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(54) Ink-jet recording sheet

(57) An ink-jet recording sheet, having an excellent ink absorption and capable of forming images with high color density and sharpness, includes a substrate and an ink-receiving layer, formed on the substrate, which includes a pigment and a self-emulsifying, cationic acrylic copolymer resin having cationic groups.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an ink-jet recording sheet. More particularly, the present invention relates to an ink-jet recording sheet having an enhanced capability of recording clear ink images at a high recording speed and a high resistance to blotching of ink.

2. Description of the Related Art

Currently, in the field of ink-jet recording, due to the development of an ink-jet color printer suitable for preparing colored hard copies at a high speed, it becomes possible to obtain an ink-jet print having a high image clarity and a high printing quality. Nevertheless, to further improve the print quality, chroma, appearance and clarity of images, a new recording sheet having an enhanced performance is required. Especially, due to the development of the ink-jet printing system in printing speed, resolution and chroma, the ink-jet recording material is required to have further enhanced properties, for example, enhanced ink-absorption speed, a high ink-absorption capacity and regular ink-blotching property. To meet to these requirements, various types of recording sheets having an ink-receiving layer formed on a surface of a substrate have been produced.

For example, Japanese Unexamined Patent Publication No. 55-51585 discloses a coating layer comprising amorphous silica particles (having a particle size of 0.1 to 10.0 μm) and a polymeric binder and formed on a substrate.

Japanese Unexamined Patent Publication No. 56-148584 discloses a recording sheet having an ink-receiving layer formed on a surface of a substrate and comprising a porous inorganic pigment, for example, natural zeorite, synthetic zeorite, diatomaceous earth, fine particulate silicic acid or synthetic mica, which has a function of absorbing and holding a coloring material in a surface of a substrate.

Nevertheless, these conventional recording sheets are disadvantageous in that when the ink-receiving layer is formed in a small amount, the printed ink irregularly spreads and blotches on the surfaces of the recording sheets, and when the ink-receiving layer is formed in a large amount, the ink-receiving layer is easily peeled off and a fine powder is formed on and scattered from the surface, while the spreading and blotching of the ink can be prevented.

To solve the above-mentioned problem, an attempt was made to provide a recording sheet provided with an ink-receiving layer containing an increased amount of a binder resin and having an enhanced mechanical strength. However, this type of recording sheet is disadvantageous in that the ink-receiving layer exhibits an insufficient ink-absorbing capacity, and the printed ink irregularly spreads on the ink-receiving layer and thus the resultant image quality is unsatisfactory. Therefore, it is difficult to provide a satisfactory resolution and reproduction of halftone colors.

Also, Japanese Unexamined Patent Publication No. 62-288,076 discloses a binder resin having an enhanced strength and comprising a water-insoluble polymer resin prepared by reacting polyvinyl alcohol with acrylic acid and methyl methacrylate. However, since this water-insoluble polymer resin is anionic, and the main components of the ink are anionic, too, the anionic ink is not easily stably fixed to the ink-receiving layer formed from the anionic, water-insoluble polymer resin. Also, if the water-insoluble polymer resin is contained too a large amount in the ink-receiving layer, the ink bleeds out with the lapse of time. Further, if the content of the water-insoluble polymer resin in the ink receiving layer is too small, the bonding strength-enhancing effect of the resin is insufficient.

As mentioned above, although various attempts have been made to produce ink jet recording sheets, it has not yet been possible to realize a new type of ink jet recording sheet having a satisfactory resistance to ink-blotching, a high ink-absorbing capacity, an excellent surface strength and the capability to form colored images with a high brightness.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an ink jet recording sheet capable of recording clear images at a high recording speed without ink-blotching, in an ink jet recording system such as, for example, an ink jet printer or an ink jet plotter, and having an excellent surface strength.

Another object of the present invention is to Provide an ink jet recording sheet useful for an ink jet recording system for printing images such as letters, characters and pictures by using an aqueous ink, having a high ink-absorbing speed, a high resistance to blotching and spread of ink dots, and a satisfactory capability of forming ink images having a high color brightness, a good dot shape and a high sharpness at the edges of the images, and thus capable of recording the ink images with high resolution at high speed.

The above-mentioned objects can be attained by the ink jet recording sheet of the present invention which comprises a substrate and an ink-receiving layer formed on at least one surface of the substrate and comprising a pigment and a binder, the binder comprising a self-emulsifying cationic resin consisting essentially of at least one water-insolu-

ble acrylic copolymer having cationic functional groups.

In the ink-jet recording sheet of the present invention as defined above, the binder may contain a water-soluble cationic resin in addition to the self-emulsifying cationic resin.

