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(54) **INK JET RECORDING SHEET**

TINTENSTRAHL-AUFZEICHNUNGSBLATT

FEUILLE PERMETTANT LA REPRODUCTION PAR JET D'ENCRE

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EP 0 655 346 B1

Description

[Technical Field]

5 The present invention relates to an ink jet recording sheet and more particularly to an ink jet recording sheet of slight-coat type which shows no uneven spread of ink, is excellent in ink absorption, is high in density and sharpness of recorded images, can provide a recorded dot close to a true circle and besides, is excellent in water resistance of recorded dots.

10 [Background Art]

The ink jet recording method performs recording of letters or images by allowing ink droplets ejected by various working principles to deposit on a recording sheet such as paper. The ink jet recording has such favorable features that it makes high-speed recording possible, that it produces little noise, that it can easily perform multi-color recording, that there is no limitation as to kind of patterns, and that it requires no developing-fixing. Thus, the ink jet recording is rapidly becoming widespread as devices for recording various characters including kanji and color images. Furthermore, the images formed by the multi-color ink jet recording method are by no means inferior to those printed by a multi-color press of those obtained by a color-photography. Besides, use of the ink jet recording extends to a field of full-color image recording where number of copies is not so many, since costs per copy are less than those employing the photographic process.

As for the recording sheets used for ink jet recording, efforts have been made from the aspects of printer hardwares or ink composition in order to use woodfree papers or coated papers used for ordinary printing or writing. However, improvements in recording sheets have come to be required increasingly in order to go side by side with developments in printer hardwares such as ever increasing speed, development of ever finer definition and images of full color.

25 That is, for recording sheets, it is required that image density of the printed ink dots be high and hue characteristics be bright and appealing, and the ink absorbing speed be high and as a result, the ink applied do not bleed or spread even though the recorded dots are put over additionally. Moreover, the diffusion of the recorded dot in the transverse direction should not be greater than needed and the circumference of dots should be sharp and demarcating.

The ink jet recording sheets as to their form can be roughly classified into those of plain paper type represented by so-called fine papers • bond papers and those of coated type which comprise a support such as paper, for example, fine paper, synthetic paper or synthetic resin film and an ink-receiving layer provided on the support.

The coated type includes ink jet recording sheets of low-coat type of about 1-10 g/m², intermediate-coat type of about 10-20 g/m² and high-coat type of more than 20 g/m².

Especially, recently, among low-coat type sheets, slight-coat type sheets of 0.5-5.0 g/m² which is the coating amount of the lower limit are close to plain papers and are preferred in both the appearance and the handling, and the slight-coat type sheets are increasingly desired. However, in the case of color recording, not only monochromatic recording of yellow, magenta, cyan or black, but also overlapping recording of these colors are effected and the deposition amount of ink is very large. Therefore, in the case of slight-coat type sheet, ink cannot be completely absorbed by the coat layer and it becomes necessary to absorb a part of the deposited ink by the base paper per se used as a support by using a base paper of relatively lower sizing.

Japanese Patent Kokai No.60-63191 discloses ink jet recording sheets having a high ink absorption and capable of providing recorded dots of good shape. This patent publication is characterized in that a filler and a fibrous material are contained together in the surface layer of the recording material (ink jet recording sheet). It describes that the material has a base comprising a fibrous material and filler particles which are thinly scattered and deposited on the surface of the base. It mentions the state of the filler and the fibrous material being present together in the surface layer, but does not mention the state of the fibrous material constituting the base being exposed at the surface layer.

In order to solve these problems, Japanese Patent Kokoku No.3-26665 discloses an example of ink jet recording sheet comprising a base paper having a Stöckigt sizing degree of 4 seconds or less at a standard of 60 g/m² in basis weight and, provided thereon, a coat layer containing fine particle silica and a water soluble polymer binder, Japanese Patent Kokai No.59-38087 discloses an example of ink jet recording material comprising a base having a sizing degree of 0-10 seconds and an ink absorbing layer provided thereon, and Japanese Patent Kokai No.59-9516 discloses an example of ink jet recording sheet comprising a base paper having a Stöckigt sizing degree of 0-5 seconds and impregnated with polyvinylpyrrolidone or the like.

Japanese Patent Kokai No.5-221115 discloses an ink jet recording sheet of the present applicant. The ink jet recording sheet disclosed in this publication comprises a support provided with an ink-receiving layer on one side and a backcoat layer on another side wherein the ink-receiving layer contains starch particles or processed starch particles thereof or at least one specific ethylene-vinyl acetate copolymer resin and a cationic dye fixer, said fixer being contained in such an amount that the cationic charge quantity is 0.2-40 meq./m² per unit area of the recording sheet. The object

is to attain high image density, excellent ink absorption, reduction of spread in color-overlapping portions, inhibition of yellowing and inhibition of curling. However, the ink-receiving layer of this patent publication is specified in cationic charge quantity given by the fixer and contains specific materials as essential components and the publication does not suggest use of specific particles and cationic charge quantity of ink jet recording sheet per unit weight.

