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(54) **PROCESS FOR PRODUCING INK-JET RECORDING SHEET**

(57) A process for producing an ink-jet recording sheet according to the present invention contains: a first step in which a crosslinking-agent-containing coating-fluid containing a crosslinking agent and a surfactant is applied on a support and dried to form a crosslinking-agent-containing layer; and a second step in which an ink-re-

ceiving-layer-formable coating-fluid containing inorganic fine particles and a water-soluble resin crosslinkable with the crosslinking agent is applied on the crosslinking-agent-containing layer to form an ink-receiving layer.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a process for producing a recording sheet which is available in an ink-jet recording system.

[0002] Priority is claimed on Japanese Patent Application No. 2005-169453, filed on June 9, 2005, and Japanese Patent Application No. 2006-083176, filed on March 24, 2006, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] Ink jet recording systems in which water-based ink is ejected to a recording sheet through a nozzle having fine pores to form an image on the surface of the recording sheet are widely used in terminal printers, facsimiles, plotters, sheet feeding printers, or the like, due to their low noise during recording, ease of forming full-color images, possibility of performing rapid recording, lower cost than other printers, and so forth.

[0004] On the other hand, it is required that an ink-jet recording sheet is made to have a high grade of characteristics so as to meet rapid spread, enhanced detail, and speedup of printers, and also to meet an appearance of digital cameras. That is, an ink jet recording sheet which can realize high-speed ink absorption, high recording density, excellent water-resistance, and excellent light-resistance, and also which can realize an image quality, surface gloss, and storage durability, which are equivalent to those of silver halide photography, has been strongly demanded. Moreover, it is required that the ink-jet recording sheet is made to prevent an ink-receiving layer thereof from being cracked or cracking when folded.

[0005] In order to satisfy the above-mentioned requirements, a process in which a first ink-receiving-layer-formable coating-fluid containing fine particles and a water-soluble resin is applied on a support to form an inside ink-receiving layer, a crosslinking-agent-containing coating-fluid containing a borax in an amount of 1.4% by mass or less is applied on the inside ink-receiving layer, and then a second ink-receiving-layer-formable coating-fluid is applied thereon to form an outside ink-receiving layer has been proposed (see Patent Document 1). In accordance with this process, the borax makes the water-soluble resin in the outside ink-receiving layer crosslinked, as a result of which the surface strength (hereinafter, abbreviated "strength") of the ink-receiving layer is enhanced, and thereby the cracking and fold-cracking thereof are prevented. Also, other requirements can be satisfied by the inside ink-receiving layer.

[0006] However, the process for producing an ink-jet recording sheet disclosed in Patent Document 1 requires many steps composed of at least the three steps of forming the inside ink-receiving layer, applying the crosslinking-agent-containing coating-fluid, and forming the outside ink-receiving layer.

[0007] Accordingly, in order to simplify the steps, it is supposed that a crosslinking-agent-containing coating-fluid is directly applied on a support, and then an ink-receiving-layer-formable coating-fluid is applied thereon. For example, Patent Document 2 discloses a process in which a crosslinking-agent-containing coating-fluid is directly applied on a support to form a monolayered ink-receiving layer.

Patent Document 1: Japanese Laid-Open Patent Application, No. 2004-74576.

Patent Document 2: Japanese Laid-Open Patent Application, No. 2001-246832.

DISCLOSURE OF THE INVENTION

[Problems to be Solved by the Invention]

[0008] In order to form a monolayered ink-receiving layer while realizing sufficient ink-acceptability, it is required that the ink-receiving layer be thick. In order to provide the sufficient strength to such a thick ink-receiving layer, it is required that the coating amount of the crosslinking-agent-containing coating-fluid be increased. Although the coating amount of the crosslinking-agent-containing coating-fluid is required to be increased, such an increase of the coating amount is difficult when the crosslinking-agent-containing coating-fluid is directly applied on the support, since the solubility of the crosslinking agent is low.

[0009] In particular, if the support is an impermeable support, the crosslinking-agent-containing coating-fluid does not penetrate through the support. Accordingly, it is conventionally impossible for the crosslinking agent to be applied in an amount of 0.1 g/cm² or more, and therefore it is difficult for the thick ink-receiving layer to be made to have a sufficient strength. Moreover, cissing of the crosslinking-agent-containing coating-fluid tends to occur on the surface of an impermeable support. Accordingly, if the crosslinking-agent-containing coating-fluid is directly applied on the support, it is difficult for the coating amount thereof to be increased and the crosslinking-agent-containing coating-fluid be uniformly applied.

[0010] The present invention has as an object thereof to provide a process for producing an ink-jet recording sheet by which a monolayered thick ink-receiving layer with a sufficient strength can form, more specifically, a process for producing an ink-jet recording sheet by which the occurrence of cissing of a crosslinking-agent-containing coating-fluid on the surface of a support is prevented to allow uniform application of the crosslinking-agent-containing coating-fluid in an amount required to provide sufficient strength to the ink-receiving layer when the crosslinking-agent-containing coating-fluid is directly applied on the impermeable support and then an ink-receiving-layer-formable coating-fluid is applied thereon.

[Means for Solving the Problems]

[0011] As a result of investigations carried out so as to solve the above-mentioned problems, the inventors of the present invention have found that a crosslinking-agent-containing coating-fluid is prevented from being repelled on a support by adding a surfactant thereto, as a result of which the coating amount of a crosslinking agent can be increased.

[0012] Moreover, the inventors of the present invention have found that occurrence of cissing of the crosslinking-agent-containing coating-fluid on the surface of an impermeable support is further prevented by adding thereto the surfactant and a viscosity modifier which increases the viscosity of the mixture, and the uniformity of the coating surface of the crosslinking-agent-containing layer can be improved, and also the coating amount of the crosslinking agent can be increased.

[0013] In accordance with these findings, the following process for producing an ink-jet recording sheet has been invented.

[0014] That is, a first aspect of the process for producing an ink-jet recording sheet according to the present invention is characterized by including: a first step in which a crosslinking-agent-containing coating-fluid containing a crosslinking agent and a surfactant is applied on a support and dried to form a crosslinking-agent-containing layer; and a second step in which an ink-receiving-layer-formable coating-fluid containing inorganic fine particles and a water-soluble resin crosslinkable with the crosslinking agent is applied on the crosslinking-agent-containing layer to form an ink-receiving layer.

[0015] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the crosslinking-agent-containing coating-fluid be applied in the first step so that the coating amount of the crosslinking agent in solid basis is 0.1 to 3.0 g/m².

[0016] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that a coating amount of the inorganic fine particles in the crosslinking-agent-containing layer be 1.0 g/m² or less.

[0017] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the crosslinking agent be a boric acid and/or a borax.

[0018] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the surfactant be a nonionic surfactant.

[0019] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that a content of the surfactant in the crosslinking-agent-containing coating-fluid be 0.001 to 10 parts by mass with respect to 100 parts by mass of the crosslinking agent.

[0020] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the water-soluble resin be a polyvinyl alcohol.

[0021] In the first aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the support be an impermeable support.

[0022] In the case where the support is an impermeable support, it is preferable that the ink-receiving-layer-formable coating-fluid be applied in the second step so that a coating amount of the ink-receiving layer is 10 to 40 g/m².

[0023] A second aspect of the process for producing an ink-jet recording sheet according to the present invention is a process for producing an ink-jet recording sheet characterized by including a first step in which a crosslinking-agent-containing coating-fluid having a viscosity of 2 to 20 mPa·s is applied on an impermeable support to form a crosslinking-agent-containing layer, the crosslinking-agent-containing coating-fluid containing a crosslinking agent, a viscosity modifier, and a surfactant; and a second step in which an ink-receiving-layer-formable coating-fluid is applied on the crosslinking-agent-containing layer to form an ink-receiving layer, the ink-receiving-layer-formable coating-fluid containing inorganic fine particles and a water-soluble resin crosslinkable with the crosslinking agent.

[0024] In the second aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the crosslinking agent contain a boric acid and/or a borax and the water-soluble resin contain a polyvinyl alcohol.

[0025] In the second aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that the viscosity modifier contain at least one selected from the group consisting of a gelatin, a cationized cellulose, a carboxymethyl cellulose, a hydroxyethyl cellulose, and a hydroxypropylmethyl cellulose.

[0026] In the second aspect of the process for producing an ink-jet recording sheet according to the present invention, it is preferable that a drying step be further performed in the first step after the crosslinking-agent-containing coating-fluid is applied to form the crosslinking-agent-containing layer.

[Effects of the Invention]

[0027] In accordance with the process for producing an ink-jet recording sheet according to the present invention, the crosslinking-agent-containing coating-fluid is prevented from being repelled on the support, and therefore the coating amount of the crosslinking-agent-containing coating-fluid can be increased, and a monolayered ink-receiving layer with an ensured strength can be formed.

BEST MODE FOR CARRYING OUT THE INVENTION

[0028] In the following, the first aspect of the process for producing an ink-jet recording sheet according to the present invention will be explained in detail.