Also, in the ink-jet recording sheet of the present invention, the self-emulsifying cationic resin is preferably present in a content of 5 to 70% by weight based on the total weight of the binder.

Further, in the ink-jet recording sheet of the present invention, the water-insoluble acrylic copolymer having cationic functional group is preferably a copolymerization product of at least one acrylic monomer selected from the group consisting of alkyl acrylates having 4 to 21 carbon atoms and alkyl methacrylates having 5 to 22 carbon atoms with at least one cationic, ethylenically unsaturated monomer having at least one cationic group selected from tert-amino groups and quaternary ammonium salt groups.

Further, in the ink-jet recording sheet of the present invention, the pigment preferably comprises at least one white pigment selected from the group consisting of amorphous synthetic silica, alumina, hydrated alumina sol, aluminum silicate, magnesium silicate, precipitated calcium carbonate, ground calcium carbonate, calcium silicate, aluminum hydroxide, zeorite, calcined clay, kaolin clay, talc, white carbon and organic (plastic) pigments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

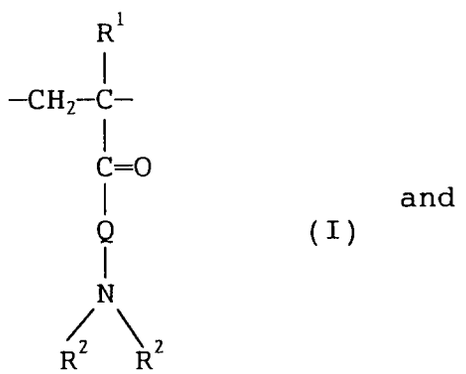
Generally speaking, in preparation of an aqueous emulsion or latex of a conventional water-insoluble acrylic copolymer resin, an anionic, cationic, nonionic or polymeric emulsifying agent is used to stably emulsify or disperse the resin in water. However, it has became clear that the emulsifying agent causes the adhesion of the resultant coating layer, formed from the resin latex or emulsion, to the substrate and the water-resistance of the coating layer to be greatly reduced. Also, it has become clear that the emulsifying agent affects the surface tension of the ink applied to the coating layer so that the ink easily blotches and spreads irregularly on the surface of the coating layer.

To remove the above-mentioned disadvantages, in the ink-jet recording sheet of the present invention, the ink-receiving layer comprises, as a binder, a self-emulsifying cationic resin consisting essentially of at least one water-insoluble acrylic copolymer having cationic functional groups. The self-emulsifying cationic resin usable for the present invention is used in the state of a self-emulsified aqueous latex or emulsion containing no emulsifying agent. Therefore, the ink-receiving layer of the present invention is free from the above-mentioned disadvantages derived from the emulsifying agent.

The water-insoluble, cationic acrylic copolymer usable for the self-emulsifying cationic resin of the present invention is preferably selected from copolymerization products of at least one acrylic monomer selected from the group consisting of alkyl acrylates having 4 to 21 carbon atoms, more preferably 6 to 19 carbon atoms, and alkyl methacrylates having 5 to 22 carbon atoms, more preferably 7 to 20 carbon atoms, with at least one cationic, ethylenically unsaturated monomer having at least one cationic group selected from tert-amino groups and quaternary ammonium groups.

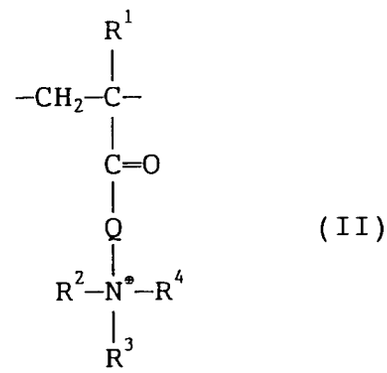
The alkyl acrylates and alkyl methacrylates usable as the acrylic monomer are preferably selected from methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate.

The cationic groups in the cationic, ethylenically unsaturated monomer are not limited to specific groups. The cationic, ethylenically unsaturated monomer is preferably selected from those having at least one cationic groups of the following formulae (I) and (II):



(I)

and



(II)

wherein R^1 represents a hydrogen atom or a lower alkyl group with 1 to 6 carbon atoms (, for example, methyl, ethyl or n-hexyl group), R^2, R^3 and R^4 represent respectively and independently from each other an alkyl group with 1 to 6 carbon atoms (, for example, methyl, ethyl or propyl group) or an aralkyl group with 7 to 10 carbon atoms, the groups R^2 and R^3 in the formula (I) or the groups R^2, R^3 and R^4 of the formula (II) may be fuse-bonded with the nitrogen atom to form a cyclic structure, Q represents a divalent organic group with 1 to 20 carbon atoms (, for example, $-OCH_2CH_2-$

group) and X^- represents an anion.