Moreover, various proposals have been made to improve water resistance of dyes. For example, Japanese Patent Kokai No.56-84992 discloses a method of adding polycationic polyelectrolytes to the surface and Japanese Patent Kokai No.55-150396 discloses a method of imparting water resistance by producing chelates with dyes in the aqueous ink. Furthermore, Japanese Patent Kokai No.60-11389 discloses an ink jet recording sheet characterized by containing a basic oligomer to improve both the water resistance and the light resistance of dyes. As an example of using polyvinylamine copolymers, Japanese Patent Kokai No.64-8085 discloses a recording material (ink jet recording sheet) improved in water resistance and light resistance by containing cationic polymers or salts thereof (polyvinylamine derivatives). However, the polyvinylamine derivatives are polymers or copolymers containing substantially no (meth)acrylic acid monomer unit.

As described above, when coating amount of the ink-receiving layer is small, a base paper of relatively low sizing degree is used to allow the support per se to absorb a part of the deposited ink. However, when the excess ink which cannot be absorbed by the ink-receiving layer is absorbed by the support per se, the recorded image is low in density and lacks sharpness. In addition, as aforementioned, the ink jet recording sheet specified in the cation charge quantity comprises combination of specific materials of the ink-receiving layer and differs in function and effect from the ink jet recording sheet of the present invention which is slight-coat type.

In JP-A-60219084, an ink jet recording medium is disclosed, wherein the ink receiving layer comprises cationic colloidal silica coated at an amount of 3-10 g/m².

In JP-A-60219083, an ink jet recording medium is disclosed, wherein the ink receiving layer comprises a mixture of cationic and anionic colloidal silica.

The object of the present invention is to provide a slight-coat type ink jet recording sheet which shows no uneven spread of ink, is excellent in ink absorption, is high in density and sharpness of the recorded image, can provide a recorded dot close to a true circle and besides, is excellent in water resistance of recorded dots.

[Disclosure of Invention]

As a result of intensive research, the inventors have invented an ink jet recording sheet which shows no uneven spread of ink, is excellent in ink absorption, is high in density and sharpness of the recorded image, can provide a recorded dot close to a true circle and besides, is excellent in water resistance of recorded dots.

That is, the first embodiment of the present invention relates to an ink jet recording sheet comprising a support and an ink-receiving layer coated thereon wherein the ink-receiving layer is a coated layer mainly composed of a non-spherical cationic colloidal silica and is contour-coated along the surface of the support, the coating amount being 0.5-5.0 g/m².

The contour-coated layer is a layer coated at a covering rate of at least 70% on the surface of the support.

The ink-receiving layer comprises a composition mainly composed of a non-spherical cationic colloidal silica and a binder.

The ink-receiving layer comprises 100 parts by weight of a non-spherical cationic colloidal silica and 5-20 parts by weight of a binder.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-20% by weight in coating liquid concentration on a support.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-10% by weight in coating liquid concentration on a support by a size press.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a rod coater.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a transfer roll coater.

The non-spherical cationic colloidal silica is acicular or columnar.

The ink jet recording sheet of the second embodiment of the present invention comprises a support and an ink-receiving layer coated thereon wherein the component of the ink-receiving layer is mainly composed of a non-spherical cationic colloidal silica and the ink-receiving layer is a coated layer which is contour-coated along the surface of the support, the coating amount being 0.5-5.0 g/m² and the total cationic charge quantity of the recording sheet is 0.5-20 meq/100 g.

The contour-coated layer is a layer coated at a covering rate of at least 70% on the surface of the support.

The ink-receiving layer comprises a composition mainly composed of a non-spherical cationic colloidal silica and a binder.

The ink-receiving layer comprises 100 parts by weight of a non-spherical cationic colloidal silica and 5-20 parts by weight of a binder.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-20% by weight in coating liquid concentration on a support.

5 The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-10% by weight in coating liquid concentration on a support by a size press.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a rod coater.

10 The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a transfer roll coater.

The non-spherical cationic colloidal silica is acicular or columnar.

15 The ink jet recording sheet of the third embodiment of the present invention comprises a support and an ink-receiving layer coated thereon wherein the support contains a polyvinylamine copolymer prepared by copolymerization reaction of N-vinylformamide and acrylonitrile and having a molecular weight of 50000 or more and a molar ratio of vinylamine of 20 mol% or more, the ink-receiving layer component is mainly composed of non-spherical cationic colloidal silica and the ink-receiving layer is contour-coated along the surface of the support, the coating amount being 0.5-5.0 g/m².

The total cationic charge quantity of the recording sheet is 0.5-20 meq/100 g.

The contour-coated layer is a layer coated at a covering rate of at least 70% on the surface of the support.

20 The ink-receiving layer comprises a composition mainly composed of a non-spherical cationic colloidal silica and a binder.

The ink-receiving layer comprises 100 parts by weight of a non-spherical cationic colloidal silica and 5-20 parts by weight of a binder.

25 The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-20% by weight in coating liquid concentration on a support.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 4-10% by weight in coating liquid concentration on a support by a size press.

The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a rod coater.

30 The ink-receiving layer is obtained by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on a support by a transfer roll coater.

The non-spherical cationic colloidal silica is acicular or columnar.

The ink jet recording sheet of the present invention will be explained in detail below.

35 The ink jet recording sheet of the present invention comprises a support and a slightly coated ink-receiving layer which is contour-coated along the surface of the support wherein the components of the ink-receiving layer are specified.

