40% by weight of the (meth) acrylate monomer (a_1) having a polyalkylene oxide group, 0.1-50% by weight of the monomer (a_2) having a hydrophilic group, 0.5-20% by weight of the monomer (a_3) having a crosslinkable group, 1-40% by weight of the cationic monomer (a_4), 10-60% by weight of a hard monomer (a_6), and 10-60% by weight of a soft monomer (a_7) (total thereof is 100% by weight), and a weight average molecular weight is 0.2×10^4 - 100×10^4 in the cationic (meth)acrylic copolymer (A-IV) having a crosslinkable group.

[0063] The present invention 14 provides a resin composition for an ink jet recording sheet which constructs an image-receiving layer which is formed at at least one surface of surface of a base material for an ink jet recording sheet, in which there are formulated 70-100% by weight of a cationic (meth)acrylic copolymer (A-V) obtained by copolymerizing a (meth)acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), 0-30% by weight of the saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0-15 parts by weight of the modifier (R) based on 100 parts by weight of total of the (A-V) and the (B).

[0064] The present invention 15 provides a resin composition for an ink jet recording sheet as described in the present invention 14, in which the cationic (meth)acrylic copolymer (A-V) is a copolymer obtained by copolymerizing a (meth) acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), and a nonionic monomer (a_5).

[0065] The present invention 16 provides a resin composition for an ink jet recording sheet as described in the present invention 14, in which there are formulated 75-95% by weight of the cationic (meth)acrylic copolymer (A-V), 5-25% by weight of the saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0.5-5 parts by weight of the modifier (R) based on 100 parts by weight of total of the (A-V) and the (B).

[0066] The present invention 17 provides a resin composition for an ink jet recording sheet as described in the present invention 14, in which there are formulated 75-95% by weight of the cationic (meth)acrylic copolymer (A-V), 5-25% by weight of the saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0.5-3 parts by weight of the modifier (R) based on 100 parts by weight of total of the (A-V) and the (B).

[0067] The present invention 18 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 14-17, in which the cationic (meth)acrylic copolymer (A-V) contains 8-40% by weight of the (meth)acrylate monomer (a_6) having a polyalkylene oxide group, 1-30% by weight of the monomer (a_2) having a hydrophilic group, 0.2-10% by weight of the monomer (a_3) having a crosslinkable group, 10-50% by weight of the cationic monomer (a_4), and 10-80% by weight of the nonionic monomer (a_5) (total thereof is 100% by weight).

[0068] The present invention 19 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 11, 13, 14, 15, and 18, in which a polyalkylene oxide group in the (meth)acrylate monomer (a_1) having a polyalkylene oxide group has a structure shown by a general formula: $-(CHR^1)_n-O)_m-R^2$.

[in the general formula, R^1 represents a hydrogen atom, methyl group, or hydroxyl group, R^2 represents a hydrogen atom or methyl group, n is an integer of 1-5, m is an integer of 1-20, respectively, n and m pieces of R^1 may be even identical to or different from each other.]

[0069] The present invention 20 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 7, 11, 13, 14, 15, and 18, in which the hydrophilic group in the monomer (a_2) having a hydrophilic group is at least one selected from the group consisting of carboxylic group or a salt thereof, an anhydride group, hydroxyl group, sulphonc acid group or a salt thereof, an amide group, and an ether group.

[0070] The present invention 21 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 7, 11, 13, 14, 15, and 18, in which the monomer (a_3) having a crosslinkable group is a monomer having a hydrolyzable condensable group.

[0071] The present invention 22 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 7, 11, 13, 14, 15, and 18, in which the monomer (a_3) having a crosslinkable group is a monomer having an alkoxysilyl group.

[0072] The present invention 23 provides a resin composition for an ink jet recording sheet as described in any one of the present inventions 7, 11, 13-15, and 18, in which the cationic monomer (a_4) is a monomer having a tertiary amino group or a monomer having a quaternary ammonium salt group.

[0073] The present invention 24 provides a resin composition for an ink jet recording sheet as described in any one of the present invention 15 or 18, in which the nonionic monomer (a_5) is any one of (meth)acrylates, aromatic vinyls, and vinyl esters.

[0074] The present invention 25 provides a resin composition for an ink jet recording sheet as described in any one of the present invention 1, 6, 8, 11, 12, 14, 16 or 17, in which a polymerization degree is 200-1000 in the saponified product (B) of a vinyl acetate copolymer.

[0075] The present invention 26 provides a resin composition for an ink jet recording sheet as described in any one of the present invention 1, 11, or 16, in which the modifier (R) contains a water-based polyurethane (C) and/or a water-based polyester resin (e_1).

[0076] The present invention 27 provides an ink jet recording sheet characterized in that an ink-receiving layer formed on at least one surface of a base material for an ink jet recording sheet is constructed by a composition (P) containing a (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group prepared by copolymerization of monomers containing a polymerizable unsaturated monomer (a_8) and a (meth)acrylic-based polymerizable unsaturated monomer (a_9), and inorganic compound fine particles (G).

[0077] The present invention 28 provides an ink jet recording sheet as in the present invention 27, in which an ink-fixing layer is formed between a base material for the ink jet recording sheet and the ink-receiving layer.

[0078] The present invention 29 provides an ink jet recording sheet as in the present invention 27, in which the (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group is a water-based copolymer.

[0079] The present invention 30 provides an ink jet recording sheet as in the present invention 27, in which weight proportion of monomer units based on the (a_8) and the (a_9) contained in the (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group is (a_8)/(a_9)=(0.1-30%)/(70-99.9%) (total is 100% by weight).

[0080] The present invention 31 provides an ink jet recording sheet as in the present invention 27, in which the inorganic compound fine particles (G) is a rosary-like colloidal silica which is dispersed in water.

[0081] The present invention 32 provides an ink jet recording sheet as in the present invention 27, in which weight ratio of the (A-VI) and (G) contained in the composition (P) containing the (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group and the inorganic compound fine particles (G) is the (A-VI)/(G)=(1-50%)/(50-99%) (total is 100% by weight).

[0082] The present invention 33 provides an ink jet recording sheet as in the present invention 27, in which the ink-fixing layer is composed of a resin composition containing a formulated product of at least one resin selected from the group consisting of a cationic group-contained resin or a saponified product of a copolymer of the cationic group-contained resin with a vinyl acetate-based copolymer, a water-based polyester-based resin and a water-based polyurethane-based resin.

[0083] The present invention 34 provides an ink jet recording sheet as in the present invention 33, in which the cationic group-contained resin is a cationic group-contained copolymer prepared by copolymerization of monomers containing a polymerizable unsaturated monomer having a hydrolyzable silyl group, a polymerizable unsaturated monomer having a tertiary amino group and/or a quaternary ammonium group, and a (meth)acrylate-based polymerizable unsaturated monomer.

[0084] The present invention 35 provides a resin composition for recording, which is a resin composition for recording for forming an ink recording layer, characterized by containing in a ratio of 100 parts by weight of a resin composition composed of (1) 1-30% by weight of a cellulose derivative (H) and (2) 70-99% by weight of a good solvent (I) for the cellulose derivative (total is 100% by weight), 0.1-20 parts by weight of (3) an organic acid (J) which can dissolve in the good solvent (I) or a weak solvent (K) for the cellulose derivative, and optionally, 0-150 parts by weight of (4) the weak solvent (K) for the cellulose derivative.

[0085] The present invention 36 provides a resin composition for recording as in the present invention 35, in which the cellulose derivative (H) is a cellulose acetate.

[0086] The present invention 37 provides a resin composition for recording as in the present invention 35, in which proportion of the weak solvent (K) for the cellulose acetate is 50-150 parts by weight.

[0087] The present invention 38 provides a resin composition for recording as in the present invention 35, characterized in that the good solvent (I) for the cellulose derivative is at least one kind selected from the group consisting of ketones, esters, ethers, cellosolves, cellosolve acetates, halogenated hydrocarbons, and nitro compounds, and a boiling point of the solvent is 35-160°C.

[0088] The present invention 39 provides a resin composition for recording as in the present invention 35, characterized in that a melting point of the organic acid (J) is not less than 60°C.

[0089] The present invention 40 provides a resin composition for recording as in the present invention 35 or 37, characterized in that the weak solvent (K) for the cellulose derivative is at least one kind selected from esters, alcohols, ketones and ethers, and a boiling point of the solvent is 100-300°C.

[0090] The present invention 41 provides a resin composition for recording as in the present invention 35, characterized in that the good solvent (I) for the cellulose derivative is at least one kind selected from a C_{1-5} dialkyl ketone, a C_{1-4} alkyl acetate, a C_{4-6} cyclic or linear ether, and a C_{1-4} alkyl cellulose and a C_{1-4} alkyl cellulose acetate, and the weak solvent (K) for the cellulose derivative is at least one kind selected from a C_{5-8} alkyl formate, a C_{1-4} alkyl benzoate, a C_{4-8} cycloalkanol, a C_{6-10} dialkyl ketone, and a C_{7-10} ether.

[0091] The present invention 42 provides a resin composition for recording as in the present invention 35 or 41, characterized in that boiling point difference (TK-TI) between the good solvent (I) and the weak solvent for the cellulose derivative is $10^{\circ}\text{C} < (\text{TK-TI}) < 200^{\circ}\text{C}$.

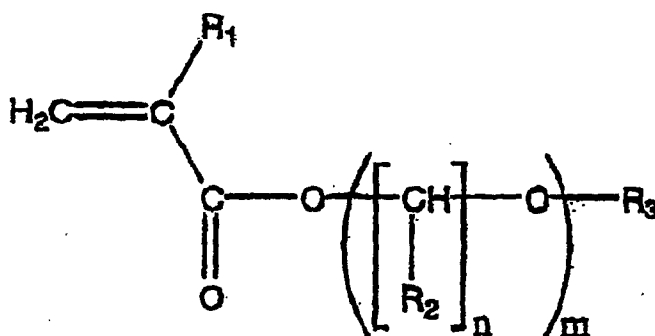
[0092] The present invention 43 provides a resin composition for recording as in the present invention 35 or 39, characterized in that solubility of the organic acid (J) to water is not more than 2 g/100 ml at 20°C.

[0093] The present invention 44 provides an ink jet recording sheet characterized in that there is employed a resin

composition for an ink jet recording sheet as in any one of the present inventions 1-43, and an image-receiving layer is formed over at least one surface of a base material.

[0094] The present invention 45 provides an ink jet recording sheet as in the present inventions 44, in which glossiness (60°-gloss measured according to JIS Z8741) in the surface of an ink-receiving layer is not less than 30%.

[0095] The present invention 46 provides a resin composition for a heat transfer sheet containing a polymer (L) containing monomer units shown by formula (14) described below and a hot-melt adhesive resin (M).



R_1 : -H or -CH₃

R_2 : -H, -CH₃ or -OH

n is 1-5, and m is 1-20.

[0096] A plurality of R_2 may be identical to or different from each other, and m pieces of $-(CHR_2)_nO-$ may be combined in random or block.

[0097] The present invention 47 provides a resin composition for a heat transfer sheet as in the present invention 46, in which the polymer (L) is constructed by a copolymer of a monomer of the formula (14) with at least one kind monomer selected from a monomer having a cationic functional group, a monomer having a crosslinkable group, and a monomer having a hydrophilic group.

[0098] The present invention 48 provides a resin composition for a heat transfer sheet as in the present invention 46 or 47, in which content of the monomer of the formula (14) is 1-40% by weight based on total monomers in the polymer (L).

[0099] The present invention 49 provides a resin composition for a heat transfer sheet as in the present invention 47, in which the monomer having a cationic functional group is at least one kind selected from a monomer having a group composed of a tertiary amino group or a salt thereof, a monomer having a quaternary ammonium salt group, and a monomer which forms a quaternary ammonium salt group, the monomer having a hydrophilic group is at least one kind selected from a monomer having a group composed of carboxylic group or a salt thereof, a monomer having an acid anhydride group, a monomer having hydroxyl group, a monomer having a group composed of sulphonic group or a salt thereof, a monomer having amide group, and a monomer having ether group, and the monomer having a crosslinkable group is at least one kind selected from a monomer having an epoxy group, a monomer having a methylol group, and a monomer having silyl group or an alkoxysilyl group.

[0100] The present invention 50 provides a resin composition for a heat transfer sheet as in any one of the present inventions 46-48, in which T_g is -85 to 30°C in the copolymer which constructs the polymer (L).

[0101] The present invention 51 provides a resin composition for a heat transfer sheet as in the present invention 46, in which the hot-melt adhesive resin (M) is at least one kind selected from a nylon-based resin, a polyester-based resin, and a polyurethane-based resin.

[0102] The present invention 52 provides a resin composition for a heat transfer sheet as in the present invention 46, in which proportion of the hot-melt adhesive resin (M) is 10-1500 parts by weight based on 100 parts by weight of the polymer (L).

[0103] The present invention 53 provides a heat transfer sheet, which is a sheet in which an ink-receiving layer being strippable from a base material is formed at one surface of the base material, in which the ink-receiving layer is constructed by a resin composition for a heat transfer sheet as in any one of the present invention 46-52.

[0104] The present invention 54 provides a heat transfer sheet as in the present invention 53, in which the ink-receiving layer is formed at a base material through a protecting layer which is strippable from the base material.

[0105] The present invention 55 provides a heat transfer sheet as in the present invention 54, in which the protecting layer is constructed by at least one kind selected from a thermoplastic resin, a thermosetting resin, and an elastomer.

[0106] The present invention 56 provides a heat transfer sheet as in any one of the present invention 53 or 54, in

which the ink-receiving layer contains at least one component of a dye-fixing agents and a plasticizer.

[0107] The present invention 57 provides a method for the preparation of a heat transfer sheet, which is a method for the preparation of a sheet by forming an ink-receiving layer through coating a solution of a material which forms the ink-receiving layer which is capable of being stripped from a base material, in which the ink-receiving layer is constructed by a resin composition as in any one of the present inventions 46-56.

BEST MODE FOR CARRYING OUT THE INVENTION

[0108] Hereinafter, examples of embodiments for carrying out the present inventions are illustrated in detail.

[0109] In order to simplify descriptions in the present inventions, respective constructing components are commonly illustrated and, in the case that order and disorder, etc. are occasionally caused in view of describing, there is clearly shown a range to which illustrative items attain in the respective inventions by describing the number of the present invention Nos. I-VIII.

[0110] The present inventions relate to a novel resin composition for an ink jet recording sheet and an ink jet recording sheet in which an image-receiving layer is formed on the surface of a base material for the sheet using thereof.

[0111] The ink jet recording sheet in relation to the present inventions possess a base material and an image-receiving layer and, in at least one surface of the base material, the image-receiving layer is formed in at least one surface of the base material by the resin composition of the present inventions.

[Base material]

[0112] In the present invention, a kind of materials for the base material (hereinafter, occasionally referred to as "a base material for recording" or merely "a base material") in the ink jet recording sheet is not particularly limited, and there are enumerated, in addition to usual papers in which natural fibers are employed, a coated paper in which the papers is employed, a nonwoven web in which natural fibers and synthetic fibers are employed solely or in combination, a plastic film, and a synthetic paper (there is included a fiber-made one in addition to a plastic film-made one), etc. and, of the material examples, the plastic film and the synthetic paper are particularly preferred.

[0113] As a polymer which constructs the plastic film and the synthetic paper, for example, there are enumerated a polyolefine such as a polyethylene and polypropylene, an ethylene-vinyl acetate copolymer, a polyvinyl chloride, a vinyl chloride-vinyl acetate copolymer, a poly(meth)acrylate, a polystyrene, a polyvinyl alcohol, an ethylene-vinylalcohol copolymer, a cellulose derivative such as a cellulose acetate, a polyester (a polyalkylene terephthalate such as a polyethylene terephthalate, a polybutylene terephthalate, a polyalkylene naphthalate such as a polyethylene naphthalate and a polybutylene naphthalate, etc.), a polycarbonate, a polyamide (nylon 6, nylon 6/6, nylon 6/10, and nylon 6/12, etc.), a polyester amide, a polyether, a polyimide, a polyamide-imide, and a polyether-polyester, etc., and there can be also appropriately employed a copolymer thereof, a blend thereof, a crosslinked product thereof. Of the films and synthetic papers, usually, there are particularly preferably employed a polyolefine (particularly, polypropylene), a polyester (particularly, a polyethylene terephthalate), and a polyamide and, there is most preferred the polyester (particularly, a polyethylene terephthalate) from a viewpoint of mechanical strength and workability, etc.

[0114] Transparency is not particularly limited in the base material for the ink jet recording sheet in relation to the present invention, indistinct, transparent, or semitransparent ones are appropriately employed depending upon uses thereof. For example, in the case that it is employed as a sheet for an overhead projector (OHP), transparent ones are usually preferred. Also, as a paper and a coated paper, for example, there can be employed a high quality paper, an art paper, and an RC paper, etc.

[0115] Thickness of the base material is not also particularly limited and, it is appropriately selected depending upon uses thereof, and it is usually 5-500 μm , preferably 10-300 μm or so.

[0116] It is to be noted that in the plastic film or synthetic paper, optionally, there may be even added additives such as a sizing agent, an antioxidant, an ultraviolet ray absorbent, a thermal stabilizer, a lubricant, and pigments, etc. which are commonly-used.

[0117] In the use in which water resistance is strongly required, there are preferably employed a film and synthetic paper which are more excellent in water resistance than in a paper base material.

[0118] Further, in order to elevate an adhesive property with an image-receiving layer, it is a preferred embodiment that surface of the base material is in advance treated by a corona discharging or an under-coating.

[0119] In the recording sheet in relation to the present invention, particularly, there can be preferably applied a treatment for forming an ink-fixing layer as described hereinafter.

[Image receiving layer]

[0120] The image receiving layer in relation to the present invention No. I is formed by the cationic (meth)acrylic

copolymer (A-I) having a crosslinkable group, the saponified product (B) of a vinyl acetate copolymer having a specified polymerization degree, and the modifier (R).

[0121] The image receiving layer in relation to the present invention No. II is formed by a composition composed of a cationic (meth)acrylic copolymer (A-II) having a crosslinkable group and a saponified product (B) of a vinyl acetate-based copolymer, a water-based polyurethane resin (C), a polyurethane-based graft polymer mixture (D) and/or a polyester-based graft polymer mixture (E).

[0122] The image receiving layer in relation to the present invention No. III is formed by a composition composed of a cationic (meth)acrylic copolymer (A-III) having a crosslinkable group and a saponified product (B) of a vinyl acetate-based copolymer, a water-based polyurethane resin (C), a polyurethane-based graft polymer mixture (D) and/or a polyester-based graft polymer mixture (E).

[0123] The image-receiving layer in relation to the present invention No. III is formed by a composition composed of a cationic (meth)acrylic copolymer (A-III) having a crosslinkable group and a saponified product (B) of a vinyl acetate-based copolymer, a water-based polyurethane resin composition (C), and a block isocyanate compound (F).

[0124] The image-receiving layers in relation to the present invention No. IV and No. V are formed by a resin composition for a recording sheet composed of a cationic (meth)acrylate monomer (A-IV or A-V) obtained by copolymerization of a (meth)acrylate monomer (a_1) having a specified polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), a saponified product (B) of a vinyl acetate-based copolymer, and a modifier (R).

[0125] The image-receiving layer in relation to the present invention No. VI is formed from a resin composition for a recording sheet constructed by a composition (P) containing a (meth)acrylic-based copolymer (A-VI) having a hydrolyzable silyl group prepared by copolymerization of monomers containing a polymerizable unsaturated monomer (a_8) and a (meth)acrylic-based polymerizable unsaturated monomer (a_9), and inorganic compound-based fine particles (G).

[0126] The image-receiving layer in relation to the present invention No. VII is formed from a resin composition for a recording sheet constructed composed of a cellulose derivative (H) and a good solvent (I) for the cellulose derivative, an organic acid (J) which can dissolve in the good solvent (I) or a weak solvent (K) for the cellulose derivative, and optionally, a weak solvent (K) for the cellulose derivative.

[0127] A method for forming the image-receiving layer is not particularly limited, and publicly-known and a variety of means can be applied. It is to be noted that details are described hereinafter.

[Resin composition for an ink jet recording sheet]

[0128] The resin composition (hereinafter, occasionally referred to as merely "resin composition for recording") for forming an image-receiving layer which is formed over at least one surface of a base material for an ink jet recording sheet in relation to the present invention is constructed by a resin composition for recording which is orderly illustrated hereinafter.

(1) Resin compositions for an ink jet recording sheet in relation to the present invention Nos. I-III

[0129] Hereinafter, there are illustrated the resin compositions for an ink jet recording sheet in relation to the present invention Nos. I-III.

[0130] The resin compositions for an ink jet recording sheet in relation to the present invention Nos. I and II are constructed by 2-80% by weight, and preferably 5-50% by weight of the cationic (meth)acrylic copolymer (A-I or A-II) having a crosslinkable group, 5-80% by weight, and preferably 15-70% by weight of the saponified product (B) of a vinyl acetate-based copolymer having a polymerization degree of 200-1000, and 0-80% by weight, and preferably 5-60% by weight of a modifier (R). Herein, constructing ratio of respective components is represented based on a solid content.

[0131] Constructing components for the modifier (R) in relation to the present invention Nos. I and II satisfy conditions that (n_1 -80)% by weight of the water-based polyurethane resin (C), (n_2 -60)% by weight of the polyurethane-based graft polymer mixture (D) [the mixture (D) is a graft polymer mixture obtained through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (d_3) and other radical polymerizable vinyl monomer (d_4) to a mixed aqueous solution or dispersed liquid of a water-based polyurethane (d_1) with a saponified product (d_2) of a vinyl acetate-based copolymer in a proportion of (100-60% by weight):(0-40% by weight)], and (n_3 -60)% by weight of the polyester-based graft polymer mixture (E) [the mixture (E) is a graft polymer mixture obtained from a graft polymerization through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (e_3) and other radical polymerizable vinyl monomer (e_4) to a mixed aqueous solution or dispersed liquid of a water-based polyester resin (e_1) with a saponified product (e_2) of a vinyl acetate-based copolymer in a proportion of (100-60% by weight):(0-40% by weight)], and total of the resin composition for an ink jet recording sheet is 100% by weight based on the solid content ratio, a minimum value in n_1 , n_2 and n_3 is 0% by weight, respectively, and ($n_1+n_2+n_3$) \geq 5% by weight.

[0132] Preferably, the water-based polyurethane resin (C) is (n_1 -50)% by weight, the polyurethane-based graft polymer mixture (D) is (n_2 -50)% by weight, the polyester-based graft polymer mixture (E) is (n_3 -60)% by weight, and ($n_1+n_2+n_3$) \geq 10% by weight.

[0133] As a preferred embodiment, it is also enumerated that the modifier (R) is a resin composition of the water-based polyurethane resin (C) or the polyester graft mixture (E).

[0134] The resin composition for an ink jet recording sheet in relation to the present invention No. III is constructed by 2-80% by weight of the cationic (meth)acrylic copolymer (A-III) having a crosslinkable group, 5-60% by weight of the saponified product (B) of a vinyl acetate-based copolymer, 0-80% by weight of the water-based polyurethane resin (C1) [total of (A-III), (B), (C1) is 100% by weight], 0.05-10 parts by weight of the block isocyanate compound (F) based on 100 parts by weight of the saponified product (B) of a vinyl acetate-based copolymer.

[0135] More preferably, the cationic acrylic copolymer (A-III) having a crosslinkable group is 10-60% by weight, the saponified product (B) of a vinyl acetate-based copolymer is 15-50% by weight, the water-based polyurethane resin (C1) is 5-60% by weight, and the block isocyanate compound (F) is 0.3-5 parts by weight based on 100 parts by weight of the (B).

[0136] Constructing ratio of respective components based on the solid content ranges in a scope in which there are obtained properties such as an excellent ink-absorbing ability, water resistance, and printing image quality in an ink jet recording, and it is appropriately selected from the scope.

[0137] The cationic acrylic copolymers ((A-I)-(A-III)) having a crosslinkable group and content proportion thereof affect to an ink-fixing ability, water resistance, and printing quality, and the saponified product (B) of a vinyl acetate-based copolymer affects to an ink-absorbing ability, and polymerization degree affects to printing ability such as bead-ing.

[0138] Further, the modifier (R) is employed in order to improve properties such as water resistance and an adhesion to a base material. The water-based polyurethane resin (C) affects to water resistance and an adhesion to a base material, and the polyurethane-based graft polymer mixture (D) and the polyester-based graft polymer mixture (E) mainly affect to an ink-absorbing ability.

[0139] Hereinafter, respective components which construct the resin composition for recording in relation to the present invention Nos. I-III are illustrated in detail.

[Cationic (meth)acrylic copolymer (A-I to A-III) having a crosslinkable group]

[0140] The cationic acrylic copolymers (A-I to A-III) having a crosslinkable group to be employed in the present inventions Nos. I-III, if those are a cationic acrylic copolymer having a crosslinkable group, are not particularly limited, and as an embodiment, there can be enumerated a copolymer containing respective monomer units of (1) or (2) described below, that is,

- (1) a copolymer containing a crosslinkable monomer unit and a hydrophilic group-contained monomer unit
- (2) a copolymer containing a cationic monomer unit, a crosslinkable monomer unit, and a hydrophilic group-contained monomer unit.

(Cationic monomer component)

[0141] As the cationic monomer, there can be employed, in addition to a variety of monomers having a tertiary amino group or a salt thereof, a variety of monomers having a quaternary ammonium salt or a variety of monomers which can form a quaternary ammonium salt and, for example, it is a diC₁₋₄alkylamino-C₂₋₃alkyl(meth)acrylic amide or a salt thereof, specifically, dimethylaminoethyl (meth)acrylic amide, diethylaminoethyl(meth)acrylic amide, dimethylamino-propyl(meth)acrylic amide, diethylaminopropyl (meth)acrylic amide, and a salt thereof, etc. Further, there can be enumerated a diC₁₋₄alkylamino-C₂₋₃alkyl(meth)acrylate or a salt thereof, dimethyl aminoethyl(meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylate, diethylaminopropyl(meth)acrylate, and a salt thereof, etc. Still further, there can be enumerated a diC₁₋₄alkylamino-C₂₋₃alkyl-substituted aromatic vinyl or a salt thereof, specifically, 4-(2-dimethylaminoethyl)styrene, 4-(2-diethylaminopropyl)styrene or a salt thereof. Besides, it is a nitrogen-contained heterocyclic monomer or a salt thereof, specifically, there can be enumerated vinyl pyridine, vinylimidazole, vinyl pyrrolidone or a salt thereof, etc.

[0142] It is to be noted that as the salts, there can be exemplified a halogenated hydrogen acid salt (hydrochloric acid and hydrobromic acid), a sulphate, an alkyl sulphate (methyl sulphate, ethyl sulphate, etc.), an alkyl sulphonc acid salt, an aryl sulphonc acid salt, and a carboxylic acid salt, etc. and, in the quaternary ammonium salt, there may be conducted a method in which it is produced by allowing to react an alkylation agent (epichlorohydrin, methyl chloride, and benzyl chloride, etc.) with a tertiary amino group.

(Monomer components containing a crosslinkable group)

[0143] As the monomer components containing a crosslinkable group, there are enumerated monomers having a variety of functions which have a self-crosslinkable or reactive functional group and, specifically, there can be exemplified an epoxy group-contained monomer such as glycidyl(meth)acrylate, (meth)allyl glycidylether, 1-allyloxy-3,4-epoxy butane, 1-(3-butenyloxy)-2,3-epoxy propane, and 4-vinyl-1-cyclohexene-1,2-epoxide, a methylol group-contained monomer such as N-methylol(meth)acrylic amide and N-butylol(meth)acrylic amide, or a derivative thereof, a monomer having a hydrolyzable condensible group (such as silyl group) such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltributoxysilane, vinylmethoxy dimethylsilane, vinylmethoxy dimethylsilane, vinylisobutoxy dimethylsilane, vinyltrimethoxy methylsilane, vinyltriethoxy methylsilane, vinyltris(β -methoxyethoxy)silane, vinylbisphenylethoxysilane, vinyltriphenoxysilane, γ -(vinylphenylaminopropyl)trimethoxy silane, γ -(vinylbenzylaminopropyl)trimethoxy silane, γ -(vinylphenylaminopropyl)triethoxy silane, γ -(vinylbenzylaminopropyl)triethoxy silane, divinyltrimethoxy silane, divinyltriethoxysilane, β -divinyl(methoxyethoxy)silane, vinylacetoxymethyl silane, vinyltriacetoxysilane, vinylbis(dimethylamino)methylsilane, vinylmethyldichlorosilane, vinyldimethylchloro silane, vinyltrichloro silane, vinylmethylphenylchloro silane, allyltriethoxy silane, 3-allylaminopropyl trimethoxy silane, allyldiacetoxymethyl silane, allyltriacetoxysilane, allylbis(dimethylamino)methylsilane, allylmethyldichloro silane, allyldimethylchloro silane, allyltrichloro silane, methallyl phenyldichloro silane, β -(meth)acryloxyethyl trimethoxy silane, β -(meth)acryloxyethyl triethoxy silane, γ -(meth)acryloxy propyl trimethoxy silane, γ -(meth)acryloxypropyl triethoxy silane, γ -(meth)acryloxypropyl methyltrimethoxy silane, γ -(meth)acryloxy propylmethyltrimethoxy silane, and γ -(meth)acryloxy propyltris(β -methoxyethoxy) silane, further, an adylidynyl group-contained monomer such as 2-(1-adyldynyl)ethyl(meth)acrylate and 2-(1-adyldynyl)propyl(meth)acrylate, etc. A preferred monomer having a crosslinkable group is a hydrolyzable condensible group-contained monomer having such as a hydrolyzable condensible group, particularly, an alkoxysilyl group (more specifically, a C_{1-4} alkoxysilyl group, etc. such as methoxysilyl group and ethoxysilyl group).

[0144] It is to be noted the monomers containing a crosslinkable group can be employed solely or in combination of two or more kinds.