In the cationic, self-emulsifying acrylic copolymer usable for the present invention, the cationic monomer is contained preferably in a molar content of 0.05 to 80%, more preferably 3 to 50%. Any other comonomer may be used unless the target effect of the present invention is obstructed.

There is no specific limitation to the polymerization method for producing the self-emulsifying cationic resin. For example, the self-emulsifying resin can be produced by a seed polymerization method in which a water-soluble or water-dispersible polymer is prepared as a seed polymer, and then the seed polymer is further polymerized with a monomer added to the polymerization system, a reactive emulsifying agent-polymerization method in which a chemical compound having an ethylenically unsaturated structure and a hydrophilic group is added as an emulsifying agent in place of the conventional emulsifying agent to the polymerization system, or an oligomer-polymerization method in which an oligomer generated in the polymerization system and having a surface active property, is utilized as an emulsifying agent.

The self-emulsifying acrylic copolymer usable as a binder resin for the ink-receiving layer of the present invention exhibits a cationic property and thus the resultant ink-receiving layer formed from the cationic acrylic copolymer exhibits an enhanced fixing property for the coloring material in the ink and an excellent water resistance, and the ink images formed on the ink-receiving layer have an enhanced color density.

In the ink-receiving layer of the present invention, the binder may contain a water-soluble resin in addition to the cationic, self-emulsifying acrylic copolymer resin. The water-soluble resin is preferably cationic or non-ionic.

The non-ionic, water soluble resin preferably comprises at least one polymer selected from polyvinyl alcohol, polyvinyl alcohol derivatives, for example, silanol group-modified polyvinyl alcohols, proteins, for example, casein, starch and starch derivatives, for example, oxidized starch, etc. These water-soluble resins are generally contributory to enhancing the ink-absorbing speed of the resultant ink-receiving layer.

The water soluble cationic resin preferably comprises at least one member selected from cation-modified polyvinyl alcohol, polyethyleneimine, polyvinyl pyridine, polydialkylaminoethyl methacrylates, polydialkylaminoethyl acrylates, polydialkylaminoethyl methacrylamides, polydialkylaminoethyl acrylamides, polyepoxyamines, polyamideamines, dicyandiamideformaldehyde condensation reaction products, dicyandiamidepolyalkyl-polyalkylenepolyamine condensation reaction products, polydimetyldiallyl ammonium chloride, polyvinyl amine, polyallylamine and modified products of the above-mentioned compounds.

The water-soluble cationic resin is contributory to enhancing the color density of the images formed on the resultant image-receiving layer. Any other binder resin may be used unless the target effect of the present invention is hindered.

In the ink-receiving layer of the present invention, there is no limitation to the content of the cationic, self-emulsifying acrylic copolymer resin. Preferably, the cationic, self-emulsifying acrylic copolymer resin is contained in a content of 3% by weight or more, more preferably from 5 to 70% by weight based on the total weight content of the binder in the ink-receiving layer. If the content of the cationic, self-emulsifying acrylic polymer resin is too small, the blotch-preventing effect may become insufficient. If the non-ionic or cationic water-soluble resin is not used or used in too small an amount, the time necessary to absorb the ink in the ink-receiving layer may become long, while the blotch-preventing effect is high.

Preferably, the water-soluble non-ionic resin is employed in an amount of 20 to 2000 parts by weight per 100 parts by weight of the cationic, self-emulsifying acrylic copolymer resin.

Also, the water-soluble cationic resin is employed preferably in an amount of 50 to 1500 parts by weight per 100 parts by weight of the cationic, self-emulsifying acrylic copolymer resin.

The pigment to be contained in the image-receiving layer of the present invention preferably comprises at least one white pigment selected from the group consisting of amorphous synthetic silica, alumina, hydrated alumina sol, aluminum silicate, magnesium silicate, precipitated calcium carbonate, ground calcium carbonate, calcium silicate, aluminum hydroxide, zeorite, calcined clay, kaolin clay, talc, white carbon, and organic (plastic) pigments. The above-mentioned white pigments may be employed alone or in a mixture of two or more thereof.

Among the above-mentioned white pigments, the amorphous synthetic silica, alumina and hydrated alumina sol are contributory to enhancing the ink-absorption of the resultant ink-receiving layer and the color density of the images formed on the ink-receiving layer, and thus are preferred for the present invention.