(First Step)

[0029] In the first step of this aspect, a crosslinking-agent-containing coating-fluid is applied on a support, and then dried to form a crosslinking-agent-containing layer. The crosslinking-agent-containing coating-fluid is a liquid containing a crosslinking agent and a surfactant. As a solvent in the crosslinking-agent-containing coating-fluid, water, a water-based solvent in which an organic solvent is added to water in a small amount, or the like is exemplified.

[Support]

[0030] Although any of permeable supports and impermeable supports may be used as the support, the impermeable supports are preferably used. The reason for this is that if the impermeable support is used, the occurrence of what is referred to as cockling, in which a recording sheet is stretched and waved due to the influence of a moisture component of the solvent in ink when printing is performed, can be prevented. However, since the impermeable support cannot absorb ink, it is required that the ink-receiving layer exhibit a sufficient ink-absorptivity.

[0031] Also, the support may be permeable or impermeable. Moreover, the support may be transparent or opaque.

[0032] Examples of the support include: films of cellophane, polyethylene, polypropylene, soft polyvinyl chloride, hard polyvinyl chloride, polyester or the like; paper such as high-quality paper, art paper, coated paper, cast-coated paper, foil paper, craft paper, paper coated with a polyolefin resin, impregnated paper, vapor deposition paper, water-soluble paper, and the like; sheets such as metal foil, synthetic paper, and the like. In order to obtain an ink-jet recording sheet with a photograph-tone, art paper, coated paper, baryta paper, raw paper for photographic paper, synthetic paper, or paper coated with a polyolefin resin is preferably used. Among them, synthetic paper or paper coated with a polyethylene resin is preferably used. In particular, a paper coated with a polyethylene resin in which titanium oxide is incorporated, referred to as RC paper, is preferably used as a support, since a finished appearance equivalent to that of photographic paper is realized. Moreover, if the RC paper is used as a support, effects of this aspect are significantly realized. In order to suppress the glossiness of an obtained ink-jet recording sheet, the surface of the support may be roughed.

[0033] In the paper coated with a polyethylene resin, the thickness of a polyethylene layer is preferably within the range of 3 to 50 μm , more preferably 5 to 30 μm . If the thickness of the polyethylene layer is less than 3 μm , there tends to occur an undesirable phenomenon such that holes being generated in applying the polyethylene resin, and thereby adjusting the thickness and smoothening polyethylene layer tends to be difficult. On the other hand, if the thickness is more than 50 μm , the realized effects are small in comparison with the cost-increase, which is not economical.

[Crosslinking Agent]

[0034] Examples of the crosslinking agent contained in the crosslinking-agent-containing coating-fluid include boron compounds, epoxy compounds, glycidyl compounds, zirconium compounds, aluminum compounds, chrome compounds, and the like. Among these crosslinking agents, the boron compounds, more preferably boric acid and/or borax, are preferable, because the viscosity-increase or gelation rapidly proceeds when used in combination with polyvinyl alcohol.

[0035] Examples of the boric acid include an orthoboric acid, metaboric acid, hypoboric acid, tetraboric acid, pentaboric acid, and the like, and sodium salts, potassium salts, and ammonium salts thereof. Among them, an orthoboric acid and disodium tetraborate are preferable.

[0036] The borax is a mineral of sodium borate hydrate and is formulated as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In this structure, $\text{Na}_2\text{B}_4\text{O}_7$ (disodium tetraborate) is a component which serves as the crosslinking agent.

[Surfactant]

[0037] As the surfactant contained in the crosslinking-agent-containing coating-fluid, any of anionic surfactants, cationic surfactants and nonionic surfactants may be used.

[0038] As the anionic surfactants, sulfuric ester salt-based surfactants, sulfonate-based surfactants, phosphate-based surfactants, or the like, may be used, for example.

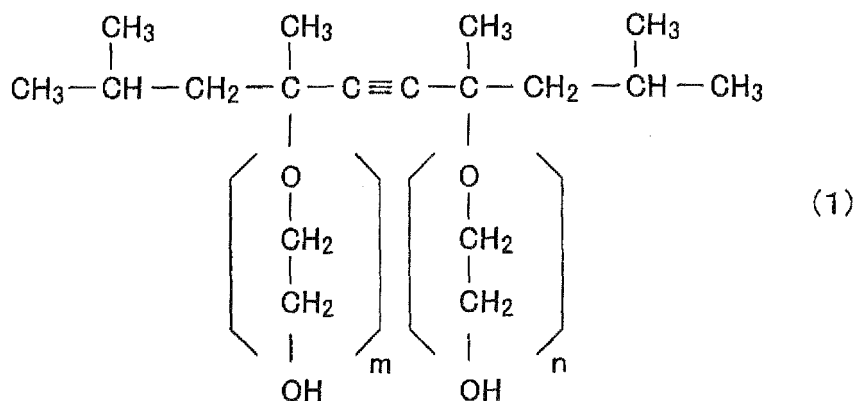
[0039] As the cationic surfactants, amine salt-based surfactants, tetraammonium salt-based surfactants, or the like, may be used, for example.

[0040] As the nonionic surfactants, acetylene glycol-based surfactants, polyethylene glycol-based surfactants (such as ethylene oxide adducts of higher alcohols, ethylene oxide adducts of fatty acids, ethylene oxide adducts of alkylphenols, ethylene oxide adducts of polypropylene glycols, ethylene oxide adducts of higher aliphatic amines or fatty acid amides, or the like), polyhydric alcohol-based surfactants (such as fatty acid esters of glycerin and pentaerythritol, fatty acid esters of sorbitol and sorbitan, fatty acid esters of sucrose, ethylene oxide adducts of polyhydric alcohols, fatty acid alkanolamides, or the like), or the like, may be used, for example.

[0041] Among the above-mentioned surfactants, the nonionic surfactants, more preferably the acetylene glycol-based surfactants, are preferable, since they exhibit high compatibility with ink used for recording with an ink-jet printer.

[0042] Although the acetylene glycol-based surfactants are nonionic, they have extremely strong polarity, since adjacent carbon atoms forming an acetylenic triple bond are bonded to each oxygen atom. Accordingly, high surface activating effects are realized and the wettability of the crosslinking-agent-containing coating-fluid with respect to the support is improved even with a small amount of the acetylene glycol-based surfactants. Since surfactants have generally high bubble-forming properties, the surfactants tend to cause a bubbling phenomenon. However, the acetylene glycol-based surfactants have anti-foaming properties, and therefore the occurrence of the bubbling phenomenon can be prevented.

[0043] The acetylene glycol-based surfactants are compounds having in the molecule thereof an acetylene bond and an alcoholic hydroxy group, and addition reaction products of alkynylene glycol compounds with ethylene oxide are preferable among them. Particularly preferable acetylene glycol-based surfactants are compounds obtained by adding ethylene oxide to 2,4,7,9-tetramethyl-5-decyl-4,7-diol, the compounds being having a chemical structure represented by the following formula (1). Among them, it is preferable that the sum of m and n in the formula (1) be 6 or less, more preferably 2 to 5. Although m and n each represents an integer, the average thereof may not be an integer.



[0044] The concentration of the crosslinking agent in the crosslinking-agent-containing coating-fluid is preferably 0.001 to 20% by mass. If the concentration of the crosslinking agent is 0.001% by mass or more, a water-soluble resin described below is sufficiently crosslinked by the crosslinking agent. On the other hand, if the concentration of the crosslinking agent is 20% by mass or less, excess crosslinking can be prevented.

[0045] The content of the surfactant in the crosslinking-agent-containing coating-fluid is preferably 0.001 to 10 parts by mass, with respect to 100 parts by mass of the crosslinking agent. If the content of the surfactant with respect to 100 parts by mass of the crosslinking agent is 0.001 parts by mass or more, the wettability of the crosslinking-agent-containing coating-fluid with respect to the support can be sufficiently realized. On the other hand, if the content of the surfactant is 10 parts by mass or less, problems such as blocking after coating or transition to the rear surface hardly occur.

[Coating Method]

[0046] In order to apply the crosslinking-agent-containing coating-fluid to the support, a blade coater, air knife coater, roll coater, bar coater, gravure coater, rod blade coater, lip coater, die coater, curtain coater, slide bead coater, or the like, may be used, for example.

[0047] It is preferable that the crosslinking-agent-containing coating-fluid be applied so that the coating amount of the crosslinking agent in solid basis is 0.1 to 3.0 g/m². If the coating amount of the crosslinking agent in solid basis is 0.1 g/m² or more, the strength and water-resistance can be sufficiently provided to the ink-receiving layer. On the other hand, if the coating amount of the crosslinking agent in solid basis is 3.0 g/m² or less, excess crosslinking of the water-soluble resin can be prevented and fold-cracking of the ink-receiving layer can be prevented.

[Drying Method]

[0048] Drying methods are not particularly limited, and drying with hot air, drying by radiating infrared rays, or the like, may be performed, for example. At the step of drying the applied crosslinking-agent-containing coating-fluid, it is not required that the solvent contained therein be completely removed, and the solvent may remain provided that the crosslinking agent is crystallized.

[0049] It is preferable that the coating amount of the inorganic fine particles in the crosslinking-agent-containing layer be 1.0 g/m² or less, and it is more preferable that no inorganic fine particles be contained. If the coating amount of the inorganic fine particles exceeds 1.0 g/m², the formulation of a binder is required, which makes it difficult for the crosslinking agent to be formulated.