(Monomer components having a hydrophilic group)

[0145] As the monomer components having a hydrophilic group, there can be exemplified, for example, a monomer having a free carboxylic group or an acid anhydride group such as (meth)acrylic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, and crotonic acid, or a monomer containing a salt thereof (an alkaline metal salt, an alkaline earth metal salt, an ammonium salt, and an amine salt, etc.), a half ester-contained monomer of an unsaturated polycarboxylic acid or an anhydride thereof with a linear or branched alcohol having a carbon number of 1-20 or so such as monomethyl maleate, monoethyl maleate, monobutyl maleate, monooctyl maleate, and mono-2-ethylhexyl maleate, a monomer having a hydroxyl group such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate which belong to a C_{2-6} alkyl (meth)acrylate, a monomer having amide group such as (meth)acrylic amide, α -ethyl(meth)acrylic amide, N-methyl(meth)acrylic amide, N-butoxymethyl(meth)acrylic amide, and diacetone(meth)acrylic amide, a monomer having sulphonic acid group such as styrene sulphonic acid and vinylsulphonic acid, a monomer having ether group such as vinylmethylether, vinylethylether, and vinylisobuylether which belong to vinyl ethers, a monomer having a polyoxyalkylene group such as diethyleneglycol mono(meth)acrylate, triethyleneglycol mono(meth)acrylate, and a polyethyleneglycol mono(meth)acrylate, etc. As a preferred one of the above various monomers having a hydrophilic group, there are enumerated monomers having a polyoxalkylene ester such as diethyleneglycol mono(meth)acrylate, triethyleneglycol mono(meth)acrylate, and the polyethyleneglycol mono(meth)acrylate.

[0146] The monomers having hydrophilic group can be employed solely or simultaneously in combination of two or more kinds.

[0147] The cationic monomers, the monomers containing a crosslinkable group, and the monomers having hydrophilic group are usually employed in combination with nonionic monomers described below in order to adjust a film-formability and film-forming property.

(Nonionic monomer components)

[0148] As the nonionic monomer components described herein, there are enumerated a C_{1-18} alkyl (meth)acrylate such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, t-butyl(meth)acrylate, n-butyl(meth)acrylate, hexyl(meth)acrylate, octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, lauryl(meth)acrylate, and stearyl(meth)acrylate, a cycloalkyl ester such as cyclohexyl(meth)acrylate, an aryl ester such as phenyl(meth)acrylate, an aralkyl ester such as benzyl(meth)acrylate, aromatic vinyls such as styrene, vinyl toluene, and α -methylstyrene, vinyl acetate, vinyl propionate, vinyl versate, allyl esters such as allyl acetate, a monomer

having a halogen such as vinylidene chloride and vinyl chloride, vinyl cyanates such as (meth)acrylonitrile, olefines such as ethylene and propylene, etc.

[0149] As the nonionic monomers, there are usually employed the C_{1-18} alkyl(meth)acrylate, particularly, a C_{2-10} alkyl ester of acrylic acid or a C_{1-6} alkyl ester of methacrylic acid, aromatic vinyls, particularly, styrene, or vinyl esters, particularly, vinyl acetate.

[0150] The nonionic monomers can be employed solely or in combination of two or more kinds.

(Constructing ratio of A-I, A-II, and A-III monomers)

[0151] Use amount the above-described cationic monomer and monomers containing a crosslinkable group or use amount in the case of combining the monomers having a hydrophilic group can be selected within a range in which water resistance and ink-absorbing ability are not deteriorated, although it is not particularly limited, the use amount of the cationic monomer is 0.1-50% by mol (for example, 1-45% by mol), preferably 0.5-40% by mol (for example, 2-35% by mol), and more preferably 1-30% by mol (for example, 3-25% by mol) based on total amount of monomers, and usually 2-25% by mol or so.

[0152] Further, the use amount of the monomer containing a crosslinkable group is, for example, 0.1-25% by mol, preferably 0.2-20% by mol, and more preferably 0.5-15% by mol based on total amount of monomers, and usually 0.3-10% by mol or so.

[0153] Still further, the use amount the monomer having hydrophilic group is 0-50% by mol, preferably 0-45% by mol (0.5-45% by mol), and more preferably 0-40% by mol (1-35% by mol) based on total amount of monomers, and usually 1-20% by mol or so.

[0154] It is to be noted that in the case that the above-described two or three kinds of monomers are employed, the total is adjusted to 100% by mol, and in the case that it is less than 100% by mol, residual portion is usually constructed by the anionic monomers.

[0155] Of those, a copolymer is employed as the cationic acrylic copolymer containing a crosslinkable group in the present invention No. I-III (A-I to A-III), and the copolymer contains 0.1-50% by mol of monomers containing tertiary amino group or quaternary ammonium base and 0.1-25% by mol of monomers containing a crosslinkable group.

(Glass transition temperature of the A-I to A-III)

[0156] The glass transition temperature can be selected within a range in which a film-formability, etc., is not deteriorated in the cationic acrylic copolymers (A-I to A-III) containing a crosslinkable group, and it is preferably -20 to 50°C, more preferably -10 to 40°C, and further preferably 0 to 30°C or so.

[0157] The copolymer having such the glass transition temperature can be prepared by combining the above-described cationic monomer with the monomers containing a crosslinkable group, and optionally, the monomers having a hydrophilic group. Usually, it can be copolymerized in combination with a hard monomer, for example, a homopolymerizable monomer having a glass transition temperature of 80 to 120°C, preferably, 90 to 105°C such as methyl (meth)acrylate and styrene and a soft monomer, for example, a homo-polymerizable monomer having a glass transition temperature of -85 to -10°C, preferably, -85 to -20°C such as a C_{2-10} alkyl ester of acrylic acid.

[0158] In the case that the copolymer is obtained by employing in combination with the various monomers, use proportion of the various monomers is not particularly limited, and an example can be enumerated below as the use proportion.

(a) the cationic monomer is 1-40% by mol, preferably 3-35% by mol, and more preferably 5-30% by mol, (b) the monomer containing a crosslinkable group is 0.5-20% by mol, preferably 1-15% by mol, and more preferably 2-10% by mol, (c) the monomer containing a hydrophilic group is 0-50% by mol, preferably 2-45% by mol, and more preferably 5-40% by mol, (d) the hard monomer is 10-60% by mol, preferably 20-55% by mol, and more preferably 25-50% by mol, and

(e) the soft monomer is 10-60% by mol, preferably 15-50% by mol, and more preferably 20-45% by mol.

[0159] On the other hand, a weight average molecular weight is not particularly limited in the cationic acrylic monomers (A-I to A-III) containing a crosslinkable group, and it ranges in preferably 0.2×10^4 to 100×10^4 , and more preferably 1×10^4 to 50×10^4 or so.

(Preparation of a water-based emulsion)

[0160] Form in the cationic acrylic monomers (A-I to A-III) containing a crosslinkable group may be an organic solvent solution, an aqueous solution and, usually, preferably a cationic emulsion (particularly, a water-based emulsion).

[0161] In the cationic emulsion, surface potential (ξ potential) is +20 to +60 mV, preferably +12 to +55 mV, and more preferably +20 to +55 mV in polymer particles contained in the emulsion and, particularly preferably +15 to +55 mV or so. When the surface potential becomes lower in polymer particles, an ink-fixing ability and water resistance lower, and when the surface potential becomes higher, an ink-fixing ability lowers.

[0162] The surface potential in polymer particles can be measured, for example, by the following apparatus and conditions.

[0163] Apparatus for measurement: An electrophoresis light scattering photometer (ELS-800) manufactured by Otsuka Denshi, Ltd.

Temperature in measurement: 25°C

Concentration: Emulsion was diluted to a solid concentration of 0.01-0.05% by weight by a distilled water.

Distance between electrodes: 32 mm

Applied electric field: 50 V/cm

(method for the preparation of polymer particles in the cationic emulsion)

[0164] Average particle diameter of polymer particles in the cationic emulsion is 1-200 nm, preferably 3-100 nm, and more preferably 5-50 nm or so.

[0165] The cationic emulsion containing the cationic acrylic copolymers (A-I to A-III) containing a crosslinkable group can be obtained by a commonly-used method, for example, a method in which the above-described two or three monomers are emulsion-polymerized in an emulsion polymerization-system containing a nonionic surface active agent and/or a cationic surface active agent, or a method in which a water-based emulsion is prepared by allowing to form a tertiary amine salt or a quaternary ammonium salt after copolymerization of the monomers.

[0166] In the resin composition for an ink jet recording sheet in relation to the present invention Nos. I-III, a printing quality and water resistance can be elevated in combination of a hydrophilic polymer compound (a water-soluble polymer compound or a water-insoluble and water-absorbable polymer compound) with other constructing components without losing an ink-absorbing ability so much.

(Hydrophilic polymer compound components)

[0167] As the hydrophilic polymer compounds described hereinabove and below, there is employed the saponification product (B) of a vinyl acetate-based polymer, and the saponification product may be even employed together with a plurality of saponification products of a vinyl acetate-based polymer and, other hydrophilic polymer compounds may be even further employed.

(Other hydrophilic polymer compound components)

[0168] As the other hydrophilic polymer compound components, for example, there are enumerated hydrophilic natural polymers or derivatives thereof (starches, corn starches, a sodium alginate, gum arabic, gelatine, casein, and dextrin, etc.), cellulose derivatives (a methyl cellulose, an ethyl cellulose, a hydroxyethyl cellulose, a carboxymethyl cellulose, a cellulose sulphate, and a cyanoethyl cellulose, etc.), a vinylalcohol-based derivative (a polyvinyl alcohol and an ethylene-vinyl acetate copolymer, etc.), an ethylene-based polymer (an ethylene-maleic anhydride copolymer, etc.), a vinyl acetate-based copolymer (a vinyl acetate-methylmethacrylate copolymer, etc.), a polyalkylene oxide (a polyethylene oxide, an ethylene oxide-propylene oxide block copolymer, etc.), a polymer having carboxylic group or sulphonic group or salts thereof [an acrylic-based polymer (a poly(meth)acrylic acid or a salt thereof (an alkaline metal salt such as ammonium and sodium), a methylmethacrylate-(meth)acrylic acid copolymer, an acrylic acid-polyvinyl alcohol copolymer, etc., a vinyl ether-based copolymer (a polyvinyl alkyl ether such as polyvinyl methyl ether and a polyvinyl isobutyl ether, a vinyl methyl ether-maleic anhydride copolymer), a styrene-based copolymer (a styrene-maleic anhydride copolymer, a styrene-(meth)acrylic acid copolymer, a styrene sodium sulphonate, etc.), a sodium polyvinyl sulphonate, et.], a nitrogen-contained polymer (or a cationic polymer) or a salt thereof (a quaternary ammonium salt such as polyvinylbenzyl trimethyl ammonium chloride and polydiallyl dimethyl ammonium chloride), a hydrochloric acid salt of a polydimethyl aminoethyl (meth)acrylate, a polyvinyl pyridine, a polyvinyl imidazole, a polyethylene imine, a polyamide polyamine, a polyacrylic amide, polyvinyl pyrrolidone, etc.

[0169] In the exemplified other hydrophilic polymer compound, there are preferred the cellulose derivatives (particularly, a hydroxyethyl cellulose, etc.), the vinylalcohol-based derivative, the vinyl ester-based polymer, and polyvinyl pyrrolidone, etc.

[0170] Further, there are also preferably employed a hydrophilic polymer having at least one functional group selected from a polyoxyalkylene group, acetoacetyl group, carboxylic group, acid anhydride group, and amino group.

[0171] The other hydrophilic polymer compounds are employed solely or in combination of two or more kinds.

(Saponified product (B) of a vinyl acetate-based polymer)

[0172] The saponified product (B) of a vinyl acetate-based copolymer in relation to the present invention Nos. I-VI includes a vinyl acetate homopolymer or a partially- or completely-saponified product of a copolymer of a vinyl acetate with other copolymerizable monomers, and a saponification degree is 70-95%, preferably 75-92%, and more preferably 79-89%. However, in the present invention No. II, it is 70-100%, preferably 75-95%, and more preferably 79-92%.

[0173] Still further, as the saponified product (B) of a vinyl acetate-based copolymer, there is preferably employed a saponified product of a vinyl acetate-based copolymer having a polymerization degree of 200-1000, and preferably 300-800.

[0174] In the case that the polymerization is less than 200 in the polymer, an effect for improving water resistance is not occasionally shown and, in the case of exceeding 1000, beading is caused, resulting in that it is afraid that uniformity in a picture image is deteriorated.

(Other copolymerizable monomer components)

[0175] As the other copolymerizable monomer, there is preferred a monomer having a hydrophilic group (for example, carboxylic group and a salt thereof, sulphonic acid group and a salt thereof, an acid anhydride group, amide group, hydroxyl group, and ether group, etc.), particularly, a vinyl monomer having an ether group, of those, an oxyalkylene group such as a (meth)acrylate and allyl ether and, in the case, the number of alkyleneoxide unit (the mol number to be added) is preferably 1-100, more preferably 2-80, and further preferably 5-70.

(Vinyl monomer components having an oxyalkylene group)

[0176] As the vinyl monomer having an oxyalkylene group, there are included, for example, diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, dipropylene glycol mono(meth)acrylate, tripropylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, diethylene glycol mono(meth)allylether, triethylene glycol mono(meth)allylether, polyethylene glycol mono(meth)allylether, dipropylene glycol mono(meth)allylether, tripropylene glycol mono(meth)allylether, polypropylene glycol mono(meth)allylether, polyethylene glycol polypropylene glycol mono(meth)acrylate, hydroxypropyl(meth)acrylate, polyethylene glycol polytetramethylene glycol(meth)acrylate, and glycerol(meth)acrylate, etc.

[0177] Of those, as a preferred monomer, there is included a (meth)acrylate which is a vinyl monomer in which the oxyalkylene group is oxyethylene group, particularly, a polyoxyalkylene (meth)allylether (of those, a polyoxyethylene allylether). The vinyl monomer can be employed solely or in combination of two or more kinds.

(Constructing ratio of the copolymerizable monomers for B)

[0178] The ratio of the copolymerizable monomers which are copolymerized with vinyl acetate can be freely selected within a range in which clearness and water resistance are not deteriorated in order to obtain the saponified product (B) of a vinyl acetate-based copolymer in relation to the present inventions I-VI, and it is preferably 0.1-50% by mol, more preferably 1-30% by mol, and further preferably 2.5-25% by mol (for example, 3-20% by mol). It is to be noted that a copolymer (a modified vinyl acetate-based resin) of vinyl acetate with the monomer components having an oxyalkylene group can be obtained, for example, as "OKS-7158G" which is a trade name of Nihon Gosei Kagaku, Ltd.

(Hydrophilic polymer components to be employed together)

[0179] It is to be noted that as the hydrophilic polymer components to be employed together for the saponified product (B) of a vinyl acetate-based copolymer, there is also included a hydrophilic polymer compound having a functional group which reacts with a reactive functional group (for example, an epoxy group such as glycidyl group and alkoxy silyl group, etc.) in the above-described cationic acrylic copolymer containing a crosslinkable group.

[Modifier (R) for a resin composition for a recording sheet]

[0180] As the modifier in relation to the present invention Nos. I-VI, there are preferably employed at least one components selected from a water-based polyurethane resin (C), a urethane-based graft polymer mixture (D), a polyester-based graft polymer mixture (E), and a block isocyanate compound (F). Further, as other preferred embodiments,

there is employed a resin composition composed of the water-based polyurethane resin (C) and/or the polyester-based graft polymer mixture (E).

[0181] Hereinafter, there are illustrated respective components constructing the modifier (R).

[Water-based polyurethane resin (C)]

[0182] The water-based polyurethane resin (C) in relation to the present invention Nos. I-VI is obtained by dissolving or dispersing a polyurethane resin synthesized from a polyol component, a polyisocyanate component, and a low molecular weight chain extender having at least two active hydrogens in the molecule which reacts with the polyisocyanate component into water, and it is synthesized by publicly-known methods. For example, there are a method in which a polyurethane having a relatively high molecular weight is synthesized in a solvent which does not react with isocyanate group, followed by emulsifying through phase conversion while gradually adding water and optionally removing the solvent under reduced pressure, a method in which the polyurethane is dispersed into water by vigorously agitating after adding an emulsifier, and a method in which a reaction is conducted by adding a chain extender after dissolving or dispersing into water a urethane prepolymer into which a hydrophilic group, for example, a polyethylene glycol and carboxylic group are introduced.

(Polyisocyanate components)

[0183] As the polyisocyanate components to be employed for the preparation of the water-based polyurethane resin (C), there are included an aromatic polyisocyanate (for example, a diisocyanate such as m-phenylene diisocyanate, p-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylmethane-4,4'-diisocyanate, and 1,5-naphthalene diisocyanate, a polyisocyanate such as triphenylmethane triisocyanate, etc.), an aromatic-aliphatic polyisocyanate (for example, a diisocyanate such as 1,3-xylilene diisocyanate, 1,4-xylilene diisocyanate, tetramethyl xylilene diisocyanate, and a polyisocyanate such as 1,3,5-trisocyanatemethyl benzene, etc.), an alicyclic polyisocyanate (for example, a diisocyanate such as isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate and cyclohexane-1,4-diisocyanate, a polyisocyanate such as 1,3,5-trisocyanate cyclohexane, etc.), an aliphatic polyisocyanate (for example, an aliphatic diisocyanate such as 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, and ridine diisocyanate, and an aliphatic polyisocyanate such as 1,3,6-hexamethylene diisocyanate, etc.), etc., and as the polyisocyanate components, the diisocyanate components are often employed.

[0184] Further, the polyisocyanate components may be even an adduct in which a polyisocyanate compound is added to a polyvalent alcohol and has isocyanate group at terminals, an isocyanurate compound produced by a buret reaction, a dimer, and a trimer.

[0185] It is to be noted that the polyisocyanate components can be solely or also in combination of two or more kinds.

(Polyol component)

[0186] As the polyol component to be employed for constructing the water-based polyurethane resin (C), there are included a polyester polyol, a polyether polyol (for example, a polyether diol having an oxy-C₂₋₄alkylene such as a polyoxytetramethylene glycol), and a polycarbonate polyol (for example, a polycarbonate diol, etc.), etc. The polyester polyol is a polyester having hydroxyl group which is obtained by a reaction of a polyvalent alcohol with a polycarboxylic acid or a low alkyl ester thereof or an acid anhydride, and it may be even a derivative from a lactone. As the polyol components, the diol components (for, example, a polyester diol, etc.) are preferably employed.

[0187] It is to be noted that the polyol component can be employed solely or in combination of two or more kinds.

[0188] As the polyvalent alcohol for preparing the polyester polyol which is the polyol component, there are included an aliphatic polyvalent alcohol (for example, a C₂₋₁₀alkylene diol such as ethylene glycol, trimethylene glycol, propylene glycol, 1,3-butane diol, tetramethylene glycol, hexamethylene glycol, and neopentyl glycol, a polyoxy-C₂₋₄alkylene glycol such as diethylene glycol and triethylene glycol, and a polyol such as trimethylol propane and pentaerythritol, etc.), a cycloaliphatic polyvalent alcohol (for example, a cycloaliphatic diol such as 1,4-cyclohexane dimethanol and hydrogenated bisphenol A), and an aromatic polyvalent alcohol [for example, an aromatic diol, etc. such as 2,2-bis(2-hydroxyethylphenyl)propane], etc., and as the polyvalent alcohol, the aliphatic diol is usually employed.

[0189] It is to be noted that the polyvalent alcohol can be employed solely or in combination of two or more kinds.

(Polyvalent carboxylic acid for the polyester polyol)

[0190] On the other hand, as the polyvalent carboxylic acid for the preparation of the polyester polyol, there can be exemplified an aliphatic polyvalent carboxylic acid (for example, a saturated aliphatic carboxylic acid such as adipic acid, sebacic acid, azelaic acid, sebacic acid, and dodecane dicarboxylic acid, and an unsaturated aliphatic carboxylic

acid such as maleic acid), a cycloaliphatic polyvalent carboxylic acid (for example, a cycloaliphatic dicarboxylic acid, etc. such as 1,4-cyclohexane dicarboxylic acid), an aromatic polyvalent carboxylic acid (for example, an aromatic dicarboxylic acid such as phthalic acid, terephthalic acid, isophthalic acid, and 1,5-naphthalene dicarboxylic acid, an aromatic polycarboxylic acid such as trimellitic acid), etc. The polyvalent carboxylic acid can be employed solely or in combination of two or more kinds.

[0191] Further, the above-described polyester alcohol can be derived from a lactone, and as the lactone, there may be included butyrolactone, varelolactone, and caprolactone, etc. and, of those, one or more kinds may be even employed in combination.

[0192] It is to be noted that a short chain polyol (for example, the above-described aliphatic polyvalent alcohol, etc.) may be even optionally employed as a portion of the polyol components.

(Chain extender)

[0193] As the chain extender be employed for the preparation of the water-based polyurethane resin (C), there are a polyamine component and, as the polyamine, there are enumerated diamines such as ethylene diamine, triethylene diamine, tetramethylene diamine, pentamethylene diamine, 1,7-diamino heptane, 1,8-diamino octane, xylilene diamine, 1,4-diamino cyclohexane, isophorone diamine, and phenylene diamine, and polyamines such as triaminopropane.

[0194] The polyurethane obtained by such the raw materials and the method for the preparation may be solely, and a plurality of polyurethane resins may be even employed together. Further, optionally, other resins and additives can be also formulated.

[0195] It is to be noted that the polyurethane resin composition (C1) to be employed in the present invention No. III, in addition to the water-based polyurethane resin (C), may be even a composition containing the polyurethane-based graft polymer mixture (D) and/or the polyester-based graft polymer mixture (E) which are described hereinafter.

[Polyurethane-based graft polymer mixture (D)]

[0196] Further, the polyurethane-based graft polymer mixture (D) may be even employed as the modifier (R). For example, there is enumerated a composition in which a hydrophilic radical polymerizable vinyl monomer (d_3) and other radical polymerizable vinyl monomer (d_4) are polymerized in a mixed aqueous solution or dispersion composed of a water-based polyurethane (d_1) for grafting and a saponified product (d_2) of a vinyl acetate-based copolymer for grafting.

[0197] As the water-based polyurethane (d_1) for grafting, there can be preferably employed the water-based polyurethane resin (C) exemplified in the illustration of the above-described water-based polyurethane resin.

[0198] As the saponified product (d_2) of a vinyl acetate-based copolymer for grafting, there can be preferably employed the saponified product (B) of a vinyl acetate-based copolymer exemplified in the illustration of the above-described saponified product of a vinyl acetate-based copolymer.

[0199] As the hydrophilic radical polymerizable vinyl monomer (d_3), there can be preferably employed the monomer having a hydrophilic group which contains a polyalkylene side chain and a crosslinkable group exemplified in the illustration of the above-described cationic acrylic copolymer.

[0200] As the other radical polymerizable vinyl monomer (d_4), there can be preferably employed the nonionic monomer exemplified in the illustration of the above-described cationic acrylic copolymer.

(Proportion of constructing components in the D)

[0201] There is not particularly limited a proportion of the water-based polyurethane (d_1), the saponified product (d_2) of a vinyl acetate-based copolymer, the radical polymerizable vinyl monomer (d_3) and the (d_4), and the saponified product (d_2) of a vinyl acetate-based copolymer is preferably 10-500 parts by weight, and more preferably 20-300 parts by weight and, as the radical polymerizable vinyl monomer (d_3), total of the (d_3) and (d_4) is preferably 10-500 parts by weight, and more preferably 20-300 parts by weight, which are all based on 100 parts by weight of the water-based polyurethane (d_1) in a solid ratio.

[0202] In the case, the saponified product (d_2) of a vinyl acetate-based copolymer is less than 10 parts by weight, clearness of a picture image and ink-absorbing ability become insufficient and, in the case of exceeding 500 parts by weight, there lower adhesion to a polyester film and a synthetic paper, water resistance, and blocking resistance. Further, in the case that the radical polymerizable vinyl monomers (d_3) and (d_4) are less than 10 parts by weight, an ink-absorbing ability tends to become worse and, in the case of exceeding 500 parts by weight, there tends to lower water resistance, and there is apt to lower adhesion to a base material such as a plastics film and a synthetic paper.

(Polymerization method of the D)

[0203] The polyurethane-based graft polymer mixture (D) is obtained by graft-polymerization of the water-based polyurethane (d_1) and the saponified product (d_2) of a vinyl acetate-based copolymer with 100-60% by weight of the hydrophilic radical polymerizable vinyl monomer (d_3) and 0-40% by weight (preferably, 95-60:5-40% by weight) of the other radical polymerizable vinyl monomer (d_4). In the case that the hydrophilic vinyl monomer (d_3) is not more than 60% by weight, absorbing ability of a water-based ink becomes worse.

[0204] As the polymerization method for obtaining the polyurethane-based graft polymer mixture (D), conventionally publicly-known methods can be applied. For example, there is enumerated a method in which a polymerization initiator and optionally a small amount of an emulsifier are added into a water dispersion composed of the water-based polyurethane (d_1) and the saponified product (d_2) of a vinyl acetate-based copolymer, and the radical polymerizable vinyl monomers (d_3) and (d_4) are gradually added while maintaining at 70-80°C and agitating, followed by aging for 2-5 hours to complete the polymerization and to obtain the polyurethane-based graft polymer mixture (D). Since the hydrophilic radical polymerizable vinyl monomers (d_3) is graft-polymerized in the water-based polyurethane (d_1) and the saponified product (d_2) of a vinyl acetate-based copolymer, the polyurethane-based graft polymer mixture (D) is excellent in the absorbing ability of a water-soluble ink and, in addition, it has adhesion, water resistance, transparency, and ductility, etc. which are a characteristic in a polyurethane resin.

(Polymerization initiator in the D)

[0205] As the polymerization initiator, there can be exemplified a usual radical polymerization initiator, for example, an azo compound [azobisisobutyronitrile, 2,2-azobis (2,4-dimethylvalero) nitrile, azobiscyano valeric acid, 2,2-azobis (2-amidinopropane) hydrochloride, and 2,2-azobis(2-amidinopropane)acetate, etc.], an inorganic peroxide (persulphates such as potassium persulphate, sodium persulphate, and ammonium persulphate, and hydrogen peroxide), an organic peroxide [benzoyl peroxide, di-t-butyl peroxide, cumenhydroperoxide, di(2-ethoxyethyl)peroxycarbonate], and a redox catalyst [a sulphite or a bisulphite (an alkaline metal salt and ammonium salt, etc.), etc.], a reducing agent such as L-ascorbic acid, elisorbic acid, persulphates (an alkaline metal salt and ammonium salt, etc.), and oxidants such as peroxides, etc. The polymerization initiator can be employed solely or in combination of two or more kinds.

(Additives to the D)

[0206] Into the polyurethane-based graft polymer mixture (D) obtained as described hereinabove, there can be optionally added resinous components such as an epoxy resin, an amino resin, an acrylic resin, a polyurethane-based resin, a polyester-based resin, starches, and a polyamine-based resin, crosslinking agents such as an isocyanate-based compound, an epoxy-based compound, carbodiimide, and a silane-coupling agent, inorganic fillers such as silica, talc, kaoline clay, calcium carbonate, and mica, inorganic pigments and organic pigments, a film-forming auxiliary agent, a thickener, a leveling agent, an antiblocking agent, an antistatic agent, an ultraviolet ray absorbent, and an oxidant, etc. which are conventionally publicly-known additives.

[Water-based polyester resin composition (E1)]

[0207] The water-based polyester resin composition (E1) to be employed in the present invention is prepared by esterification (or a transesterification) through a condensation polymerization of a dicarboxylic acid with a diol, and a method for the preparation thereof is not limited at all.

(Dicarboxylic acid components in the E1)

[0208] As the dicarboxylic acid components, there is preferably and mainly employed an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, phthalic acid, and naphthalene dicarboxylic acid, or an ester thereof. A reason depends upon an advantage of an improvement in adhesion because an aromatic ring in the aromatic dicarboxylic acid has a large affinity to a hydrophobic plastics. Particularly, since a water-based polyester in which terephthalic acid is employed has a large adhesion to a molded article made from a polyethylene terephthalate-based polyester, it is an excellent water-based polyester.

[0209] As the dicarboxylic acid components which construct the water-based polyester resin composition (E1), there are also employed the above-described aromatic dicarboxylic acid or the ester thereof and, in addition, there can be employed an aliphatic dicarboxylic acid such as adipic acid, succinic acid, sebacic acid, and dodecanoic diacid and a hydroxycarboxylic acid such as hydroxybenzoic acid or the ester thereof as the dicarboxylic acid components or a portion thereof. In the case of employing the ester, there is employed a lower alkyl ester such as a methyl ester and

an ethyl ester. The ester may be even a monoester and diester.

(Diol components in the E1)

[0210] On the other hand, as the diol components, there are employed ethylene glycol, propylene glycol, 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, cyclohexane dimethanol, and bisphenols, etc.

(Introduction of a hydrophilic group into the E1)

[0211] The water-based polyester resin composition (E1) to be employed in the present invention is polymerized so as containing sulphonic acid salt group or carboxylic acid salt group in the molecule in order to give a water-soluble or water-dispersible property.

[0212] As a specific example for allowing to contain the sulphonic acid salt group, there is enumerated a method in which a dicarboxylic acid component such as 5-sodium sulphisophthalic acid is employed as a portion of the dicarboxylic acid component, and the use amount is preferably 2-15% by mol in the dicarboxylic acid component.

[0213] As a specific example for allowing to contain the carboxylic acid salt group, there is enumerated a method in which a polyvalent carboxylic acid having three or more functionalities is employed as a condensed acid component in the preparation of the water-based polyester resin composition (E1), or a method in which a water-based polyester resin composition (E1) is prepared by a method in which a polymerizable unsaturated carboxylic acid is grafted on a polyester resin, and then, there are prepared salts of a substance which forms a water-soluble salt together with an alkaline metal, a variety of amines, and an ammonium compound etc. Amount of the carboxylic salt in the water-based polyester resin composition (E1) is preferably 15-250 KOH mg/g as an acid value in the water-based polyester resin composition (E1) produced.

[0214] In the polyester to be employed in the water-based polyester resin composition (E1), a molecular weight is 4000-30,000 and, in the case, in the case that the molecular weight is less than 4000, there are apt to lower physical properties in resins such as water resistance, blocking resistance, and adhesion, and in the case of exceeding 30,000, uniform dissolution or dispersion into water is difficult, resulting in that gelation tends to be caused with a lapse of time. Particularly, the molecular weight is preferably 5,000-25,000. The water-based polyester resin composition (E1) is changed to an aqueous solution or a water dispersion and, as a means thereof, in the case of a water-based polyester resin composition (E1) containing a sulphonic acid salt, it is preferably dispersed into warm water of 50-90°C under agitation. In the case, an water-soluble organic solvent may be even employed together in order to readily dissolve or disperse the resin composition.