The pigment is employed preferably in a content of 40 to 90% by weight based on the total solid weight of the ink-receiving layer. If the content of the pigment is too small, the resultant ink-receiving layer may exhibit an unsatisfactory ink-absorption, and if the pigment content is too large, the resultant ink-receiving layer may have an insufficient mechanical strength.

The ink-receiving layer of the present invention optionally contains an additive comprising at least one member selected from pigment-dispersing agent, defoaming agent, coloring material, antioxidant, ultraviolet ray-absorbing agent, viscosity modifier and cross-linking agent, in response to the ink-receiving layer-forming conditions, the required image quality and the required performance of the ink jet recording sheet.

The substrate usable for the ink jet recording sheet of the present invention is preferably formed from a paper sheet comprising cellulose pulp, synthetic paper sheet, or a transparent or opaque sheet made from a synthetic resin. The

cellulose pulp to be contained in the paper sheet may be selected from ground wood pulps, sulfite pulps, kraft pulps, semi-chemical pulps, chemi-ground pulps and refiner-ground pulps produced mainly from soft woods, for example, Japanese red pine, Japanese black pine, silver fir, abies, and cedar tree woods and hard woods, for example, beech, birch and chinquapin tree woods and waste paper pulps.

When a paper sheet is used as a substrate of the ink jet recording sheet of the present invention, the paper sheet usually contains, in addition to the cellulose pulp, a pigment which is added to the pulp slurry. The pigment includes at least one member selected from inorganic pigments, for example, clay, talc, calcium carbonate, calcined kaolin, aluminum oxide, aluminum hydroxide, and titanium dioxide, and organic pigments, for example, urea resin particles. The paper sheet for the substrate optionally contains an additive selected from sizing agents, for example, rosin compounds, alkylketene dimer and alkenyl succinic acids, fixing agents, for example, aluminum sulfate and cationic starchs, and paper strengthening agent, for example, polyacrylamide polymers and starch. The additive is added to the pulp slurry. The pulp slurry containing the pigment and optionally the additive is subjected to paper-forming and is converted to a paper sheet.

The paper sheet usable for the substrate is optionally sized with a surface-sizing agent comprising at least one member selected from rosin compounds, petroleum resins, starch, starch derivatives, for example, oxidized starch, acetylated starch and hydroxyethylated starch, polyvinyl alcohol, polyvinyl alcohol derivatives, synthetic resin latexes comprising at least one of polymers and copolymers of styrene, ethylenically unsaturated amide compounds, acrylic esters, olefins, maleic acids and vinyl acetate, alkyl resins, and waxes.

The paper sheet is optionally calendered by a conventional calender, for example, a machine calender or a super calender, to control the thickness thereof.

The synthetic resin sheet of film, usable as a substrate for the present invention, may be produced from a thermoplastic resin, typically polyester or polyolefin resin. The polyester resin includes polyethylene terephthalate, polybutylene terephthalate and polycyclohexene terephthalate. Also, the polyolefin resin includes polyethylene, polypropylene, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, and blends of two or more thereof. The thermoplastic resin usable for the synthetic resin sheet or film may be a mixture of a polystyrene with an acrylic acid ester copolymer. The synthetic resin sheet or film may be oriented in a longitudinal or a transverse direction.

The substrate for the ink-jet recording sheet of the present invention may be formed from a synthetic paper sheet which has a paper-like appearance and can be produced by mixing inorganic fine particles into a thermoplastic resin, forming a film from the mixture and orienting the film, for example, in biaxial directions. In the present invention, the substrate may be formed from a laminate containing a plurality of the synthetic paper sheets. For example, the laminate may be a two or three-layered composite sheet composed of a base sheet and at least one synthetic paper sheet laminated on at least one surface of the base sheet. Also, the laminate is preferably a three to five layered composite sheet composed of the above-mentioned two or three-layered composite sheet and one or two surface layers formed on the one or two surfaces of the two or three-layered composite sheet. The synthetic paper sheet made from a thermoplastic resin in the above-mentioned manner has a paper-like appearance and a good texture. The thermoplastic resin film or sheet usable as a substrate for the present invention is not limited to one having a specific opaqueness.

The ink-receiving layer can be formed on at least one surface of the substrate by using a conventional coating method and apparatus, for example, a bar coater, air knife coater, blade coater, or gravure coater. The resultant coated sheet having the ink-receiving layer coated on the substrate can be used as an ink-jet recording sheet of the present invention. Optionally, the resultant coated sheet is surface-treated with a calender, for example, a super calender or gloss calender, to impart an enhanced smoothness to the surface of the sheet.