40 In the first ink jet recording sheet of the present invention, the ink-receiving layer is a coated layer contour-coated along the surface of a base paper. The term "contour-coated layer" means a surface of a coated layer coated with components of the ink-receiving layer along the projected portions (mountains) and the dented portions (valleys) of the surface of a base paper, and the coated surface has the surface contour similar to that of the base paper.

The "contour-coating" generally means coating on the surface of a base paper by an air knife coater, thereby to form a thick-coated layer which is reflective of the surface contour of the base paper. This expression is cited for the slight-coat type ink jet recording sheet of the present invention.

45 The "contour-coated layer" can be compared by another expression to a row of mountains covered with snow which are seen far away, namely, the row of mountains in the surface of the base paper and the snowscape of the mountains is the surface of the ink-receiving layer. If the snowfall is small, trees not covered with snow are seen in places. Similarly, if the coating amount is small, there is seen the state of pulp fibers being exposed at the surface of the ink-receiving layer. If the snowfall is large, the contour of the mountains is recognized and a somewhat larger amount of snow lies on the slope of the mountains. Similarly, if the coating amount is large, shape of the pulp fibers can be recognized on the surface of the ink-receiving layer and a somewhat larger amount of ink-receiving layer component covers the dented portions (valleys) between the pulp fibers.

50 If the snowfall is larger, the slope of the mountains is covered with a large amount of snow and the contour of the mountains cannot be definitely seen. Similarly, if the coating amount is larger, the dented portions (valleys) between the pulp fibers are filled up with the ink-receiving layer component and the shape of the pulp fibers cannot be recognized and the surface of the ink-receiving layer flattens. In this case, the ink jet recording sheet as a coated paper is reminded of from a plain paper and is outside the scope of the ink jet recording sheet of the present invention.

55 The contour-coated layer in the ink jet recording sheet of the present invention is a layer coated on the surface of the support at a covering rate of at least 70% and this means that the support is coated to such an extent that the shape

of pulp fibers of the surface of the ink-receiving layer present on the support, namely, the base paper can be sufficiently recognized. The support is uniformly covered with ink-receiving layer, namely, with non-spherical cationic colloidal silica along the surface of the pulp fibers and is thinly covered therewith in conformity with the shape of the surface of the pulp fibers. The surface covering rate of the ink-receiving layer is such that 70% or more of the surface of the pulp fibers is covered. Thereby, the characteristics aimed at by the present invention can be sufficiently exhibited. The covering rate is preferably at least 80%, more preferably at least 90%.

The reason therefor is as follows. In the case of the surface of the ink-receiving layer coated being uniform, when ink is applied to the surface of the ink-receiving layer by an ink jet printer, the ink does not spread in the planar direction of the ink-receiving layer because of the uniform surface of the ink-receiving layer and the recorded dot can be expressed in the form of nearly a true circle and the excess ink permeates in the thickness direction of the base paper from the surface. On the other hand, if the covering rate of the ink-receiving layer over the pulp fibers is less than 70%, the ratio of the ink spreading in planar direction at the surface of the ink-receiving layer is high and as a result, the shape of the recorded dot is out of true circle. Furthermore, permeation into the base paper is irregular and ink bleeds.

In the present invention, the contour-coated layer is preferably coated on the surface of support in the form of continuous layer of a uniform thickness and when the continuous layer is formed, this is prescribed to be a covering rate of 100%. Thickness of the coated layer relates to the coating amount, but the layer is preferably a continuous layer even if the thickness is thin. Thickness of the coat layer is about 0.3-3 μm . However, the contour-coated layer does not necessarily completely cover the surface of the support and a covering rate of at least 70% is preferred. For measuring the covering rate, a scanning electron microscope can be used and image analysis is carried out to calculate area ratio.

In the ink jet recording sheet of the present invention, as a means to measure the covering rate of the coat layer on the surface of pulp fibers at the ink-receiving layer, a scanning electron microscope can be used and image analysis is conducted to calculate the area ratio.

The ink jet recording sheet according to the present invention is characterized by having a type close to slight-coat type paper and plain paper by forming an ink-receiving layer contour-coated along the surface of a support. When the ink jet recording sheet is subjected to recording using an ink jet printer, recorded dots close to true circles can be obtained. The applied ink is instantaneously absorbed by the non-spherical cationic colloidal silica which is superior in absorbability and excess ink permeates in the direction of thickness which is sectional direction of the coated layer. Therefore, there are obtained recorded dots free from uneven ink spread.

The ink jet recording sheet of the present invention has component of ink-receiving layer mainly composed of a non-spherical cationic colloidal silica.

The non-spherical cationic colloidal silica used in the present invention is non-spherical colloidal silica which is cation-modified by coating the surface with a hydrated metal oxide which is a cation modifier. The term "non-spherical" used here means "substantially not spherical" and means various forms such as acicular, columnar, rosary-like, rod-like, platy, bulky, fibrous and spindle-like forms. Moreover, it includes fibrous form made by agglomeration into a long chain form. Especially preferred are acicular and columnar ones.

As the non-spherical cationic colloidal silica used in the present invention, there may be preferably used colloidal silica covered with a cation modifier comprising a metal oxide hydrate such as aluminum oxide hydrate, zirconium oxide hydrate, tin oxide hydrate or the like and especially preferred is one cation-modified with aluminum oxide hydrate.