(Water-soluble organic solvent)

[0215] As the water-soluble organic solvent, there are enumerated lower alcohols, polyvalent alcohols, and alkyl ethers or alkyl esters thereof and, specifically, there can be employed the lower alcohols such as methanol, ethanol, normal propanol, and isopropanol, the polyvalent alcohols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, and glycerine, ethylene glycol monomethylether, ethylene glycol monoethylether, propylene glycol monomethylether, propylene glycol monoethylether, propylene glycolacetate, diethylene glycol monomethylether, and dipropylene glycol monomethylether, etc.

[0216] Further, in the case of the polyester resin containing a carboxylic acid salt, it is preferably dissolved or dispersed into water of 50-90°C under agitation, in which there are added alkaline compounds such as an aqueous ammonia, sodium hydroxide, potassium hydroxide, and a variety of amines. Also in the case, the water-soluble organic solvent may be even employed together.

[0217] Thus-obtained water-based polyester resin composition (E1) may be even employed solely or in combination of two or more kinds of the water-based polyester resin composition (E1). Other resins and additives can be optionally formulated.

[Polyester-based graft polymer mixture (E)]

[0218] Further, the polyester-based graft polymer mixture (E) may be even employed as the modifier (R). It is, for example, a composition in which a hydrophilic radical polymerizable vinyl monomer (e_3) is polymerized with other radical polymerizable vinyl monomer (e_4) in an aqueous solution or dispersion composed of a water-based polyurethane (e_1) for grafting and a saponified product (e_2) of a vinyl acetate-based copolymer.

[0219] As the water-based polyester resin (e_1) for grafting, there can be preferably employed the water-based polyester resin composition (E1) exemplified in the illustration of the above-described water-based polyester resin composition.

[0220] As the saponified product (e_2) of a vinyl acetate-based copolymer, there can be preferably employed the saponified product (B) of a vinyl acetate-based copolymer exemplified in the illustration of the above-described saponified product of a vinyl acetate-based copolymer.

[0221] As the hydrophilic radical polymerizable vinyl monomer (e_3), there can be preferably employed the monomer (a_2) having a hydrophilic group composed of the monomer having a polyalkyleneoxide group exemplified in the illustration of the above-described cationic (meth)acrylic copolymer.

[0222] Further, as the other radical polymerizable vinyl monomer (e_4), there can be preferably employed the nonionic monomer (a_5) exemplified in the illustration of the above-described cationic (meth)acrylic copolymer.

[0223] The polyester-based graft polymer mixture (E) is obtained by graft polymerization of 100-60% by weight of the hydrophilic radical polymerizable vinyl monomer (e_3) with 0-40% by weight of other radical polymerizable vinyl monomer (e_4) in an aqueous solution or dispersion of a mixture of the above-described water-based polyester resin (e_1) for grafting with the above-described saponified product (e_2) of a vinyl acetate-based copolymer. In the case that the hydrophilic radical polymerizable vinyl monomer (e_3) is not more than 60% by weight, an absorbing ability of a water-based ink becomes worse.

(Constructing proportion of monomers in the E)

[0224] As the proportion of the water-based polyester resin (e_1) with respect to the saponified product (e_2) of a vinyl acetate-based copolymer and the radical polymerizable vinyl monomer [$(e_3)+(e_4)$], the saponified product (e_2) of a vinyl acetate-based copolymer is 10-500 parts by weight, and preferably 20-300 parts by weight, the radical polymerizable vinyl monomer (e_3) is 10-500 parts by weight, and preferably 20-300 parts by weight, which are based on and 100 parts by weight of the water-based polyester resin (e_1) and which based on solid ratio. In the case that the saponified product of a vinyl acetate-based copolymer is less than 10 parts by weight, a clearness and ink-absorbing ability are apt to lower and, in the case of exceeding 500 parts by weight, there becomes worse an adhesion to a plastic film-synthesized paper such as a polyester film which is a base material. Further, in the case that the radical polymerizable vinyl monomer (e_3) is less than 10 parts by weight, an ink-absorbing ability becomes worse and, in the case of exceeding 500 parts by weight, water resistance becomes worse and there is shown a tendency that there lowers an adhesion of a plastic film to a base material.

(Polymerization method of the E)

[0225] As the polymerization method for obtaining the polyester-based graft polymer mixture (E), conventionally publicly-known methods can be applied. For example, there is enumerated a method in which a polymerization initiator and optionally a small amount of an emulsifier are added into an aqueous solution/dispersion of a mixture of the above-described water-based polyester resin (e_1) for grafting with the above-described saponified product (e_2) of a vinyl acetate-based copolymer, and the hydrophilic radical polymerizable vinyl monomer (e_3) is gradually added while maintaining at 70-80°C, followed by aging for 2-5 hours to complete the polymerization and to obtain the polymer mixture (E).

[0226] Since the hydrophilic radical polymerizable vinyl monomers (e_3) is graft-polymerized in the water-based polyester resin (e_1) and the saponified product (e_2) of a vinyl acetate-based copolymer, the polyester-based graft polymer mixture (E) is excellent in the absorbing ability of a water-soluble ink and, in addition, it has adhesion, water resistance, and toughness, etc. which are a characteristic in a polyurethane resin.

(Polymerization initiator for the E)

[0227] As the polymerization initiator, there can be employed a usual radical polymerization initiator, for example, there can be employed the polymerization initiator exemplified in the above-described polyurethane-based graft polymer mixture (D).

(Additives in the E)

[0228] In the polyester-based graft polymer mixture obtained, optionally, there can be likewise employed the additives exemplified in the illustration of the above-described polyurethane-based graft polymer mixture (D).

[Block isocyanate compound (F)]

[0229] The block isocyanate compound (F) in relation to the present invention No. III is obtained by allowing to react an isocyanate compound with a blocking agent until free isocyanate groups disappears by a usual method.

[0230] As the polyisocyanate, there can be preferably employed the isocyanate compound exemplified in the illus-

tration of the above-described water-based polyurethane resin (C).

[0231] As the blocking agent, there can be employed a large number of publicly-known ones, for example, there are enumerated oximes such as methylethyl ketoxime, acetoxime, cyclohexanone oxime, acetophenone oxime, and benzophenone oxime; phenols such as m-cresol and xylene; alcohols such as methanol, ethanol, butanol, 2-ethylhexanol, cyclohexanol, and ethyleneglycol monomethylether; lactams such as ϵ -caprolactam; diketones such as diethyl malonate, acetoacetic acid ester; and mercaptans such as thiophenol, etc. In addition, there are many kinds such as ureas such as thiourea; imidazoles; and carbamic acids, etc.

[0232] The block isocyanate compounds are commercially supplied, for example, there can be obtained Desmodur series (Sumitomo Bayer Urethane, Ltd.), Bernox D series (Dainippon Ink Kagaku Kogyo, Ltd.), Takenate B series (Takeda Yakuhin Kogyo, Ltd.), Aquanate 200 series (Nihon Polyurethane Kogyo, Ltd.), and Elastolon BN series (Daiichi Kogyo Seiyaku, Ltd.), etc. there is preferred a block isocyanate compound blocked by an oxime or a lactam.

[Formulation of a resin composition for an ink jet recording sheet]

[0233] In the resin composition for an ink jet recording sheet in relation to the present invention Nos. I-III, as described hereinabove, there are formulated the cationic acrylic-based copolymers (A-I to A-III) having a crosslinkable group, the saponified product (B) of a vinyl acetate copolymer having a polymerization degree of 200-1000 and, further, the modifier (R) under fixed conditions described hereinafter. Herein, the modifier (R) is 0-80% by weight, preferably 5-60% by weight, and more preferably 5-65% by weight. Further, as the modifier (R), there can be applied the preferred embodiment as described hereinabove. For example, under fixed conditions described hereinafter, the modifier (R) is constructed by the water-based polyurethane resin (C), the polyurethane-based graft polymer mixture (D), and the polyester-based graft polymer mixture (E) and, formulating is conducted in 2-80% by weight of the (A-I to A-III), and preferably 5-50% by weight, 5-80% by weight of the (B), and preferably 15-75% by weight, (n_1 -80)% by weight of the (C), and preferably (n_1 -50)% by weight, (n_2 -60)% by weight of the (D), and preferably (n_2 -50)% by weight, (n_3 -60)% by weight of the (E) in 100% by weight of the resin composition for an ink jet recording sheet. Herein, in the n_1 , n_2 , and n_3 , minimum number is 0% by weight, respectively, and ($n_1+n_2+n_3$) is ≥ 5 , preferably not less than 10% by weight.

[0234] In the case that the (A-I to A-III) is outside of a range of 2-80% by weight, there lower ink-fixing ability, water resistance, and printing quality, and in the case that the (B) is outside of a range of 5-80% by weight, ink-absorbing ability lowers and, further, under the fixed conditions described hereinabove, in the case that the (C) is outside of a range of (n_1 -80)% by weight, there lower water resistance and adhesion to a base material and, in the case that both of the (D) and (E) are outside of a range of (n_2 -60)% by weight, there lower water resistance, ink-absorbing ability, and printing quality.

(2) Resin composition for recording in relation to the present invention Nos. IV-V

[0235] Hereinafter, there is illustrated the resin composition for ink jet recording in relation to the present invention Nos. IV-V.

[0236] In the resin composition for ink jet recording in relation to the present invention No. IV, there are formulated 2-100% by weight of a cationic (meth)acrylic copolymer (A-IV) obtained by copolymerizing a monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), 0-90% by weight of a saponified product (B) of a vinyl acetate copolymer, and 0-80% by weight of a modifier (R).

[0237] As a preferred embodiment for the resin composition for ink jet recording in relation to the present invention No. IV, there can be enumerated a resin composition composed of 5-80% by weight of the cationic (meth)acrylic copolymer (A-IV), 15-80% by weight of the saponified product (B) of a vinyl acetate copolymer, and 5-60% by weight of the modifier (R).

[0238] Further, in the resin composition for ink jet recording in relation to the present invention No. V, there are formulated 70-100% by weight of the cationic (meth)acrylic copolymer (A-V), 0-30% by weight of the saponified product (B) of a vinyl acetate copolymer (total of those is 100% by weight), and 0-15 parts by weight of the modifier (R) based on 100 parts by weight of the total of the (A-V) and the (B). Herein, constructing ratio of respective components is represented based on solid components.

[0239] In the present invention Nos. IV and V, the ratio of respective components which construct the resin composition for a recording sheet can be selected within a range in which there are not deteriorated an ink-absorbing ability, water resistance, printing quality, glossiness, and roll-mark resistance, etc.

[0240] Incidentally, the cationic (meth)acrylic copolymer (A-IV or A-V) affects to an ink-fixing ability, water resistance, an ink-absorbing ability, and printing quality, which is obtained by copolymerizing a monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), the saponified product (B) of a vinyl acetate copolymer affects to an ink-absorbing ability and an em-

bossed roll mark adherence property, the polymerization degree in the saponified product (B) of a vinyl acetate copolymer affects to a printing quality such as beading, and the modifier (R) affects to water resistance, adhesion to a base material, and a printing quality such as beading.

[0241] Composition ratio of the respective components in the composition in relation to the present invention enables to well-balance in a high level of respective performances in consideration thereof.

[0242] Concerning a relationship between the constructing ratio in the above-described three kinds of constructing components in the resin composition for ink jet recording in relation to the present invention and a characteristic in the recording sheet in the case that the composition is employed as a material for an image receiving layer, the invention No. V is illustrated as a typical example.

[0243] Formulation ratio of the cationic (meth)acrylic copolymer (A-V) with respect to the saponified product (B) of a vinyl acetate copolymer is (70-100% by weight)/(0-30% by weight) (total of both is 100% by weight). In the case that the (B) exceeds 30% by weight, although an ink-absorbing ability elevates, since the (B) tends to be softened by absorbing an ink, an embossed roll-mark is unpreferably apt to become adhered. On the other hand, even though the (A-V) absorbs an ink, since a softening degree is small, it has a characteristic that an embossed roll-mark is not marked. It is to be noted that although a usual cationic (meth)acrylic copolymer other than the (A-V) has a low absorbing ability of an ink, since the monomer (a_1) having a polyalkyleneoxide group and the monomer (a_2) having a hydrophilic group are employed as constructing monomers in the (A-V) in relation to the present invention, it has a relatively high ink-absorbing ability, and an excellent printed picture image is obtained.

[0244] The modifier (R) is formulated in 0-15 parts by weight based on 100 parts by weight of the total of the (A-V) and the (B), and in the case of exceeding 15 parts by weight, an ink-absorbing ability is apt to be reduced in an image-receiving layer, and there is shown a tendency affecting to a printing quality.

[0245] Accordingly, as the composition ratio of the resin composition for ink jet recording in relation to the present invention No. V, if there are considered a variety of affections and tendency which become problematic as described hereinabove, the cationic (meth)acrylic copolymer (A-V) is preferably 70-100% by weight, the saponified product (B) of a vinyl acetate copolymer is preferably 0-30% by weight (total of both is 100% by weight), the modifier (R) is preferably 0.2-10 parts by weight of based on 100 parts by weight of the total of the (A-V) and the (B). More preferably, the (A-V) is 75-95% by weight, the (B) is 5-25% by weight, the modifier (R) is preferably 0.5-5 parts by weight of based on 100 parts by weight of the total of the (A-V) and the (B).

(Monomers constructing A-IV to A-V)

[0246] As the monomer (a_1) having a polyalkylene oxide group (a polyoxyalkylene group) which constructs the cationic (meth)acrylic copolymers (A-IV to A-V), there can be exemplified a (meth)acrylate monomer containing a polyalkyleneoxide group such as a monoester of a mono, di, tri, or polyalkylene glycol with a (meth)acrylic acid, which is a monomer copolymerizable with the monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, a cationic monomer (a_4), or a nonionic monomer (a_5).

[0247] As the mono, di, tri, or polyalkylene glycol, for example, there can be preferably employed a vinyl monomer having an oxyalkylene group, etc. exemplified in the illustration of the constructing components for the saponified product (B) of a vinyl acetate copolymer.

[0248] Of those, as a preferred monomer, there is included a (meth)acrylate which is a vinyl monomer in which the oxyalkylene group is an oxyethylene group, particularly, a polyoxyalkylene (meth)allyl ether (of those, a polyoxyethylene allyl ether). The vinyl monomers can be employed solely or in combination of two or more kinds.

[0249] In the monomers, a structural formula of the alkyleneoxide group is shown by a general formula: $-[(CHR^1)_n-O]_m-R^2$

[In the formula, R^1 is a hydrogen atom, methyl group, or hydroxyl group, R^2 is a hydrogen atom or methyl group, "n" is an integer of 1-5, "m" is an integer of 1-20, "n and m" pieces of R^1 may be even identical to or different from each other]

[0250] In the general formula, in the case that "n" exceeds 5, an ink-absorbing ability lowers and, in the case that "m" exceeds 20, tackiness becomes unpreferably remarkable. As a more preferred range, "n" is 2-3, and "m" is 2-9.

[0251] As the monomer (a_2) having a hydrophilic group which constructs the cationic (meth)acrylic copolymers (A-IV to A-V), there can be employed the monomer having a hydrophilic group exemplified in the illustration of the above-described cationic (meth)acrylate copolymers (A-I to A-III) containing a crosslinkable group.

[0252] Of the above monomers, there are preferably enumerated a monomer having carboxylic group [a (meth)acrylic acid, etc.] and a monomer having hydroxyl group [2-hydroxyethyl(meth)acrylate and 2-hydroxypropyl(meth)acrylate, etc.].

[0253] As the monomer (a_3) having a crosslinkable group to be employed in the cationic (meth)acrylic copolymers (A-IV to A-V), there can be likewise employed the monomer having a crosslinkable group exemplified in the illustration of the above-described cationic (meth)acrylate copolymers (A-I to A-III) containing a crosslinkable group.

[0254] Of the above monomers, there is preferably enumerated a monomer having a crosslinkable group such as a

monomer having a hydrolyzable condensible group, particularly, an alkoxysilyl group (a C_{1-4} alkoxysilyl group such as methoxysilyl group and ethoxysilyl group, etc.).

[0255] As the cationic monomer (a_4) which constructs the cationic (meth)acrylic copolymers (A-IV to A-V), there can be likewise employed the cationic monomer exemplified in the illustration of the above-described cationic (meth)acrylate copolymers (A-I to A-III) containing a crosslinkable group.

[0256] The monomers are employed in combination with the nonionic monomer (a_5) in addition to the above-described various monomers as the cationic (meth)acrylate copolymers (A-I to A-III) in order to adjust film-formability and film properties.

[0257] As the nonionic monomer (a_5), there can be likewise employed the nonionic monomer exemplified in the illustration of the above-described cationic (meth)acrylate copolymers (A-I to A-III) containing a crosslinkable group.

[0258] As the nonionic monomer (a_5), there can be usually employed a C_{1-18} alkyl(meth)acrylate [particularly, a C_{2-10} alkylacrylate and a C_{1-6} alkylmethacrylate], aromatic vinyls [particularly, styrene], and vinyl esters [particularly, vinyl acetate]. The nonionic monomers (a_5) can be also employed solely or in combination of two or more kinds.

[0259] In the present invention No. IV, use amount of the cationic monomers (a_4) and the monomer (a_3) having a crosslinkable group can be selected within a range in which water resistance and ink-absorbing ability are not deteriorated, and the cationic monomer (a_4) is preferably 0.1-50% by weight (for example, 1-45% by weight), more preferably 0.5-40% by weight (for example, 2-35% by weight), and most preferably 1-30% by weight (for example, 3-25% by weight) based on total monomers which construct the cationic acrylic copolymer (A-IV), and it is usually 2-25% by weight or so. Further, use amount of the monomer (a_3) having a crosslinkable group is preferably 0.1-25% by weight, more preferably 0.2-20% by weight, and most preferably 0.5-15% by weight based on all monomers, and it is usually 0.3-10% by weight or so.

(Monomer proportion in the A-IV to A-V)

[0260] In the case that the above-described respective monomers are combined, proportion of the respective monomers can be selected in consideration of a preferred range of the respective components in the above-described (a_1)-(a_5) which construct the (A-IV to A-V).

[0261] In a preferred embodiment for the cationic acrylic copolymer (A-IV), the monomer (a_1) having a polyalkylene oxide group is preferably 0.1-40% by weight, more preferably 3-35% by weight, and most preferably 5-30% by weight, the monomer (a_2) having a hydrophilic group is preferably 0.1-50% by weight, more preferably 2-45% by weight, and most preferably 5-40% by weight, the monomer (a_3) having a crosslinkable group is preferably 0.5-20% by weight, more preferably 1-15% by weight, and most preferably 2-10% by weight, the cationic monomer (a_4) is preferably 1-40% by weight, more preferably 3-35% by weight, and most preferably 5-30% by weight, the hard monomer (a_6) is preferably 10-60% by weight, more preferably 20-55% by weight, and most preferably 25-50% by weight, and the soft monomer (a_7) is preferably 10-60% by weight, more preferably 15-50% by weight, and most preferably 20-45% by weight.

[0262] In a preferred embodiment for the cationic acrylic copolymer (A-V), the monomer (a_1) having a polyalkylene oxide group is preferably 8-40% by weight, more preferably 12-30% by weight, and most preferably 15-25% by weight, the monomer (a_2) having a hydrophilic group is preferably 1-30% by weight, more preferably 2-20% by weight, and most preferably 4-15% by weight, the monomer (a_3) having a crosslinkable group is preferably 0.2-10% by weight, more preferably 0.4-6% by weight, and most preferably 0.7-3% by weight, the cationic monomer (a_4) is preferably 10-50% by weight, more preferably 20-40% by weight, and most preferably 25-35% by weight, and the nonionic monomer (a_5) is preferably 10-80% by weight, more preferably 20-70% by weight, and most preferably 30-60% by weight.

[0263] In the cationic (meth)acrylic copolymers (A-IV to A-V), a weight average molecular weight is not particularly limited, and it is selected from a range of preferably 0.2×10^4 - 100×10^4 , and more preferably 1×10^4 - 50×10^4 . In the case of being less than 0.2×10^4 , tackiness is apt to be caused by increased low molecular weight components. On the other hand, in the case of exceeding 100×10^4 , viscosity becomes high, and inconvenience is caused in view of production.

(Glass transition temperature of the A-IV to A-V)

[0264] The glass transition temperature in the cationic (meth)acrylic copolymers (A-IV to A-V) can be selected within a range in which film-formability is not deteriorated. For example, it is preferably -20 to 50°C, more preferably -10 to 40°C, particularly preferably 0 to 30°C or so. A polymer having such the glass transition temperature can be appropriately prepared in combination of the above-described cationic monomer (a_4), monomer (a_3) having a crosslinkable group, and other monomers. The monomers often usually construct a copolymer in combination with a hard monomer [for example, a monomer having a glass transition temperature of 80 to 120°C (particularly, 90 to 105°C) such as methyl(meth)acrylate and styrene which forms a homopolymer] which is the above-described nonionic monomer (a_5) and a soft monomer [for example, a monomer having a glass transition temperature of -85 to -10°C (particularly, -85 to -20°C) such as a C_{2-10} alkylacrylate which forms a homopolymer].

[0265] In the present invention Nos. IV and V, there is not particularly limited a polymerization style for the cationic (meth)acrylic copolymers (A-IV to A-V) which are constructed by the above-described monomers, and a polymer obtained may be even any one of a random copolymer, a graft copolymer, and a block copolymer, etc.

(Polymerization style for the A-IV to A-V)

[0266] Form of the cationic (meth)acrylic copolymers (A-IV to A-V) may be even a solution such as an organic solvent solution and an aqueous solution, and it is usually a cationic emulsion (particularly, an aqueous emulsion).

[0267] The cationic emulsion containing the cationic (meth)acrylic copolymers (A-IV to A-V) can be obtained by a commonly-used method, for example, a method in which the above-described monomers are emulsion-polymerized in an emulsion system containing a nonionic-based surface active agent and/or a cationic-based surface active agent, and a method in which a water-based emulsion is prepared by allowing to form a tertiary amine salt or a quaternary ammonium salt after polymerization of the above-described monomers.

[0268] In polymer particles contained in the cationic emulsion, surface potential (ξ potential) is +20 to +60 mV, preferably +12 to +55 mV (for example, +15 to +55 mV), and particularly preferably +20 to +55 mV or so. When the surface potential becomes smaller in polymer particles, an ink-fixing ability and water resistance lower, and when the surface potential becomes larger, an ink-absorbing ability lowers. The surface potential of polymer particles in the cationic emulsion can be measured by the above-described conditions.

[0269] Average particle diameter of polymer particles in the cationic emulsion is 1-200 nm, preferably 3-100 nm, and more preferably 5-50 nm or so.

[0270] The cationic emulsion containing the cationic acrylic copolymers (A-IV to A-VI) can be obtained by a commonly-used method, for example, a method in which the above-described two or three monomers are emulsion-polymerized in an emulsion polymerization-system containing a nonionic surface active agent and/or a cationic surface active agent, or a method in which a water-based emulsion is prepared by allowing to form a tertiary amine salt or a quaternary ammonium salt after copolymerization of the monomers.

[Saponified product (B) of a vinyl acetate-based copolymer]

[0271] As the saponified product (B) of a vinyl acetate copolymer in the present inventions No. IV and No. V, there can be preferably employed the saponified product (B) of a vinyl acetate copolymer illustrated in the present inventions No. I-III.

[Modifier (R)]

[0272] Substance to be employed as the modifier (R) in the present inventions No. IV and No. V is a water-based polyurethane resin composition (C1) and/or a water-based polyester resin composition (E1). The water-based polyurethane resin composition (C1) and the water-based polyester resin composition (E1) are the same water-based polyurethane resin composition (C1) and water-based polyester resin composition (E1) as in the present invention No. III.

(3) Resin composition for recording in relation to the present invention No. VI

[0273] Hereinafter, the resin composition for recording in relation to the present invention No. VI is illustrated.

(Polymerizable unsaturated monomer (A-VI) having a hydrolyzable silyl group)

[0274] In the present invention No. VI, a primary component in the composition (P) which constructs an ink-receiving layer is a polymerizable unsaturated monomer (A-VI) having a hydrolyzable silyl group prepared by copolymerization of monomers containing a polymerizable unsaturated monomer (a_8) having a hydrolyzable silyl group and a (meth)acrylic-based polymerizable unsaturated monomer (a_9).

(Polymerizable unsaturated monomer (a_8) having a hydrolyzable silyl group)

[0275] As the polymerizable unsaturated monomer (a_8) having a hydrolyzable silyl, a polymerizable unsaturated monomer having a hydrolyzable silyl group shown by general formula (1) described below is enumerated.



(in the formula, R¹, R² and R³ may be identical or different from each other, and any one of a halogen atom, an alkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, an acyloxy group, a hydroxyl group, an amino group, an aminoxy group, and an alkylthio group)

[0276] The R¹, R² and R³ which construct a silyl group shown by the general formula (1) can be selected from the above-described various groups and, usually, at least one thereof is preferably a halogen atom, an alkoxy group, and a hydroxyl group.

[0277] The halogen atom described herein includes fluorine, chlorine, bromine, and iodine, and it is usually preferably chlorine atom.

[0278] Further, as the alkyl group, there can be preferably exemplified a C₁₋₁₀alkyl group such as methyl, ethyl, propyl, butyl, pentyl, and hexyl.

[0279] Still further, as the aryl group, there can be exemplified a C₆₋₁₀aryl group such as phenyl group and, as the aralkyl group, there can be exemplified a C₆₋₁₀aralkyl group such as benzyl group as a preferred group.

[0280] In addition, as the alkoxy group, there can be exemplified a C₁₋₁₆alkoxy group such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy, pentyloxy, hexyloxy, octyloxy, decyloxy, and dodecyloxy as a preferred group, and a C₁₋₄alkoxy group is preferred, and methoxy and ethoxy groups are particularly preferred. It is to be noted that the alkoxy group also includes an alkoxy-alkoxy group such as methoxyethoxy group.

[0281] Besides, as the aryloxy group, a C₆₋₁₀aryloxy group such as phenoxy group can be exemplified as a preferred group, and as the acyloxy group, there can be exemplified a C₂₋₆acyloxy group such as acetyloxy (acetoxy), propionyloxy, and butyryloxy groups as a preferred group.

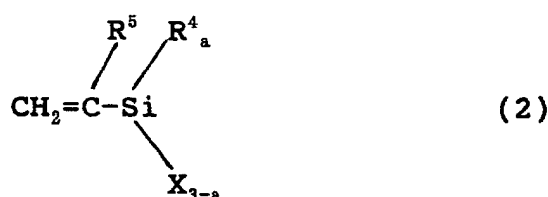
[0282] Also, as amino group, there is included an amino group which may have a substituted group such as dimethylamino group and, aminoxy group may have a substituted group such as dimethylaminoxy group, and dimethylaminoxy group and diethylaminoxy group can be exemplified as a preferred group.

[0283] And also, as the alkylthio group, there can be exemplified a C₁₋₆alkylthio group such as methylthio group and diethylthio group as a preferred group.

[0284] The polymerizable unsaturated monomer (a₈) having a hydrolyzable silyl group includes, for example, the following monomers.

(a) halogen-contained monomer

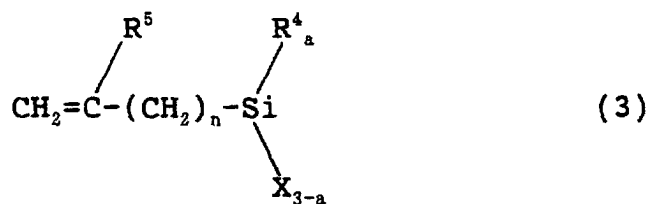
(a-1) Compound represented by general formula (2) described below,



(in the formula, R⁴ a C₁₋₁₀alkyl group, a C₆₋₁₀ aryl group, a C₇₋₁₀ aralkyl group, R⁵ represents a hydrogen atom or a methyl group, X represents fluorine, chlorine, bromine, and iodine, and "a" represents an integer of 0-2.

As specific examples of the compound shown by the formula (2), there are enumerated vinyltrichlorosilane, vinyl dimethyl chlorosilane, vinylmethyl phenylchlorosilane, isopropenyl trichlorosilane, isopropenylmethyl dichlorosilane, isopropenyl dimethyl chlorosilane, and isopropenylmethylphenyl chlorosilane, etc.

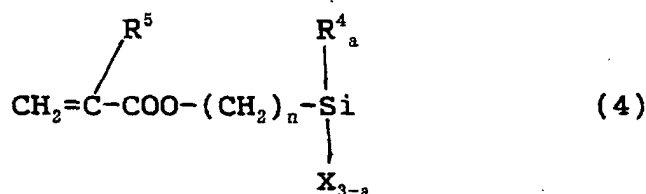
(a-2) Compound represented by general formula (3) described below,



(in the formula, R^4 , R^5 , X, and "a" are the same as the above descriptions, and "n" represents an integer of 1-12)

As specific examples of the compound shown by the formula (3), there are enumerated allyltrichlorosilane, allylmethyl dichloromethane, and allyldimethyl chloromethane, etc.

(a-3) Compound represented by general formula (4) described below,

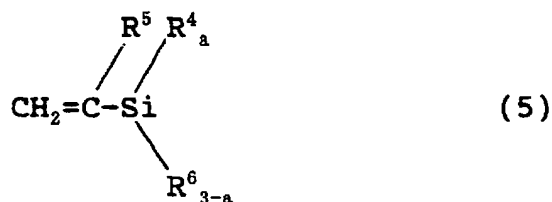


(in the formula, R^4 , R^5 , X, "a", and "n" are the same as the above descriptions)

As specific examples of the compound shown by the formula (4), there are enumerated 2-(meth)acryloxyethyl trichlorosilane, 3-(meth)acryloxypropyl trichlorosilane, 2-(meth)acryloxyethylmethyl dichlorosilane, 3-(meth)acryloxypropyl methyl dichlorosilane, 2-(meth)acryloxyethyl dimethyl chlorosilane, and 3-(meth)acryloxy propyldimethyl chlorosilane, etc.