(Second Step)

[0050] After the above-mentioned first step is performed, an ink-receiving-layer-formable coating-fluid containing inorganic fine particles and a water-soluble resin crosslinkable with the crosslinking agent is applied on the crosslinking-agent-containing layer to form an ink-receiving layer in the second step.

[Inorganic Fine Particles]

[0051] Examples of the inorganic fine particles include amorphous silica (such as synthetic amorphous silica prepared by wet-process or dry-process, and cationized silica prepared using alumina or the like), agglomerated particles composed of amorphous silica and a cationic compound, which are prepared by mixing and agglomerating amorphous silica with the cationic compound, kaolin, clay, sintered clay, zinc oxide, tin oxide, titanium oxide, magnesium sulfate, aluminum hydroxide, alumina, alumina hydrate, calcium carbonate, satin white, aluminum silicate, smectite, zeolite, magnesium silicate, magnesium carbonate, magnesium oxide, diatomaceous earth, styrene-based plastic pigment, urea resin-based plastic pigment, benzoguanamine-based plastic pigment, and the like. Among them, amorphous silica, agglomerated particles composed of amorphous silica and a cationic compound, which are prepared by mixing and agglomerating amorphous silica with the cationic compound, aluminosilicate, alumina, or alumina hydrate is preferably used, in that they tend to achieve favorable balance between glossiness and ink-absorptivity.

[0052] The average secondary particle diameter of the inorganic fine particles is preferably 0.7 μm or less, in terms of glossiness.

[Water-soluble Resin]

[0053] Examples of the water-soluble resin crosslinkable with the above-mentioned crosslinking agent include polyvinyl alcohol, cationized polyvinyl alcohol, silyl-modified polyvinyl alcohol, polyvinyl acetal, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, casein, soybean protein, synthetic proteins, starches, polypropylene oxide, polyethylene glycol, polyvinyl ether, polyvinyl acrylamide, polyvinyl pyrrolidone, and the like.

[0054] Among them, polyvinyl alcohol is preferably used in terms of ink-absorptivity, water-resistance, and preventability of cracking. It is preferable that the polyvinyl alcohol has a polymerization degree of 3,000 to 5,000. If the polymerization degree is less than 3,000, the water-resistance of the formed ink-receiving layer tends to be insufficient. In contrast, polyvinyl alcohol with a polymerization degree of more than 5,000 cannot be obtained in practice.

[0055] It is preferable that the water-soluble resin be formulated in an amount of 1 to 100 parts by mass, more preferably 5 to 50 parts by mass, with respect to 100 parts by mass of the inorganic fine particles.

[0056] It is preferable that the mass ratio of the water-soluble resin to the crosslinking agent be between 20:1 and 1:20, more preferably 10:1 and 1:10. If the mass ratio is within the above-mentioned range, an ink-jet recording sheet with excellent preventability of cracking and bleeding over time, and excellent ink-absorptivity can be obtained.

[Other Components]

[0057] The ink-receiving-layer-formable coating-fluid may contain various adhesives generally used in the art of coating paper, such as, for example, water-dispersible resins (such as, for example, conjugated-diene-based polymer latexes, such as styrenebutadiene copolymers, or methyl methacrylate-butadiene copolymers, acrylic polymer latexes, or vinyl-based copolymer latexes such as styrene-vinyl acetate copolymers), provided that the object of the present aspect is achieved.

[0058] Also, the ink-receiving-layer-formable coating-fluid may contain a cationic compound. Examples of the cationic compound include polyalkylene polyamines such as, for example, polyethyleneamines or polypropylene polyamines, derivatives thereof, acrylic resins having a tertiary amino group or a quaternary ammonium group, diacrylic amines, and the like. It is preferable that the content of the cationic compound be 1 to 30 parts by mass, more preferably 5 to 20 parts by mass, with respect to 100 parts by mass of the inorganic fine particles.

[0059] Moreover, the ink-receiving-layer-formable coating-fluid may contain various auxiliaries such as, for example, dispersants, thickeners, antifoaming agents, coloring agents, antistatic agents, or antiseptics.

[Coating Method and Drying Method]

[0060] As a method for applying the ink-receiving-layer-formable coating-fluid on the crosslinking-agent-containing layer and a method for drying the applied ink-receiving-layer-formable coating-fluid, the same method as that for coating the crosslinking-agent-containing coating-fluid and drying the same may be adopted.

[0061] In the case where the support is an impermeable support, the ink-receiving-layer-formable coating-fluid is preferably applied so that the coating amount of the ink-receiving layer be 10 to 40 g/m². In the case where the support is a permeable support, the ink-receiving-layer-formable coating-fluid is preferably applied so that the coating amount of the ink-receiving layer be 5 to 25 g/m². If the coating amount is the above-mentioned lower limit or more, sufficient ink-absorptivity and image-quality can be realized. If the coating amount is the above-mentioned upper limit or less, cracking of the ink-receiving layer can be prevented. If the coating amount is within the above-mentioned range, image-quality equivalent to that of silver halide photography can be realized.

[Glossy Layer]

[0062] In the present aspect, a glossy layer containing fine particles may be formed on the ink-receiving layer so as to increase glossiness. Although the fine particles in the glossy layer are not particularly limited, colloidal silica, fumed silica, or alumina is preferably used, in that they contribute to the realization of an excellent glossiness.

[0063] Since the glossy layer has as the main object thereof to provide glossiness, the glossy layer may not have dye-fixing capabilities. However, the dye-fixing capabilities can be enhanced by formulating cationic fine particles. As the cationic fine particles, cationized colloidal silica, fumed silica, or alumina is preferably used. Among the alumina, fumed alumina is particularly preferable.

[0064] It is preferable that the fine particles be in the colloidal form. Although the fine particles may be monodispersing particles or agglomeratingly dispersing particles, monodispersing particles or agglomeratingly dispersing particles with a small particle diameter are mainly preferably used so that high printing density and high glossiness are realized. In more detail, it is preferable that the fine particles be selected from those with an average primary particle diameter of 3 to 100 nm and an average (secondary) particle diameter of 700 nm or less.

[0065] The glossy layer may suitably contain the above-mentioned water-soluble resin, provided that the ink-absorptivity is not degraded. Also, the glossy layer may contain the above-mentioned cationic compound, as needed.

[0066] As a method for forming the glossy layer, a casting method in which a glossy-layer-formable coating-fluid containing fine particles and a solvent is applied on an ink-receiving layer, and the applied coating-fluid in a wet state is pressed against a heated mirrored drum to dry may be adopted, for example. The glossy-layer-formable coating-fluid may suitably contain various mold release agents so as to enhance the releaseability thereof from the mirrored drum. It is preferable that the mold release agent be formulated in an amount of 0.5 to 10 parts by mass, with respect to 100 parts by mass of the fine particles.

[0067] If the support is an air-impermeable support or a low-air-permeable support, it is preferable that the glossy-layer-formable coating-fluid be dried using a drier during a post-process, immediately after the glossy-layer-formable coating-fluid is applied, or during the application of the glossy-layer-formable coating-fluid while pressing it against the mirrored drum (for example, nipping as shown in International Publication No. 03/039881 pamphlet).

[0068] It is preferable that the coating amount of the glossy-layer-formable coating-fluid in solid basis be 0.1 to 10 g/m², more preferably 0.2 to 5 g/m², even more preferably 0.5 to 2 g/m². If the coating amount is extremely small, the coating film tends to be thin, which causes interference color by light. On the other hand, if the coating amount is extremely great, there is a possibility in which the ink-absorbing rate significantly decreases and the transparency decreases.

[0069] In accordance with the process for producing an ink-jet recording sheet as described above, since the crosslinking-agent-containing coating-fluid to be applied on the support contains the surfactant, the crosslinking-agent-containing coating-fluid is hardly repelled on the support. Accordingly, the crosslinking-agent-containing layer containing a great amount (0.1 g/m² or more) of the crosslinking agent can be formed. When the ink-receiving-layer-formable coating-fluid is applied on the crosslinking-agent-containing layer, the crosslinking-agent-containing layer is dissolved by the solvent contained in the ink-receiving-layer-formable coating-fluid, and thereby the dissolved crosslinking agent is transferred into the ink-receiving-layer-formable coating-fluid. As a result, the water-soluble resin in the ink-receiving layer is crosslinked. Even if the ink-receiving layer is thick, the water-soluble resin can be sufficiently crosslinked due to the presence of the great amount of the crosslinking agent in the crosslinking-agent-containing layer. Accordingly, the sufficient strength of the ink-receiving layer is realized. Thus, a monolayered thick ink-receiving layer with a sufficient strength can be formed in accordance with the above-mentioned production process.

[0070] Since the crosslinking-agent-containing layer is dissolved when the ink-receiving-layer-formable coating-fluid is applied, the crosslinking-agent-containing layer does not distinguishably exist in the obtained ink-jet recording sheet. That is, the ink-jet recording sheet obtained in accordance with the production process has a structure in which the ink-receiving layer is formed on the support.