Methods of cation modification used include those described in U.S. Patent No.3,007,878 and Japanese Patent Kokoku No.47-26959.

The diameter of pulp fibers which form a base paper is in the order of several 10 μm and the maximum shorter diameter of the non-spherical cationic colloidal silica used in the present invention is 50 nm or less, preferably 30 nm or less and the length of the colloidal silica is 300 nm or less, preferably 100 nm or less.

Since the ratio of the diameter of pulp fibers and the particle diameter of the colloidal silica is several hundredth or less, even the surface of pulp fibers projected over the surface of base paper can be thinly coated with such a small coating amount as described above.

The non-spherical cationic colloidal silica is normally used in the form of colloidal dispersion in water with keeping the size of primary particles.

In the non-spherical cationic colloidal silica used in the ink jet recording sheet of the present invention, coating amount of the metal oxide hydrate as a cation modifier is advantageously in the range of 1-30% by weight in terms of metal oxide on the basis of silica (in terms of SiO_2). If the coating amount is less than 1% by weight, water resistance of the image recorded with ink on the ink jet recording sheet is conspicuously deteriorated and if it is too much, film properties on the coated surface become brittle to cause cracking. The coating amount is preferably 2.5-25% by weight, more preferably 5-20% by weight.

Furthermore, the dispersion of the non-spherical cationic colloidal silica may further contain an acid component such as acetic acid, citric acid, sulfuric acid, phosphoric acid or the like for colloid stability.

The component of the ink-receiving layer of the ink jet recording sheet of the present invention is mainly composed of the non-spherical cationic colloidal silica and is further constituted of the non-spherical cationic colloidal silica and a

binder, the amount of the binder being 5-20 parts by weight, preferably 7-15 parts by weight for 100 parts by weight of the colloidal silica.

That the effect of the present invention can be exhibited with use of a small amount of binder in the coating liquid for the ink-receiving layer is due to the binder effect of the colloidal silica per se. Even though there is the binding effect of the colloidal silica per se, if the amount of binder is less than 5 parts by weight, this is insufficient and if it exceeds 20 parts by weight, the binder damages the ink absorbability.

In the ink jet recording sheet of the present invention, concentration of the coating liquid for the ink-receiving layer is preferably 4-20% by weight. If the concentration is less than 4% by weight, it is difficult to coat the layer in a given amount on the support and if it is more than 20% by weight, the coating amount exceeds the desired amount in the case of some coating methods and the resulting sheet becomes like the coated paper type. This is not preferred.

For coating the ink-receiving layer using a coating liquid of the above specific concentration, there may be used various apparatuses such as blade coater, roll coater, air knife coater, bar coater, rod coater, gate roll coater, curtain coater, short-dowel coater, gravure coater, flexogravure coater, and size press in the manner of on- or off-machine. Of these coaters, size press, rod coater, transfer roll coater and air knife coater are preferred.

After coating, the coated sheet may be finished by calenders such as machine calender, temperature gradient (TG) calender, super calender and soft calender.

Especially, when the coating liquid of the ink-receiving layer comprising the above composition has a concentration of 4-10% by weight, it is preferred to use a size press. If the concentration of the coating liquid is less than 4% by weight here, it is difficult to coat the liquid in a given amount on the support and if it is more than 10% by weight, the coating amount exceeds the desired amount and the resulting sheet becomes close to coated paper type. This is not preferred.

Further, when the coating liquid of the ink-receiving layer comprising the above composition has a concentration of 10-20% by weight, it is preferred to use rod coater, transfer roll coater or air knife coater. If the concentration of the coating liquid is less than 10% by weight, it is difficult to coat the layer in a given amount on the support and if it is more than 20% by weight, the coating amount exceeds the desired amount and the resulting sheet becomes like the coated paper type. This is not preferred.

As aforementioned, with reference to the ink jet recording sheet of the present invention, the surface state of the ink-receiving layer is explained above figuratively, and specifically the coating amount of the ink-receiving layer is 0.5-5.0 g/m², preferably 1.0-4.0 g/m². Within this range, the ink jet recording sheet of the present invention can be obtained and can be handled as a type near the plain papers. If the coating amount is more than 5.0 g/m², no ink jet recording sheet close to plain papers can be obtained. On the other hand, if it is less than 0.5 g/m², the component of the ink-receiving layer cannot cover uniformly the surface of the support and this is undesirable.

The ink jet recording sheet of the present invention can contain ultrafine inorganic pigments in addition to the non-spherical cationic colloidal silica. Examples of the ultrafine inorganic pigments are as shown below.

That is, mention may be made of silica (colloidal silica), alumina or alumina hydrates (alumina sol, colloidal alumina, cationic aluminum oxide or hydrates thereof, pseudoboehmite), surface-treated cationic colloidal silica, aluminum silicate, magnesium silicate and magnesium carbonate.

Furthermore, inorganic pigments usable in combination with the ultrafine inorganic pigments may be any of those which are known. As examples thereof, mention may be made of precipitated calcium carbonate, ground calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, synthetic amorphous silica, aluminum hydroxide, lithopone, zeolite, hydrated halloysite and magnesium hydroxide.