(b) Monomer containing an alkoxy group or allyoxy group

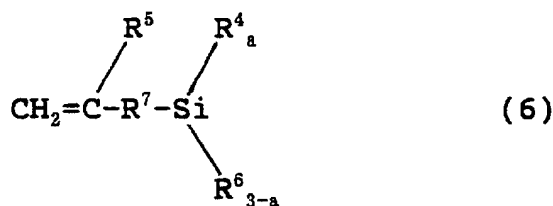
(b-1) Compound represented by general formula (5) described below,



(in the formula, R^4 , R^5 , and "a" are the same as the above descriptions, and R^6 represents a C_{1-16} alkoxy group)

As specific examples of the compound shown by the formula (5), there are enumerated vinyltrimethoxy silane, vinyltriethoxy silane, vinyltributoxy silane, vinyltri(hexyloxy) silane, vinyltri(octyloxy)silane, vinyltri(decyloxy)silane, vinyltri(dodecyloxy)silane, vinyldimethoxymethyl silane, vinyl-diethoxymethyl silane, vinylbutoxydimethyl silane, vinyl-diphenylethoxy silane, isopropenyltrimethoxy silane, isopropenyltriethoxy silane, isopropenyltributoxy silane, isopropenyltri(hexyloxy)silane, isopropenyltri(octyloxy)silane, isopropenyltri(decyloxy)silane, isopropenyltri(dodecyloxy)silane, isopropenyldimethoxy methylsilane, isopropenyldiethoxy methylsilane, isopropenyl methoxydimethyl silane, isopropenyl ethoxydimethyl silane, isopropenyl butoxydimethyl silane, and vinyltris(2-methoxyethoxy)silane, etc.

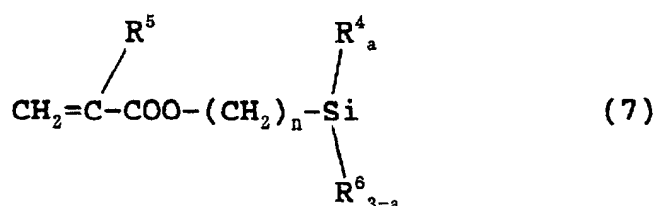
(b-2) Compound represented by general formula (6) described below,



(in the formula, R^4 , R^5 , R^6 , and "a" are the same as the above descriptions, and R^7 represents any one of an alkylene group or a phenylene group)

As specific examples of the compound shown by the formula (6), there are enumerated allyltrimethoxy silane, vinyldecyl trimethoxy silane, vinyloctyl trimethoxy silane, vinylphenyl trimethoxy silane, vinylphenyl dimethoxymethyl silane, vinylphenylmethoxydimethyl silane, isopropenylphenyl trimethoxy silane, isopropenylphenyl dimethoxymethyl silane, and isopropenylphenyl methoxydimethyl silane, etc.

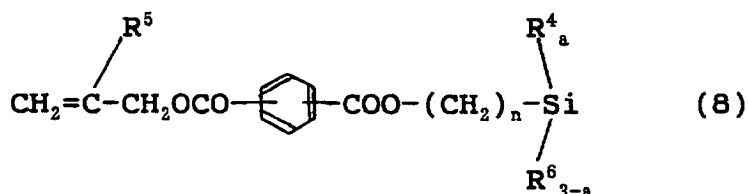
(b-3) Compound represented by general formula (7) described below,



(in the formula, R^4 , R^5 , R^6 , "a", and "n" are the same as the above descriptions)

As specific examples of the compound shown by the formula (7), there are enumerated 2-(meth)acryloxyethyl trimethoxy silane, 2-(meth)acryloxyethyl triethoxy silane, 3-(meth)acryloxypropyl trimethoxy silane, 3-(meth)acryloxypropyl triethoxy silane, 3-(meth)acryloxypropyl methyldimethoxy silane, 3-(meth)acryloxypropyldiethoxy silane, and 3-(meth)acryloxypropyl tris(2-methoxyethoxy)silane, etc.

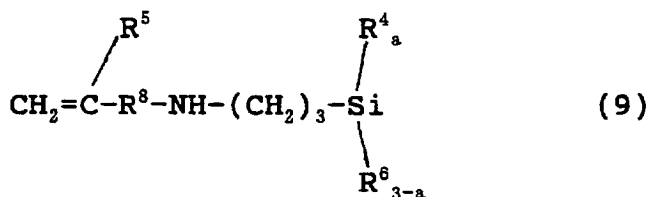
(b-4) Compound represented by general formula (8) described below,



(in the formula, R^4 , R^5 , R^6 , "a", and "n" are the same as the above descriptions)

As specific examples of the compound shown by the formula (8), there are enumerated 3-[2-(allyloxycarbonyl)phenylcarbonyloxy] propyldimethoxy methylsilane, 3-[2-(allyloxycarbonyl) phenylarbonyloxy]propyldimethoxydimethyl silane, 3-[2-(allyloxycarbonyl)phenylenecarbonyloxy]propyltrimethoxy silane, 3-[2-(isopropenylmethoxycarbonyl)phenylarbonyloxy] propyldimethoxymethylsilane, and 3-[2-(isopropenylmethoxycarbonyl)phenylcarbonyloxy]propyl methoxydimethyl silane, etc.

(b-5) Compound represented by general formula (9) described below,

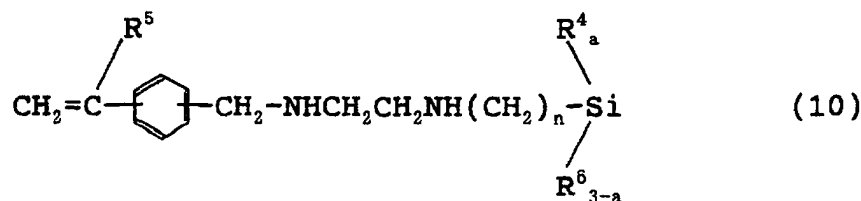


(in the formula, R^4 , R^5 , R^6 , and "a" are the same as the above descriptions, and R^8 represents a phenylene group or



As specific examples of the compound shown by the formula (9), there are enumerated 3-(vinylphenylamino)propyltrimethoxy silane, 3-(vinylphenylamino)propyltriethoxy silane, 3-(vinylbenzylamino)propyltrimethoxy silane, and 3-(vinylbenzylamino)propyltriethoxy silane, etc.

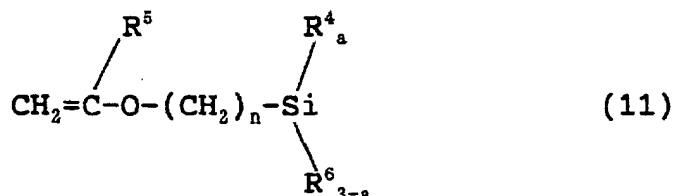
(b-6) Compound represented by general formula (10) described below,



(in the formula, R^4 , R^5 , R^6 , and "a" are the same as the above descriptions)

As specific examples of the compound shown by the formula (10), there are enumerated 3-[2-(N-vinylphenylmethylamino) ethylamino]propyltrimethoxy silane and 3-[2-(N-isopropenylphenyl methylamino)ethylamino]propyltrimethoxy silane, etc.

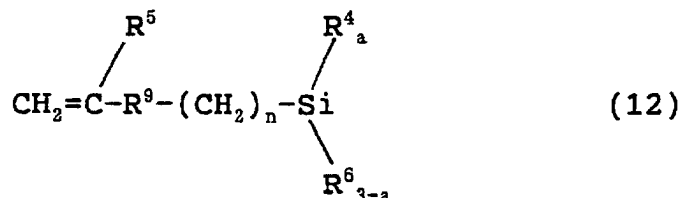
(b-7) Compound represented by general formula (11) described below,



(in the formula, R^4 , R^5 , R^6 , "a", and "n" are the same as the above descriptions)

As specific examples of the compound shown by the formula (11), there are enumerated 2-(vinylloxy) ethyltrimethoxy silane, 3-(vinylloxy)propyl trimethoxysilane, 4-(vinylloxy)butyl triethoxysilane, and 2-isopropenylloxy)ethyl trimethoxysilane, etc.

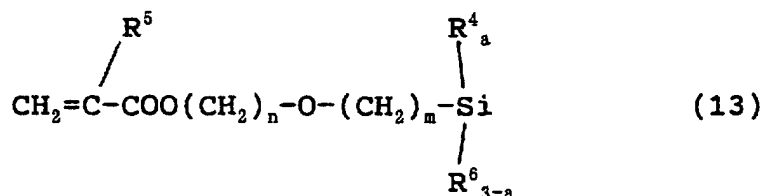
(b-8) Compound represented by general formula (12) described below,



(in the formula, R^4 , R^5 , R^6 , "a", and "n" are the same as the above descriptions, and R^9 represents $\text{---CH}_2\text{O---}$ or $\text{---CH}_2\text{OCO---}$)

As specific examples of the compound shown by the formula (12), there are enumerated 3-(allyloxy)propyltrimethoxy silane, 10-(allyloxycarbonyl)decyl trimethoxysilane, 3-(isopropenylmethoxy)propyltrimethoxy silane, and 10-(isopropylmethoxycarbonyl)decyltrimethoxy silane, etc.

(b-9) Compound represented by general formula (13) described below,



(in the formula, R⁴, R⁵, R⁶, "n", and "a" are the same as the above descriptions, and "m" is an integer of 1-12)

As specific examples of the compound shown by the formula (13), there are enumerated 3-[(meth)acryloxyethoxy] propyltrimethoxy silane and 3-[(meth)acryloxyethoxy] propyldimethoxymethylsilane, etc.

[0285] Further, as the polymerizable unsaturated monomer (a₈) having a hydrolyzable silyl group, in addition to the examples, for example, there may be even a monomer containing a divinyl group such as divinyltrimethoxy silane, divinyltriethoxy silane, and divinyltri(β-methoxyethoxy)silane.

[0286] Such the monomer having a silyl group preferably includes, for example, a vinyl-based monomer containing an alkoxysilyl group from a viewpoint of a handling ability, profitability, and suppression of side reactions, etc.

[(meth)acrylate-based polymerizable unsaturated monomer (a₉)]

[0287] As described hereinabove in the present invention, the composition (P) contains as a primary component the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group prepared by a copolymerization of monomers containing the polymerizable unsaturated monomer (a₈) having a hydrolyzable silyl group and the (meth)acrylate-based polymerizable unsaturated monomer (a₉) described hereinafter.

[0288] In the composition (P) in relation to the present invention, the (meth)acrylate-based polymerizable unsaturated monomer (a₉) can be employed even solely or in combination of two or more kinds.

[0289] It is to be noted that the (meth)acrylate-based copolymerizable unsaturated monomer (a₉) includes, for example, a (meth)acrylate, (meth)acrylic amides, and a (meth)acrylonitrile, etc.

[0290] As the (meth)acrylate, there can be exemplified an alkyl(meth)acrylate [for example, C₁₋₁₈alkyl(meth)acrylates such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, t-butyl(meth)acrylate, hexyl(meth)acrylate, octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, and lauryl(meth)acrylate], a cycloalkyl(meth)acrylate [for example, cyclohexyl(meth)acrylate, etc.], an aryl(meth)acrylate [for example, phenyl(meth)acrylate, etc.], an aralkyl(meth)acrylate [for example, benzyl(meth)acrylate, etc.], a hydroxyalkyl(meth)acrylate [for example, hydroxy-C₂₋₄alkyl(meth)acrylates such as 2-hydroxyethyl(meth)acrylate and 2-hydroxypropyl(meth)acrylate, etc.], a hydroxyalkyl(meth)acrylate, glycidyl(meth)acrylate, a dialkylamino-alkyl(meth)acrylate [for example, a di-C₁₋₄alkylaminoalkyl(meth)acrylate such as 2-(dimethylamino)ethyl(meth)acrylate and 2-(diethylamino)ethyl(meth)acrylate], etc.

[0291] Further, as the (meth)acrylamides, there can be exemplified (meth)acrylamide, a hydroxyalkyl(meth)acrylamide [for example, an N-hydroxy-C₁₋₄alkyl(meth)acrylamide such as N-methylol(meth)acrylamide], an alkoxyalkyl(meth)acrylamide [for example, N-hydroxy-C₁₋₄alkoxy-C₁₋₄alkyl(meth)acrylamides such as N-methoxymethyl(meth)acrylamide], and diacetone(meth)acrylamide, etc.

[0292] As a preferred (meth)acrylic-based polymerizable unsaturated monomer (a₉) in relation to the present invention, there can be exemplified a (meth)acrylate [for example, a C₁₋₁₈alkyl(meth)acrylate, a hydroxy-C₂₋₄alkyl(meth)acrylate, glycidyl(meth)acrylate, di-C₁₋₄alkylamino-C₂₋₄alkyl(meth)acrylate, etc.] and (meth)acrylamides, etc. and, as a more preferred (meth)acrylic-based monomer, there can be enumerated a C₂₋₁₀alkylacrylate, C₂₋₁₀alkylmethacrylate, a hydroxy-C₂₋₃alkyl(meth)acrylate, glycidyl(meth)acrylate, and di-C₁₋₃alkylamino-C₂₋₃alkyl(meth)acrylate.

(Monomer which constructs the A-VI)

[0293] The (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group in relation to the present invention is obtained by a copolymerization of monomers containing the (a₈) and (a₉), and as the latter (a₉) or in addition to the (a₉), there may be often employed a hard monomer [for example, a monomer component which forms a homopolymer having a glass transition temperature of 80 to 120°C. (particularly, 90 to 105°C) or so such as methyl(meth)acrylate and styrene] and a soft monomer [for example, a monomer component which forms a homopolymer having a glass transition temperature of -85 to -10°C (particularly, -85 to -20°C) or so such as a C₂₋₁₀alkylacrylate] in combination thereof.

(Other copolymerizable unsaturated monomer)

[0294] On the other hand, there is a merit that there can be obtained a water-based resin composition without using an emulsifier by using a monomer component containing an ionic functional group such as carboxylic group and amino group [for example, a dialkylaminoalkyl(meth)acrylate, etc.] as the (a₉) as well as the above descriptions or in addition to the (a₉).

[0295] It is to be noted that in addition to the monomer (a₉) copolymerized with the (a₈), a copolymerizable unsaturated monomer which is further added is hereinafter represented as other copolymerizable unsaturated monomer (a₁₀).

[0296] In the case that the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group is constructed by the polymerizable unsaturated monomer (a₈) having a hydrolyzable silyl group, the (meth)acrylate-based polymerizable unsaturated monomer (a₉), and the other copolymerizable unsaturated monomer (a₁₀), use amount of respective monomer components is not limited.

(Constructing proportion of the monomers in the A-VI)

[0297] A respective preferred range of the (a₈) and (a₉) is a range described below (herein, total of the (a₈) and (a₉) is 100% by weight), and it is appropriately preferably selected in the range.

[0298] Component (a₈): 0.1-30% by weight [preferably 0.5-20% by weight, more preferably 1-15% by weight, and particularly preferably 2-10% by weight].

[0299] Component (a₉): 70-99.9% by weight [preferably 80-99.5% by weight, more preferably 85-99% by weight, and particularly preferably 90-98% by weight].

[0300] In the case that construction of the copolymerizable unsaturated monomers containing the (a₉) and (a₁₀) is separated into a hard monomer, a soft monomer, and a monomer containing an ionic functional group, a ratio of use amount between each other is not particularly limited, and a preferred range is a range (herein, total is 100% by weight) as described below, it is appropriately preferably selected in the range.

(1) Hard monomer: 0-90% by weight [preferably 10-80% by weight, more preferably 15-75% by weight, and particularly preferably 20-70% by weight]

(2) Soft monomer: 0-90% by weight [preferably 10-80% by weight, more preferably 15-75% by weight, and particularly preferably 20-70% by weight]

(3) Monomer containing an ionic group: 0-90% by weight [preferably 1-50% by weight, more preferably 2-20% by weight, and particularly preferably 2-10% by weight]

(Embodiment in the use of the A-VI)

[0301] The (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group, which is one of primary components in the composition (P) in relation to the present invention, may be any one of embodiments of a water-based product such as an aqueous solution, a water-based emulsion (a water-based polymer emulsion), a nonaqueous solution such as an organic solvent solution and an organic solvent emulsion, and a solid powder, etc., and which are not problematic in use. However, the water-based product is preferred in view of handling, preparation, and handling in the preparation of the composition (P) from inorganic compound fine particles (G) of other primary components.

[0302] It is to be noted that it is the water-based product, since it is constructed by a water-based resin component constructed from a copolymer of the polymerizable unsaturated monomer (a₈) having a hydrolyzable silyl group with the (meth)acrylate-based polymerizable unsaturated monomer (a₉) without using a crosslinked resin such as a crosslinked product of an acrylic silicone oligomer containing a hydrolyzable alkoxysilyl group, it can be readily handled.

(Average particle diameter in particles of the copolymer A-VI)

[0303] In the case that the component (A-VI) is a water-based emulsion, the average particle diameter in particles of the copolymer is selected from a range of 0.01-2 μm, preferably 0.01-1 μm, more preferably 0.01-0.5 μm, and further preferably 0.01-0.3 μm- or so, so that dispersion stability and adhesion are not deteriorated.

(Method for the preparation of a water-based emulsion)

[0304] As a method for the preparation of the aqueous solution or water-based emulsion of the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group, it is not particularly limited, and commonly-used methods can be applied, for example, (1) a method in which the monomer containing a hydrolyzable silyl group represented by the above-described general formula (1) is copolymerized with a polymerizable unsaturated (meth)acrylate-based mono-

mer having a functional group such as carboxylic group or amino group to prepare a copolymer, and the copolymer is dissolved or dispersed using an alkali (for example, an alkyl amine such as triethylamine, a cyclic amine such as morpholine, an alkanol amine such as triethanolamine, pyridine, and ammonia, etc.), an acid [for example, there can be exemplified an inorganic acid (for example, hydrochloric acid and sulfuric acid, etc.) and an organic acid (for example, a carboxylic acid such as acetic acid and propionic acid, and sulfonic acid, etc.)],

- (2) a method in which the above-described copolymer is emulsified and dispersed using an emulsifier, and
- (3) an emulsion polymerization, etc.

[0305] In the methods (1) and (2), the copolymer may be prepared even by a solution-polymerization method, an emulsion polymerization method, a suspension polymerization method, and a bulk polymerization method, etc. It is to be noted that a style in the polymerization may be any one of a batchwise or continuous one.

(Organic solvent for copolymerizing the A-VI)

[0306] In the method for the preparation of the copolymer by a solution-polymerization of both components, the polymerization may be conducted under the presence of organic solvents [for example, an alcohol (ethanol, isopropanol, and n-butanol, etc.), an aromatic hydrocarbon (benzene, toluene, and xylene, etc.), an aliphatic hydrocarbon (pentane, hexane, and heptane, etc.), acycloaliphatic hydrocarbon (cyclohexane, etc.), an ester (ethyl acetate and n-butyl acetate, etc.), a ketone (acetone and methylethylketone, etc.), and an ether (diethylether, dioxane, and tetrahydrofuran, etc.)]. It is to be noted that the organic solvent may be employed solely or even in combination of two or more kinds.

[0307] As the organic solvent, there may be usually employed an alcohol such as isopropanol, an aromatic hydrocarbon such as toluene, and a ketone such as methylethylketone, etc.

[0308] Use amount of the organic solvent is not particularly limited, and it can be selected from, for example, a range of total amount of (the organic solvents)/(total amount of monomers)=preferably 0.1/1-5/1 (weight ratio), and more preferably 0.5/1-2/1 (weight ratio).

(Polymerization initiator for the A-VI)

[0309] In the solution polymerization, although a polymerization may be initiated by irradiation of an electron beam or an ultraviolet ray and heating, it is often initiated using a polymerization initiator.

[0310] As the polymerization initiator, there can be employed the polymerization initiators exemplified in the illustration of the polyurethane-based graft polymer mixture (D).

[0311] Use amount of the polymerization initiator can be selected from, for example, a range of preferably 0.001-20% by weight, and more preferably 0.01-10% by weight (for example, 0.1-10% by weight) or so based on total amount of the monomers (the monomer having a silyl group and the copolymerizable components) and, usually, it is selected from such the range.

[0312] Reaction temperature in the solution polymerization is preferably 50-150°C, and more preferably 70-130°C or so. Further, reaction time of period is preferably 1-10 hours, and more preferably 2-7 hours or so.

[0313] It is to be noted that a terminating point of the polymerization can be identified by disappearance in the absorption (for example, 1648 cm⁻¹) by double bonds in infrared absorption spectra or a decrease of unreacted monomers using a gas chromatography.

(Emulsifier for the A-VI)

[0314] In the case of a change to an aqueous property by emulsifying the copolymer in relation to the present invention, there can be employed an emulsifier, for example, an alkyl sulphate, an alkylaryl sulphonate, an alkyl phosphate or an anionic surface active agent such as a fatty acid salt, a cationic surface active agent such as an alkyl amine salt and an alkyl quaternary ammonium salt, a nonionic surface active agent such as a polyoxyethylene alkylarylether, a polyoxyethylene alkylether, or a pulmonic-type nonionic surface active agent such as a polyoxyethylene-polyoxypropylene condensate which is a product by Asahi Denka, Ltd., or an ampholytic surface active agent such as a carboxylic acid salt-type (an amino acid-type or betaine-type) or a sulphonic acid salt-type agent. It is to be noted that pH adjustment of the emulsion may be even conducted by a pH control agent.

(Acid and basic compound for improving hydrophilicity)

[0315] In modification for giving an aqueous property to the above-described copolymer, in the case that the polymer contains a cationic group such as a cation-formable group, amino group, and imide group, the polymer can be readily

dissolved or emulsified because of an increase of hydrophilic property by the use of acids.

[0316] As such the acids, there can be exemplified an inorganic acid (hydrochloric acid, phosphoric acid, sulfuric acid, and nitric acid, etc.) and an organic acid [a saturated aliphatic monocarboxylic acid such as formic acid, acetic acid, and propionic acid; a saturated aliphatic polycarboxylic acid such as oxalic acid and adipic acid; an unsaturated aliphatic monocarboxylic acid such as (meth)acrylic acid; an unsaturated aliphatic polycarboxylic acid such as maleic acid and itaconic acid; and an aliphatic oxycarboxylic acid such as lactic acid and citric acid, etc.].

[0317] Use amount of the acid can be selected from, for example, a range of the acid/cationic group=0.3/1-1.5/1 (molar ratio) or so based on total amount of the cationic groups.

[0318] In the case that the polymer contains an acidic group such as carboxylic group, the polymer can be readily dissolved or emulsified by the use of a base. As such the base, for example, there can be included an organic base (an alkyl amine such as triethylamine, a cyclic amine such as morpholine, an alkanol amine such as triethanol amine, and pyridine, etc.) and an inorganic base (ammonia and a hydroxide of an alkali metal, etc.), etc.

[0319] Use amount of the base can be selected from, for example, a range of the acid/cationic group=1-1.5/1 (molar ratio) or so based on total amount of the acidic groups.

(Emulsification of the copolymer)

[0320] The polymer obtained by a solution polymerization can be emulsified under the presence or the absence of organic solvents.

[0321] In the case that the polymer is dissolved or immediately emulsified without dissolving under the presence of organic solvents, a water-soluble organic solvent (for example, an alcohol such as isopropanol) is often employed as an organic solvent. In the case that the polymer was emulsified under the presence of organic solvents, the organic solvent may be even removed by evaporation, etc. after emulsifying, and an emulsion may also contain the organic solvent. It is to be noted that in the case that the organic solvent is removed before emulsifying the polymer, an organic solvent (a ketone such as methylethylketone) having a low boiling point is often employed.

[0322] In the case that the polymer obtained by solution polymerization is emulsified under the presence of organic solvents, it can be emulsified by adding water after adding an additive (for example, an emulsifier, a pH regulator, and an acid, etc.) to an organic solution containing the polymer. In the case, it is preferred to gradually add water by dropping. Emulsifying is preferably carried out at a low temperature, for example, it can be selected from a range of not more than 70°C (for example, 5-70°C), and preferably not more than 50°C or so (for example, 10-50°C).

[0323] After having emulsified by the addition of water, removal of the organic solvents is often carried out at, for example, not more than 80°C (for example, 5-80°C) and an ordinary or reduced pressure (for example, 0.0001-1 normal atmosphere or so).

(Method for emulsion polymerization)

[0324] In the case that the copolymer is obtained by conducting the emulsion polymerization of the respective monomers ((a₈) and (a₉), (a₈), (a₉), and (a₁₀)) in relation to the present invention, a commonly-used method can be applied and, for example, there can be applied a method for collectively-feeding the respective monomers (for example, a method in which the respective monomers are collectively fed into a water-based medium to allow to copolymerize) and a method for adding monomers (a method in which the respective monomers are separately fed while mixing into a water-based medium to allow to polymerize).

[0325] The monomers may be prepared as a pre-emulsion which is in advance emulsified. In the preparation of the emulsion, emulsifying may be even conducted using a polymerizable emulsifier and may be emulsified using an emulsifier.

(Polymerizable emulsifier)

[0326] Herein, as the polymerizable emulsifier, for example, commonly-used various polymerizable emulsifiers [compounds which contain (meth)allyl group or (meth)acrylic group as a polymerizable group and contain a cationic group such as a quaternary ammonium salt, a tertiary amine salt, amino group, and imide group, an anionic group such as a sulfonic acid salt and a carboxylic acid salt, a nonionic group such as an ethyleneoxide group, etc. as a emulsifying-functional group] can be employed. It is to be noted that use amount of the emulsifier can be appropriately selected from a range of, for example, preferably 0.1-20% by weight, and more preferably 0.5-10% by weight based on total amount of monomers.

(Polymerization initiator)

[0327] As the polymerization initiator to be employed in the emulsion polymerization, of the polymerization initiators exemplified in the above-described polyurethane-based graft polymer mixture (D), there can be employed the water-soluble polymerization initiators such as inorganic peroxides, and water-soluble redox-type polymerization initiator-system may be also employed.

(Emulsifier for emulsion polymerization)

[0328] As the emulsifier to be employed in the emulsion polymerization, there are enumerated emulsifiers, etc. which can be employed in the case of emulsifying the above-described solution polymer. Further, for the purpose of stabilizing the emulsion polymerization, a protective colloidal agent (a partially-saponified polyvinyl alcohol, a carboxymethyl cellulose, a methyl cellulose, a hydroxyethyl cellulose, and a hydroxypropyl cellulose,) may be employed. It is to be noted that a pH controlling agent may be employed in emulsifying.

[0329] In the emulsion polymerization, conditions such as temperature may be same conditions as in the solution polymerization described hereinabove.

(Chain transfer agent)

[0330] In the solution polymerization and the emulsion polymerization, there may be employed a chain transfer agent in order to adjust a molecular weight of the copolymer, for example, such as alcohols such as catechol, thiols, mercaptans (n-lauryl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, 3-mercaptopropyl trimethoxy silane, 3-mercaptopropyl methyldimethyl silane).

[0331] It is to be noted that as an ionic property of the emulsion, nonionic property is preferred and, of those, an anionic property is more preferred.

(Additives)

[0332] In the case that the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group is a water-based resin, there may be added a variety of additives in order to elevate weatherability of a recorded picture image, for example, which includes a lubricant such as a fluorine resin, a silicone resin, an organic sulphonate compound, an organic phosphate compound, and an organic carboxylate compound, a stabilizer such as an antioxidant, an ultraviolet ray absorbent, and a thermal stabilizer, a variety of additives such as a radical scavenger, a delustering agent, an antistatic agent, a plasticizer, a thickener, and a defoaming agent.

[0333] The composition (P) which constructs an ink-receiving layer in relation to the present invention primarily contains the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group and inorganic compound-based fine particles (G).

(Inorganic compound-based fine particles (G))

[0334] As the inorganic compound-based fine particles (G), for example, there are enumerated fine particles composed of silica, alumina, white carbon, a calcine diatomaceous, and an oxide (including a composite oxide and a hydrate) such as titanium oxide; a hydroxide such as aluminum hydroxide, calcium hydroxide, and magnesium hydroxide; a carbonate such as calcium bicarbonate, a heavy calcium carbonate, a light calcium carbonate, and magnesium carbonate; a sulphate such as calcium sulphate; calcium silicate, magnesium silicate, talc, kaoline, delami kaoline, clay, bentonite, smectite, zeolite, a silicate or alumino silicate such as magnesium alumino silicate and celcicite; and clay minerals, etc. which are an inorganic compound or a mixture thereof.

[0335] The inorganic compounds to be employed in the present invention are not particularly limited and, as preferred inorganic compound-based fine particles, there are inorganic-based fine particles such as silica and alumina, and of those, silica is preferred. Particularly, there is preferred a colloidal silica dispersed in water which is connected in a rosary-state. Herein, the colloidal silica dispersed in water which is connected in a rosary-state is a colloidal suspension of a silicone dioxide or a hydrate thereof, and usually, it is obtained by allowing to react an aqueous solution of a silicate with a diluted hydrochloric acid, and even colloidal silica by any methods for the preparation can be employed.

[0336] Average primary particle diameter in the inorganic compound-based fine particles is preferably 1-200 nm, more preferably 5-100 nm, and most preferably 15-50 nm. Secondary particle diameter is preferably 10-1000 nm, more preferably 20-500 nm, and most preferably 100-300 nm.

(Composition of the composition (P))

[0337] As weight ratio (%) of the (A-VI) with the (G) which construct an ink-receiving layer and which is a primary component in the (P), since there are possibly a case that the (A-VI) is water-soluble and a case that it is a colloidal silica in which the (G) is dispersed in water, respective components are preferably represented based on a solid component value (weight), and the (A-VI)/(G) preferably ranges in (1-50)/(50-99) (respective values are % by weight, and total is 100% by weight).

[0338] Further, although depending upon a method for forming the ink-receiving layer, the composition (P) is preferably a water-based liquid, and it is preferably a water-based liquid adjusted to 10-50% by weight.

(Method for the preparation of the composition (P))

[0339] The method for the preparation of the composition (P) comprises the (A-VI) and the (G) is not particularly limited and, in the case that both of the components (A-VI) and (G) are a solid, the (A-VI) and the (G) are preferably dispersed into water by a homogenizer, etc. after having crushed the (A-VI) and the (G), respectively. In the case that any one of the components (A-VI) and (G) is water-based, for example, the (A-VI) is a colloidal silica in which a water-based emulsion (G) is dispersed in water and it is connected in a rosary-state, there is preferably a method in which mixing is conducted by agitating as it is. Further, in the case that any one of the components (A-VI) and (G) is a solid and another one is water-based, there is preferred a method that the solid is added to the water-based component after having crushed, followed by dispersing by a homogenizer, etc.

(Resin for employing for an ink-fixing layer)

[0340] Resin or resin composition to be employed for the ink-receiving layer is not particularly limited and, there is preferably employed a resin composition containing a mixture of at least one resin selected from the group consisting of the (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group, a mixture of the (meth) acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group, the saponified product (B) of a vinyl acetate-based copolymer, and the water-based polyurethane-based graft polymer mixture (D), and the water-based polyester-based graft polymer mixture (E).