[0071] Next, the second aspect of the process for producing an ink-jet recording sheet according to the present invention will be explained in detail.

<First Step>

[0072] In the first step of the present aspect, a crosslinking-agent-containing coating-fluid is applied on an impermeable support to form a crosslinking-agent-containing layer.

[Support]

[0073] The impermeable support used in the present aspect is a sheet through which moisture content does not infiltrate, more specifically a sheet which results in the mass change of 0.1 g or less between before and after the sheet is made to contact with water in a water-absorption test in which 50 ml of water is made to contact with the surface of the support on which the crosslinking-agent-containing coating-fluid is to be applied, the mass of the support being previously measured, so that the contact area is 100 cm², and then held in that situation for 10 seconds, followed by removing water from the support, wiping out water on the surface completely by slightly pressing down blotting paper thereon, and then measuring the mass of the support.

[0074] Examples of the impermeable support (hereinafter, may be abbreviated as a support) include: film of cellophane, polyethylene, polypropylene, soft polyvinyl chloride, hard polyvinyl chloride, polyester or the like; resin-coated paper of which a base material such as paper is coated with polyolefin such as, for example, polyethylene, or polypropylene; synthetic paper prepared by drawing polypropylene so that voids are formed inside thereof; and sheets such as, for example, metal-foil paper. The support is suitably selected from the above-mentioned examples depending on a method for forming an ink-receiving layer or a glossy layer thereon or intended use thereof.

[0075] Among the above-mentioned supports, synthetic paper or resin-coated paper is preferable in order to obtain an ink-jet recording sheet with a photograph-tone. In particular, a support composed of paper coated with resin in which titanium oxide is kneaded, that is, so-called RC paper, is preferably used, since a finished appearance equivalent to that of photographic paper is realized.

[0076] As the synthetic paper, synthetic paper prepared by extruding a polypropylene resin containing an inorganic pigment such as, for example, calcium carbonate, followed by subjecting to biaxial orientation, is preferably used, and synthetic paper with a skin layer free from roughness on the surface thereof is particularly preferable.

[0077] In order to obtain an ink-jet recording sheet with a suppressed glossiness, the surface of the support may be roughened.

[0078] In the case where the support is resin-coated paper of which a base material is coated with a polyethylene layer, it is preferable that the coating amount of the polyethylene layer be 3 to 50 g/m², more preferably 5 to 30 g/m². If the coating amount of the polyethylene layer is less than 3 g/m², defects such as holes occurring in the polyethylene when coating the resin tend to occur, the control of thickness tends to be difficult, and smoothness tends not to be realized. On the other hand, if the coating amount exceeds 50 g/m², exhibited effects are small in comparison with cost-increase, which is not economical.

[0079] Also, it is preferable that corona discharge treatment be provided on the surface of the resin layer, or an anchor coat layer be formed on the surface or the resin layer in order to enhance adhesive properties with respect to an ink-receiving layer.

[0080] In the case where paper is used as a base material of the above-mentioned resin-coated paper, paper prepared using wood pulp as the main raw material thereof is preferably used as the paper base material. As the wood pulp,

various chemical pulp, mechanical pulp, regenerated pulp, or the like, may be suitably used. The beating degree of the pulp may be adjusted using a beater so as to adjust paper strength, smoothness, paper making suitability, or the like. Although the beating degree is not particularly limited, it is generally preferable that the beating degree be approximately within the range of 250 to 550 ml (CSF: JIS-P-8121). Also, chlorine-free pulp, such as so-called ECF pulp, TCF pulp, or the like, may be preferably used.

[0081] Moreover, a pigment may be formulated in the wood pulp, as needed. As the pigment, a talc, calcium carbonate, clay, kaolin, sintered kaolin, silica, zeolite, or the like, may be preferably used. The formulated pigment contributes to increasing the opacity or smoothness. However, there is a case in which an excessively formulated pigment degrades the paper strength. Accordingly, it is preferable that the formulation amount of the pigment with respect to the wood pulp be approximately 1 to 20% by mass.

[0082] The color of the support may be modified using a fluorescent brightening agent such as a fluorescent dye, fluorescent pigment, or the like. Also, an antistatic layer may be formed on the support. The support may be transparent or opaque.

[Crosslinking-agent-containing Coating-fluid]

[0083] The crosslinking-agent-containing coating-fluid is a liquid containing a crosslinking agent, viscosity modifier, and surfactant, and the viscosity thereof is 2 to 20 mPa·s. The viscosity of the crosslinking-agent-containing coating-fluid of the present aspect is measured at a liquid temperature of 23°C using a B-type viscometer BL-model, manufactured by TOKI SANGYO CO., LTD. If the viscosity of the crosslinking-agent-containing coating-fluid is 2 mPa·s or more, the occurrence of cissing of the crosslinking-agent-containing coating-fluid on the surface of the support is prevented, and a sufficient amount of the crosslinking-agent-containing coating-fluid can be uniformly applied. Also, even if hot-air drying is performed, the phenomenon in which the hot-air causes a ripple on the coating face is prevented, and thereby rapid-drying is realizable. On the other hand, if the viscosity of the crosslinking-agent-containing coating-fluid is 20 mPa·s or less, a uniform crosslinking-agent-containing layer with a smoothness can be easily formed.

[0084] The viscosity of the crosslinking-agent-containing coating-fluid is more preferably 5 to 10 mPa·s.

[Crosslinking Agent]

[0085] As the crosslinking agent formulated in the crosslinking-agent-containing coating-fluid, the same crosslinking agent exemplified in the above-mentioned first aspect may be preferably used in the same concentration of that of the first aspect.

[Viscosity Modifier]

[0086] The viscosity modifier is not particularly limited, provided that it can increase the viscosity of the crosslinking-agent-containing coating-fluid, and examples thereof include a gelatin, biogums, cellulose derivatives, guar gums, sodium alginates, polyacrylic acids, and the like.

[0087] Examples of the biogums include a xanthan gum, welan gum, gellan gum, and the like. Examples of the cellulose derivatives include a cationized cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose, hydroxypropyl cellulose, ethyl cellulose, and the like. Examples of the guar gums include a guar gum, hydroxypropylated guar gum, cationized guar gum, and the like.

[0088] Among these, it is preferable that the viscosity modifier contain at least one selected from the group consisting of a gelatin, cationized cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, and hydroxypropylmethyl cellulose.

[0089] The cellulose derivatives are preferable in that a favorable balance in which the viscosity of the crosslinking-agent-containing coating-fluid is relatively high and the gelation strength thereof is relatively low is realized.

[0090] It is preferable that the polymerization degree of the cellulose derivatives be 500 to 2,000, more preferably 800 to 1,800, in that the viscosity-control of the crosslinking-agent-containing coating-fluid is relatively easy.

[0091] In the present aspect, the content of the viscosity modifier in the crosslinking-agent-containing coating-fluid is not particularly limited, provided that the viscosity of the crosslinking-agent-containing coating-fluid is adjusted to be within the determined range. However, in the case where a small amount of a formulated viscosity modifier makes the viscosity of the crosslinking-agent-containing coating-fluid be within the determined range, fine-adjustment of the viscosity is difficult, and therefore such a case is not preferable. On the other hand, in the case where an excessively great amount of a viscosity modifier is formulated, the ink-absorptivity is degraded. Accordingly, it is preferable that the viscosity modifier be formulated in an amount of 1 to 100 parts by mass, with respect to 100 parts by mass of the crosslinking agent.

[Surfactant]

[0092] Formulation of the surfactant in the crosslinking-agent-containing coating-fluid prevents the crosslinking-agent-containing coating-fluid from being repelled on the surface of the impermeable support, and therefore makes it possible for the crosslinking-agent-containing coating-fluid to be sufficiently coated, and realize the evenness of the coating face of the crosslinking-agent-containing layer even if the viscosity of the crosslinking-agent-containing coating-fluid is increased by adding the viscosity modifier.

[0093] As the surfactant, the same surfactant exemplified in the above-mentioned first aspect may be preferably formulated in the same content as that of the first aspect.

[Other Components]

[0094] Although a small amount of inorganic fine particles may be formulated in the crosslinking-agent-containing coating-fluid, it is preferable that no inorganic fine particles be formulated, in a similar manner to that of the first aspect.

[0095] Also, the crosslinking-agent-containing coating-fluid may suitably contain a solvent.

[0096] The crosslinking-agent-containing coating-fluid may be prepared by mixing a crosslinking-agent solution in which the crosslinking agent is dissolved in a solvent, a surfactant solution in which the surfactant is dissolved in a solvent, and a viscosity-modifier solution in which the viscosity modifier is dissolved in a solvent, for example.

[0097] Examples of the solvent include water and water-based solvents in which a small amount of an organic solvent is formulated in water.

[Coating Method]

[0098] As an apparatus used to apply the crosslinking-agent-containing coating-fluid on the support, the same apparatuses exemplified in the first aspect may be used.

[0099] Also, it is preferable that the crosslinking-agent-containing coating-fluid be applied so that the coating amount of the crosslinking agent in solid basis is 0.1 to 3.0 g/m², for the same reasons as those of the first aspect.