There is no limitation to the amount of the ink-receiving layer to be formed on the substrate. Preferably, the ink-receiving layer is in a dry weight of 1 to 30 g/m^2, more preferably 2 to 20 g/m^2.

If the amount of the ink-receiving layer is too small, the resultant ink-receiving layer may exhibit an insufficient ink-absorbing capacity and the ink may spread or blotch outside of the desired images, the resultant ink images have unclear countours, and the drying time of the ink images may become long. Thus, the sheet delivery rolls of the printer may be stained by the wet ink images and then may soil following recording sheets.

Also, if the amount of the image-receiving layer is too large, the thick image-receiving layer may exhibit a reduced bonding strength to the substrate and thus may scale off from the substrate so that the resultant scales blotch the ink-jetting nozzle of the printer. Also, the thick image-receiving layer may cause an economical disadvantage.

In the ink jet recording sheet of the present invention, the ink-receiving layer may have a multilayered structure.

EXAMPLES

The present invention will be further explained by the following examples which are merely representative and are not intended to restrict the scope of the present invention in any way.

Example 1

An aqueous pulp slurry was prepared from 100 parts by weight of hard wood bleached kraft pulp mixed with 20 parts by weight of precipitated calcium carbonate particles, 0.8 part by weight of a cationic starch and 0.11 part by weight of a neutral sizing agent containing an alkenylsuccinic anhydride compound. The aqueous pulp slurry was fully stirred and subjected to a paper-forming process using a multi-cylinder Fourdrivier paper machine, the resultant wet paper sheet was dried to a water content of 10% by weight. Then, an aqueous solution of 6% by weight of an oxidized starch was applied to both the surfaces of the dried paper sheet by a size-press method to size the both surfaces of the paper sheet with the sizing agent in a total amount of 5 g/m^2, and the sized paper sheet was dried into a water content of 7% by weight. A fine paper sheet having a basis weight of 82 g/m^2 was obtained.

An aqueous coating liquid (1) was prepared in the following composition.

Coating liquid (1)	
Amorphous synthetic silica $(*)_1$	73 wt%
Polyvinyl alcohol $(*)_2$	16.2 wt%
Self-emulsifying, water-insoluble, cationic acrylic copolymer resin latex $(*)_3$	10.8% by solid weight

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_3$ ... Trademark: Sumikaflex 3911, made by Sumitomo Kagakukogyo

The aqueous coating liquid (1) was coated on a surface of the wood free paper sheet by using a bar coater to form an ink-receiving layer in an absolute dry weight of 10 g/m^2. An ink-jet recording sheet was obtained.

Example 2

An ink-jet recording sheet was produced by the same procedures and the same wood free paper sheet as in Example 1, with the following exceptions.

The coating liquid (1) of Example 1 was replaced by an aqueous coating liquid (2) having the following composition.

Coating liquid (2)	
Amorphous synthetic silica $(*)_1$	72 wt%
Polyvinyl alcohol $(*)_2$	2.2 wt%
Oxidized starch $(*)_4$	8 wt%
Polydiallyldimethylammonium chloride $(*)_5$	6 wt%
Self-emulsifying, water-insoluble, cationic acrylic copolymer resin latex $(*)_3$	10.8% by solid weight

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_3$ ... Trademark: Sumikaflex 3911, made by Sumitomo Kagakukogyo
$(*)_4$ ... Trademark: Ace A, made by Oji Corn Starch
$(*)_5$ ... A water-soluble cationic resin having a molecular weight of about 50,000, trademark: PAS-H-5L, made by Nito Boseki K.K.

The coating liquid (2) was coated on a surface of the wood free paper by using a bar coater to produce a ink-jet recording sheet having an ink-receiving layer with an absolute dry weight of 15 g/m^2.

Example 3

An ink-jet recording sheet was produced by the same procedures and the same wood free paper sheet as in Example 1, with the following exceptions. The coating liquid (1) was replaced by an aqueous coating liquid (3) having the following composition.

Coating liquid (3)	
Amorphous synthetic silica $(*)_1$	20 wt%
Calcium carbonate $(*)_6$	20 wt%
Silanol-modified polyvinyl alcohol $(*)_{13}$	49 wt%
Polyoxypropylenemethyldiethyl ammonium chloride $(*)_7$	8 wt%
Self-emulsifying, water-insoluble, cationic acrylic copolymer resin latex $(*)_3$	3% by solid weight

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_3$ ... Trademark: Sumikaflex 3911, made by Sumitomo Kagakukogyo
$(*)_6$ ... Trademark: Unibar 70, made by Shiraishi Kogyo
$(*)_7$ ... A water-soluble cationic resin having 9 oxypropylene chain groups per molecule, trademark: Adecacol CC-9, made by Asahi Denkakogyo K.K.
$(*)_{13}$ ... Trademark: PVA R-1130, made by Kuraray

The coating liquid (3) was coated on a surface of the wood free paper sheet by using a bar coater to form an ink receiving layer having an absolute dry weight of 5 g/m^2.