(Resin containing a cationic group)

[0341] As described hereinabove, in the case that the ink-fixing layer is formed, there is employed the resin alone or a resin composition of the resin with the above-described other resins.

[0342] Herein, as the resin containing a cationic group, there can be preferably exemplified a dicyan-based resin (a dicyandiamide-formaldehyde polycondensate, etc.), a polyamine-based resin [a condensate (a dicyandiamide-diethylenetriamine polycondensate, etc.) of an aliphatic polyamine such as diethylenetriamine, triethylenetetramine, an aromatic polyamine such as phenylene diamine, or a condensed product (a dicyandiamide-diethylenetriamine polycondensate, etc.) of dicyan diamide with a polyC₂₋₄alkylene polyamine], and a polycationc-based resin, etc.

(Polycationc-based resin)

[0343] As the polycationc-based resin, there can be exemplified an epichlorohydrin-diC₁₋₄alkylamine-added polymer (an epichlorohydrin-dimethylamine-added polymer, etc.), a polymer of an alkylamine or a salt thereof (a polymer of polyallylamine or a hydrochloric acid salt thereof, etc.), a polymer of a diallylC₁₋₄alkylamine or a salt thereof (a polymer of a dialkylmethylamine or a hydrochloric acid salt thereof, etc.), a polymer of a diallyldiC₁₋₄alkyl ammonium salt (a polymer of a diallyldimethyl ammonium chloride, etc.), a copolymer of diallylamine or a salt thereof with sulphur dioxide (a diallylamine hydrochloric acid salt-sulphur dioxide copolymer, etc.), a diallyldiC₁₋₄alkyl ammonium salt-sulphur dioxide copolymer (a diallyldimethyl ammonium chloride-sulphur dioxide copolymer, etc.), a copolymer of a diallyldiC₁₋₄alkyl ammonium salt with diallylamine or a salt thereof or a derivative thereof (a diallyldimethyl ammonium chloride-diallylamine hydrochloric acid salt derivative copolymer, etc.), a diallyldiC₁₋₄alkyl ammonium salt polymer, a copolymer of a diC₁₋₄alkyl aminoethyl(meth)acrylate quaternary salt, a diallyldiC₁₋₄alkyl ammonium salt-acrylamide copolymer (a diallyldimethyl ammonium chloride-acrylamide copolymer, etc.), and an amine-carboxylic acid copolymer, etc.

[0344] The resins containing a cationic group can be employed solely or in combination of two or more kinds.

[0345] Further, in order to improve water resistance of the ink-fixing layer itself, a cationic group-contained resin having a crosslinkable reactive group is preferably employed. As such the resin, there can be enumerated a copolymer in which there is employed a monomer having a cationic group or a monomer producing a cationic property by acid

neutralization in the above-described (meth)acrylate-based copolymer (A-VI) containing a hydrolyzable silyl group.

[Saponified product (B) of a vinyl acetate-based copolymer]

[0346] As the saponified product (B) of a vinyl acetate-based copolymer to be employed in the present invention No. VI, there can be preferably employed the saponified product (B) of a vinyl acetate-based copolymer in relation to the present invention Nos. I-III.

[0347] In the saponified product (B) of a vinyl acetate-based copolymer, proportion of the copolymerizable monomer can be selected within a range in which clearness and water resistance of an image are not deteriorated, and it is preferably 0.1-50% by mol, more preferably 1-30% by mol, and further preferably 2.5-25% by mol, particularly, preferably 3-20% by mol based on total monomers to be employed for constructing the copolymer.

[0348] It is to be noted that the saponified product (B) of a vinyl acetate-based copolymer can be employed solely or in combination of a plurality of the products and, in addition, the other hydrophilic polymer (described hereinabove) may be even formulated depending upon purposes.

[Water-based polyurethane-based resin]

[0349] As the water-based polyurethane-based resin to be employed in the present invention No. VI, there can be preferably employed the water-based polyurethane-based resin (C) and/or the water-based polyurethane-based graft polymer mixture (D) in relation to the present invention Nos. I-III.

(4) Resin composition for recording in relation to the present invention No. VII

[0350] Hereinafter, the resin composition for recording in relation to the present invention No. VII will be illustrated.

[0351] The resin composition for recording in relation to the present invention No. VII contains 100 parts by weight of a resin (total of both is 100% by weight) composed of

- (1) 1-30% by weight of a cellulose derivative (H)
- (2) 70-99% by weight of a good solvent (I) for the cellulose derivative, and
- (3) 0.1-20 parts by weight of an organic acid (J) which can dissolve in the good solvent (I) or a weak solvent (K) for the cellulose derivative, and optionally,
- (4) 0-150 parts by weight of the weak solvent (K) for the cellulose derivative.

[0352] Further, the resin composition for recording in relation to the present invention No. VII may be a resin composition for recording in which the cellulose derivative (H) is a cellulose acetate, a resin composition for recording in which proportion of the weak solvent (K) for the cellulose derivative (H) is 50-150 parts by weight, and a resin composition for recording in which the good solvent (I) for the cellulose derivative is at least one selected from the group consisting of ketones, esters, ethers, cellosolves, cellosolve acetates, halogenated hydrocarbons, and nitro compounds, and which has a boiling point of 35-160°C.

[0353] Still further, it may be a resin composition for recording in which a melting point of the organic acid (J) is not less than 60°C, a resin composition for recording in which the weak solvent (K) for the cellulose derivative is at least one selected from esters, alcohols, ketones, and ethers, and which has a boiling point of 100-300°C, and a resin composition for recording in which the good solvent (I) for the cellulose derivative is at least one of a C₁₋₅dialkyl ketone, a C₁₋₄dialkyl acetate, a C₄₋₆Cyclic or linear chain ether, a C₁₋₄dialkyl cellosolve, and a C₁₋₄dialkyl cellosolve acetate, and the weak solvent (K) for the cellulose derivative is at least one of a C₁₋₄alkyl formate, a C₁₋₄alkyl benzoate, a C₄₋₈cycloalkanol, a C₆₋₁₀dialkyl ketone, and a C₇₋₁₀ether.

[0354] Still further, the present invention may be a resin composition for recording in which the difference (TK-TI) of a boiling point is 10°C<(TK-TI)<200°C in the good solvent (I) and the weak solvent (K) for the cellulose derivative (H), and may be even a resin composition for recording in which solubility to the organic acid (J) to water is not more than 2 g/100 ml at 20°C.

(Cellulose derivative (H))

[0355] As the cellulose derivative (H) to be employed in the present invention, there are enumerated cellulose esters, for example, organic acid esters such as a cellulose acetate, a cellulose propionate, a cellulose butylate, a cellulose acetate propionate, and a cellulose acetate butylate, inorganic acid esters such as a cellulose nitrate, a cellulose sulphate, and a cellulose phosphate, mixed acid esters such as a cellulose nitrate-acetate, cellulose ethers, for example, a methyl cellulose, an ethyl cellulose, an isopropyl cellulose, a butyl cellulose, a benzyl cellulose, a hydroxyethyl

cellulose, a carboxymethyl cellulose, a carboxyethyl cellulose, and a cyanoethyl cellulose, etc.

[0356] Of those, the cellulose esters, further, the cellulose acetate are preferably employed. These may be employed solely or in combination. Further, other polymers may be optionally added.

(Good solvent (I) for the cellulose derivative)

[0357] As the good solvent (I) for the cellulose derivative, for example, there can be exemplified C_{1-5} dialkyl ketones such as acetone, methylethyl ketone, methylpropyl ketone, methylbutyl ketone, methylisobutyl ketone, and ketones such as cyclohexanone, a C_{1-4} alkyl formate such as ethyl formate, a C_{1-4} alkyl acetate such as methyl acetate, ethyl acetate, and butyl acetate, esters such as ethyl propionate and ethyl lactate, ethers such as a cyclic or linear chain C_{4-6} ether including 1,4-dioxane, tetrahydrofuran, tetrahydropyran, diethylether, diisopropylether, and dimethoxyethane, cellosolves such as a C_{1-4} cellosolve including methyl cellosolve, ethyl cellosolve, and butyl cellosolve, cellosolve acetates (a C_{1-4} alkyl cellosolve acetate such as methyl cellosolve acetate and ethyl cellosolve acetate), aromatic hydrocarbons such as benzene, toluene, and xylene, halogenated hydrocarbons such as methylene chloride and ethylene chloride, amides such as formamide, acetoamide, N-methyl formamide, N-methyl acetoamide, N,N-dimethyl formamide, and N,N-dimethyl acetoamide, sulphoxides such as dimethyl sulphoxides, nitriles such as acetonitrile, propionitrile, butyronitrile, and benzonitrile, organic acids such as formic acid, acetic acid, propionic acid, etc., and organic anhydrides (maleic anhydride and acetic anhydride, etc.), and a mixture thereof, etc.

[0358] It is to be noted that the good solvents, for example, lower alcohols (a C_{1-4} alkyl alcohol such as methanol, ethanol, isopropanol, and butanol, diacetone alcohol, etc.), and cycloalkanol (a C_{4-8} alkanol such as cyclopentanol, cyclohexanol, methylcyclohexanol, and dimethylcyclohexanol which is substituted with a C_{1-4} alkyl group), etc. occasionally become a weak solvent depending upon a kind of the resins. The good solvent may even contain a nitro compound (nitromethane, nitroethane, and nitropropane, etc.). There are preferably employed at least one solvents selected from the group consisting of the solvents, and solvents having a boiling point of 35°C-160°C.

[0359] More specifically, in the case that the cellulose acetate is employed as a polymer, a preferred good solvent is acetone, methylethyl ketone, ethyl acetate, dioxane, dimethoxyethane, methyl cellosolve, methyl cellosolve acetate, and a mixture thereof.

(Weak solvent (K))

[0360] The weak solvent (K) means a solvent which does not have solubility to the cellulose derivatives to be employed, or which have a lower solubility than the good solvents to be employed and, if it has a higher boiling point than the good solvents to be employed in combination, it is not particularly limited.

[0361] As the weak solvent (K) for the cellulose derivative, there can be exemplified, for example, water, esters (a C_{5-8} alkyl formate such as amyl formate, isoamyl formate, an aliphatic C_{6-10} alkyl C_{2-4} carboxylate which may have C_{1-4} alkoxyl group such as amyl acetate, hexyl acetate, octyl acetate, 3-methoxybutyl acetate, 3-ethoxybutyl acetate, butyl propionate, 3-methoxybutyl propionate, a C_{1-4} alkyl benzoate such as methyl benzoate, ethyl benzoate, and propyl benzoate, etc.), alcohols (C_{6-10} alcohols such as amyl alcohol and heterocyclic alcohols, etc.), aliphatic polyvalent alcohols (ethylene glycol, diethylene glycol, propylene glycol, a polyethylene glycol, and glycerine, etc.), and a mixture thereof.

[0362] As preferred weak solvents, there are enumerated amyl formate, cyclohexanol, methyl cyclohexanol, ethyl benzoate, or a mixture thereof, and cyclohexanol is particularly preferred. Moreover, there is further preferred a solvent having a boiling point of 100-300°C.

(Organic acid (J))

[0363] As the organic acid (J), there can be enumerated formic acid, acetic acid, propionic acid, lactic acid, citric acid, oxalic acid, benzoic acid, sulphamic acid, fumaric acid, maleic acid, phthalic acids (phthalic acid and isophthalic acid), and paratoluene sulphonic acid, etc.

[0364] Of those, the phthalic acids and derivatives thereof are particularly preferred. Of those, there is further preferred an organic acid having a melting point of not less than 60°C.

(Combination of the good solvent with the weak solvent)

[0365] Further, as the combination of the good solvent with the weak solvent, there is preferred a combination of the good solvent (I) including at least one of the C_{1-5} dialkyl ketone, the C_{1-4} alkyl acetate, the cyclic or linear chain C_{4-6} ether, the C_{1-4} alkyl cellosolve, and the C_{1-4} alkyl cellosolve acetate with the weak solvent (K) for the cellulose derivative including at least one of the C_{5-8} alkyl formate, the C_{1-4} alkyl benzoate, the C_{4-8} cycloalkanol, the C_{1-5} dialkyl ketones,

and the C₇₋₁₀ether.

[0366] As a method for mixing the resin composition for recording of the present invention, there can be conducted a method in which there are dissolved the cellulose derivative (H) and the organic acid (J) into the good solvent (I), followed by adding and agitating the weak solvent (K).

[0367] In the resin composition for recording, there may be added common additives within a range in which a characteristic of the present invention is not deteriorated, and the additives include, for example, a defoaming agent, an improving agent for coatability, a thickener, a thermal stabilizer, a lubricant, an ultraviolet ray absorbent, a light stabilizer, an antistatic agent, a crosslinking agent, and an antiblocking agent, etc.

[0368] A coating method onto a base sheet of the resin composition for recording is not particularly limited, and there can be employed a roll coating, an air knife-coating, a blade-coating, a bar-coating comma-coating, and a gravure coating methods which are a publicly-known method.

[0369] By drying the resin layer coated, a recording sheet is obtained in which an image-receiving layer is formed on a body to be recorded.

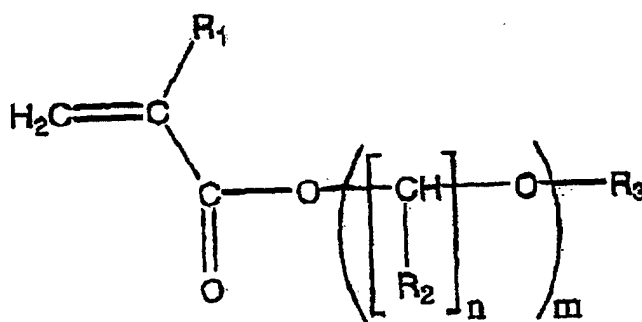
[0370] Drying method is not particularly limited and, in the case that a dry phase-conversion method is employed, first of all, temperature and vapor pressure, etc. are controlled so that the good solvent is evaporated to produce micelles themselves of the cellulose derivative, subsequently, the micelles themselves are brought into contact with each other by evaporation of the weak solvent to produce a network structure.

(5) Resin composition for recording in relation to the present invention No. VIII

[0371] Hereinafter, the resin composition for recording in relation to the present invention No. VIII is illustrated.

[0372] The resin composition of the present invention No. VIII is comprised a polymer (L) represented by general formula (14) described below and a hot-melt adhesive resin (M),

Formula (14)



R₁: -H or -CH₃

R₂: -H, -CH₃, or -OH

"n" is 1-5, and "m" is 1-20.

a plurality of R₂ may be identical to or different from each other, "m" pieces of -(CHR₂)_nO- may be connected in random or block.

[Polymer (L)]

[0373] The polymer (L) may be constructed by the monomer of at least one selected from the formula (14) [hereinafter, referred to as "(poly)alkyleneoxide-modified monomer"], a monomer containing a cationic functional group, a monomer containing a crosslinkable group, and a monomer containing a hydrophilic group.

((poly)alkyleneoxide-modified monomer)

[0374] As the monomer shown by the formula (14) to be employed in the present invention, there can be likewise employed the vinyl monomer component having an oxyalkylene group employed for the above-described product (B) of a vinyl acetate-based copolymer.

(Monomer containing a cationic functional group)

[0375] As the monomer containing a cationic functional group to be employed in the present invention, there can be likewise employed the cationic monomer employed in the above-described cationic (meth)acrylate-based copolymers (A-I to A-III) having a crosslinkable group.

(Monomer containing a crosslinkable group)

[0376] As the monomer containing a crosslinkable group to be employed in the present invention, there can be likewise employed the monomer containing a crosslinkable group employed in the above-described cationic (meth)acrylate-based copolymers (A-I to A-III) having a crosslinkable group.

(Monomer containing a hydrophilic group)

[0377] As the monomer containing a hydrophilic group to be employed in the present invention, there can be likewise employed the monomer containing a hydrophilic group employed in the above-described cationic (meth)acrylate-based copolymers (A-I to A-III) having a crosslinkable group.

[0378] The cationic functional group-contained monomer, the monomer containing a crosslinkable group, and the monomer containing a hydrophilic group can be employed solely or in combination of two or more kinds. A preferred combination of the monomers is as follows.

[0379] The monomer of the formula (14): R_1 is -H or -CH₃, R_2 is -H, R_3 is -H, $n=1-5$, and $m=1-20$.

[0380] The monomer containing a cationic functional group: a dic₁₋₄alkylamino-C₂₋₈alkyl(meth)acrylate or a quaternary salt thereof.

[0381] The monomer containing a crosslinkable group: a (meth)acryoxy-C₂₋₈alkyltriC₁₋₈alkoxy silane.

[0382] The monomer containing a hydrophilic group: an unsaturated carboxylic acid.

[0383] The monomers are usually employed in combination with a nonionic monomer in order to adjust a film-formability and a coating layer property.

(Nonionic monomer)

[0384] As the nonionic monomer, there can be likewise employed the nonionic monomer employed in the above-described cationic (meth)acrylate-based copolymers (A-I to A-III) having a crosslinkable group.

[0385] In a copolymer constructed by the monomers, a polymerization style thereof is not particularly limited, for example, there may be a random copolymer, a graft copolymer, and a block copolymer, etc.

(Composition of the polymer (L))

[0386] Content of the monomer of the formula (14) is preferably 1-40% by mol, more preferably 5-30% by mol, and most preferably 15-25% by mol based on total monomers in the polymer (L). Content of the monomer containing a cationic functional group is preferably 1-50% by mol, and more preferably 5-45% by mol based on total monomers in the polymer (L). Content of the monomer containing a crosslinkable group is preferably 0.1-20% by mol, more preferably 0.1-10% by mol, and most preferably 1-5% by mol based on total monomers in the polymer (L). Content of the monomer containing a hydrophilic group is preferably 0.1-30% by mol, more preferably 0.1-20% by mol, and most preferably 0.5-15% by mol based on total monomers in the polymer (L). Residual components are the nonionic monomer, and preferably 10-80% by mol, more preferably 20-70% by mol or so.

[0387] As proportion of the respective monomers, the monomer containing a cationic functional group is preferably 5-300 parts by weight, and more preferably 10-250 parts by weight, the monomer containing a crosslinkable group is preferably 1-30 parts by weight, and more preferably 5-20 parts by weight, and the monomer containing a hydrophilic group is preferably 5-80 parts by weight, and more preferably 10-60 parts by weight or so, respectively, based on 100 parts by weight of the (poly)alkylene oxide-modified monomer of the formula (14).

(Glass transition temperature of a copolymer)

[0388] The glass transition temperature (T_g) of the copolymer which constructs the polymer (L) can be selected within a range in which a film-formability, etc. is not deteriorated, and it is preferably -85 to 30°C, more preferably -60 to 0°C, and most preferably -50 to -10°C or so. The polymer having such the glass transition temperature can be prepared by appropriately combining the monomer containing a cationic functional group and the monomer containing a crosslinkable group with the monomer containing a hydrophilic group and the nonionic monomer.

[0389] The monomers preferably construct the copolymer in combination of, usually, a hard monomer, for example, a monomer component which forms a homopolymer having a glass transition temperature of 80 to 120°C, particularly, 90 to 105°C or so such as methyl(meth)acrylate and styrene and a soft monomer, for example, a monomer (soft monomer) which forms a homopolymer having a glass transition temperature of -85 to -10°C, particularly, -85 to -20°C or so such as a C₂₋₁₀ alkylacrylate.

(Hot-melt adhesive resin (M))

[0390] As the hot-melt adhesive resin (M) to be employed in the present invention, there can be exemplified a variety of resins, for example, an olefinic-based resin such as a polyethylene, an ethylene-propylene copolymer, and an atactic polypropylene, an ethylene copolymer resin such as an ethylene-vinyl acetate copolymer, an ethylene-(meth)acrylic acid copolymer, an ethylene-ethylacrylate copolymer, and an ionomer, a nylon-based resin, a polyester-based resin, a polyurethane-based resin, an acrylic-based resin, and a rubber, etc. The hot-melt adhesive resins can be employed solely or in combination of two or more kinds. The hot-melt adhesive resins are usually water-insoluble. The hot-melt adhesive resins may be even a reactive hot-melt adhesive resin having a reactive group such as carboxylic groups, hydroxyl groups, amino groups, isocyanate groups, and silyl groups at terminals thereof.

(Resin for giving a heat transfer property and durability)

[0391] A preferred resin for giving a heat transfer property and durability (washing resistance) is a nylon-based resin, a polyester-based resin, and a polyurethane-based resin, etc.

[0392] Particularly, a hot-melt adhesive resin constructed by the nylon-based resin, in the case that a body to be transferred is clothes, can give an excellent washing resistance to a picture image transferred, water resistance, and a high feeling.

[0393] As a nylon-based hot-melt adhesive resin, there are included a polyamide resin (for example, a homopolyamide such as a nylon 11 and nylon 12, a nylon 6/11, a nylon 6/12, a nylon 66/12, etc.) containing at least one unit selected from a nylon 11 and nylon 12, a copolyamide such as a copolymer of a dimer acid with a diamine and lauro-lactam or amino undecanoic acid, and a polyamide resin produced by a reaction of a dimer acid with a diamine, etc.

[0394] As a polyester-based hot-melt adhesive resin, there are included a homopolyester resin or a copolyester resin in which an aliphatic diol is employed. As the homopolyester resin, there is included a saturated aliphatic polyester resin produced by a reaction of a C₂₋₁₀alkylene diol such as ethylene glycol, propylene glycol, 1,4-butane diol, and 1,6-hexane diol, an aliphatic diol such as diethylene glycol which is a polyoxyC₂₋₁₀alkylene glycol with an aliphatic dicarboxylic acid such as adipic acid, sebacic acid, azelaic acid, sebacic acid, and dodecanoic dicarboxylic acid, and, optionally, a lactone. As a copolyester resin, there is included a saturated polyester resin in which constructing components composed of a polyethylene terephthalate or polybutylene terephthalate are partially substituted with other diols such as a C₂₋₆alkylene glycol including ethylene glycol, propylene glycol, and 1,4-butane diol or a dicarboxylic acid including the above-described aliphatic dicarboxylic acid, an asymmetric aromatic dicarboxylic acid such as phthalic acid and isophthalic acid, or a lactone.

[0395] As the polyurethane-based hot-melt adhesive resin, there is included a polyester resin in which there is employed a polyester diol corresponding to the polyester-based hot-melt adhesive resin and, as a diisocyanate component, there can be employed an aromatic, aromatic-aliphatic, and cycloaliphatic or aliphatic diisocyanate.

[0396] The hot-melt adhesive resin may optionally contain, for example, commonly-used additives described herein after and waxes.

[0397] In the hot-melt adhesive resin, a melting point can be selected from a range of preferably 70-250°C, more preferably 70-200°C, and most preferably 100-150°C.

[0398] The hot-melt adhesive resin is employed as powder or particles. The hot-melt adhesive resin is usually constructed by a powder- or particle-state resin having larger average particle diameter than thickness of an ink-receiving layer in order to effectively show a hot-melt adhesive property by projecting from surface of the ink-receiving layer. In the hot-melt adhesive resin, the larger average particle diameter is, for example, preferably 1-100 μm, more preferably 3-80 μm, and most preferably 5-50 μm or so. In order to improve an ink-absorbing property and washing resistance, the powder- or particles in the hot-melt adhesive resin may be even a porous body.

(Proportion of the polymer (L) with the hot-melt adhesive resin (M))

[0399] As the proportion of the polymer (L) containing the monomer units of the formula (14) with the hot-melt adhesive resin (M), it is preferably selected from a range of (L)/(M)=1/99-60/40 (weight ratio), further 5/95-60/40 or so based on solid components. In the case that the polymer (L) is constructed by a copolymer of the monomers as described hereinabove, the resin composition of the present invention can be obtained by the using the hot-melt adhesive

resin in preferably 10-1500 parts by weight, more preferably 10-900 parts by weight, and particularly preferably 80-900 parts by weight based on 100 parts by weight of the polymer (L) (the above-described copolymer).

[0400] Hereinafter, there will be illustrated a method for forming an image-receiving layer in the ink-jet recording sheet in relation to the present invention Nos. I-VIII.

[Preparation of a resin composition for an ink-jet recording sheet]

(Curing agent for the resin composition)

[0401] In the ink-jet recording sheet in relation to the present invention Nos. I-VII, a curing agent (a curing catalyst or a curing accelerator) may be even added in order to accelerate a curing reaction.

[0402] As the curing agent, there are enumerated an organic tin compound (dibutyltin dilaurate, dibutyltin dimaleate, dioctyltin dilaurate, dioctyltin dimaleate, dibutyltin diacetate, dibutyltin dimethoxide, tributyltin sulphide, dibutyltin thioglycolate, and tin octylate, etc.), an organic aluminum compound (aluminum isopropylate, aluminum tris(ethylacetate), aluminum tris(acetylacetonate), ethylacetoacetatealuminum diisopropylate, etc.), an organic titanium compound (isopropyltrisstearyl titanate, tetraisopropyl bis(dioctylphosphite)titanate, bis(dioctylpyrophosphate)oxyacetate titanate, etc.), an organic zirconium compound (tetra-n-butoxyzirconium, zirconyl octylate, a reaction product of an alkoxy zirconium with acetylacetone or an acetoacetate, etc.), an acidic compound (an organic acid, for example, an aliphatic organic carboxylic acid such as acetic acid and propionic acid, an aromatic carboxylic acid such as an oxycarboxylic acid and benzoic acid, a sulphonic acid such as benzene sulphonic acid, p-toluene sulphonic acid, dodecylbenzene sulphonic acid, etc.), a basic compound (a base, for example, an organic base such as triethyl amine, an inorganic base such as sodium hydroxide and potassium hydroxide), an acidic phosphate (monobutyl phosphate, dibutyl phosphate, isopropyl acid phosphate, butyl acid phosphate, octyl acid phosphate, and dodecyl acid phosphate, etc.), and a mixture or a reaction product of the acidic phosphate with an amine (hexyl amine, triethyl amine, N,N-dimethyldodecyl amine, and 3-propanol amine, etc.).

[0403] The curing agents can be employed solely or in combination of two or more kinds.

[0404] Use amount of the curing agents is a range in which curing can be accelerated, for example, preferably 0.01-10 parts by weight, and more preferably 0.1-5 parts by weight with respect to 100 parts by weight of the resin composition constructed by the cationic acrylic copolymers (A-I to A-VI) containing a crosslinkable group and a hydrophilic polymer compound such as the saponified product (B) of a vinyl acetate-based copolymer based on solid components.

(Dye-fixing agent)

[0405] Further, in order to elevate a fixing ability of a coloring agent (a dye), there is advantageously employed a dye-fixing agent, particularly, a polymeric dye-fixing agent. The dye-fixing agent (a polymeric dye-fixing agent) usually has a cationic group (particularly, a strong cationic group such as guanidyl group and a quaternary ammonium salt type) in the molecule. The dye-fixing agent may be water-soluble.

[0406] As the dye-fixing agent, there can be exemplified, for example, a dicyan-based fixing agent (dicyandiamide-formalin polycondensate, etc.), a polyamine-based fixing agent [a condensate (a dicyan diamide-diethylenetriamine polycondensate, etc.) of an aliphatic polyamine such as diethylenetriamine, triethylene tetramine, dipropylene triamine, a polyallylamine, an aromatic polyamine such as phenylene diamine, and dicyandiamide with a poly C_{2-4} alkylene polyamine], and a polycationic-based fixing agent, etc.

[0407] As the polycationic-based fixing agent, there can be exemplified, for example, an epichlorohydrin-di C_{1-4} alkyl amine-added polymer (an epichlorohydrin-dimethyl amine-added polymer, etc.), a polymer of allyl amine or a salt thereof (a polymer of a polyallylamine or a hydrochloric acid salt thereof, for example, PA-10C, PAA-HCL-3L, and PAA-HCL-10L by Nittoboseki, Ltd.), a polymer of a diallyl C_{1-4} alkyl amine or salt thereof (a polymer of a diallylmethyl amine or a hydrochloric acid salt thereof, for example, PAS-M-1, etc. by Nittoboseki, Ltd.), a polymer of a diallyldi C_{1-4} alkyl ammonium salt (a polymer of a diallyldimethyl ammonium chloride, for example, PAS-H-5L and PAS-H-10L, etc. by Nittoboseki, Ltd.), a copolymer of diallylamine or a salt thereof with sulphur dioxide (a diallylamine hydrochloric acid salt-sulphur dioxide copolymer, for example, PAS-A-1, PAS-A-5, PAS-A-120L, and PAS-A-120A by Nittoboseki, Ltd.), a copolymer of a diallyldi C_{1-4} alkyl ammonium salt with diallylamine or a salt thereof, or a derivative thereof (a diallyl dimethylammonium chloride-diallylamine hydrochloric acid salt copolymer, for example, PAS-880, etc. by Nittoboseki, Ltd.), a diallyldi C_{1-4} alkyl ammonium salt polymer, a polymer of a diallyldi C_{1-4} alkyl aminoethyl(meth)acrylate quaternary salt, a diallyldi C_{1-4} alkyl ammonium salt-acryl amide copolymer (a diallyl dimethylammonium chloride-acryl amide copolymer, for example, PAS-J-81, etc. by Nittoboseki, Ltd.), and an amine-carboxylic acid copolymer (for example, PAS-410, etc. by Nittoboseki, Ltd.), etc. The dye-fixing agent can be also employed solely or in combination of two or more kinds.

[0408] Use amount of the dye-fixing agent is a range in which ink-fixing ability can be elevated, for example, preferably

0.1-40 parts by weight, more preferably 1-30 parts by weight and, further preferably 2-20 parts by weight with respect to 100 parts by weight of the resin composition prepared by addition of the saponified product (B) of a vinyl acetate-based copolymer, the water-based polyurethane resin composition (C) and, in the case of the invention No. III, further, the block isocyanate (D) to the cationic acrylic copolymers (A-I to A-VI) containing a crosslinkable group based on solid components.

[0409] Further, in the present invention Nos. IV and V, it can be selected from a range of preferably 0.1-40 parts by weight, more preferably 1-30 parts by weight and, further preferably 2-20 parts by weight or so with respect to 100 parts by weight of the resin composition constructed by the cationic (meth)acrylic copolymers (A-IV to A-V), the saponified product (B) of a vinyl acetate-based copolymer, and the modifier (R). In the case of exceeding 40 parts by weight, coloring becomes worse in the dye and, moreover, an ink-absorbing property ends to lower.

[0410] In an ink-receiving layer obtained by coating onto a base material using the resin composition in relation to the present invention No. VI, 60°-glossiness is preferably not less than 30%, more preferably not less than 50%, and further preferably not less than 70%.