Among these inorganic pigments, preferred are porous inorganic pigments and examples are porous synthetic amorphous silica, porous magnesium carbonate and porous alumina and especially preferred is porous synthetic amorphous silica of great volume of micro pore.

Moreover, organic pigments such as styrene plastic pigments, acrylic plastic pigments, polyethylene, microcapsules, urea resin and melamine resin may be used together with the ultrafine inorganic pigments.

The binders used together with the non-spherical cationic colloidal silica include polyvinyl alcohol, vinyl acetate, oxidized starch, etherified starch, cellulose derivatives such as carboxymethyl cellulose and hydroxyethyl cellulose, casein, gelatin, soybean protein, silyl-modified polyvinyl alcohol; conjugated diene copolymer latexes such as maleic anhydride resin, styrene-butadiene copolymer and methyl methacrylate-butadiene copolymer; acrylic polymer latexes such as polymers or copolymers of acrylic esters and methacrylic esters and polymers or copolymers of acrylic acid and methacrylic acid; vinyl polymer latexes such as ethylene-vinyl acetate copolymer; functional group-modified polymer latexes obtained by modifying the above-mentioned various polymers with monomers containing functional group such as carboxyl group; aqueous binders such as thermosetting synthetic resins, for example, melamine resin and urea resin; synthetic resin binders such as polymethyl methacrylate, polyurethane resin, unsaturated polyester resin, vinyl chloride-vinyl acetate copolymer, polyvinyl butyral and alkyd resin. These may be used alone or in combination of two or more.

Moreover, known cationic resins may also be used together for fixing the dyes.

Furthermore, as other additives there may be used pigment dispersant, thickener, flowability improver, antifoamer, foam inhibitor, releasing agent, foaming agent, penetrant, coloring dye, coloring pigment, fluorescent whitener, ultraviolet absorber, antioxidant, preservative, antifungal agent, water-resisting agent, wet strengthening agent and dry strengthening agent.

The second ink jet recording sheet of the present invention comprises a support and a slight-coat type ink-receiving layer which is contour-coated along the surface of the support where components of the ink-receiving layer are specified and the total cationic charge quantity of the recording sheet is within a specific range per 100 g of the recording sheet.

The total cationic charge quantity of the ink jet recording sheet of the present invention is 0.5-20 meq/100 g, preferably 1.0-15 meq/100 g in conformity with the slight-coat type ink jet recording sheet. If the total cationic charge quantity is less than 0.5 meq/100 g, it is insufficient for attaining the object of the present invention and if it is more than 20 meq/100 g, the coating amount of the ink-receiving layer must also be increased and the resulting ink jet recording sheet is outside the scope of the slight-coat type ink jet recording sheet of the present invention.

The total cationic charge quantity concerns with fixability of ink dyes and in the case of the slight-coat type ink jet recording sheet of the present invention within the scope of the present invention, when an ink is applied by an ink jet printer, the anionic ink dye can be fixed in the ink-receiving layer and besides, the solvent for the ink can be rapidly absorbed into the support. As a result, it becomes possible to carry out ink jet recording of images of high image density and sharpness.

The components of ink-receiving layer which contributes to the total cationic charge quantity include the non-spherical colloidal silica of the present invention as a main component and cationic dye fixing agents and the like. The total cationic charge quantity within the range of the present invention is the total cationic charge quantity per 100 g of the ink jet recording sheet coated with the ink-receiving layer containing the above-mentioned cationic materials. Furthermore, the cationic charge quantity resulting from other materials than the components of the ink-receiving layer, namely, the cationic materials, for example, fillers comprising basic pigments such as calcium carbonate which are contained in the support per se can be added to the total cationic charge quantity and the resulting value can be employed as the total cationic charge quantity of the whole ink jet recording sheet and this is included in the present invention.

The total cationic charge quantity of the ink jet recording sheet can be measured by the following method. First, a recording sheet comprising a base paper as a support and an ink-receiving layer coated thereon is taken and subjected to maceration by adding an deionized water. A given amount thereof is taken and adjusted to pH 4-5 with addition of a buffer. Then, an anionic substance for colloidal titration is added, followed by filtration to obtain a sample of a given concentration. The total cationic charge quantity is measured using this sample by colloidal titration method.

The total cationic charge quantity is a cationic charge quantity of the recording sheet per 100 g and expediently, this is calculated by multiplying the sum of the cationic charge quantity of the support and that of the ink-receiving layer by a factor obtained by converting the total weight of the basis weight of the support and the coating amount of the ink-receiving layer into the weight per 100 g. The unit is meq/100 g.

The third ink jet recording sheet of the present invention comprises a support containing a specific polyvinylamine copolymer and a slight-coat type ink-receiving layer which is contour-coated along the surface of the support.

The support used in the ink jet recording sheet of the present invention contains a polyvinylamine copolymer which is prepared by copolymerization reaction of N-vinylformamide and acrylonitrile and has a molar ratio of vinylamine of 20 mol% or more and a molecular weight of 50000 or more. The ink jet recording sheet of the present invention comprises the above-mentioned support and the ink-receiving layer coated thereon and is excellent in water resistance of the recorded image.