[Drying Method]

[0100] After the crosslinking-agent-containing coating-fluid is applied on the support, a drying step in which the solvent in the coating-fluid is thoroughly removed is preferably performed. After the drying step, the resultant may be once wound up for storage.

[0101] The ink-receiving-layer-formable coating-fluid may be applied on a layer of the applied crosslinking-agent-containing coating-fluid (crosslinking-agent-containing layer) without drying the layer. However, in such a case, the water-soluble resin in the ink-receiving layer is crosslinked immediately after the ink-receiving-layer-formable coating-fluid is applied, and thereby a head of a die coater used as an apparatus for applying the ink-receiving-layer-formable coating-fluid may be blocked by crosslinked matter, as a result of which it may be difficult that application thereof is suitably performed.

[0102] The drying method is not particularly limited, and drying with hot air, drying by irradiation of infrared rays, or the like may be adopted.

[0103] Since the crosslinking-agent-containing coating-fluid with a viscosity adjusted to the above-mentioned range is used in the present aspect, the crosslinking-agent-containing coating-fluid on the support is hardly blown away by hot air at the time of drying with hot air, and phenomenon in which the hot-air causes a ripple on the coating face is prevented. Accordingly, intensification of the hot-air is possible to perform rapid-drying.

[0104] If a borax is used as the crosslinking agent, the moisture retention of the crosslinking-agent-containing layer after drying is improved by adjusting the viscosity of the crosslinking-agent-containing coating-fluid to the above-mentioned range, and thereby crystallization of the borax during storing can be prevented.

<Second Step>

[0105] After the crosslinking-agent-containing layer is formed in the first step, an ink-receiving-layer-formable coating-fluid containing a water-soluble resin crosslinkable with the crosslinking agent and inorganic fine particles is applied on the crosslinking-agent-containing layer to form an ink-receiving layer in the second step.

[Inorganic Fine Particles]

[0106] As the inorganic fine particles, the same inorganic fine particles exemplified in the first aspect may be preferably

used.

[Water-soluble Resin]

- 5 **[0107]** As the water-soluble resin crosslinkable with the crosslinking agent, the same water-soluble resin exemplified in the first aspect may be preferably used in the same content as that of the first aspect.

[Other Components]

- 10 **[0108]** The ink-receiving-layer-formable coating-fluid may contain other components described in the first aspect, provided that the objects of the present aspect are achieved.

[Coating Method and Drying Method]

- 15 **[0109]** As a method for applying the ink-receiving-layer-formable coating-fluid on the crosslinking-agent-containing layer and a method for drying the same, the same methods as those of the first aspect may be adopted.

[0110] In the present aspect, although the favorable ink-absorptivity is realized, even if the ink-receiving layer is a monolayer, another ink-receiving layer may be further laminated thereon. Also, a glossy layer may be formed in the same way as that of the first aspect.

- 20 **[0111]** In the second aspect described above, since the viscosity modifier is formulated in the crosslinking-agent-containing coating-fluid applied on the support to adjust the viscosity thereof within the determined range, and also the surfactant is formulated therein, the crosslinking-agent-containing coating-fluid is hardly repelled on the support or carried away, and the favorable coating properties can be realized. Accordingly, the crosslinking-agent-containing layer in which the coating amount of the crosslinking agent is great is uniformly formed by applying a great amount of the crosslinking-agent-containing coating-fluid on the impermeable support. Also, rapid drying is realizable by intensifying drying conditions.

- 25 **[0112]** When the ink-receiving-layer-formable coating-fluid is applied on the crosslinking-agent-containing layer, the crosslinking-agent-containing layer is dissolved by the solvent contained in the ink-receiving-layer-formable coating-fluid, and the dissolved crosslinking agent is transferred into the ink-receiving-layer-formable coating-fluid. As a result, the water-soluble resin in the ink-receiving layer is crosslinked. Since the crosslinking-agent-containing layer contains a great amount of the crosslinking agent, the water-soluble resin can be sufficiently crosslinked and the sufficient strength of the ink-receiving layer can be provided, even if the ink-receiving layer is thick. Accordingly, the thick ink-receiving layer with a sufficient strength can be formed in accordance with the above-mentioned production process.

- 30 **[0113]** Since the crosslinking-agent-containing layer is dissolved as described above when the ink-receiving-layer-formable coating-fluid is applied, the crosslinking-agent-containing layer is indistinguishably present in the obtained ink-jet recording sheet. That is, the ink-receiving layer is formed on the support in the ink-jet recording sheet prepared in accordance with this production process.

Examples

- 40 **[0114]** In the following, the present invention will be explained in more detail by illustrating some examples. However, the present invention is not limited to these. Herein, the terms "parts" and "%" in the examples indicates "parts by mass" and "% by mass", respectively, unless otherwise so indicated.

- 45 (Silica Sol A)

- [0115]** A commercially available fumed silica (manufactured by TOKUYAMA Corp., under the trademark of REOSIL QS-30, with an average primary particle diameter of 10 nm and a specific surface area of 300 m²/g) was dispersed and pulverized in water using a sand mill and then pulverized and dispersed using a nanomizer (manufactured by Nanomizer Co., Ltd., under the trademark of NANOMIZER). These processes were combinationally repeated, and then the obtained dispersion liquid was classified to prepare a 10% silica dispersion liquid with an average secondary diameter of 80 nm. To the silica dispersion liquid, 10 parts of diallyldimethyl ammonium chloride (manufactured by SENKA CORPORATION under the trademark of UNISENCE CP-103) as a cationic compound was added to cause agglomeration of the silica and viscosity-increase of the dispersion liquid, followed by repeatedly performing pulverization and dispersion again using a nanomizer, to obtain an 8% dispersion liquid with an average secondary particle diameter of 300 nm as a silica sol A.

(Support A)

[0116] A needle-leaved tree bleached kraft pulp (NBKP) beaten to 250 ml CSF (JIS P-8121) and a broad-leaved tree bleached kraft pulp (LBKP) beaten to 250 ml CSF were mixed in a mass ratio of 2:8 to prepare a 0.5% pulp slurry. To the pulp slurry, 2.0% of cationized starch, 0.4% of alkyl ketene dimer, 0.1% of anionized polyacrylamide resin, and 0.7% of polyamide polyamine epichlorohydrin resin, with respect to the total dry mass of the pulp, were added, and sufficiently stirred to disperse them.

[0117] The pulp slurry with the above-mentioned components was made into paper using a Fourdrinier machine, passed through a drier, size-presser, and machine calendar to obtain a base paper with a basis weight of 180 g/m² and a density of 1.0 g/cm³. The size-pressing liquid used in the size-pressing step was a 5% solution prepared by mixing a carboxyl-modified polyvinyl alcohol and sodium chloride in a mass ratio of 2:1, followed by adding water to the mixture, and then heating to dissolve them. The size-pressing liquid was applied on both surfaces of the paper in the total amount of 25 ml/m² to obtain a support A (with an air-permeability of 300 seconds).

(Support B)

[0118] Both surfaces of the support A were subjected to corona discharge treatment, and then the felt side of the support A was coated with a polyolefin resin composition 1 mixed and dispersed using a Banbury mixer, as described below, in a coating amount of 25 g/m² using a melt extruder equipped with a T-die (melting temperature: 320°C). The wire side of the support A was coated with a polyolefin resin composition 2 described below in a coating amount of 20 g/m² using the above-mentioned melt extruder. Then, the felt side was cooled and fixed using a cooling roll with a specular surface, and the wire side was cooled and fixed using a cooling roll with a rough surface. Thus, a support B coated with resin, of which the smoothness (Ohken-type, J. TAPPI No. 5) was 6,000 seconds and the opacity (JIS P 8138) was 93%, was obtained.

(Polyolefin Resin Composition 1)

[0119] 35 parts of a linear-chain type low-density polyethylene (with a density of 0.926 g/cm³ and a melt index of 20 g/ 10 minutes), 50 parts of a low-density polyethylene (with a density of 0.919 g/cm³ and a melt index of 2 g/ 10 minutes), 15 parts of anatase-type titanium dioxide (manufactured by ISHIHARA SANGYO KAISHA, LTD., under the trade name of A-220), 0.1 parts of zinc stearate, 0.03 parts of antioxidant (manufactured by Ciba Specialty Chemicals Inc., under the trademark of IRGANOX 1010), 0.09 parts of ultramarine blue (manufactured by DAIICHI KASEI CO., LTD., under the trade name of blue ultramarine blue No. 2000), and 0.3 parts of a fluorescent brightening agent (manufactured by Ciba Specialty Chemicals Inc., under the trademark of UVITEX OB) were mixed to prepare a polyolefin resin composition 1.

(Polyolefin Resin Composition 2)

[0120] 65 parts of a high-density polyethylene (with a density of 0.954 g/cm³ and a melt index of 20 g/ 10 minutes) and 35 parts of low-density polyethylene (with a density of 0.919 g/cm³ and a melt index of 2 g/ 10 minutes) were melted and mixed to prepare a polyolefin resin composition 2.