[0411] It is to be noted that there may be optionally formed a porous layer, a blocking protecting layer, a slipping layer, and an antistatic agent layer on the image-receiving layer.

[0412] The recording sheets in relation to the present invention Nos. I-VII are useful as a recording sheet by an ink-jet style in which small droplets of an ink are sprayed, and can be also utilized as a printing sheet (particularly, a sheet for a water-based ink) for an offset printing and a flexo printing, etc.

[Method for the preparation of an ink jet recording sheet]

(Additives)

[0413] The ink jet recording sheet in relation to the present invention is obtained by coating the above-described resin composition onto a base material for the recording sheet and, the image-receiving layer formed by coating may optionally contain other components, for example, a water-based emulsion (for example, an acrylic resin emulsion, an ethylene-vinyl acetate copolymer emulsion, and a vinyl acetate emulsion, etc.) containing a polymer not having a crosslinkable group and polymer particles.

(Powder and particles)

[0414] Further, the image-receiving layer may even further contain powder and particles (pigments, etc.). As the powder and particles, there are enumerated inorganic powder and particles (mineral powder and particles, etc. such as white carbon, a fine particle-state calcium silicate, zeolite, magnesium aluminosilicate, calcined diatomaceous, a fine particle-state magnesium carbonate, a fine particle-state alumina, silica, talc, kaoline, delamikaoline, clay, heavy calcium carbonate, light calcium carbonate, magnesium carbonate, titanium dioxide, aluminum hydroxide, calcium hydroxide, magnesium hydroxide, calcium sulphate, celicite, bentonite, and smectite), organic powder and particles (organic powder and particles such as a crosslinked or noncrosslinked organic fine particles such as a polystyrene resin, an acrylic resin, a urea resin, a melamine resin, a benzoguanamine resin, etc., and a micro balloon). The powder and particles can be also selectively employed solely or in combination of two or more kinds.

[0415] It is to be noted that in the case of employing the powder and particles, the above-described various hydrophilic polymer can be employed as a binder resin.

[0416] Proportion of the powder and particles with respect to the binder resin is not particularly limited and, the powder and particles are preferably 0.1-80 parts by weight, and more preferably 0.2-50 parts by weight.

(Common additives)

[0417] In the image-receiving layer, there may be even added common additives within a range in which a characteristic is not deteriorated, and the additives include, for example, a defoaming agent, an improving agent for coatability, a thickener, a surface active agent, a lubricant, a stabilizer (an antioxidant, an ultraviolet ray absorbent, and a thermal stabilizer, etc.), an antistatic agent, and an antiblocking agent, etc.

(Plasticizer)

[0418] The ink-receiving layer in the heat transfer sheet of the present invention No. VIII is constructed by the above-described resin composition. The ink-receiving layer may even contain a plasticizer in order to give a high ductility to a transferred picture image. As the plasticizer, there can be exemplified a phthalic acid-based plasticizer such as ethyl phthalate, butyl phthalate, hexyl phthalate, octyl phthalate, 2-ethylhexyl phthalate, and lauryl phthalate, an aliphatic

dicarboxylic acid-based plasticizer such as 2-ethylhexyl adipate, dibutyl sebacate, and 2-ethylhexyl sebacate, a glycol-based plasticizer such as ethyl-phthallyl ethyl glycolate and a polyethylene glycol ester, a phosphate-based plasticizer such as triphenyl phosphate, tricresyl phosphate, and 2-ethylhexyl phosphate, a polyester-based plasticizer, and an epoxide-based plasticizer such as an epoxy fatty acid ester, etc. The plasticizer can be employed solely or in combination of two or more kinds.

[0419] Use amount of the plasticizer, for example, preferably 0.1-30 parts by weight, more preferably 1-25 parts by weight, and particularly preferably 1-20 parts by weight with respect to 100 parts by weight of total amount of the resins such as a polymer constructing the ink-receiving layer and the hydrophilic polymer, the hot-melt adhesive resin, the cationic polymer, and the polyurethane-based polymer resin. Further, the ink-receiving layer may even contain a dye-fixing agent independently or together with the above-described plasticizer in order to elevate a fixing ability of a coloring agent (a dye).

[0420] Since the recording sheet of the present invention possesses the above-described receiving layer, an ink-absorbing ability and ink-fixing ability are high and water resistance, printing quality, and a roll mark-adhering problem are especially improved.

[0421] That is, a letters-printing portion or a picture image portion is formed by a water-based ink without causing inferiority in a picture image such as beading and roll mark-adhering owing to an ink-jet recording method, and when a dried printing portion or a picture image portion is immersed in water of 30°C for 1 minute, retention ratio of color concentration is not less than 80% (for example, 85-100% or so), and preferably not less than 85% (for example, 90-99% or so).

[Method for the preparation of a recording sheet]

[0422] The recording sheet of the present invention can be prepared by forming an image-receiving layer composed of the resin composition for recording on at least one surface of the above-described base material. Ink-absorbing layer can be prepared by coating a coating liquid which is prepared using an appropriate solvent (water, a hydrophilic solvent which may be water-soluble, a hydrophobic solvent or a mixture thereof) on a supporting material. Particularly, in the case that a resin composition containing the cationic (meth)acrylic copolymers (A-I to A-VI) having a crosslinkable group is a form of a water-based emulsion, a water-based coating liquid is employed.

[0423] The coating liquid is coated by common coating methods including a casting-coating method, for example, on at least one surface of the base material by a roll coater, air-knife coater, blade coater, rod coater, bar coater, comma coater, gravure coater, and silk-screen coater method, etc.

[0424] The image-receiving layer can be formed by coating a liquid containing the above-described respective components onto at least one surface of a base material, followed by drying. Further, after coating the coating liquid, there may be optionally formed an ink-absorbing layer crosslinked by heating at an appropriate temperature selected from a range of 50-150°C or so.

[0425] In the image-receiving layer formed by the resin composition for an ink jet recording sheet in relation to the present invention, thickness can be selected depending upon uses, and it is preferably 3-50 μm, more preferably 6-30 μm, and usually 5-30 μm or so.

[0426] Since the ink jet recording sheet obtained using the resin composition in relation to the present invention possesses an image-receiving layer, an ink-absorbing ability and ink-fixing ability are high, and water resistance and printing quality are especially improved and, even though it is employed in a printing machine having a large printing speed, there can be obtained a clear and sharp image without beading. That is, a letters-printing portion or an image portion is formed by a water-based ink without causing inferiority in an image such as beading and roll mark-adhering owing to an ink-jet recording method, and when a dried printing portion or a picture image portion is immersed in water of 30°C for 1 minute, retention ratio of color concentration is preferably not less than 80% (for example, 85-100% or so), and more preferably not less than 85% (for example, 90-99% or so).

[0427] It is to be noted that there may be optionally formed a porous layer, a blocking protecting layer, a slipping layer, and an antistatic agent layer on the ink-receiving layer.

[0428] The recording sheet of the present invention is useful as a recording sheet by an ink-jet style in which small droplets of an ink are sprayed, and it can be also utilized as a printing sheet (particularly, a sheet for a water-based ink) for an offset printing and a flexo printing, etc.

[0429] Further, in order to elevate a fixing ability of a coloring agent (a dye), there is advantageously employed a dye-fixing agent, particularly, a polymeric dye-fixing agent. The dye-fixing agent (a polymeric dye-fixing agent) usually has a cationic group (particularly, a strong cationic group such as guanidyl group and a quaternary ammonium salt type) in the molecule. The dye-fixing agent may be even water-soluble.

(Protecting layer)

[0430] In the heat transfer sheet of the present invention No. VIII, a protecting layer is formed on the ink-receiving layer.

[0431] The protecting layer can be stripped from the base material, and it protects the ink-receiving layer. So far as quality of a picture image transferred is not largely disturbed, there can be employed a variety of thermoplastic resins and thermosetting resins, particularly, a polymer having a film-formability. As the thermoplastic resins, there can be exemplified a polyamide resin such as nylon 11, nylon 12, and nylon 612, a polyester resin such as a PET based-copolyester and a PBT based-copolyester, a styrene-based resin such as a styrene-(meth)acrylic acid ester resin, a polyolefine-based resin such as a polyethylene, a polypropylene, an ethylene-propylene resin, a polyvinyl acetate-based resin such as an ethylene-vinyl acetate-based copolymer, an acrylic-based resin such as a poly(meth)acrylic acid ester, a polyacetal resin, a vinyl chloride-based resin such as a polyvinyl chloride-vinyl acetate copolymer, and a fluorine-based resin, etc. The thermoplastic resins can be employed solely or in combination of two or more kinds. As the thermosetting resins, there can be exemplified a variety of resins such as a urethane resin, an epoxy resin, a phenol resin, a xylilene resin, a melamine resin, a urea resin, and a silicone resin.

[0432] In order to effectively protect the ink-receiving layer after having been transferred, the protecting layer is advantageously constructed by a soft polymer, particularly, a nonsticking polymer.

[0433] Although the soft polymer may be even a nonelastomer, it is preferably an elastomer.

[0434] In the present invention, "elastomer" means a polymer having a rubber elasticity in addition to rubbers such as a natural rubber and synthetic rubber. As the elastomer, there are enumerated at least one polymers selected from the synthetic rubber, natural rubber, and a thermoplastic elastomer.

[0435] As the synthetic rubber, there can be exemplified, for example, a variety of rubbers which include a diene-based rubber such as a styrene-butadiene rubber, a butadiene rubber, an isoprene rubber, a chloroprene rubber, and an acrylonitrile-butadiene rubber, for example, a butyl rubber, an ethylene-propylene rubber such as an EPM and an EPDM, an olefine-based rubber such as a fluorine rubber, an acrylic rubber, an ethylene-acrylic rubber, and a chloro-sulphonated ethylene rubber, and other rubbers (for example, a silicone rubber, a urethane rubber, an ethylene-vinyl acetate copolymer, and a polynorbornene rubber, etc.).

[0436] As the thermoplastic elastomer, there are enumerated a variety of elastomers which include an elastomer constructed by a hard segment (or a block) and a soft segment (or a block), for example, a polystyrene-based elastomer which is a block copolymer such as a polybutadiene/polystyrene elastomer and a polyisoprene/polystyrene elastomer, a polyurethane-based elastomer which is a block copolymer such as a polyester or polyether-based polyurethane elastomer, a polyamide elastomer which is a block copolymer such as a polyester or polyether-based polyamide elastomer, a polyolefine-based elastomer such as an EPR/polypropylene elastomer, an EPDM/polypropylene elastomer, and a polyolefine block copolymer, a polyester-based elastomer which is a block copolymer such as a polyethylene terephthalate-based elastomer and a polybutylene terephthalate-based elastomer, and a polyvinylchloride-based elastomer, etc.

[0437] In the case that the heat transfer sheet of the present invention is thermally-transferred on an expansible and contractible body to be transferred such as clothes, the protecting layer and the ink-receiving layer can flexibly follow even though the body to be transferred are expanded and contracted, resulting in that there is prevented generation of micro cracks in an image to be transferred and, for that reason, it is preferred that the protecting layer is constructed by the synthetic rubber, a natural rubber, and the thermoplastic elastomer. The elastomer may be even vulcanized by sulphur and a peroxide, etc.

[0438] A preferred protecting layer can be constructed by an elastomer having Young's modulus of preferably 0.1-100 MPa (for example, 1-100 MPa), and more preferably 0.1-50 MPa (for example, 1-50 MPa). Further, as a polymer for the protecting layer, there can be employed an elastomer selected from a range of an extension ratio of not less than 300% (for example, 300-1000% or so) and, particularly, preferably not less than 400% (for example, 400-1000% or so), and the extension ratio is usually 400-900% or so in the polymer.

[0439] Further, in the polymer which constructs the protecting layer, a glass transition temperature is preferably -100 to 100°C, more preferably -50 to 50°C and, particularly preferably -30 to 30°C. In the case that the polymer is an elastomer, a glass transition temperature in the elastomer is preferably not more than -10°C (for example, -100 to -10°C or so), more preferably not more than -15°C (for example, -100 to -15°C or so) and, particularly preferably not more than -20°C (for example, -100 to -20°C or so), and the polymer is not preferably tacky at room temperatures (for example, -10 to 30°C or so).

[0440] By forming such the protecting layer, flexibility can be largely improved, and water resistance, durability, and washing resistance are remarkably elevated and, further, generation of micro cracks and cracks by expansion and shrinkage can be remarkably suppressed in a picture image transferred.

(Additives for the protecting layer)

[0441] The polymer which constructs the protecting layer may even optionally contain a variety of additives employed for the image-receiving layer.

[0442] Thickness of the protecting layer is, for example, preferably 1-90 μm or so, and more preferably 3-70 μm or so, and it is usually 5-50 μm or so (for example, 5-30 μm or so).

[0443] Thickness ratio of the protecting layer with respect to the ink-receiving layer is the former/the latter=preferably 1/1-1/10 or so, more preferably 1/2-1/8 or so, and particularly preferably 1/3-1/6 or so.

(Method for the preparation of a heat transfer sheet)

[0444] The heat transfer sheet of the present invention No. VIII can be prepared by forming an ink-receiving layer which can be stripped from a base material on at least one surface of a strippable base material. The ink-receiving layer can be prepared by coating a coating agent constructed by the polymer (L) containing at least the monomer units represented by the formula (14), the hot-melt adhesive resin (M), and optionally other components on a releasable surface of the base material. At least, the polymer (L) can be usually employed in a form of a water-based solution or an emulsion, and the hot-melt adhesive resin (M) can be employed in a form of powder and particles. For that reason, the water-based solution or the emulsion of the polymer (L) and the powder and particles of the hot-melt adhesive resin (M) are optionally mixed with other components to prepare the coating agent for the ink-receiving layer. Solvent for the water-based solution or the emulsion may be water alone, or may optionally contain hydrophilic solvents such as alcohols. In the case that the ink-receiving layer is formed on the base material through the protecting layer, there is coated a coating liquid for the protecting layer constructed by an elastomer, etc., and it is optionally dried to prepare a protecting layer, and the ink-receiving layer may be even formed on the protecting layer as described hereinabove. The coating liquid for the protecting layer can be prepared using an organic solvent and water-based solvent depending upon the kind of the polymer, and it may be even a form of an aqueous solution or an emulsion.

[0445] The coating liquid can be coated by the common methods (described hereinabove). The ink-receiving layer and the protecting layer can be formed by drying a coating layer at 50-150°C (preferably 80-120°C) or so.

[0446] Thus-formed ink-receiving layer is appropriate for forming a picture image by an ink-jet method in which small droplets of an ink (particularly, a water-based ink) are sprayed. Picture image to be recorded can be smoothly transferred or moved by compressing at an appropriate temperature (for example, preferably 140-250°C, and more preferably 140-200°C) and a pressure of 0.5-50 kPa (5-500 gf/cm² or so) for an appropriate time of period and stripping the ink-receiving layer from the base material. A body to be transferred including a picture image transferred may be optionally even crosslinked by heating.

[0447] As materials to be transferred, there can be utilized a two dimensional or three dimensional structural material formed by a variety of materials such as fibers, paper, woods, plastics, ceramics, and metals. Usually, there can be utilized plastic films, plastic sheet, paper, and clothes as the materials to be transferred.

[0448] By forming an ink-receiving layer which is strippable from a base material at one surface of a base material, it can be utilized using the resin composition, for example, as a heat transfer sheet for an ink-jet recording in which a picture image is recorded by an ink-jet recording method, and the picture image is transferred onto the materials to be transferred to form a picture image transferred and, even though it is transferred onto an expansible and shrinkable material to be transferred, the picture image recorded can excellently follow an expansion and shrinkage, and micro cracks are not produced in the picture image.

[0449] The heat transfer sheet of the present invention is useful as an ink-receiving sheet (particularly, a sheet for a water-based ink) by an ink-jet method in which recording is conducted by spraying small droplets of an ink, and it can be also utilized also as a heat transfer sheet for an offset printing and a flexo printing.

Examples

[0450] Hereinafter, although the present invention is illustrated in more detail based on Examples, the present invention is not limited to the Examples. It is to be noted that "part" is shown by weight in the Examples,

[0451] Further, evaluation methods of a variety of properties are as follows in relation to recording sheets obtained in the Examples and Comparative Examples, and items which cannot be normalized are illustrated in the respective inventions.

[0452] An ink-jet printer (PM-770C manufactured by Seiko Epson, Ltd.) was employed, and a recorded picture image was formed by printing a color pattern using colors such as cyan, yellow, magenta, and black in a photoglossy paper mode on recording sheets obtained in Examples and Comparative Examples.

[0453] An ink-jet printer (BJ-410J manufactured by Canon, Ltd.) was employed, and a recorded picture image was formed by printing a color pattern using colors such as cyan, yellow, magenta, and black in an HQ mode on recording

sheets obtained in Examples and Comparative Examples.

[0454] It is to be noted that as the ink-jet printer in the HQ mode printing, BJC-420J manufactured by Canon, Ltd. was employed in the present invention No. II, and Desljet895cxi manufactured by Hewlett Packard, Ltd. was employed in the present invention No. III.

Clearness: (applied in the present invention No. I to No. III)

Recorded picture image was visually observed, and clearness was evaluated by the following standard.

○: Printing is clearly shown without mixing of respective colors.

△: Different colors are partially mixed with each other, and clearness is partially lost.

x: Different colors are mixed with each other in a wide range, and clearness is lost.

[0455] Uniformity in a picture image: A (applied in the present invention No. I)

[0456] Recorded picture image was visually observed, and clearness was evaluated by the following standard. Uniformity in a picture image was evaluated under conditions of a high speed printing.

○: Portion in an identical color concentration is uniform, and there was not observed inferiority in the picture image such as unevenness and beading.

x: Ink became unequal in a wide range, and there was observed inferiority in the picture image such as unevenness and beading.

[0457] Uniformity in a picture image: B (applied in the present inventions No. I to No. IV)

[0458] Recorded picture image was visually observed, and clearness was evaluated by the following standard.

○: Portion in an identical color concentration is uniform, and there was not observed inferiority in the picture image such as unevenness and beading.

△: Ink became partially unequal, and there was observed inferiority in the picture image such as unevenness and beading.

x: Ink became unequal in a wide range, and there was observed inferiority in the picture image such as unevenness and beading.

[0459] Water resistance (A): (applied in the present inventions No. I to No. III)

[0460] Printed portion was immersed in water of 30°C for 1 hour and, it was vertically pulled up, and water was sufficiently removed and dried. After having dried, water resistance was visually evaluated by the following standard.

○: Printed picture image is completely remained.

△: Printed picture image is partially blurred, and color becomes light.

x: Printed picture image is not mostly remained.

[0461] Water resistance (B): (applied in the present inventions No. III).

[0462] Printed portion was immersed in water of 30°C for 1 hour and, it was vertically pulled up, and water was sufficiently removed and dried. After having dried, water resistance was visually evaluated by the following standard.

○: Loss of gloss is not remarkable in an image-receiving layer.

x: Loss of gloss is severe and remarkable in an image-receiving layer.

[0463] Hereinafter, Examples for the present invention No. I are illustrated.

[Preparation of an cationic acrylic copolymer (A-I-1) containing a crosslinkable group]

[0464] A 2000 ml reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts of isopropylalcohol (IPA), and 1.23 part of azobisisobutyronitrile (AIBN) was added while agitating to dissolve, followed by heating to 80°C. As copolymerizable components, there were mixed 93.7 parts of methylmethacrylate (MMA), 98.7 parts of n-butylacrylate (BA), 49.3 parts by weight of diethylaminoethyl methacrylate (DEAEMA), and 4.93 parts of trimethoxysilane propylmethacrylate (A-174 manufactured by Nihon Unicar, Ltd.), followed by adding dropwise into the reaction vessel over approximately 4 hours. After the completion of the dropwise addition, 0.25 part of AIBN which is an additional catalyst was dissolved in 25 parts of IPA, followed by adding dropwise into the reaction vessel, and reaction was further continued for 2 hours to

complete the reaction. After the completion of the polymerization, 16 parts of acetic acid was added into the reaction vessel, and 705 parts of water was added dropwise into the reaction vessel over approximately 2 hours while agitating to emulsify. After having emulsified, an emulsion of the cationic acrylic copolymer containing a crosslinkable group was obtained by evaporating IPA using a rotary evaporator (solid content concentration: 34.7% by mass).

[Saponified product (B-I) of a vinyl acetate-based copolymer]

[0465] As a saponified product of a vinyl acetate-based copolymer, the following products (B-I-1 to B-I-4 according to described order) manufactured by Kuraray, Ltd.

PVA-405 (saponified degree: 80.0-83.0%, polymerization degree: 500)
 PVA-420 (saponified degree: 78.0-81.0%, polymerization degree: 2000)
 PVA-205 (saponified degree: 86.5-89.5%, polymerization degree: 500)
 PVA-217 (saponified degree: 87.0-89.0%, polymerization degree: 1700)

[Water-based polyurethane resin (C-I)]

[0466] As the water-based polyurethane resin, HUX-670 was employed which is manufactured by Asahi Denka Kogyo, Ltd.

[Polyurethane-based graft polymer mixture (D-I)]

[0467] There was employed a composition in which 100-60% by weight of a hydrophilic monomer was graft-polymerized with 0-40% by weight of a copolymerizable monomer in an aqueous solution or an aqueous dispersion in which the water-based polyurethane resin are mixed with the saponified product of a vinyl acetate-based copolymer. It is to be noted that as the composition, there was employed NS-141LX which is a water-based polyester resin composition manufactured by Takamatsu Yushi Kogyo, Ltd.

[Polyester-based graft polymer mixture (E-I)]

[0468] There was employed a composition in which 100-60% by weight of a hydrophilic monomer was graft-polymerized with 0-40% by weight of a copolymerizable monomer in an aqueous solution or an aqueous dispersion in which the water-based polyester resin are mixed with the saponified product of a vinyl acetate-based copolymer. It is to be noted that as the composition, there was employed NS-141LX which is a water-based polyester resin composition manufactured by Takamatsu Yushi Kogyo, Ltd.

(Example I-1)

[0469] There were mixed 30 parts (based on solid component) of the cationic acrylic copolymer (A-I-1) containing a crosslinkable group obtained in the above-described step, 40 parts (based on solid component) of the PVA-405 (B-I) manufactured by Kuraray, Ltd., and 30 parts (based on solid component) of HUX-670 (C-I) manufactured by Asahi Denka Kogyo, Ltd. to obtain a water-based coating liquid. The water-based coating liquid was coated on an adhesive-treated polyethylene terephthalate film having the thickness of 100 μm (Merinex 705 manufactured by ICI Japan, Ltd., hereinafter, it is occasionally referred to as merely PET film), and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet I-1.

(Example I-2)

[0470] The same procedures were followed as in the Example I-1, except that the NS-120X (D-I) manufactured by Takamatsu Yushi Kogyo, Ltd. was employed in place of the HUX-670 (C-I) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet I-2.

(Example I-3)

[0471] The same procedures were followed as in the Example I-1, except that the NS-141LX (E-I) manufactured by Takamatsu Yushi Kogyo, Ltd. was employed in place of the HUX-670 (C-I) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet I-3.

(Example I-4)

[0472] The same procedures were followed as in the Example I-1, except that the PVA-205 (B-I) was employed in place of the PVA-405 manufactured by Kuraray, Ltd. to obtain a recording sheet I-4.

(Comparative Example I-1)

[0473] The same procedures were followed as in the Example I-1, except that the PVA-420 (B-I) was employed in place of the PVA-405 manufactured by Kuraray, Ltd. to obtain a recording sheet I-5.

(Comparative Example I-2)

[0474] The same procedures were followed as in the Example I-1, except that the PVA-217 (B-I) was employed in place of the PVA-405 manufactured by Kuraray, Ltd. to obtain a recording sheet I-6.

(Comparative Example I-3)

[0475] The cationic acrylic copolymer (A-I) containing a crosslinkable group obtained in the above-described step was coated on a PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet I-7.

(Comparative Example I-4)

[0476] An aqueous solution of the PVA-217 (B-I) manufactured by Kuraray, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet I-8.

(Comparative Example I-5)

[0477] The HUX-670 (C-I) manufactured by Asahi Denka Kogyo, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet I-9.

(Comparative Example I-6)

[0478] The NS-120X (D-I) manufactured by Takamatsu Yushi Kogyo, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet I-10.

[0479] Hereinafter, evaluation results in relation to the above Examples I-1 to I-3 and Comparative Examples I-1 to I-6 are shown in Table I-1.

Table I-1

Example No.	Sheet No.	Uniformity of Picture image A	Uniformity of Picture image B	Clearness	Water Resistance
Example I-1	Sheet I-1	○	○	○	○
Examples I-2	Sheet I-2	○	○	○	○
Example I-3	Sheet I-3	○	○	○	○
Example I-4	Sheet I-4	○	○	○	○
Comparative Example I-1	sheet I-5	×	○	○	○
Comparative Example I-2	Sheet I-6	×	○	○	○
Comparative Example I-3	Sheet I-7	×	×	×	○

Table I-1 (continued)

Example No.	Sheet No.	Uniformity of Picture image A	Uniformity of Picture image B	Clearness	Water Resistance
Comparative Example I-4	Sheet I-8	×	○	○	×
Comparative Example I-5	Sheet I-9	×	Δ	×	Δ
Comparative Example I-6	Sheet I-10	×	×	Δ	Δ

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0480] According to the present invention No. I, all the recording sheets employed in the Examples show a higher clearness and a higher level in water resistance and printed quality than those in the Comparative Examples.

[0481] It was confirmed that in the recording sheet in which there is employed the resin composition for an ink-jet recording sheet of the present invention and which has a picture image-receiving layer on at least one surface of a base material, water resistance can be largely improved without beading even in an ink-jet printer having a high printing speed, in addition to clearness and an ink-absorbing ability such as uniformity of a picture image and, further, water resistance and an ink-absorbing ability are successfully consistent with each other while improving a printing quality, which are a contrary characteristic each other.

[0482] Hereinafter, there are illustrated Examples in relation to the present invention No. II.

[0483] As the cationic (meth)acrylic copolymer (A-II-1) containing a crosslinkable group, there was employed the same one as in the cationic (meth)acrylic copolymer (A-I-1) containing a crosslinkable group.

[Saponified product (B-II) of a vinyl acetate-based copolymer]

[0484] As the saponified product (B-II) of a vinyl acetate-based copolymer, the PVA-210 manufactured by Kuraray, Ltd. was employed.

[Water-based polyurethane resin (C-II)]

[0485] As the water-based polyurethane resin (C-II), the HUX-670 manufactured by Asahi Denka Kogyo, Ltd. was employed.

[Polyurethane-based graft polymer mixture (D-II)]

[0486] There was employed a composition in which 100-60 wt% of a hydrophilic vinyl monomer is graft-polymerized with 0-40 wt% of a copolymerizable vinyl monomer in an aqueous solution or an aqueous dispersion in which the water-based polyurethane resin are mixed with the saponified product of a vinyl acetate-based copolymer. It is to be noted that as the composition, there was employed NS-120X which is a water-based polyester resin composition manufactured by Takamatsu Yushi Kogyo, Ltd.

[Polyester-based graft polymer mixture (E-II)]

[0487] There was employed a composition in which 100-60% by weight of a hydrophilic monomer was graft-polymerized with 0-40% by weight of a copolymerizable monomer in an aqueous solution or an aqueous dispersion in which the water-based polyester resin are mixed with the saponified product of a vinyl acetate-based copolymer. It is to be noted that as the composition, there was employed NS-141LX which is a water-based polyester resin composition manufactured by Takamatsu Yushi Kogyo, Ltd.

(Example II-1)

[0488] There were mixed 30 parts (based on solid components) of the cationic acrylic copolymer (A-II-1) containing a crosslinkable group obtained in the above-described step, 40 parts (based on solid components) of the PVA-210 (B-II) manufactured by Kuraray, Ltd., and 30 parts (based on solid component) of HUX-670 (C-II) manufactured by Asahi

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Denka Kogyo, Ltd. to obtain a water-based coating liquid. The water-based coating liquid was coated on an adhesive-treated polyethylene terephthalate film having the thickness of 100 μm (Merinex 705 manufactured by ICI Japan, Ltd., hereinafter, it is occasionally referred to as merely PET film), and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-1.

(Example II-2)

[0489] The same procedures were followed as in the Example II-1, except that the NS-120X which is the component (D-II) manufactured by Takamatsu Yushi Kogyo, Ltd. was employed in place of the HUX-670 which is the component (C-II) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet II-2.

(Example II-3)

[0490] The same procedures were followed as in the Example II-1, except that the NS-141LX which is the component (E-II) manufactured by Takamatsu Yushi Kogyo, Ltd. was employed in place of the HUX-670 which is the component (C-II) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet II-3.

(Comparative Example II-1)

[0491] The cationic acrylic copolymer (A-II) containing a crosslinkable group obtained in the above-described step was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-4.

(Comparative Example II-2)

[0492] The PVA-210 which is the component (B-II) manufactured by Kuraray, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-5.

(Comparative Example II-3)

[0493] The HUX-670 which is the component (C-II) manufactured by Asahi Denka Kogyo, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-6.

(Comparative Example II-4)

[0494] The NS-120X which is the component (D-II) manufactured by Takamatsu Yushi Kogyo, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-7.

(Comparative Example I-5)

[0495] The NS-141LX which is the component (E-II) manufactured by Takamatsu Yushi Kogyo, Ltd. was coated on the PET film having the thickness of 100 μm , and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet II-8.

[0496] Hereinafter, evaluation results in relation to the above Examples II-1 to II-3 and Comparative Examples II-1 to II-5 are shown in Table II-1.

Table II- 1

	Recording Sheet	Clearness	Uniformity of Picture image	Water Resistance
Example II-1	Sheet II-1	○	○	○
Example II-2	Sheet II-2	○	○	○
Example II-3	Sheet II-3	○	○	○
Comparative Example II-1	Sheet II-4	×	×	○

Table II- 1 (continued)

	Recording Sheet	Clearness	Uniformity of Picture image	Water Resistance
Comparative Example II-2	Sheet II-5	○	○	×
Comparative Example II-3	Sheet II-6	×	Δ	Δ
Comparative Example II-4	Sheet II-7	Δ	×	Δ
Comparative Example II-5	Sheet II-8	Δ	Δ	×

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0497] According to the present invention No. II, all the recording sheets employed in the Examples show a higher clearness and a higher level in water resistance and printed quality than those in the Comparative Examples.