The ink for ink jet recording comprises an aqueous ink mainly composed of a direct dye and an acid dye and the dye can be fixed by the reaction of the anionic portion of the dye with the cationic substance such as polyvinylamine copolymer used in the present invention. When a polyvinylamine copolymer is used as the cationic substance in making a base paper (support), the polyvinylamine copolymer strongly adsorbs to the pulp and is retained in the base paper (support). Since the dye in the recording ink is fixed by the polyvinylamine copolymer adsorbed into the support, water resistance of the recorded image is developed.

In the ink jet recording sheet comprising a support containing the polyvinylamine copolymer and an ink-receiving layer provided thereon, when the ink for ink jet recording is first applied to the ink-receiving layer, the ink is absorbed in the ink-receiving layer and excess ink is absorbed in the thickness direction of the recording sheet, namely, into the support and the polyvinylamine copolymer contained in the support contacts with the dye in the ink whereby the dye is fixed. Since the fixed dye is firmly set with the support, it is never dissolved away even when water is applied from outside. That is, a recorded image having water resistance is obtained.

Even in the case the polyvinylamine copolymer is one obtained by copolymerization of N-vinylformamide with acrylonitrile, if the vinylamine ratio is less than 20 mol%, a sufficient water resistance can hardly be obtained and if the molecular weight is less than 50000, fixability of the polyvinylamine copolymer in the pulp and ink-receiving layer decreases and the recorded image tends to deteriorate in water resistance.

The polyvinylamine copolymers used in the present invention can be contained in an amount of 1% by weight or more, preferably in an amount of 3% by weight or more based on the solid content of pulp in the support.

The polyvinylamine copolymers used in the present invention are copolymers as exemplified in Japanese Patent Kokai Nos.64-40694 and 4-11094.

5 As the monomers used for synthesis of the polyvinylamine copolymers, mention may be made of, for example, N-vinylacetamide, N-vinylpropionamide, methyl N-vinylcarbamate, ethyl N-vinylcarbamate and isopropyl N-vinylcarbamate in addition to N-vinylformamide.

10 As the monomers copolymerized with N-vinylformamide, mention may be made of, for example, acrylonitrile, (meth)acrylic esters of alcohols of 1-4 carbon atoms with (meth)acrylic acid, acrylamide and (meth)acrylic acid. Especially preferred are acrylonitrile and acrylamide.

15 Supports used in the present invention include base papers prepared by mixing wood pulp, for example, chemical pulp such as LBKP and NBKP, mechanical pulp such as SGW, PGW, RMP, TMP, CTMP, CMP and CGP or recycled pulp such as DIP and known pigments in addition to the above polyvinylamine copolymer as main components with at least one of known additives such as binder, sizing agent, fixing agent, retention aid, cationizing agent and strengthening agent and making paper from the resulting mixture by a paper former such as Foudrinier machine, cylinder machine and twin wire machine.

More preferred are the above base papers subjected to surface sizing with water-soluble polymers such as starch and polyvinyl alcohol. When the sized base papers are used, coatability and fixability of the ink-receiving layer can be improved.

20 The ink-receiving layer may be provided on such base papers as they are or after subjected to calendering using calendering apparatuses such as machine calender, temperature gradient (TG) calender and soft calender to control the flattening.

The ink for ink jet recording used in the present invention is an aqueous ink comprising the following colorants, solvents and other additives.

25 The colorants include water-soluble dyes such as direct dyes, acid dyes, basic dyes, reactive dyes and food dyes.

30 The solvents for the aqueous ink include water and various water-soluble organic solvents, for example, alkyl alcohols of 1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and isobutyl alcohol; amides such as dimethylformamide and dimethylacetamide; ketones or ketone alcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols having 2 to 6 alkylene groups such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol and diethylene glycol; and lower alkyl ethers of polyhydric alcohols such as glycerin, ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether and triethylene glycol monomethyl ether. Of these many water-soluble organic solvents, preferred are polyhydric alcohols such as diethylene glycol and lower alkyl ethers of polyhydric alcohols such as triethylene glycol monomethyl ether and triethylene glycol monoethyl ether.

35 As other additives, mention may be made of, for example, pH regulators, chelating agents, preservatives, viscosity modifiers, surface tension modifiers, wetting agents, surface active agents and anticorrosive agents.

The ink jet recording sheet of the present invention can be used not only as sheet for ink jet recording, but also as any recording sheets on which an ink which is liquid state at the time of recording is put for recording.

40 For example, these recording sheets include an image-receiving sheet for heat transfer recording which comprises heating an ink sheet comprising a thin support such as a resin film, a high-density paper or a synthetic paper coated with a heat-meltable ink mainly composed of dye or pigment from the back side to melt the ink and transferring the molten ink; an ink jet recording sheet which makes use of droplets of a heated and molten ink and splashing them, an ink jet recording sheet which uses an ink prepared by dissolving an oil-soluble dye in a solvent and an image-receiving sheet on which images are transferred from a photosensitive and pressure-sensitive donor sheet coated with microcapsules containing a photopolymerizable monomer and colorless or colored dye or pigment.

45 These recording systems are common in that the ink is in a liquid state at the time of recording. A liquid ink permeates or diffuses vertically and horizontally through the ink-receiving layer until it hardens, solidifies or becomes fixed. Ink absorbing ability of the recording sheets in conformity with the respective recording system is required, so that the ink jet recording sheet of the present invention can be utilized successfully in these recording systems.