Example 1 (Application of Crosslinking-agent-containing Coating-fluid)

[0121] 100 parts of an aqueous solution containing 5% borax and 3 parts of an aqueous solution containing 0.1% acetylene glycol-based surfactant (manufactured by Nissin Chemical Co., Ltd., under the trade name of Olfin E1004) were mixed while stirring to obtain a crosslinking-agent-containing coating-fluid. Then, the crosslinking-agent-containing coating-fluid was applied on the support B in a coating amount of 10 g/m² using a Mayer bar and then dried to form a crosslinking-agent-containing layer. The coating amount of the crosslinking agent in solid basis was 0.5g/m².

(Formation of Ink-receiving Layer)

[0122] 100 parts of the silica sol A and 24 parts of an aqueous solution containing 5% polyvinyl alcohol (manufactured by KURARAY CO., LTD., under the trade name of PVA-135H, with a polymerization degree of 3,500 and a saponification degree of 99% or more) were mixed to obtain an ink-receiving-layer-formable coating-fluid A. Then, the ink-receiving-layer-formable coating-fluid A was applied on the crosslinking-agent-containing layer in a coating amount of 22 g/m² using a die coater, and then dried to form an ink-receiving layer. The total thickness of the ink-receiving layer was 37 μm.

Example 2

[0123] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that the support A was used instead of the support B. The total thickness of the ink-receiving layer was 37 μm .

Example 3

[0124] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that a commercially available polypropylene synthetic paper (manufactured by Yupo Corporation under the trademark of YUPO GWG-140) was used instead of the support B. The total thickness of the ink-receiving layer was 37 μm .

Example 4

[0125] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that 100 parts of an aqueous solution containing 10% borax, the aqueous solution being heated at 60°C, was used instead of 100 parts of the aqueous solution containing 5% borax.

Example 5

[0126] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that 170 parts of an aqueous solution containing 3% boric acid was used instead of 100 parts of the aqueous solution containing 5% borax.

Example 6

[0127] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that an alumina sol A described below was used instead of the silica sol A.

[Alumina Sol A]

[0128] A high-purity alumina with an average particle diameter of approximately 3.0 μm (manufactured by Sumitomo Chemical Co., Ltd., under the trade name of AKP-G015, γ -crystalline alumina, with a specific surface area of 150 m^2/g) was dispersed using a sand mill. Then, the resultant was further dispersed using a high speed colliding type homogenizer, repeatedly dispersed using the sand mill and a liquid-colliding type homogenizer until the average particle diameter became 0.25 μm , and then a 10% aqueous dispersion thereof was prepared as the alumina sol A.

Example 7

[0129] An ink-jet recording sheet was prepared in a similar way to that of Example 1, except that a gelatin was applied in a coating amount of 0.3 g/m^2 on the felt-side resin-coating layer of the support B, and then a crosslinking-agent-containing layer was formed thereon.

Example 8

[0130] 100 parts of cationic colloidal silica (manufactured by NISSAN CHEMICAL INDUSTRIES, LTD., under the trademark of Snowtex AK) and 3 parts of distearyl dimethyl ammonium chloride were mixed and then diluted to prepare a 10% silica dispersion liquid. Then, this silica dispersion liquid was applied on the ink-receiving layer of the ink-jet recording sheet prepared in Example 1. While the applied face was in a wet state, the applied face was pressed against a mirrored drum finished by chrome-plating, the surface temperature thereof being 100°C, at a linear pressure of 2,000 N/cm to form a glossy layer, followed by drying using a drier to obtain an ink-jet recording sheet. The thickness of the glossy layer was 1 μm .

Example 9

[0131] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that the coating amount of the crosslinking agent was changed to 0.3 g/m^2 .

Example 10

[0132] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that the coating amount of the crosslinking agent was changed to 0.3 g/m², and the coating amount of the ink-receiving layer was changed to 15 g/m².

Comparative Example 1

[0133] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that a crosslinking-agent-containing coating-fluid composed of an aqueous solution containing 5% borax, the crosslinking-agent-containing coating-fluid being free from any acetylene glycol-based surfactants, was applied on the support B.

Comparative Example 2

[0134] An ink-jet recording sheet was prepared in a way similar to that of Example 1, except that the crosslinking-agent-containing coating-fluid was applied on the support B using a Mayer bar, and then, before the crosslinking-agent-containing coating-fluid was dried, the ink-receiving-layer-formable coating-fluid was applied thereon in accordance with a wet-on-wet process, followed by drying the resultant.

Comparative Example 3 (Preparation of inside-ink-receiving-layer-formable coating-fluid B)

[0135] 500 parts of a dispersion liquid containing 20% wet-process synthetic amorphous silica (manufactured by Grace Davison under the trademark of SYLOJET 703A), 400 parts of an aqueous solution containing 5% polyvinyl alcohol (manufactured by KURARAY CO., LTD., under the trade name of PVA-145), and a small amount of an antifoaming agent, a dispersant, and water were mixed to obtain an inside-ink-receiving-layer-formable coating-fluid B of which the solid concentration was 15%.

(Formation of Ink-jet Recording Sheet)

[0136] On the support B, the inside-ink-receiving-layer-formable coating-fluid B was applied in a coating amount of 10 g/m² in solid basis using a wire bar to form an inside ink-receiving layer. Then, on the inside ink-receiving layer, an aqueous solution containing 3% borax was applied in a wet coating amount of 15 g/m², and then, before the applied face was dried, the ink-receiving-layer-formable coating-fluid A was applied thereon in a coating amount of 15 g/m² in solid basis using a wire bar, followed by drying to form an outside ink-receiving layer. Thus, an ink-jet recording sheet was formed. The total thickness of the ink-receiving layer formed on the support was 35 μm. The viscosity of the borax aqueous solution (crosslinking-agent-containing coating-fluid) was 1 mPa·s.

Example 11 (Application of crosslinking-agent-containing coating-fluid)

[0137] 80 parts of an aqueous solution containing 5% borax, 20 parts of an aqueous solution containing 2% cationized cellulose (with a polymerization degree of 1,500) (manufactured by KAO CORPORATION under the trade name of POIZ C-154L), and 2 parts of an aqueous solution containing 0.1% acetylene glycol-based surfactant (manufactured by Nissin Chemical Co., Ltd., under the trademark of Olfin E1004) were mixed and stirred to prepare a crosslinking-agent-containing coating-fluid with a viscosity of 5 mPa·s. Then, the crosslinking-agent-containing coating-fluid was applied on the support B using a Mayer bar in an amount of 16 g/m² and then dried at a drying temperature of 100°C and a line rate of 50 m/min to form a crosslinking-agent-containing layer. At that time, the coating amount of the crosslinking agent was 0.7 g/m² in solid basis.

(Formation of ink-receiving layer)

[0138] The ink-receiving-layer-formable coating-fluid A was applied on the crosslinking-agent-containing layer using a die coater so that the coating amount thereof was 22 g/m², and then dried to form an ink-receiving layer. The total thickness of the ink-receiving layer was 37 μm.

Example 12

[0139] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that a commercially available polypropylene synthetic paper (manufactured by Yupo Corporation under the trademark of YUPO GWG-140)

was used instead of the support B. The total thickness of the ink-receiving layer was 37 μm .

[0140] As a result of the water absorption test carried out as described above, the mass change of the polypropylene synthetic paper used as a support was 0.1 g or less. Thus, it was confirmed that the polypropylene synthetic paper was an impermeable support.

Example 13

[0141] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that 100 parts of an aqueous solution containing 10% borax heated at 60°C was used instead of 80 parts of the aqueous solution containing 5% borax. The viscosity of the crosslinking-agent-containing coating-fluid was 8 mPa·s.

Example 14

[0142] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that 20 parts of an aqueous solution containing 2% hydroxyethyl cellulose (with a polymerization degree of 1,000) (manufactured by Sansho Co., Ltd., under the trade name of SANHECK H) was used instead of 20 parts of the aqueous solution containing 2% cationized cellulose. The viscosity of the crosslinking-agent-containing coating-fluid was 5 mPa·s.

Example 15

[0143] An ink-jet recording sheet was prepared in a similar way to that of Example 11, except that 20 parts of an aqueous solution containing 2% hydroxypropylmethyl cellulose (with a polymerization degree of 1,500) (manufactured by Shin-Etsu Chemical Co., Ltd., under the trade name of 60SH-15) was used instead of 20 parts of the aqueous solution containing 2% cationized cellulose. The viscosity of the crosslinking-agent-containing coating-fluid was 4 mPa·s.

[0144] The aqueous solution containing 2% hydroxypropylmethyl cellulose was prepared as follows. Specifically, 2 parts of hydroxypropylmethyl cellulose was added to 98 parts of hot water heated at 90°C while stirring, and dispersed therein, followed by gradually cooling to prepare the aqueous solution containing 2% hydroxypropylmethyl cellulose.

Example 16

[0145] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that 20 parts of an aqueous solution containing 2% carboxymethyl cellulose (with a polymerization degree of 1,000) (manufactured by DAI-ICHI KOGYO SEIYAKU CO., LTD., under the trademark of CELOGEN WSA) was used instead of 20 parts of the aqueous solution containing 2% cationized cellulose. The viscosity of the crosslinking-agent-containing coating-fluid was 6 mPa·s.