[0498] It was confirmed that in the recording sheet in which there is employed the resin composition for an ink-jet recording sheet of the present invention and which has a picture image-receiving layer on at least one surface of a base material, there can be largely improved water resistance without beading even in an ink-jet printer having a high printing speed, in addition to clearness and an ink-absorbing ability such as uniformity of a picture image and, further, water resistance and an ink-absorbing ability are successfully consistent with each other while improving a printing quality, which are a contrary characteristic each other.

[0499] Hereinafter, there are illustrated Examples in relation to the present invention No. III.

[0500] As a cationic (meth)acrylic copolymer (A-III-1) containing a crosslinkable group, there was employed the same one as in the cationic (meth)acrylic copolymer (A-I-1) containing a crosslinkable group.

[Saponified product (B-III) of a vinyl acetate-based copolymer]

[0501] As a saponified product of a vinyl acetate-based copolymer, the PVA:OKS-7158G manufactured by Nihon Gosei Kagaku, Ltd. was employed.

[Water-based polyurethane resin (C-III)]

[0502] The NS-120X manufactured by Takamatsu Yushi Kogyo, Ltd. was employed.

[Block isocyanate compound (F-III)]

[0503] Aquanate 201 manufactured by Nihon Polyurethane, Ltd. was employed.

(Example III-1)

[0504] There were mixed 35 parts (based on solid components) of the cationic acrylic copolymer (A-III-1) containing a crosslinkable group obtained in the above-described step, 20 parts (based on solid components) of the saponified product of a vinyl acetate-based copolymer (B-III):OKS-7158G, and 45 parts (based on solid components) of the water-based polyurethane resin (C-III): NS-120X, and 0.3 part of the block isocyanate compound (F-III): Aquanate 201 to obtain a water-based coating liquid having a solid content of 17 wt%. Subsequently, the water-based coating liquid was coated on an adhesive-treated polyethylene terephthalate film having the thickness of 100 μm (Merinex 705 manufactured by Dupon't, Ltd., hereinafter, it is occasionally referred to as merely PET film), and it was dried at 120°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain a recording sheet III-1.

(Example III-2)

[0505] The same procedures were followed as in the Example III-1, except that there were employed 30 parts (based on solid components) of the cationic acrylic copolymer (A-III-1) containing a crosslinkable group, 40 parts (based on solid components) of the saponified product of a vinyl acetate-based copolymer (B-III), and 30 parts (based on solid component) of the water-based polyurethane resin (C-III): NS-120X to obtain a recording sheet III-2.

(Comparative Example III-1)

[0506] The same procedures were followed as in the Example III-1, except that the block isocyanate compound (F-

III) was changed to 0 part to obtain a recording sheet III-3.

(Comparative Example III-2)

- 5 **[0507]** The same procedures were followed as in the Example III-1, except that the block isocyanate compound (F-III) was changed to 5 parts to obtain a recording sheet III-4.

(Comparative Example III-3)

- 10 **[0508]** The same procedures were followed as in the Example III-1, except that the cationic acrylic copolymer (A-III-1) containing a crosslinkable group was changed to 0 part, the saponified product of a vinyl acetate-based copolymer (B-III): OKS-7158G was changed to 100 parts, the water-based polyurethane resin (C-III): NS-120X was changed to 0 part, and the block isocyanate compound (F-III) was changed to 0 part to obtain a recording sheet III-5.

- 15 (Comparative Example III-4)

[0509] The same procedures were followed as in the Example III-1, except that a block isocyanate compound (D-III) was changed to the same amount of isophorone diisocyanate to obtain a recording sheet III-6.

- 20 **[0510]** Evaluation results in relation to the recording sheets obtained in the Examples and Comparative Examples are shown in Table III-1.

Table III-1

	Sheet No.	Uniformity of Picture image	Clearness	Water A	Resistance B
25	Example III-1	○	○	○	○
	Example III-2	○	○	○	○
	Comparative Example III-1	○	○	○	×
	Comparative Example III-2	○	-	-	-
30	Comparative Example III-3	○	○	×	×
	Comparative Example III-4	-	-	-	-
Comparative Example III-2, -4 : Coating was stopped because of viscosity increase in water-based coating liquid.					

POSSIBILITY OF UTILIZATION IN INDUSTRY

- 40 **[0511]** According to the present invention No. III, all the recording sheets employed in the Examples show a more excellent printed quality such as the uniformity of a picture image and clearness compared to those in the Comparative Examples.

[0512] In the composition for recording of the present invention and the recording sheet having a picture image-receiving layer on at least one surface of a base material prepared therefrom, there can be largely improved water resistance while improving an ink-absorbing ability and a printing quality.

- 45 **[0513]** Hereinafter, Examples for the present invention No. IV are illustrated.

[Preparation of a cationic acrylic copolymer (A-IV-1)]

- 50 **[0514]** A 2000 ml reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts of isopropylalcohol (IPA), and 1.23 part of azobisisobutyronitrile (AIBN) was added while agitating to dissolve, followed by heating to 80°C. As copolymerizable components, there were mixed 93.7 parts of methylmethacrylate (MMA), 98.7 parts of n-butylacrylate (BA), 49.3 parts of diethylaminoethyl methacrylate (DEAEMA), 49.3 parts of a polyethylene glycol methacrylate (Blemmer PE200 (CH₂=CCH₃COO(CH₂CH₂O)₄₋₅H) manufactured by Nihon Yushi, Ltd.), 24.7 parts of acrylic acid, and 4.93 parts of trimethoxysilane propylmethacrylate (A-174 manufactured by Nihon Unicar, Ltd.), followed by adding dropwise into the reaction vessel over approximately 4 hours. After the completion of the dropwise addition, 0.25 part of AIBN which is an additional catalyst was dissolved in 25 parts of IPA, and it was added dropwise into the reaction vessel, and reaction was further continued for 2 hours.

[0515] After the completion of the polymerization, 16 parts of acetic acid was added into the reaction vessel, and 705 parts of water was added dropwise over approximately 2 hours, followed by evaporating a solvent using a rotary evaporator to obtain the cationic acrylic copolymer (A-IV-1).

[Preparation of a cationic acrylic copolymer (A-IV-2) containing a crosslinkable group]

[0516] Using the same apparatus as in the preparation of the (A-IV-1), the same synthesis was conducted as in the (A-IV-1) except that as copolymerization components, methylmethacrylate (MMA) was changed to 93.7 parts, n-butylacrylate was changed to 98.7 parts by weight, diethylaminoethyl methacrylate was changed to 49.3 parts by weight, and trimethoxysilane propylmethacrylate was changed to 4.93 parts to obtain a cationic acrylic copolymer (A-IV-2) containing a crosslinkable group, and which does not contain an alkylene oxide group.

[Saponified product (B-IV) of a vinyl acetate-based copolymer]

[0517] As a saponified product of a vinyl acetate-based copolymer, the following products (B-IV-1 to B-IV-4 according to described order) manufactured by Kuraray, Ltd.

PVA-405 (saponified degree: 80.0-83.0%, polymerization degree: 500)
 PVA-420 (saponified degree: 78.0-81.0%, polymerization degree: 2000)
 PVA-205 (saponified degree: 86.5-89.5%, polymerization degree: 500)
 PVA-217 (saponified degree: 87.0-89.0%, polymerization degree: 1700)

[Modifier (C-IV)]

[0518] A water-based polyurethane resin was employed. As the water-based polyurethane (C-IV). HUX-670 was employed which is manufactured by Asahi Denka Kogyo, Ltd.

(Preparation of samples for evaluation)

[0519] There were mixed the cationic acrylic copolymer obtained in the above-described step, the saponified product of a vinyl acetate-based copolymer, and the modifier to obtain a water-based coating liquid. The water-based coating liquid was coated on an adhesive-treated polyethylene terephthalate film having the thickness of 100 μm (Merinex 705 manufactured by Dupont, Ltd., hereinafter, it is occasionally referred to as merely PET film), and it was dried at 100°C for 3 minutes to form an ink-absorbing layer having the thickness of 15 μm and to obtain the samples for evaluation.

(Method for evaluation)

[0520] Using an ink-jet printer (PM-770C manufactured by Seiko Epson, Ltd.), a recorded picture image was formed by printing a color pattern using colors such as cyan, yellow, magenta, and black in a photoprint mode on the recording sheets obtained in Examples and Comparative Examples.

(Uniformity in a picture image)

[0521] (Blot) Recorded picture image was visually observed, and clearness was evaluated by the following standard.

○: In visual observation, blot is not observed at all.
 △: In visual observation, blot is slightly observed.
 x: Blot is remarkable in a picture image.

(Water resistance)

[0522] Printed portion was immersed in water of 30°C for 1 hour and, it was vertically pulled up, and water was sufficiently removed and dried. After having dried, there was measured retention of color concentration in the picture image remained after drying.

(Example IV-1)

[0523] There were mixed 30 parts (based on solid components) of the cationic acrylic copolymer (A-IV-1) containing

a crosslinkable group obtained in the above-described step and 70 parts (based on solid components) of the PVA-405 (B-IV) manufactured by Kuraray, Ltd. which is a saponified product of a vinyl acetate to obtain a water-based coating liquid for a resin composition for recording.

[0524] The water-based coating liquid was coated on an adhesive-treated polyethylene terephthalate film having the thickness of 100 μm (Merinex 705 manufactured by Dupon't, Ltd.), and it was dried at 100°C for 3 minutes to form an ink-absorbing layer which is an image-receiving layer having the thickness of 15 μm and to obtain a recording sheet IV-1.

(Example IV-2 to IV-10 and Comparative Examples IV-1 to IV-4)

[0525] A water-based coating liquid composed of a resin composition was obtained by formulating a cationic acrylic copolymer containing a crosslinkable group, a saponified product of a vinyl acetate, and a water-based urethane in a formulating proportion shown in Table IV-1. It was likewise coated and dried as in the Example IV to form an ink-absorbing layer which is an image-receiving layer having the thickness of 15 μm and to obtain respective recording sheets IV-1.

[0526] In relation to the Example IV-1 to IV-10 and Comparative Examples IV-1 to IV-4, Table IV-1 shows formulating proportion of components in the respective resin composition and evaluation results in the recording sheets obtained.

Table IV-1

Table IV-1

Example No.		Component A-IV		Component B-IV		Component C-IV	Evaluation of image quality		
		Kind	Formulation	Kind	Formulation	Formulation	Uniformity	Blot	Water Resistance
Example	IV-1	A-IV-1	30	B-IV-1	70	0	○	○	63
	IV-2	A-IV-1	50	B-IV-1	50	0	○	○	72
	IV-3	A-IV-1	70	B-IV-1	30	0	○	○	85
	IV-4	A-IV-1	50	B-IV-3	50	0	○	○	79
	IV-5	A-IV-1	30	B-IV-1	40	30	○	○	89
	IV-6	A-IV-1	30	B-IV-3	40	30	○	○	91
	IV-7	A-IV-1	50	B-IV-2	50	0	△	○	72
	IV-8	A-IV-1	50	B-IV-4	50	0	△	△	74
	IV-9	A-IV-1	30	B-IV-2	40	30	△	△	79
	IV-10	A-IV-1	30	B-IV-4	40	30	△	△	76
Comparative Example	IV-1	A-IV-2	30	B-IV-1	70	0	×	○	61
	IV-2	A-IV-2	50	B-IV-1	50	0	×	△	69
	IV-3	A-IV-2	70	B-IV-1	30	0	×	×	80
	IV-4	A-IV-2	30	B-IV-1	40	30	×	△	75

Component A-IV : Crosslinkable group-contained cationic acrylic polymer

Component B-IV : Saponified product of acetic acid-based polymer

Component C-IV : Water-based polyurethane resin

Numerical values in formulation section show solid content % in a composition.

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0527] According to the present invention No. IV, all the recording sheets employed in the Examples show a more excellent printed quality such as the uniformity, blot, and water resistance compared to those in the Comparative Examples.

[0528] In the recording sheet in which there is employed the resin composition for an ink-jet recording sheet of the present invention and which has an image-receiving layer on at least one surface of a base material, there can be

improved water resistance, an ink-absorbing ability, and a printing quality even though under a circumstance in which a high resolution and a change to a high speed are required. Further, in the present invention, water resistance and an ink-absorbing ability are successfully consistent with each other while improving a printing quality to a same level as a photographic image quality, which are a contrary characteristic each other.

[0529] Hereinafter, there are illustrated Examples in relation to the present invention No. V.

[0530] First of all, there were prepared the resin composition for an ink-jet recording sheet of the present invention and a resin composition in which components in the resin composition are changed, and there was prepared a recording sheet having an image-receiving layer to supply for Examples and Comparative Examples.

[0531] There were prepared recording sheets V-1 to V-3 for the Examples and recording sheets V-4 to V-6 for the Comparative Examples to conduct evaluations of a variety of properties. It is to be noted that a specific method for the evaluations of a variety of properties and a method for indicating evaluation results are illustrated hereinafter.

[Preparation of a cationic methacrylic copolymer (A-V-1)]

[0532] A 2000 ml (milliliter) reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts of isopropylalcohol (IPA), and 1.23 part of azobisisobutyronitrile (AIBN) was added while agitating to dissolve, followed by heating to 80°C.

[0533] Subsequently, as constructing components of the copolymer (A-V-1), there were mixed 49.3 parts by weight of a polyethylene glycol methacrylate (Blemmer PE200 ($\text{CH}_2=\text{CCH}_3\text{COO}(\text{CH}_2\text{CH}_2\text{O})_{4.5}\text{H}$) manufactured by Nihon Yushi, Ltd.) (the component a_1), 24.7 parts of acrylic acid (the component a_2), 4.93 parts of trimethoxysilane propylmethacrylate (A-174 manufactured by Nihon Unicar, Ltd.) (the component a_3), 49.3 parts by weight of diethylaminoethyl methacrylate (the component a_4), 93.7 parts by weight of methylmethacrylate (the component a_5), and 98.7 parts by weight of n-butylacrylate (the component a_5), followed by adding dropwise into the reaction vessel over approximately 4 hours.

[0534] After the completion of the dropwise addition, 0.25 part by weight of AIBN which is an additional catalyst was dissolved in 25 parts by weight of IPA, and it was added dropwise into the reaction vessel, and reaction was further continued for 2 hours. After the completion of the polymerization, 16 parts by weight of acetic acid was added into the reaction vessel, and 705 parts by weight of water was added dropwise over approximately 2 hours while agitating, followed by evaporating a solvent using a rotary evaporator to obtain the cationic methacrylic copolymer (A-V-1).

(Example V-1)

[0535] There were mixed 80 parts by weight of the cationic methacrylic copolymer (A-V-1) containing a crosslinkable group obtained in the above-described step, 20 parts by weight of a saponified product of a vinyl acetate (B-V) (PVA-405 manufactured by Kuraray, Ltd., a saponified degree of 80.0-83.0%, a polymerization degree of 500), and 2 parts by weight of HUX-670 manufactured by Asahi Denka Kogyo, Ltd. to obtain a water-based coating liquid.

[0536] The water-based coating liquid was coated on an art paper having the thickness of 190 μm (NK Whitone Gloss 180.0), and it was dried at 110°C for 3 minutes to form an ink-absorbing layer which is a picture image receiving layer having the thickness of 15 μm and to obtain a recording sheet V-1.

[0537] The above formulation ratio is based on solid components.

[0538] Hereinafter, it is the same so far as being not particularly shown.

(Example V-2)

[0539] The same procedures were followed as in the Example V-1, except that the PVA-405 manufactured by Kuraray, Ltd. was not added to obtain a recording sheet V-2.

(Example V-3)

[0540] The same procedures were followed as in the Example V-1, except that there was employed a water-based polyurethane resin (C-V) (HUX-670 manufactured by Asahi Denka Kogyo, Ltd.) in which the amount of a cationic group is smaller than in the HUX-670-M2 in place of the water-based polyurethane resin (C-V) (HUX-670-M2 manufactured by the same company) having a characteristics that the amount of a cationic group is larger employed in the Example V-1.

(Example V-4)

[0541] The same procedures were likewise followed as in the Example V-1, except that there was not added the

HUX-670-M2 (C-V) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet V-4.

(Comparative Example V-1)

- 5 **[0542]** The same procedures were likewise followed as in the Example V-1, except that the components (A-V-1) and (B-V) employed in the Example V-1 were changed to 20 parts by weight and 80 parts by weight, respectively, to obtain a recording sheet V-5.

(Comparative Example V-2)

- 10 **[0543]** The same procedures were likewise followed as in the Comparative Example V-1, except that there was not added the HUX-670-M2 (C-V) manufactured by Asahi Denka Kogyo, Ltd. to obtain a recording sheet V-6.

[0544] Subsequently, there are illustrated evaluation methods for a variety of properties in the recording sheets obtained in the Examples and Comparative Examples, respectively, and results are shown in Table V-1 and Table V-2.

- 15 **[0545]** First of all, using an ink-jet printer (PM-770C manufactured by Seiko Epson, Ltd.), a recorded picture image was formed by printing a color pattern using colors such as cyan, yellow, magenta, and black in a photo glossy paper mode on recording sheets obtained in Examples and Comparative Examples.

(Embossed roll mark)

- 20 **[0546]** A recorded picture image was visually observed, and adherence conditions of an embossed roll mark were judged according to the following standards.

- : Embossed roll mark is not adhered at all.
 25 △: Embossed roll mark is apt to not adhere, and an outer appearance of a recorded picture image is not deteriorated.
 x: Embossed roll mark is clearly adhered, and an outer appearance of a recorded picture image is deteriorated.

(Glossiness)

- 30 **[0547]** Glossiness in a recorded picture image was measured using a gloss meter according to JIS Z8741.

- : not less than 70% in 60° gloss.
 △: not less than 40% in 60° gloss.
 x: less than 40% in 60° gloss.

35 (Water resistance)

- [0548]** One water droplet was dropped on a recorded picture image and, the water droplet was absorbed with a tissue paper after placing for 10 seconds and, the recorded picture image was visually observed and, water resistance was judged according to the following standards.

- : Ink and a resin do not dissolve and, lack is not observed in the picture image.
 △: Ink and a resin slightly dissolve and, lack is slightly observed in the picture image.
 x: Ink and a resin dissolve and, lack is slightly observed in the picture image.

45 (Ink absorbing ability and picture image quality)

[0549]

- 50 ○: Portion of identical color concentration is uniform, and there is not observed inferiority in a picture image quality such as blot, unevenness, and beading.
 △: There is partially observed inferiority in a picture image quality such as blot, unevenness, and beading.
 ×: There is widely observed inferiority in a picture image quality such as blot, unevenness, and beading.

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Table V-1

	Sheet Number	Roll mark
Example V-1	Recording Sheet V-1	△
Example V-2	Recording Sheet V-2	△
Example V-3	Recording Sheet V-3	△
Example V-4	Recording Sheet V-4	△
Comparative Example V-1	Recording Sheet V-5	×
Comparative Example V-2	Recording Sheet V-6	×

Table V-2

	Sheet Number	Gloss	Water Resistance	Absorbing ability Image quality
Example V-1	Recording sheet V-1	○	○	○
Example V-2	Recording sheet V-2	○	○	○
Example V-3	Recording sheet V-3	△	○	○
Example V-4	Recording sheet V-4	○	○	△

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0550] According to the present invention No. V, in the resin composition which forms an image-receiving layer in the recording sheet, if the formulation ratio of the respective components (A-V), (B-V) and (C-V) is within a range specified in the present invention, in a recording sheet obtained, an embossed roll mark is not apt to be adhered, and it is excellent without damaging an outer appearance of a recorded picture image.

[0551] Further, there was measured glossiness in relation to the recording sheets (V-1) to (V-4) in which conditions in adherence of the embossed roll mark are excellent, and water resistance, an ink-absorbing ability, and picture image quality were visually evaluated, and results are shown in Table V-2.

[0552] As distinctly shown in Table V-2, glossiness becomes excellent by employing even a small amount of the modifier (C-V) which is a water-based polyurethane resin, and a picture image quality becomes more excellent by employing the modifier (C-V) HUX-670-2M which is a water-based polyurethane resin having 10% larger cationic group.

[0553] Hereinafter, there are illustrated Examples VI in relation to the present invention No. VI.

[0554] Picture images for evaluation were formed in relation to sheets for recording obtained in Examples VI and Comparative Examples VI using a dye-ink jet printer (PM-770 manufactured by Seiko Epson, Ltd.) and a pigment-ink jet printer (ENCAD NOVAJET Pro).

(Printed picture image)

[0555] An ISO standard picture image was printed using the above-described printers, and it was visually judged according to the following standards.

○: Beading and blot are not observed at all.

△: Beading and blot are slightly observed.

x: Beading and blot are remarkable, and a clear picture image cannot be obtained.

(Ink-driability)

[0556] Using the above-described printers, a model picture image was printed by cyan, magenta, yellow, and black and, further, red, green, and blue which are a mixed color from yellow, etc., and a PPC copy paper was placed on a letters-printed portion at an every fixed time. The copy paper was stripped after the loading (500 g/cm²) was charged for 5 minutes, and conditions of ink-movement to the copy paper were visually observed according to the following standards.

- : Ink-movement to the copy paper is not observed at all.
- △: Ink-movement is slightly observed.
- x: Ink-movement is remarkable.

5 (Water resistance)

[0557] Using the above-described printers, a model picture image was printed by cyan, magenta, yellow, and black and, further, red, green, and blue which are a mixed color from yellow, etc., and water droplet was dropped on a picture image after an ink was dried and, the water droplet was wiped after having placed for 1 minute, and there were visually observed a picture image in a wiped portion and conditions of an image-receiving layer according to the following standards.

[Evaluation of picture image conditions]

15 [0558]

- : There was not observed at all a change in a picture image of a portion at which water droplet was wiped.
- △: Blot and decline of color concentration are slightly observed.
- x: Blot and decline of color concentration are remarkable.

[Evaluation of conditions in an image-receiving layer]

[0559]

- : Dissolution is not observed at all in an image-receiving layer.
- △: Dissolution is slightly observed.
- x: An image-receiving layer is completely dissolved and not remained.

(Glossiness)

[0560] Using a gloss meter, 60°-glossiness was measured.

[Synthesis of an acrylate resin (A-VI-1) containing an alkoxysilyl group]

[0561] A 2000 ml (milliliter) reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts by weight of isopropylalcohol and 1.23 part by weight of azobisisobutyronitrile which is a catalyst while agitating to dissolve, followed by heating to 80°C. As copolymerizable components, there were mixed 93.7 parts by weight of methylmethacrylate, 98.7 parts by weight of n-butyl acrylate, 5.0 parts by weight of acrylic acid, and 4.93 parts by weight of 3-methacryloxy propyltrimethoxysilane (A-174 manufactured by Nihon Unicar, Ltd.), followed by adding dropwise into the reaction vessel over approximately 4 hours. After the completion of the dropwise addition, there was added dropwise into the reaction vessel a solution composed of 0.25 part by weight of azobisisobutyronitrile which is an additional catalyst and 25 parts by weight of isopropylalcohol, and reaction was further continued for 2 hours to complete polymerization.

[0562] After the completion of the polymerization, 5.0 parts by weight of 25%-aqueous ammonia was added into the reaction vessel, and 705 parts by weight of water was added dropwise over approximately 2 hours to emulsify while agitating. After that, isopropylalcohol was evaporated using a rotary evaporator to obtain a resin A-VI-1 containing an alkoxysilyl group (Solid content concentration of 36.2% by weight).

[Synthesis of an acrylate resin (A-VI-2)]

[0563] The same procedures were followed as in the A-VI-1, except that 3-methacryloxy propyltrimethoxysilane was not employed to obtain an acrylate resin (A-VI-2).

[Synthesis of a resin B-VI containing a cationic group]

[0564] A 2000 ml reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts by weight of isopropylalcohol and 1.23 part of azobisisobutyronitrile which is a catalyst while agitating to dissolve, followed by heating to 80°C. As copolymerizable com-

ponents, there were mixed 93.7 parts by weight of methylmethacrylate, 98.7 parts by weight of n-butyl acrylate, 49.3 parts by weight of diethylaminoethyl methacrylate, and 4.93 parts by weight of 3-methacryloxy propyltrimethoxysilane (A-174 manufactured by Nihon Unicar, Ltd.), followed by adding dropwise into the reaction vessel over approximately 4 hours. After the completion of the dropwise addition, there was added dropwise into the reaction vessel a solution composed of 0.25 part by weight of azobisisobutyronitrile which is an additional catalyst and 25 parts by weight of isopropylalcohol, and reaction was further continued for 2 hours. After the completion of the polymerization, 16 parts by weight of acetic acid was added into the reaction vessel, and 705 parts by weight of water was added dropwise over approximately 2 hours to emulsify while agitating. After having emulsified, isopropanol was evaporated using a rotary evaporator to obtain a resin B-VI containing a cationic group (Solid concentration of 34.7%).

(Example VI-1)

[0565] A mixed product containing 55.2 parts by weight (solid content of 20 parts by weight) of the resin A-VI-1 containing a crosslinkable group and 400 parts by weight (solid content of 80 parts by weight) of a rosary-state colloidal silica (Snowtex PS-M manufactured by Nissan Kagaku, Ltd.) was coated on a white-colored PET sheet having a density of 140 g/m² (thickness of 100 μm), so that thickness in dryness becomes 15 μm to obtain a recording sheet VI-1. Evaluation results of the recording sheet are shown in Table VI-1.

(Example VI-2)

[0566] A resin B-VI containing a cationic group was coated on the white-colored PET sheet employed in the Example VI-1, so that thickness in dryness becomes 30 μm to form an ink-fixing layer.

[0567] Further, the mixed product employed in the Example VI-1 was likewise coated on the layer to obtain a recording sheet VI-2.

[0568] Evaluation results of the recording sheet are shown in Table VI-1.

(Example VI-3)

[0569] A mixed product containing 57.6 parts by weight (solid contents of 20 parts by weight) of the resin B-VI containing a cationic group, 200 parts by weight (solid contents of 50 parts by weight) of a polyvinyl alcohol (PVA-405 manufactured by Kuraray, Ltd.), and 100 parts by weight (solid contents of 30 parts by weight) of a water-based polyurethane resin (HUX-670 manufactured by Asahi Denka Kogyo, Ltd.) was coated on a white-colored PET sheet employed in the Example VI-1, so that thickness in dryness becomes 15 μm to form an ink-fixing layer. Further, the mixed product employed in the Example VI-1 was likewise coated on the ink-fixing layer to obtain a recording sheet VI-3. Evaluation results of the recording sheet are shown in Table VI-1.

(Comparative Example VI-1)

[0570] The same procedures were followed as in the Example VI-1, except that an acrylate resin (A-VI-2) was employed in place of the acrylate resin (A-VI-1) containing a crosslinkable group employed in the Example VI-1 to obtain a recording sheet VI-4. Evaluation results of the recording sheet are shown in Table VI-1.

(Comparative Example VI-2)

[0571] The same procedures were likewise followed as in the Example VI-1, except that a spherical colloidal silica (Snowtex ST-20 manufactured by Nissan Kagaku, Ltd.) was employed in place of the rosary-state colloidal silica employed in the Example VI-1 to obtain a recording sheet VI-5. Evaluation results of the recording sheet are shown in Table VI-1.

(Comparative Example VI-3)

[0572] The same procedures were likewise followed as in the Example VI-2, except that an ink-fixing layer was likewise formed as in the Example VI-2 and an ink-receiving layer was not formed to obtain a recording sheet VI-6. Evaluation results of the recording sheet are shown in Table VI-1.

Table VI-1

	Evaluation of Picture image		Ink Dryability	Water resistance			60° Gloss
	Dye Ink	Pigment Ink		Picture image		Image Receiving Layer	
				Dye Ink	Pigment Ink		
Example VI-1	○	○	Not more than 30 seconds	△	○	○	70
Example VI-2	○	○	Not more than 3 seconds	○	○	○	73
Example VI-3	○	○	Not more than 3 seconds	○	○	○	71
Comparative Example VI-1	○	○	Not more than 30 seconds	△	△	△	69
Comparative Example VI-2	×	×	Not more than 3 seconds	△	○	○	34
Comparative Example VI-3	○	×	Not less than 3 minutes	○	△	△	71

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0573] According to the present invention No. VI, it was confirmed that an ink-absorbing ability, water resistance, and glossiness in the recording sheet are remarkably improved by using a composition as an ink-receiving layer of an ink-jet recording sheet and, in the composition, a copolymer composed of a monomer having a hydrolyzable silyl group and a (meth)acrylate-based monomer is mixed with inorganic compound fine particles such as silica.

[0574] Hereinafter, there are illustrated Examples in relation to the present invention No. VII.

[0575] In relation to recording sheets obtained in Example VII and Comparative Example VII, an ink-absorbing ability, water resistance, dissolution of a picture image, and blocking resistance were evaluated as shown below.

[Ink-absorbing ability]:

[0576] Using an ink-jet printer (MasterJet-JC2008 manufactured by Graphtec Ltd.), a model letter-printing was conducted by a pigment-type water-based ink (cyan, magenta, and yellow, respectively) to form a recorded picture image on recording sheets obtained in Examples and Comparative Examples. After having letter-printed, a PPC copy paper was placed on a letters-printed portion at an every fixed time. The copy paper was stripped after the loading 24.5 kPa (250 gf/cm²) was charged for 10 seconds, and conditions of ink-movement to the copy paper were visually observed, and there was measured a time of period through which ink-movement to a back surface becomes not observed.

[Water resistance]:

[0577] In relation to recording sheets obtained in the Examples and Comparative Examples, a letter-printing was conducted as in an ink-absorbing test, followed by immersing in water of ordinary temperatures for 24 hours, and an outer appearance was visually evaluated according to the following standards.

○: Abnormality was not observed.

△: Picture image portion was slightly dissolved out.

×: Picture image portion was almost dissolved out.

[Dissolution of a picture image]

[0578] Using an ink-jet printer (MasterJet-JC2008 manufactured by Graphtec Ltd.), a magenta line of a yellow base (width of 100 μm) was printed on recording sheets obtained in Example VII and Comparative Example VII, followed

by observing 50 times-enlarged dots using a microscope, and evaluation was conducted according to the following standards.

- ⊙: Blot is almost not observed around the dots.
- : Blot is almost slightly observed around the dots, and an actual value exceeds 120 μm.
- ×: Blot is observed around the dots, and a region between yellow dots and magenta dots is indistinct, which are adjacent each other.

[Blocking resistance]

[0579] Two recording sheets obtained in Example VII and Comparative Example VII were put one upon another and, placed at 40°C and 90% RH for 1 day while loading 3.92 kPa (40 gf/cm²), and evaluated according to the following standards.