Furthermore, the ink jet recording sheets of the present invention can be used as the recording sheets for electrophotographic recording system which is widely used in copiers, printers and the like, where a toner is fixed by heating.

55 First, the ink jet recording sheet of the present invention comprises a support and an ink-receiving layer coated thereon wherein the ink-receiving layer is a coat which is mainly composed of a non-spherical cationic colloidal silica and which is contour-coated along the surface of the support at a coating amount of 0.5-5.0 g/m². When an ink is applied to the surface of the ink-receiving layer of the recording sheet, the ink does not spread in the surface direction, but permeates through the surface of the ink-receiving layer and excess ink permeates in the thickness direction of the base paper. Thereby, recorded dots close to true circle can be obtained and an ink jet recording sheet high in density

of recorded image and in sharpness can be obtained.

Secondly, the ink jet recording sheet of the present invention comprises a support and an ink-receiving layer coated thereon wherein the ink-receiving layer is a coat which is mainly composed of a non-spherical cationic colloidal silica and which is contour-coated along the surface of the support at a coating amount of 0.5-5.0 g/m² and the total cationic charge quantity of the recording sheet is 0.5-20 meq/100 g. When an ink is applied to the surface of the ink-receiving layer of the recording sheet, the anionic ink dye is rapidly fixed in the ink-receiving layer (partially in the base paper) and the ink does not spread in the direction of the surface and the excess ink permeates in the direction of thickness of the base paper. Thereby, recorded dots close to true circle can be obtained and an ink jet recording sheet high in density of recorded image and in sharpness can be obtained.

Furthermore, thirdly, the ink jet recording sheet of the present invention comprises a support and an ink-receiving layer coated thereon wherein the support contains a polyvinylamine copolymer prepared by copolymerization reaction of N-vinylformamide and acrylonitrile and having a molecular weight of 50000 or more and a molar ratio of vinylamine of 20 mol% or more, the ink-receiving layer component is mainly composed of a non-spherical cationic colloidal silica and the ink-receiving layer is contour-coated along the surface of the support at a coating amount of 0.5-5.0 g/m². When an ink is applied to the surface of the ink-receiving layer of the recording sheet, the anionic ink dye is rapidly fixed in the ink-receiving layer and the ink does not spread in the direction of the surface and then, the excess ink permeates in the direction of thickness of the support (base paper). The excess ink contacts with the polyvinylamine copolymer in the support to result in fixing of the dye. It is presumed that the excellent water resistance can be obtained by this fixation of the dye.

[Best Mode for Carrying Out the Invention]

Examples of the present invention will be explained below, but the present invention is not limited to these examples. In the examples, "part" and "%" indicate part by weight and % by weight, respectively, unless otherwise notified.

The ink jet recording sheets prepared in the following examples and comparative examples were evaluated by the following methods and the results are shown in Tables 1-6 and 8.

[Ink absorbability]

Ink absorbability and sharpness of image were conducted by visually judging the degree of ink mixing at the boundary between the solid portions printed by superposing inks, for example, the boundary between red print (magenta + yellow) and green print (cyan + yellow). When the red print portion and the green print portion did not overlap and separated, the characteristic is good and when they overlapped in a large area to form a black line, the characteristic is bad. In the case of the ink jet recording sheets which are inferior in ink absorbability, the quality of the resulting image (sharpness of image) is considerably damaged and therefore the sheets are worthless even if other characteristics such as image density are good.

The evaluation criteria are as follows.

A: The characteristics are good.

B: Practically acceptable.

C: Practically unsatisfactory.

D: The characteristics are bad.

[Image density]

The image density was measured on the solid portion printed with a black ink by a reflective densitometer (Macbeth RD918 manufactured by Macbeth Co., Ltd.). The higher value indicates the higher image density and the superior result. Normally, 1.20 or more is satisfactory.

[Covering rate]

The covering rate (%) was obtained in the following manner. X-ray photograph of a metal element of the material on the surface of pulp fibers of the ink jet recording sheet was taken by a scanning electron microscope and the covering rate on the support was measured as an area ratio using an image analyzer.

[Shape factor of dot]

Single color dot was printed with a black ink using an ink jet printer (IO-720 manufactured by Sharp Corporation)

and length of perimeter L of the dot and area A of the dot were measured by an image analyzer, and shape factor C of the dot defined by the following formula was calculated. With the shape factor C increasing and departing from 1.0, the shape of dot becomes irregular due to spread of the dot.

$$C = L^2 / (4\pi \times A)$$

where C denotes shape factor of dot, L denotes length of perimeter of dot and A denotes area of dot.

[Examples 1-5 and Comparative Examples 1-4]

Example 1

[Preparation of base paper]

To a pulp slurry comprising 83 parts of LBKP having a freeness of 450 ml cfs and 8 parts of NBKP having a freeness of 480 ml csf were added 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ketene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner machine, dried and finished by a machine calender. The resulting base paper had a basis weight of 85 g/m² and a Stöckigt sizing degree of 25 seconds.