Example 17

[0146] An ink-jet recording sheet was prepared in a way similar to that of Example 13 (where the aqueous solution containing 10% borax was used), except that 100 parts of an aqueous solution containing 10% gelatin (manufactured by Miyagi Chemical Industrial, CO., Ltd., under the trade name of Inert gelatin P-100) was used instead of 20 parts of the aqueous solution containing 2% cationized cellulose. The viscosity of the crosslinking-agent-containing coating-fluid was 10 mPa·s.

[0147] The aqueous solution containing 10% gelatin was prepared as follows. Specifically, 10 parts of gelatin was added to cold water while stirring to disperse it, and then heated at 60°C followed by hold the resultant for an hour. Then, the resultant was cooled at 40°C to prepare the aqueous solution containing 10% gelatin.

Example 18

[0148] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that 170 parts of an aqueous solution containing 3% boric acid was used instead of 80 parts of the aqueous solution containing 5% borax. The viscosity of the crosslinking-agent-containing coating-fluid was 3 mPa·s.

Example 19

[0149] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that the alumina sol A was used instead of the silica sol A.

Example 20

[0150] In a way similar to that of Example 8, a glossy layer was formed on the ink-receiving layer of the ink-jet recording sheet prepared in Example 11.

Example 21

[0151] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that the coating amount of the crosslinking agent was changed to 0.3 g/m².

Example 22

[0152] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that the coating amount of the crosslinking agent was changed to 0.3 g/m², and the coating amount of the ink-receiving layer was changed to 15 g/m².

Comparative Example 4

[0153] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that a crosslinking-agent-containing coating-fluid composed of an aqueous solution containing 5% borax, the coating-fluid being free from cationized cellulose and acetylene glycol-based surfactants, was applied on the support B. The viscosity of the crosslinking-agent-containing coating-fluid was 1 mPa·s.

Comparative Example 5

[0154] An ink-jet recording sheet was prepared in a way similar to that of Example 11, except that a 4% crosslinking-agent-containing coating-fluid composed of borax and cationized cellulose, the coating-fluid being free from acetylene glycol-based surfactants, was applied on the support B. The viscosity of the crosslinking-agent-containing coating-fluid was 5 mPa·s.

(Evaluation Method)

[0155] Each of the crosslinking-agent-containing coating-fluid and the ink-receiving layer-formable coating-fluid used in the above-mentioned examples or comparative examples were evaluated in terms of the coating suitability, and the ink-receiving layer of each ink-jet recording sheet was evaluated in terms of degree of cracking, 75° surface glossiness, ink-absorptivity, print density, and water resistance, as follows. Results thereof are shown in Tables 1 and 2.

(Coating Suitability of Crosslinking-agent-containing Coating-fluid: Cissing)

[0156] The degree of cissing in which the crosslinking-agent-containing coating-fluid was repelled on the support (hereinafter, abbreviated as cissing) was visually evaluated.

⊙: No cissing was recognized, and no problems arose on the coating surface.

○: Although cissing was slightly recognized in a ratio of less than 0.5 spots per m², no practical problems arose.

△: Cissing was recognized in a ratio of 0.5 spots per m² or more and less than 1.0 spot per m², and a slight practical problem arose.

×: Cissing was recognized in a ratio of 1.0 spot per m² or more, and practical problems arose.

(Coating Suitability of Crosslinking-agent-containing Coating-fluid: Uniformity of Surface-quality)

[0157] The surface-quality of the crosslinking-agent-containing coating-fluid applied on each support was visually evaluated.

⊙: A uniform coating surface with a glossiness was realized, and no problems arose.

○: A uniform coating surface was realized, and no problems arose.

△: The coating surface slightly rippled and the crosslinking agent was slightly unevenly-distributed.

×: The coating surface rippled, and the crosslinking agent was unevenly-distributed, or insufficiently applied.

(Die-coating Suitability)

[0158] The die-coating suitability of the ink-receiving-layer-formable coating-fluid was visually evaluated at the time of application thereof.

⊙: The ink-receiving-layer-formable coating-fluid was not gelled by the crosslinking agent, and favorable operation conditions were realized.

○: Although the ink-receiving-layer-formable coating-fluid was slightly gelled at the vicinity of both ends of its coating face, no practical problems arose.

×: The ink-receiving-layer-formable coating-fluid was gelled by the crosslinking agent and application thereof could not be performed.

(Cracking of Ink-receiving Layer)

[0159] The degree of cracking in each ink-receiving layer was visually evaluated.

⊙: No cracking occurred.

○: Although cracking slightly occurred, no practical problems arose.

△: Although the degree of cracking was more than the case evaluated as ○, no practical problems arose.

×: Cracking occurred, and practical problems arose.

(75° Surface Glossiness)

[0160] The 75° surface glossiness of the ink-receiving layer in each ink-jet recording sheet was measured in accordance with a method described in JIS-P8142.

(Ink-absorptivity)

[0161] Solid printing with a green color was performed using an ink-jet printer manufactured by Canon Inc., under the trade name of PIXUS iP4100 and the degree of ink-absorptivity at the solidly-printed portion was visually evaluated. As ink cartridges, BCI-7Bk, BCI-7C, BCI-7M, BCI-7Y, and BCI-3eBk, manufactured by Canon Inc., were used.

⊙: No unevenness was recognized at the solidly-printed portion, and favorable conditions were realized.

○: Although slight unevenness was recognized at the solidly-printed portion, there was almost no possibility that problems arose.

△: Some unevenness was recognized at the solidly-printed portion, and there was a possibility that practical problems arose by a use state.

×: Unevenness was recognized at the solidly-printed portion, and there was a possibility that practical problems arose by a use state.

(Print Density)

[0162] Solid-printing with a black color was performed using an ink-jet printer manufactured by Canon Inc., under the trade name of PIXUS iP8600, and the print density at the solidly-printed portion was measured using a Greta Macbeth reflection densitometer (manufactured by Greta Macbeth under the trade name of RD-19I). Each value shown in the following table is an average of results obtained by repeatedly performing the measurement five times. As ink cartridges, BCI-7Bk, BCI-7C, BCI-7M, BCI-7Y, BCI-7PC, BCI-7PM, BCI-7R, and BCI-7G, manufactured by Canon Inc., were used.

(Water Resistance)

[0163] Each image solidly-printed with a black, cyan, magenta, yellow, red, green, or blue color was formed, and then water at 25°C was dropped on the image. After the image was air-dried, the degree of discoloration and color fading of the image was visually observed to evaluate the water resistance thereof.

⊙: The image exhibited almost no discoloration, color-fading, and color-migration, and favorable conditions thereof were maintained.

○: Although the image exhibited slight discoloration, color-fading, or color-migration, there was no possibility that practical problems arose.

Δ: The image exhibited discoloration, color-fading, or color-migration to the extent that there was a possibility that practical problems arose.

×: The image exhibited significant discoloration, color-fading, or color-migration.

Table 1

	Cissing on coating face	Coating suitability	Cracking	75° glossiness	Ink absorptivity	Print density	Water resistance
Example 1	⊙	⊙	⊙	60	○	2.54	○
Example 2	⊙	⊙	⊙	53	○	2.48	○
Example 3	⊙	⊙	⊙	61	○	2.50	○
Example 4	⊙	⊙	⊙	62	⊙	2.55	○
Example 5	⊙	⊙	○	60	○	2.52	○
Example 6	⊙	⊙	⊙	66	○	2.57	○
Example 7	⊙	⊙	⊙	61	○	2.51	○
Example 8	⊙	⊙	⊙	80	○	2.62	○
Example 9	⊙	⊙	Δ	55	○	2.52	○
Example 10	⊙	⊙	○	59	Δ	2.49	Δ
Comparative Example 1	×	⊙	×	50	○	2.40	○
Comparative Example 2	⊙	×	-	-	-	-	-
Comparative Example 3	⊙	⊙	⊙	60	○	2.53	○

[0164] In accordance with each process for producing an ink-jet recording sheet of Examples 1 to 10 in which each crosslinking-agent-containing coating-fluid containing the crosslinking agent and the surfactant was applied on the support and then dried, followed by applying each ink-receiving-layer-formable coating-fluid thereon, no cissing of the crosslinking-agent-containing coating-fluid on the support was recognized, and the ink-receiving-layer-formable coating-fluid exhibited excellent coating-suitability. Moreover, each obtained ink-jet recording sheet was excellent in terms of the preventability of cracking, glossiness, ink-absorptivity, print density (image-quality), and water resistance. More specifically, the obtained ink-jet recording sheet exhibited the same performance as that of the ink-jet recording sheet prepared in accordance with the production process of Comparative Example 3 in which two-layered ink-receiving layer was formed, which requires time and labor.

[0165] In contrast, in accordance with the process for producing an ink-jet recording sheet of Comparative Example 1 in which the crosslinking-agent-containing coating-fluid free from any surfactants was applied on the support, cissing of the crosslinking-agent-containing coating-fluid on the support was recognized. Moreover, cracking occurred in the ink-receiving layer, and the glossiness and image-quality were low.