- ⊙: Both of matting and blocking were not observed.
- : Matting was observed, and blocking was not observed.
- ×: Blocking was observed.

(Example VII-1)

[0580] 18%-aqueous solution of a polyvinyl alcohol (OKS7158G manufactured by Nihon Gosei, Ltd.) was coated on one surface of a polyethylene terephthalate film having thickness of 100 μm (Merinex 339 manufactured by Dupon't, Ltd.), and it was dried at 120°C for 5 minutes to form a layer having thickness of 15 μm. Further, a resin composition VII-a for recording described below was coated on the layer, and dried at 80°C for 5 minutes to form a recording sheet having a porous image-receiving layer having thickness of 7 μm, in which pores of an average pore diameter of 1 μm exist in a high density. Table VII-1 shows evaluation results of the recording sheet.

[Resin composition (VII-a) for recording]

[0581] 5 parts by weight of phthalic acid which is an organic acid and 100 parts by weight of cyclohexanol which is a weak solvent were added to 100 parts by weight of 10%-solution in which a cellulose acetate (an acetylated degree: 55 and an average polymerization degree: 170) which is a cellulose derivative is dissolved in acetone which is a good solvent for the cellulose acetate to obtain a resin composition (VII-a) for recording.

(Example VII-2)

[0582] 18%-aqueous solution of a polyvinyl alcohol (OKS7158G manufactured by Nihon Gosei, Ltd.) was coated on one surface of a polyethylene terephthalate film having thickness of 100 μm (Merinex 339 manufactured by Dupon't, Ltd.), and it was dried at 120°C for 5 minutes to form a layer having thickness of 15 μm. Further, a resin composition VII-b for recording described below was coated on the layer, and dried at 80°C for 5 minutes to form a recording sheet having a porous image-receiving layer having thickness of 7 μm, in which pores of an average pore diameter of 1 μm exist in a high density. Table VII-1 shows evaluation results of the recording sheet.

[Resin composition VII-b for recording]

[0583] 2 parts by weight of phthalic acid which is an organic acid and 90 parts by weight of cyclohexanol which is a weak solvent were added to 100 parts by weight of 13%-solution in which a cellulose acetate (an acetylated degree: 51 and an average polymerization degree: 250) which is a cellulose derivative is dissolved in acetone which is a good solvent for the cellulose acetate to obtain a resin composition VII-b for recording.

(Example VII-3)

[0584] The resin composition VII-a for recording shown in the Example VII-1 was coated on one surface of a synthetic paper having thickness of 110 μm (Yupo FPG110 manufactured by Ohji Yuka Paper manufacturing, Ltd.), and it was dried at 80°C for 5 minutes to obtain a recording sheet having a porous image-receiving layer having thickness of 7 μm, in which pores of an average pore diameter of 1 μm exist in a high density. Table VII-1 shows evaluation results of the recording sheet.

(Comparative Example VII-1)

[0585] 18%-aqueous solution of a polyvinyl alcohol (OKS7158G manufactured by Nihon Gosei, Ltd.) was coated on one surface of a polyethylene terephthalate film having thickness of 100 μm (Merinex 339 manufactured by Dupont, Ltd.), and it was dried at 120°C for 5 minutes to form an image receiving layer having thickness of 15 μm . Table VII-1 shows evaluation results of the recording sheet.

Table VII-1

	Ink absorbing property	Water resistance	Dissolution of picture image	Blocking resistance
Example VII-1	Not more than 1 minute	○*	⊙	⊙
Example VII-2	Not more than 1 minute	○*	⊙	⊙
Example VII-3	Not more than 1 minute	○	⊙#	⊙
Comparative Example VII-1	3 minutes	×	○	×

Mark *: Although a polyvinyl alcohol was dissolved out and an image receiving layer was peeled from PET, an image was not abnormal.

Mark #: Although an ink receiving layer is not formed, an ink was fixed by an effect by an organic acid in the ink receiving layer, and a clear picture image was obtained.

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0586] According to the present invention No. VII, there can be prepared a body to be recorded or a recording sheet which is excellent in an ink-absorbing ability, blocking resistance, color reproducibility, water resistance in a recorded picture image or letters, and weatherability and, moreover, which has a surface glossiness.

[0587] Hereinafter, there are illustrated Examples in relation to the present invention No. VIII.

[0588] There are as follows evaluation methods of a variety of properties in relation to recording sheets obtained in Example VIII and Comparative Example VIII.

[Preparation of a polymer (L-VIII-1)]

[0589] A 2000 ml reaction vessel equipped with an agitator, a reflux condenser, a dropping funnel, a tube for introducing nitrogen, and a thermometer was charged with 219 parts of isopropyl alcohol, and 1.23 part of azobisisobutyronitrile was added while agitating to dissolve, followed by heating to 80°C. As copolymerizable components, there were mixed 93.7 parts of methylmethacrylate, 98.7 parts of n-butylacrylate, 49.3 parts by weight of diethylaminoethyl methacrylate, 49.3 parts by weight of a polyethylene glycol methacrylate (Blemmer PE200 manufactured by Nihon Yushi, Ltd.), 24.7 parts of acrylic acid, and 4.93 parts of trimethoxysilane propylmethacrylate (A-174 manufactured by Nihon Unicar, Ltd.), followed by adding dropwise into the reaction vessel using the dropping funnel over approximately 4 hours. After the completion of the dropwise addition, there was added dropwise a solution composed of 0.25 part of azobisisobutyronitrile which is an additional catalyst and 25 parts of isopropyl alcohol, and reaction was further continued for 2 hours to complete a polymerization.

[0590] After the completion of the polymerization, 16 parts of acetic acid was added into the reaction vessel, and 705 parts of water was added dropwise into the reaction vessel over approximately 2 hours while agitating. After the polymerization have completed, a polymer (L-VIII-1) was obtained by evaporating a solvent using a rotary evaporator.

[Synthesis of a polymer (L-VIII-2)]

[0591] The same synthesis was conducted as in the (A-VIII-1) except that as copolymerization components, methylmethacrylate was changed to 93.7 parts, n-butylacrylate was changed to 98.7 parts by weight, diethylaminoethyl methacrylate was changed to 49.3 parts by weight, and trimethoxysilane propylmethacrylate was changed to 4.93 parts to obtain a polymer (A-VIII-2).

[Hot-melt adhesive resin (M-VIII)]

[0592] (M-VIII) As a hot-melt adhesive resin (M-VIII), there was employed a nylon-based powder 430-P1 manufactured by Daxicel-Huels, Ltd.

(Evaluation method)

[0593] Printing method: Using an ink-jet printer (PM-770C manufactured by Seiko Epson Co. Ltd.), color patterns using cyan, magenta, yellow, and black, respectively, were set up at an iron print paper and printed on the recording sheets obtained in the Examples and Comparative Examples.

[0594] Evaluation of an ink-absorbing ability: After having printed, a PPC copy paper was placed on a printed portion at an interval of every time, and the weight of 24.5 kPa (250 gf/cm²) was loaded on the copy paper for 10 seconds, and then, the copy paper was stripped, and the presence or absence of an ink-movement was visually judged, and evaluated by a time of period until not being observed.

[0595] Evaluation of a picture image quality: Recorded image was visually observed, and clearness was judged according to the following standards.

○: Portion in an identical color concentration is uniform, and lack of uniformity is not observed in a picture image.

△: Ink is uniform in a very partial range, and lack of uniformity is partially observed in a picture image.

x: Ink is uniform in a wide range, and lack of uniformity is remarkable in a picture image.

[0596] Transferring: There was pressed a surface of an image-receiving layer in a heat transfer sheet printed on a T-shirt, and compressed at temperature of 160°C and pressure of 4.47 kPa (15 gf/cm²) for 20 seconds using a Haaxilon press machine, and a picture image was thermally-transferred on a T-shirt.

[0597] Evaluation of washing resistance: 1 g of a commercially supplied cleaning agent was added to 1 liter of water of temperature of 40°C, and there was immersed a T-shirt sample (5x10 cm) on which a picture image is transferred, followed by agitating at rotating speed of 600 rpm for 20 minutes using an agitator (Three-one motor). After having agitated, the sample was taken out, and water was completely removed, and a picture image transferred was observed, and washing resistance was evaluated according to the following standards.

○: Picture image portion transferred is completely remained.

△: Picture image portion transferred becomes slightly faint.

x: Picture image portion transferred is not remained.

(Examples VIII-1 to VIII-3 and Comparative Examples VIII-1 to VIII-3)

[0598] The polymer (L-VIII-1) and the polymer (L-VIII-2) were mixed with the hot-melt adhesive resin (M-VIII) in proportion of a solid content shown in Table VIII-1 to obtain a water-based coating liquid having 30% of nonvolatile components. The water-based coating liquid was coated on a base material (a releasing paper) having thickness of 100 μm using a barcoater to obtain heat transfer sheets. Amount of the coated resin was 40 gf m². Table VIII-1 shows results evaluated using the transfer sheets.

Table VII-1

	Polymer (L-VII)		Hot-melt adhesiveresin (M-VII) 430-P1	Ink absorbing property (minute)	Image Quality	Washing resistance
	Kind	Formulation Amount (part)				
Example VIII-1	L-VIII-1	50	50	1	○	○
Example VIII-2	L-VIII-1	30	70	1.5	○	○
Example VII-3	L-VII-1	10	90	2	○	○

Table VII-1 (continued)

	Polymer (L-VII)		Hot-melt adhesive resin (M-VII) 430-P1	Ink absorbing property (minute)	Image Quality	Washing resistance
	Kind	Formulation Amount (part)				
Comparative Example VII-1	L-VII-2	50	50	2	Δ	×
Comparative Example VIII-2	L-VII-2	30	70	3	Δ	Δ
Comparative Example VII-3	L-VII-2	10	90	3	×	○

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0599] According to the present invention No. VIII, since the resin composition of the present invention is constructed by the polymer (L) and the hot-melt adhesive resin (M), there can be largely improved a microcrack resistance, durability, water resistance, washing resistance in a picture image transferred by preparing the picture image on a strippable base material and by transferring to an elastic body, and there can be largely improved an ink-absorbing ability in the formation of a picture image.

Claims

1. A resin composition for an ink-jet recording sheet for constructing an image-receiving layer which is formed on at least one surface of a base material for an ink jet recording sheet, which comprises,

- (1) 2-80% by weight of a cationic (meth)acrylic copolymer (A) having a crosslinkable group,
- (2) 5-80% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and
- (3) 0-80% by weight of a modifier (R).

2. A resin composition for an ink-jet recording sheet as claimed in claim 1, wherein said modifier (R) satisfies conditions that (n₁-80)% by weight of a water-based polyurethane resin (C), (n₂-60)% by weight of a polyurethane-based graft polymer mixture (D) [the mixture (D) is a graft polymer mixture obtained through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (d₃) and other radical polymerizable vinyl monomer (d₄) in a proportion of (100-60% by weight): (0-40% by weight) to a mixed aqueous solution or a dispersed liquid of a water-based polyurethane (d₁) with a saponified product (d₂) of a vinyl acetate-based copolymer], and (n₃-60)% by weight of a polyester-based graft polymer mixture (E) [the mixture (E) is a graft polymer mixture obtained from a graft polymerization through graft-polymerization by adding a hydrophilic radical polymerizable vinyl monomer (e₃) and other radical polymerizable vinyl monomer (e₄) in a proportion of (100-60% by weight): (0-40% by weight) to a mixed aqueous solution or a dispersed liquid of a water-based polyester resin (e₁) with a saponified product (e₂) of a vinyl acetate-based copolymer], and total of said resin composition for an ink jet recording sheet is 100% by weight based on the solid content ratio, and (n₁+n₂+n₃) is ≥5% by weight.

3. A resin composition for an ink-jet recording sheet as claimed in claim 2, wherein a saponification degree is 75-100% and polymerization degree is 200-5000, respectively, in said saponified products (d₂) and (e₂) of a vinyl acetate-based copolymer.

4. A resin composition for an ink-jet recording sheet as claimed in claim 2, wherein said water-based polyurethane resin (C) is cationic.

5. A resin composition for an ink-jet recording sheet as claimed in claim 2, wherein said polyurethane-based graft polymer mixture (D) and the polyester-based graft polymer mixture (E) are cationic.

6. A resin composition for an ink-jet recording sheet for constructing an image-receiving layer formed over at least one surface of a base material for an ink-jet recording sheet, which comprises,

- [1] 2-80% by weight of a cationic (meth)acrylic copolymer (A) having a crosslinkable group,
- [2] 5-60% by weight of a saponified product (B) of a vinyl acetate-based copolymer, and
- [3] 0-80% by weight of a water-based polyurethane resin (C) {total of the (A-III), (B), and (C) is 100% by weight}, and
- [4] 0.05-10 parts by weight of a block isocyanate compound (F) based on 100 parts by weight of the saponified product (B) of a vinyl acetate-based copolymer.

7. A resin composition for an ink-jet recording sheet as claimed in claim 1 or 6, wherein said cationic (meth)acrylic copolymer (A) having a crosslinkable group is a copolymer containing monomer units based on a respective monomer (1) or (2) described below,

- (1) a cationic monomer and a monomer having a crosslinkable group
- (2) a cationic monomer, a monomer having a crosslinkable group, and a monomer having a hydrophilic group.

8. A resin composition for an ink-jet recording sheet as claimed in claim 1 or 6, wherein a saponification degree is 70-95% in said saponified product (B) of a vinyl acetate-based copolymer.

9. A resin composition for an ink-jet recording sheet as claimed in claim 7, wherein the monomer having a hydrophilic group is a (meth)acrylate containing an ester bond with a polyoxyalkylene.

10. A resin composition for an ink-jet recording sheet as claimed in claim 1, 6, or 7, wherein said cationic (meth)acrylic copolymer (A) having a crosslinkable group is a copolymer containing 0.1-50% by mol of a monomer having a tertiary amino group or a quaternary amino group and 0.1-25% by mol of a monomer having a crosslinkable group.

11. A resin composition for an ink-jet recording sheet which is a resin composition which constructs an image-receiving layer which is formed at at least one surface of surface of a base material for an ink jet recording sheet, which comprises 2-100% by weight of a cationic (meth)acrylic copolymer (A-IV) obtained by copolymerizing a (meth)acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), 0-90% by weight of a saponified product (B) of a vinyl acetate copolymer, and 0-80% by weight of a modifier (R) (total thereof is 100% by weight).

12. A resin composition for an ink-jet recording sheet as claimed in claim 11, which comprises 5-80% by weight of the cationic (meth)acrylic copolymer (A-IV), 15-80% by weight of the saponified product (B) of a vinyl acetate copolymer, and 5-60% by weight of the modifier (R) (total thereof is 100% by weight).

13. A resin composition for an ink-jet recording sheet as claimed in claim 11 or 12, wherein said cationic (meth)acrylic copolymer (A-IV) having a crosslinkable group is composed of 0.1-40% by weight of said (meth)acrylate monomer (a_1) having a polyalkylene oxide group, 0.1-50% by weight of said monomer (a_2) having a hydrophilic group, 0.5-20% by weight of said monomer (a_3) having a crosslinkable group, 1-40% by weight of said cationic monomer (a_4), 10-60% by weight of a hard monomer (a_6), and 10-60% by weight of a soft monomer (a_7) (total thereof is 100% by weight), and a weight average molecular weight is 0.2×10^4 - 100×10^4 in said cationic (meth)acrylic copolymer (A-IV) having a crosslinkable group.

14. A resin composition for an ink-jet recording sheet which constructs an image-receiving layer which is formed at at least one surface of a base material for an ink jet recording sheet, wherein there are formulated 70-100% by weight of a cationic (meth)acrylic copolymer (A-V) obtained by copolymerizing a (meth)acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), 0-30% by weight of a saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0-15 parts by weight of the modifier (R) based on 100 parts by weight of total of the (A-V) and the (B).

15. A resin composition for an ink-jet recording sheet as claimed in claim 14, wherein said cationic (meth)acrylic co-

polymer (A-V) is a copolymer obtained by copolymerizing a (meth)acrylate monomer (a_1) having a polyalkylene oxide group, a monomer (a_2) having a hydrophilic group, a monomer (a_3) having a crosslinkable group, and a cationic monomer (a_4), and a nonionic monomer (a_5).

- 5 **16.** A resin composition for an ink-jet recording sheet as claimed in claim 14, wherein there are formulated 75-95% by weight of said cationic (meth)acrylic copolymer (A-V), 5-25% by weight of said saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0.5-5 parts by weight of a modifier (R) based on 100 parts by weight of total of said (A-V) and said (B).
- 10 **17.** A resin composition for an ink-jet recording sheet as claimed in claim 14, wherein there are formulated 75-95% by weight of said cationic (meth)acrylic copolymer (A-V), 5-25% by weight of said saponified product (B) of a vinyl acetate copolymer (total thereof is 100% by weight), and 0.5-3 parts by weight of said modifier (R) based on 100 parts by weight of total of said (A-V) and said (B).
- 15 **18.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 14-17, wherein said cationic (meth)acrylic copolymer (A-V) contains 8-40% by weight of said (meth)acrylate monomer (a_6) having a polyalkylene oxide group, 1-30% by weight of said monomer (a_2) having a hydrophilic group, 0.2-10% by weight of the monomer (a_3) having a crosslinkable group, 10-50% by weight of said cationic monomer (a_4), and 10-80% by weight of said nonionic monomer (a_5) (total thereof is 100% by weight).
- 20 **19.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 11, 13, 14, 15, and 18, wherein a polyalkylene oxide group in said (meth)acrylate monomer (a_1) having a polyalkylene oxide group has a structure shown by a general formula: $-[(CHR^1)_n-O]_m-R^2$,
 [in the general formula, R^1 represents a hydrogen atom, methyl group, or hydroxyl group, R^2 represents a hydrogen atom or methyl group, "n" is an integer of 1-5, "m" is an integer of 1-20, respectively, "n" and "m" pieces of R^1 may be even identical to or different from each other.].
- 25 **20.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 7, 11, 13, 14, 15, and 18, wherein said hydrophilic group in said monomer (a_2) having a hydrophilic group is at least one selected from the group consisting of carboxylic group or a salt thereof, an anhydride group, hydroxyl group, sulphonic acid group or a salt thereof, an amide group, and an ether group.
- 30 **21.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 7, 11, 13, 14, 15, and 18, wherein said monomer (a_3) having a crosslinkable group is a monomer having a hydrolyzable condensable group.
- 35 **22.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 7, 11, 13, 14, 15, and 18, wherein said monomer (a_3) having a crosslinkable group is a monomer having an alkoxysilyl group.
- 40 **23.** A resin composition for an ink-jet recording sheet as claimed in any one of claims 7, 11, 13-15, and 18, wherein said cationic monomer (a_4) is a monomer having a tertiary amino group, a monomer having an acid salt of a tertiary amine, or a monomer having a quaternary ammonium base.
- 45 **24.** A resin composition for an ink-jet recording sheet as claimed in any one of claim 15 or 18, wherein said nonionic monomer (a_5) is any one of (meth)acrylates, aromatic vinyls, and vinyl esters.
- 50 **25.** A resin composition for an ink-jet recording sheet as claimed in any one of claim 1, 6, 8, 11, 12, 14, 16 or 17, wherein a polymerization degree is 200-1000 in said saponified product (B) of a vinyl acetate copolymer.
- 55 **26.** A resin composition for an ink-jet recording sheet as claimed in any one of claim 1, 11, or 16, wherein said modifier (R) contains a water-based polyurethane (C) and/or a water-based polyester resin (e_1).
- 27.** An ink-jet recording sheet characterized in that an ink-receiving layer formed on at least one surface of a base material for an ink jet recording sheet is constructed by a composition (P) containing a (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group prepared by copolymerization of monomers containing a polymerizable unsaturated monomer (a_8) having a hydrolyzable silyl group and a (meth)acrylic-based polymerizable unsaturated monomer (a_9), and inorganic compound fine particles (G).
- 28.** An ink-jet recording sheet as claimed in claim 27, wherein an ink-fixing layer is formed between a base material

for said ink-jet recording sheet and the ink-receiving layer.

29. An ink-jet recording sheet as claimed in claim 27, wherein said (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group is a water-based copolymer.

30. An ink jet recording sheet as claimed in claim 27, wherein the weight proportion of monomer units based on the (a_8) and the (a_9) contained in said (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group is (a_8)/(a_9)=(0.1-30%)/(70-99%) (total is 100% by weight).

31. An ink-jet recording sheet as claimed in claim 27, wherein said inorganic compound fine particles (G) is a rosary-state colloidal silica which is dispersed in water.

32. An ink-jet recording sheet as claimed in claim 27, wherein the weight ratio of the (A-VI) and (G) contained in said composition (P) containing said (meth)acrylic-based copolymer (A-IV) having a hydrolyzable silyl group with said inorganic compound fine particles (G) is the (A-VI)/(G)=(1-50%)/(50-99%) (total is 100% by weight).

33. An ink-jet recording sheet as claimed in claim 28, wherein said ink-fixing layer is composed of a resin containing a cationic group or a resin composition containing a formulated product of a resin containing a cationic group with at least one resin selected from the group consisting of a saponified product of a vinyl acetate-based copolymer, a water-based polyester-based resin, and a water-based polyurethane-based resin.

34. An ink-jet recording sheet as claimed in claim 33, wherein said resin containing a cationic group is a copolymer containing a cationic group prepared by copolymerization of monomers containing a polymerizable unsaturated monomer having a hydrolyzable silyl group, a polymerizable unsaturated monomer having a tertiary amino group and/or a quaternary ammonium group, and a (meth)acrylate-based polymerizable unsaturated monomer.

35. A resin composition for recording for forming an ink recording layer, characterized in that said composition contains 100 parts by weight of a resin composition composed of (1) 1-30% by weight of a cellulose derivative (H) and (2) 70-99% by weight of a good solvent (I) for the cellulose derivative (total is 100% by weight), 0.1-20 parts by weight of (3) an organic acid (J) which can dissolve in the good solvent (I) or a weak solvent (K) for the cellulose derivative, and optionally, 0-150 parts by weight of (4) a weak solvent (K) for the cellulose derivative.

36. A resin composition for recording as claimed in claim 35, wherein said cellulose derivative (H) is a cellulose acetate.

37. A resin composition for recording as claimed in claim 35, wherein a proportion of said weak solvent (K) for said cellulose acetate is 50-150 parts by weight.

38. A resin composition for recording as claimed in claim 35, characterized in that said good solvent (I) for said cellulose derivative is at least one kind selected from the group consisting of ketones, esters, ethers, cellosolves, cellosolve acetates, halogenated hydrocarbons, and nitro compounds, and a boiling point of the solvent is 35°C-160°C.

39. A resin composition for recording as claimed in claim 35, characterized in that a melting point of said organic acid (J) is not less than 60°C.

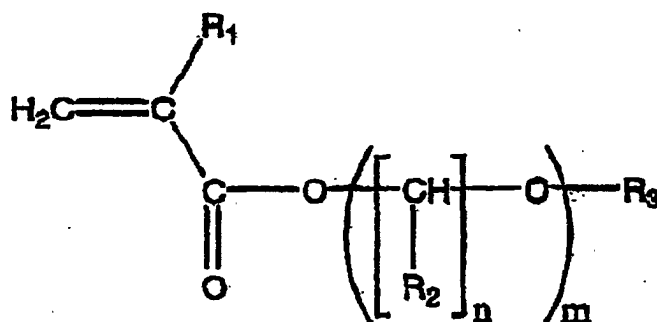
40. A resin composition for recording as claimed in claim 35 or 37, characterized in that said weak solvent (K) for said cellulose derivative is at least one kind selected from esters, alcohols, ketones and ethers, and a boiling point of the solvent is 100-300°C.

41. A resin composition for recording as claimed in claim 35, characterized in that said good solvent (I) for said cellulose derivative is at least one kind selected from a C_{1-5} dialkyl ketone, a C_{1-4} alkyl acetate, a C_{4-6} acrylic or linear ether, and a C_{1-4} alkylcellulose and a C_{1-4} alkylcellulose acetate, and said weak solvent (K) for said cellulose derivative is at least one kind selected from a C_{5-8} alkyl formate, a C_{1-4} alkyl benzoate, a C_{4-8} cycloalkanol, a C_{6-10} dialkyl ketone, and a C_{6-10} ether.

42. A resin composition for recording as claimed in claim 35 or 41, characterized in that the difference (TK-TI) of a boiling point between said good solvent (I) and said weak solvent (K) for the cellulose derivative is 10°C<(TK-TI)<200°C.

43. A resin composition for recording as claimed in claim 35 or 39, characterized in that solubility of said organic acid (J) to water is not more than 2 g/100 ml at 20°C.
44. An ink-jet recording sheet characterized in that there is employed a resin composition for an ink-jet recording sheet as claimed in any one of claims 1-43, and an image-receiving layer is formed over at least one surface of a base material.
45. An ink-jet recording sheet as claimed in claim 44, wherein glossiness (60° gloss measured according to JIS Z8741) is not less than 30% in the surface of said ink-receiving layer.
46. A resin composition for a heat transfer sheet containing a polymer (L) containing monomer units shown by formula (14) described below and a hot-melt adhesive resin (M).

Formula (14)



R₁: -H or -CH₃

R₂: -H, -CH₃ or -OH

n is 1-5, and m is 1-20,

a plurality of R₂ may be identical to or different from each other, and m pieces of -(CHR₂)_nO- may be combined by random or block.

47. A resin composition for a heat transfer sheet as claimed in claim 46, wherein said polymer (L) is constructed by a copolymer of a monomer of formula (14) with at least one kind monomer selected from a monomer containing a cationic functional group, a monomer containing a crosslinkable group, and a monomer containing a hydrophilic group.
48. A resin composition for a heat transfer sheet as claimed in claim 46 or 47, wherein the content of the monomer of formula (14) is 1-40% by weight based on total monomers in said polymer (L).
49. A resin composition for a heat transfer sheet as claimed in claim 47, wherein said monomer containing a cationic functional group is at least one kind selected from a monomer having a group composed of a tertiary amino group or a salt thereof, a monomer having a quaternary ammonium basic group, and a monomer which forms a quaternary ammonium basic group, said monomer containing a hydrophilic group is at least one kind selected from a monomer having a group composed of carboxylic group or a salt thereof, a monomer having an acid anhydride group, a monomer having hydroxyl group, a monomer having a group composed of sulphonic group or a salt thereof, a monomer having amide group, and a monomer having ether group, and said monomer having a crosslinkable group is at least one kind selected from a monomer having an epoxy group, a monomer having a methylol group, and a monomer having silyl group or an alkoxysilyl group.
50. A resin composition for a heat transfer sheet as claimed in any one of claims 46-48, wherein T_g is -85 to 30°C in said copolymer which constructs said polymer (L).
51. A resin composition for a heat transfer sheet as claimed in claim 46, wherein said hot-melt adhesive resin (M) is at least one kind selected from a nylon-based resin, a polyester-based resin, and a polyurethane-based resin.

52. A resin composition for a heat transfer sheet as claimed in claim 46, wherein a proportion of said hot-melt adhesive resin (M) is 10-1500 parts by weight based on 100 parts by weight of said polymer (L).

5 53. A heat transfer sheet, which is a sheet in which an ink-receiving layer being strippable from a base material is formed at one surface of the base material, wherein said ink-receiving layer is constructed by a resin composition for a heat transfer sheet as claimed in any one of claims 46-52.

10 54. A heat transfer sheet as claimed in claim 53, wherein said ink-receiving layer is formed on a base material through a protecting layer which is strippable from said base material.

15 55. A heat transfer sheet as claimed in claim 54, wherein said protecting layer is constructed by at least one kind selected from a thermoplastic resin, a thermosetting resin, and an elastomer.

20 56. A heat transfer sheet as claimed in claim 53 or 54, wherein said ink-receiving layer contains at least one component of a dye-fixing agents and a plasticizer.

25 57. A method for the preparation of a heat transfer sheet by forming an ink-receiving layer through coating a solution of a material which forms the ink-receiving layer which is capable of being stripped from a base material, wherein said ink-receiving layer is constructed by a resin composition as claimed in any one of claims 46-56.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03611

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ B41M5/00, B41M5/38~5/40, C08J7/04, D21H27/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ B41M5/00, B41M5/38~5/40, C08J7/04, D21H27/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 11-29738, A (Takamatsu Yushi K.K.), 02 February, 1999 (02.02.99), Full text & WO, 99/02350, A1 & EP, 995609, A1	1-34
Y	EP, 896883, A1 (DAICEL CHEMICAL INDUSTRIES CO., LTD), 17 February, 1999 (17.02.99), Full text & JP, 10-264511, A Full text & CN, 1213343, A	1-34
Y	JP, 10-195375, A (Takamatsu Yushi K.K.), 28 July, 1998 (28.07.98), Full text (Family: none)	1-34
Y	JP, 10-309874, A (Daicel Chemical Industries, Ltd.), 24 November, 1998 (24.11.98), Full text (Family: none)	1-34
	JP, 9-165552, A (Takamatsu Yushi K.K.), 24 June, 1997 (24.06.97),	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 29 August, 2000 (29.08.00)		Date of mailing of the international search report 05 September, 2000 (05.09.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03611

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Full text (Family: none)	1-34
Y	JP, 5-229246, A (Takamatsu Yushi K.K.), 07 September, 1993 (07.09.93), Full text (Family: none)	1-34
Y	JP, 10-309865, A (Daicel Chemical Industries, Ltd.), 24 November, 1998 (24.11.98), Full text (Family: none)	21,22,27,30
Y	JP, 4-201286, A (Toray Industries, Inc.), 22 July, 1992 (22.07.92), Full text (Family: none)	31
Y	EP, 896883, A1 (SCHOELLER TECHNICAL PAPERS, INC.), 17 February, 1999 (17.02.99), Full text & JP, 10-114146, A Full text & DE, 19623432, A1	35-44
Y	JP, 9-76626, A (BANDO CHEMICAL INDUSTRIES LTD), 25 March, 1997 (25.03.97), Full text; all drawings (Family: none)	35-44
Y	JP, 11-138980, A (Daicel Chemical Industries, Ltd.), 25 May, 1999 (25.05.99), Full text (Family: none)	46-57
Y	JP, 1178269, A (Daicel Chemical Industries, Ltd.), 23 March, 1999 (23.03.99) Full text (Family: none)	46-57
Y	JP, 9-169085, A (Daicel Chemical Industries, Ltd.), 30 June, 1997 (30.06.97) Full text (Family: none)	46-57

Form PCT/ISA/210 (continuation of second sheet) (July 1992)