Example 4

An ink-jet recording sheet was produced by the same procedure and the same wood free paper sheet as in Example 1 with the following exceptions.

The coating liquid (1) was replaced by an aqueous coating liquid (4) having the following composition.

Coating liquid (4)	
Alumina $(*)_8$	90 wt%
Polyvinyl alcohol $(*)_2$	2.4 wt%
Polydiallyldimethylammonium chloride $(*)_5$	2 wt%
Water-insoluble, self-emulsifying, cationic acrylic copolymer resin emulsion $(*)_9$	5.6% by solid weight

Note:
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_5$ ... A water-soluble cationic resin having a molecular weight of about 50,000, trademark: PAS-H-5L, made by Nito Boseki K.K.
$(*)_8$ ... Trademark: CAH-3000, made by Sumitomo Kagakukogyo
$(*)_9$ ... Trademark: Boncoat SFC-302, made by Dainihon Inki. An emulsified polymer having an average particle size of 260 nm and a Tg of 0°C

The coating liquid (4) was coated on a surface of the wood free paper sheet to form an ink-receiving layer having an absolute dry weight of 10 g/m^2.

Example 5

An ink-jet recording sheet was produced by the same procedures as in Example 2 with the following exceptions.

The wood free paper sheet was replaced by a multi-layered biaxially oriented synthetic paper sheet comprising a thermoplastic resin, provided with a surface layer containing an inorganic pigment, having a thickness of 110 μm and available under the trademark of Yupo FPG-110, from Oji Yukagoseishi K.K.

The coating liquid (2) was coated on a surface of the synthetic paper sheet by using a bar coater to form an ink-receiving layer having an absolute dry weight of 15 g/m^2.

Example 6

An ink-jet recording sheet was produced by the same procedures as in Example 2 with the following exceptions.

The wood free paper sheet was replaced by a polyethyleneterephthalate resin film having a thickness of 75 μm and available from Toray.

The coating liquid (2) was coated on a surface of the PET film by using a bar coater to form an ink-receiving layer having an absolute dry weight of 20 g/m^2.

Example 7

An ink-jet recording sheet was produced by the same procedures and the same wood free paper sheet as in Example 1 with the following exceptions.

The coating liquid (1) was replaced by an aqueous coating liquid (5) having the following composition.

Coating liquid (5)	
Amorphous synthetic silica $(*)_1$	60 wt%
Water-insoluble, self-emulsifying, cationic acrylic copolymer resin latex $(*)_9$	28% by solid weight
Polydiallyldimethylammonium chloride $(*)_5$	12 wt%

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_5$ ... A water-soluble cationic resin having a molecular weight of about 50,000, trademark: PAS-H-5L, made by Nito Boseki K.K.
$(*)_9$ ... Trademark: Boncoat SFC-302, made by Dainihon Inki. An emulsified polymer having an average particle size of 260 nm and Tg of 0°C

The coating liquid (5) was coated on a surface of the wood free paper sheet to form an ink-receiving layer having an absolute dry weight of 10 g/m^2.

Comparative Example 1

An ink-jet recording sheet was produced by the same procedures as in Example 1 except that the self-emulsifying, cationic acrylic copolymer resin latex (Sumikaflex 3911) was not employed.

Comparative Example 2

An ink-jet recording sheet was produced by the same procedures as in Example 2 except that the self-emulsifying, cationic acrylic copolymer resin latex (Sumikaflex 3911) was not employed.

Comparative Example 3

An ink-jet recording sheet was produced by the same procedures as in Example 1, with the following exception.

A surface of the same wood free paper sheet as in Example 1 was coated, by using a bar coater, with an aqueous coating liquid (6) having the following composition.

Coating liquid (6)	
Amorphous synthetic silica $(*)_1$	40 wt%
Polyvinyl alcohol $(*)_2$	12 wt%
Water-insoluble, cationic acrylic copolymer emulsion $(*)_{10}$	48% by solid weight

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_{10}$ ... An aqueous emulsion of a cationic acrylic copolymer resin prepared by an emulsion copolymerization using an emulsifying agent, trademark: Boncoat VO-8, made by Dainihon Inki.

The resultant ink-receiving layer on the wood free paper sheet had an absolute dry weight of 10 g/m^2.

Comparative Example 4

An ink-jet recording sheet was produced by the same procedures as in Example 1 with the following exceptions.