[0166] In accordance with the process for producing an ink-jet recording sheet of Comparative Example 2 in which the crosslinking-agent-containing coating-fluid containing the crosslinking agent and the surfactant was applied and then the ink-receiving layer was formed without drying the crosslinking-agent-containing coating-fluid, the water-soluble resin contained in the ink-receiving-layer-formable coating-fluid was immediately crosslinked when the ink-receiving-layer-formable coating-fluid was applied. Then, the crosslinked products blocked the die-head and the supply of the ink-receiving-layer-formable coating-fluid was difficult. That is, the die-coating suitability of the ink-receiving-layer-formable coating-fluid was low.

Table 2

	Viscosity	Cissing on coating face	Surface quality of coating face	Coating suitability	Cracking	75° glossiness	Ink absorptivity	Print density	Water resistance
Example 11	5 mPa·s	⊙	○	⊙	⊙	63	○	2.55	○
Example 12	5 mPa·s	⊙	○	⊙	⊙	61	○	2.50	○
Example 13	8 mPa·s	⊙	○	⊙	⊙	62	⊙	2.55	○
Example 14	5 mPa·s	⊙	○	⊙	⊙	60	○	2.54	○
Example 15	4 mPa·s	⊙	○	⊙	⊙	64	○	2.53	○
Example 16	6 mPa·s	⊙	○	⊙	⊙	59	○	2.54	○
Example 17	10 mPa·s	⊙	⊙	○	Δ	50	Δ	2.49	○
Example 18	3 mPa·s	⊙	○	⊙	○	60	○	2.52	○
Example 19	5 mPa·s	⊙	○	⊙	⊙	66	○	2.57	○
Example 20	5 mPa·s	⊙	○	⊙	⊙	80	○	2.62	○
Example 21	5 mPa·s	⊙	○	⊙	Δ	55	○	2.52	○
Example 22	1 mPa·s	⊙	○	⊙	○	59	Δ	2.49	○
Comparative Example 3	1 mPa·s	⊙	○	⊙	⊙	60	○	2.53	○
Comparative Example 4	5 mPa·s	×	×	○	×	50	○	2.40	○
Comparative Example 5	5 mPa·s	×	×	○	×	50	○	2.41	○

[0167] The results shown in Table 2 revealed that no cissing of each crosslinking-agent-containing coating-fluid on each impermeable support was recognized and the surface-quality of each coating face was uniform in Examples 11 to 22 according to the present invention. Moreover, the die-coating suitability of each ink-receiving-layer-formable coating-fluid was excellent. Each ink-jet recording sheet prepared in these examples was excellent in terms of the preventability of cracking, glossiness, ink-absorptivity, print density (image-quality), and water resistance, and exhibited the same performance as that of Comparative Example 3 in which time and labor were required. Accordingly, it was revealed that the crosslinking-agent-containing coating-fluid was favorably applied in an amount required to realize sufficient strength of the ink-receiving layer, and the number of the steps and cost required for the preparation were reduced.

[0168] Moreover, the results of Examples 13 and 17 revealed that the formulation of the gelatin as the viscosity modifier excellently contributed to the uniform application of the crosslinking-agent-containing coating-fluid, and the formulation of the cellulose derivative as the viscosity modifier excellently contributed to make the ink-receiving layer have preventability of cracking, glossiness, and printing-suitability.

[0169] In contrast, cissing of each crosslinking-agent-containing coating-fluid on each impermeable support was recognized in Comparative Example 4 in which neither the viscosity modifier nor the surfactant was contained in the crosslinking-agent-containing coating-fluid and Comparative Example 5 in which the viscosity modifier was contained but no surfactants were contained in the crosslinking-agent-containing coating-fluid. Moreover, uneven running of the crosslinking-agent-containing coating-fluid occurred during drying, and therefore the coating face was rippled. Moreover, cracking occurred in the ink-receiving layer, and the glossiness and image-quality thereof were low.

INDUSTRIAL APPLICABILITY

[0170] In accordance with the process for producing an ink-jet recording sheet according to the present invention, cissing of the crosslinking-agent-containing coating-fluid on the support is prevented, and therefore the coating amount of the crosslinking-agent-containing coating-fluid can be increased to form a monolayered ink-receiving layer with a sufficient strength.

Claims

1. A process for producing an ink-jet recording sheet, comprising:

a first step in which a crosslinking-agent-containing coating-fluid comprising a crosslinking agent and a surfactant is applied on a support and dried to form a crosslinking-agent-containing layer; and
a second step in which an ink-receiving-layer-formable coating-fluid comprising inorganic fine particles and a water-soluble resin crosslinkable with the crosslinking agent is applied on the crosslinking-agent-containing layer to form an ink-receiving layer.

2. A process for producing an ink-jet recording sheet according to Claim 1, wherein the crosslinking-agent-containing coating-fluid is applied in the first step so that a coating amount of the crosslinking agent in solid basis is 0.1 to 3.0 g/m².

3. A process for producing an ink-jet recording sheet according to Claim 1 or 2, wherein a coating amount of the inorganic fine particles in the crosslinking-agent-containing layer is 1.0 g/m² or less.

4. A process for producing an ink-jet recording sheet according to any one of Claims 1 to 3, wherein the crosslinking agent is a boric acid and/or a borax.

5. A process for producing an ink-jet recording sheet according to any one of Claims 1 to 4, wherein the surfactant is a nonionic surfactant.

6. A process for producing an ink-jet recording sheet according to any one of Claims 1 to 5, wherein a content of the surfactant in the crosslinking-agent-containing coating-fluid is 0.001 to 10 parts by mass with respect to 100 parts by mass of the crosslinking agent.

7. A process for producing an ink-jet recording sheet according to any one of Claims 1 to 6, wherein the water-soluble resin is a polyvinyl alcohol.

8. A process for producing an ink-jet recording sheet according to any one of Claims 1 to 7, wherein the support is an impermeable support.

9. A process for producing an ink-jet recording sheet according to Claim 8, wherein the ink-receiving-layer-formable coating-fluid is applied in the second step so that a coating amount of the ink-receiving layer is 10 to 40 g/m².

10. A process for producing an ink-jet recording sheet, comprising:

a first step in which a crosslinking-agent-containing coating-fluid having a viscosity of 2 to 20 mPa·s is applied on an impermeable support to form a crosslinking-agent-containing layer, the crosslinking-agent-containing coating-fluid comprising a crosslinking agent, a viscosity modifier, and a surfactant; and
a second step in which an ink-receiving-layer-formable coating-fluid is applied on the crosslinking-agent-containing layer to form an ink-receiving layer, the ink-receiving-layer-formable coating-fluid comprising a water-soluble resin crosslinkable with the crosslinking agent and inorganic fine particles.

11. A process for producing an ink-jet recording sheet according to Claim 10, wherein the crosslinking agent comprises a boric acid and/or a borax, and the water-soluble resin comprises a polyvinyl alcohol.

12. A process for producing an ink-jet recording sheet according to Claim 10 or 11, wherein the viscosity modifier comprises at least one selected from the group consisting of a gelatin, a cationized cellulose, a carboxymethyl cellulose, a hydroxyethyl cellulose, and a hydroxypropylmethyl cellulose.

13. A process for producing an ink-jet recording sheet according to any one of Claims 10 to 12, wherein a drying step is further performed in the first step after the crosslinking-agent-containing coating-fluid is applied to form the crosslinking-agent-containing layer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/311450

A. CLASSIFICATION OF SUBJECT MATTER <i>B41M5/00(2006.01) i, B41M5/50(2006.01) i, B41M5/52(2006.01) i</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) <i>B41M5/00, B41M5/50-5/52</i>		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched <i>Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006</i> <i>Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006</i>		
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.
X Y A	JP 2003-164798 A (Toyobo Co., Ltd.), 10 June, 2003 (10.06.03), Claims 1 to 2; Par. Nos. [0063] to [0066] (example 1), [0074] to [0075] (example 4); Fig. 1 (Family: none)	1-3, 5-9 4 10-13
Y A	JP 2003-11496 A (Fuji Photo Film Co., Ltd.), 15 January, 2003 (15.01.03), Par. Nos. [0096] to [0098] (example 1) (Family: none)	4 1-3, 5-13
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 24 July, 2006 (24.07.06)		Date of mailing of the international search report 01 August, 2006 (01.08.06)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/311450

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-277897 A (Canon Inc.), 12 October, 1999 (12.10.99), Full text & EP 933226 A2 & KR 99068187 A & KR 287087 B & US 2002098326 A1 & US 6652928 B2 & EP 933226 B1 & DE 69915908 E	1-13
A	JP 5-104848 A (Sanyo-Kokusaku Pulp Co., Ltd.), 27 April, 1993 (27.04.93), Full text; all drawings (Family: none)	1-13
A	JP 4-223190 A (Sanyo-Kokusaku Pulp Co., Ltd.), 13 August, 1992 (13.08.92), Full text; all drawings & EP 493100 A1 & AU 9188060 A	1-13
A	JP 2004-230599 A (Kyanon Faintekku Kabushiki Kaisha), 19 August, 2004 (19.08.04), Full text (Family: none)	1-13

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2005169453 A [0002]
- JP 2006083176 A [0002]
- JP 2004074576 A [0007]
- JP 2001246832 A [0007]
- WO 03039881 A [0067]