A surface of the wood free paper sheet is coated by an aqueous coating liquid (7) having the following composition, by using a bar coater.

Coating liquid (7)	
Alumina $(*)_8$	67 wt%
Polyvinyl alcohol $(*)_2$	16.2 wt%
Polyoxypropylenemethyldiethyl ammonium chloride $(*)_7$	6 wt%
Water-insoluble, cationic vinyl acetate copolymer resin emulsion $(*)_{11}$	10.8% by solid weight

Note:
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_7$ ... A water-soluble cationic resin having 9 oxypropylene chain groups per molecule, trademark: Adecacol CC-9, made by Asahi Denkakogyo K.K.
$(*)_8$ ... Trademark: CAH-3000, made by Sumitomo Kagakukogyo
$(*)_{11}$ ... An aqueous emulsion of a water-insoluble, cationic vinyl acetate copolymer resin prepared by an emulsion polymerization using an emulsifying agent, trademark: Yodosol CE-58, made by Kanebo NSC K.K.

The resultant ink-receiving layer had an absolute dry weight of 10 g/m^2.

Comparative Example 5

An ink-jet recording sheet was prepared by the same procedures as in Comparative Example 4 with the following exceptions.

The coating liquid (7) was coated on a surface of the same synthetic paper sheet (Yupo FPG 110) as in Example 5 by using a bar coater, to form an ink-receiving layer with an absolute dry weight of 18 g/m^2.

Comparative Example 6

An ink-jet recording sheet was produced by the same procedures as in Example 1 with the following exceptions.

An aqueous coating liquid (8) having the composition as shown below was prepared.

Coating liquid (8)	
Amorphous synthetic silica $(*)_1$	67 wt%
Polyvinyl alcohol $(*)_2$	16.2 wt%
Polydiallyldimethyl ammonium chloride $(*)_5$	6 wt%
Water-insoluble, anionic carboxyl-modified styrene-butadiene copolymer emulsion $(*)_{12}$	10.8% by solid weight

Note:
$(*)_1$ ... Trademark: Fineseal, made by Tokuyama
$(*)_2$ ... Trademark: PVA 117, made by Kuraray
$(*)_5$ ... A water-soluble cationic resin having a molecular weight of about 50,000, trademark: PAS-H-5L, made by Nito Boseki K.K.
$(*)_{12}$ ... An aqueous emulsion of a water-insoluble, anionic carboxyl-modified styrene-butadiene copolymer produced by an emulsion polymerization using an emulsifying agent, trademark: JSR0593, made by Nihon Goseigomu

During the preparation of the coating liquid (8), the components agglomerated, and thus the coating procedure could not be carried out.

TESTS

In each of the examples and comparative examples, the properties of the resultant ink-jet recording sheet were measured and evaluated by the following tests.

(1) Ink absorption

An ink-jet recording sheet was printed in an ink-jet printer (trademark: BJC-820J, made by Canon) and the drying time of the printed ink images was determined by checking for reflected light from the ink images by the naked eye and measuring a time from a printing stage to a stage at which the reflected light from the ink image disappeared due to the completion of the drying of the ink images. The ink absorption was evaluated in the following five classes.

Class	Drying time
5	Less than 4 seconds
4	4 seconds or more but less than 7 seconds
3	7 seconds or more but less than 10 seconds
2	10 seconds or more but less than 15 seconds
1	15 seconds or more

(2) Brightness of colored images

By using the ink-jet printer (BJC-820J), an ink-jet recording sheet was printed with each of yellow, magenta and cyan inks, and the resultant colored images was observed by the naked eye, and evaluated in the following five classes.

Class	Sharpness of colored images
5	Extremely excellent
4	Excellent
3	Good
2	Slightly dark
1	Dark and unclear

(3) Form and size of dots

By using the ink-jet printer (BJC-820J, made by Canon), an ink-jet recording sheet was ink-jet-printed, and the form and size of the dots were observed by using a zoom stereoscope (made by Sener K.K.) at a magnification of 50, and evaluated in the following classes.

Class	Form and size of dots
5	Form: True circle
	Size: No increase occurred
4	Form: Approximately true circle
	Size: Very small increase occurred
3	Form: Circular
	Size: Small increase occurred
2	Form: Irregular
	Size: Considerable increase occurred
1	Form: Very bad
	Size: Significant increase occurred

(4) Blotching of colored inks when mixed

By using the ink-jet printer (BJC-820J), an ink-jet recording sheet was printed with cyan and yellow colored inks so that the colored ink images were overlapped on each other, and the resultant overlapped colored images were observed by the naked eye and evaluated into the following five classes.

Class	Blotching of colored inks
5	None
4	Very small
3	Permissible
2	Significant
1	Very significant

(5) Surface strength

An adhesive tape was adhered to an ink-receiving layer surface of a ink-jet recording sheet and rapidly peeled off the surface. The total area of the peeled portions of the ink-receiving layer was observed by the naked eye. The surface strength of the ink-jet recording sheet was indicated in the following three classes.

Class	Surface strength
3	Excellent
2	Satisfactory
1	Bad

The test results are shown in Table 1.

Table 1

Item / Example No.		Ink absorption	Sharpness of colored images	Form and size of dots	Blotching of overlapped colored ink images	Surface strength
Example	1	5	4	5	5	3
	2	5	5	5	5	3
	3	5	4	5	5	3
	4	5	5	5	5	3
	5	5	5	5	5	3
	6	5	5	5	5	3
	7	4	5	5	5	3
Comparative Example	1	5	1	1	1	2
	2	5	3	3	3	1
	3	2	3	2	2	2
	4	4	2	2	2	2
	5	4	2	2	2	2
	6	-	-	-	-	-

Table 1 clearly shows that the ink-jet recording sheets of Examples 1 to 7 in accordance with the present invention exhibited excellent ink absorption and sharpness of colored images, a satisfactory form of dots, a high resistance to increase in size of the dots, a high resistance to blotching of the ink images overlapped on each other and a superior surface strength, whereas the comparative ink-jet recording sheets of Comparative Examples 1 to 5 were unsatisfactory in one or more of the above-mentioned test results. In the comparative coating liquid (8) of Comparative Example 6, the components agglomerated and thus the coating liquid (8) could not be employed for coating.

The ink-jet recording sheet of the present invention exhibits not only excellent ink absorption and sharpness of the colored images but also a satisfactory form of dots, a high resistance to increase in size of the dots, a high resistance to blotching of the overlapped colored ink images and superior surface strength. Therefore, the ink-jet recording sheet of the present invention is useful for forming fine and sharp images at a high speed not only in monochromatic printing but also in multichromatic or full color printing.

Claims

1. An ink-jet recording sheet comprising a substrate and an ink-receiving layer formed on at least one surface of the substrate and comprising a pigment and a binder, the binder comprising a self-emulsifying cationic resin consisting essentially of at least one water-insoluble acrylic copolymer having cationic functional group.

2. The ink-jet recording sheet as claimed in claim 1, wherein the binder contains a water-soluble cationic resin in addition to the self-emulsifying cationic resin.

3. The ink-jet recording sheet as claimed in claim 1, wherein the self-emulsifying cationic resin is present in a content of 5 to 70% by weight based on the total weight of the binder.

4. The ink-jet recording sheet as claimed in claim 1, wherein the water-insoluble acrylic copolymer having cationic functional group is a copolymerization product of at least one acrylic monomer selected from the group consisting of alkyl acrylates having 4 to 21 carbon atoms and alkyl methacrylates having 5 to 22 carbon atoms with at least one cationic, ethylenically unsaturated monomer having at least one cationic group selected from tert-amino groups and quaternary ammonium salt groups.

5. The ink-jet recording sheet as claimed in claim 1, wherein the pigment comprises at least one white pigment selected from the group consisting of amorphous synthetic silica, alumina, hydrated alumina sol, aluminum silicate, magnesium silicate, precipitated calcium carbonate, ground calcium carbonate, calcium silicate, aluminum hydroxide, zeorite, calcined clay, kaolin clay, talc, white carbon and organic (plastic) pigments.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 5970

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 477 (M-885) [3825] , 27 October 1989 & JP-A-01 188387 (CANON K.K.), 27 July 1989, * abstract *	1-5	B41M5/00
X	WO-A-95 13194 (BASF AG.) * page 2, line 18 - line 44 * * page 4, line 4 - page 6, line 19 * * page 9, line 18 - line 26; claims 1,4 *	1-5	
X	DE-A-31 32 248 (FUJI PHOTO FILM COMPANY LIMITED) * page 14, line 21 - page 20, line 28 * * page 28, line 12 - page 30, line 29 * * page 32, line 4 - line 23; claims 1-11 *	1-5	
A	EP-A-0 627 324 (MITSUBISHI PAPER MILLS, LIMITED) * page 3, line 6 - page 5, line 50 * * claims 1-5 *	1-5	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M
A	EP-A-0 634 284 (CANON K.K.) * page 5, line 32 - line 45 * * page 6, line 18 - line 31 * * claims 1-7 *	1-5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 January 1997	Bacon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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