[Preparation of ink jet recording sheet]

On the thus obtained base paper was coated, as a composition of ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of an aqueous dispersion of acicular cation-modified colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.41 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 6.2% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂) and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601; cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a size press so that the dry solid content was 0.5 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Example 2

An ink jet recording sheet was prepared in the same manner as in Example 1 except that the coating was carried out using a rod coater so that the dry solid content was 1.0 g/m².

Example 3

An ink jet recording sheet was prepared in the same manner as in Example 1 except that the coating was carried out using a transfer roll coater so that the dry solid content was 3.0 g/m².

Example 4

An ink jet recording sheet was prepared in the same manner as in Example 1 except that the coating was carried out using an air knife coater so that the dry solid content was 5.0 g/m².

Comparative Example 1

An ink jet recording sheet was prepared in the same manner as in Example 1 except that the coating was carried out using a size press so that the dry solid content was 0.3 g/m².

Comparative Example 2

An ink jet recording sheet was prepared in the same manner as in Example 1 except that the coating was carried out using an air knife coater so that the dry solid content was 5.5 g/m².

Example 5

An ink jet recording sheet was prepared in the same manner as in Example 1 except that a 10% aqueous disper-

sion of columnar cationic colloidal silica (particle size: 40 nm in width $\times$ 100-300 nm in length; cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2) was used in place of the acicular cation-modified colloidal silica used in Example 1 and the coating was carried out using a transfer roll coater so that the dry solid content was 3.0 g/m².

Comparative Example 3

An ink jet recording sheet was prepared in the same manner as in Example 1 except that 250 parts of a 40% aqueous dispersion of spherical colloidal silica (primary particle size: 300 ± 30 nm; cationic charge quantity: -0.01 meq/g) was used in place of the acicular cation-modified colloidal silica used in Example 1 and the coating was carried out using a transfer roll coater so that the dry solid content was 3.0 g/m².

Comparative Example 4

An ink jet recording sheet was prepared in the same manner as in Example 1 except that 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm ; cationic charge quantity: -0.09 meq/g) was used in place of the acicular cation-modified colloidal silica used in Example 1 and the coating was carried out using a transfer roll coater so that the dry solid content was 3.0 g/m².

The ink jet recording sheets obtained in Examples 1-5 and Comparative Examples 1-4 were evaluated and the results are shown in Table 1.

Table 1

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 1	A	1.38	A	81	1.12
Example 2	A	1.30	B	72	1.15
Example 3	A	1.40	A	84	1.10
Example 4	A	1.52	A	96	1.08
Comparative Example 1	C	1.27	C	68	1.27
Comparative Example 2	A	1.52	A	95	1.10
Example 5	A	1.45	A	84	1.12
Comparative Example 3	B	1.23	C	65	1.20
Comparative Example 4	B	1.10	C	62	1.29

As can be seen from the results of Table 1, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer, superior in ink absorbability, image density and sharpness, and small in shape factor of dot which indicates shape of the recorded dot close to true circle.

On the other hand, Comparative Examples 1 and 2 are examples where coating amount of the ink-receiving layer was outside the range of the present invention. In Comparative Example 1, ink absorbability and sharpness were inferior and in Comparative Example 2, the results were good, but the sheet was not preferable to be handled as a plain paper. In Comparative Example 3, spherical colloidal silica was used and since it was not cation-modified, sharpness of image was inferior, the covering rate was low and the shape factor of dot was inferior. In Comparative Example 4, since the particle size of the inorganic pigment used was great, sharpness of the image was inferior, the covering rate was low and the shape factor of dot was inferior.

[Examples 6-11 and Comparative Examples 5-9]

Example 6

5 [Preparation of base paper]

To a pulp slurry comprising 83 parts of LBKP having a freeness of 450 ml cfs and 8 parts of NBKP having a free-
ness of 480 ml csf were added 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ket-
ene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner
10 machine, dried and finished by a machine calender. The resulting base paper had a basis weight of 85 g/m² and a
Stöckigt sizing degree of 25 seconds.

[Preparation of ink jet recording sheet]

15 On the thus obtained base paper was coated, as a composition of ink-receiving layer, an aqueous dispersion of
10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cation-
modified colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.41 meq/g)
prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 6.2% by weight in
terms of Al₂O₃ based on silica (in terms of SiO₂), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117
20 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix
601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so
that the dry solid content was 1 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was
obtained.

25 Example 7

An ink jet recording sheet was prepared in the same manner as in Example 6 except that the coating was carried
out using a size press so that the dry solid content was 0.5 g/m².

30 Example 8

An ink jet recording sheet was prepared in the same manner as in Example 6 except that the coating was carried
out using a rod coater so that the dry solid content was 2 g/m².

35 Example 9

An ink jet recording sheet was prepared in the same manner as in Example 6 except that the solid concentration
of the aqueous dispersion was 15% and the coating was carried out using an air knife coater so that the dry solid con-
tent was 5 g/m², followed by drying and calendering.

40

Example 10

On the base paper prepared in Example 6 was coated, as a composition of ink-receiving layer, an aqueous disper-
sion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular
45 cation-modified colloidal silica (Snowtex UP-AK (1) manufactured by Nissan Chemical Industries, Ltd., agglomerate,
particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.71 meq/g) prepared by modifying
acicular colloidal silica with aluminum oxide hydrate in an amount of about 11% by weight in terms of Al₂O₃ based on
silica (in terms of SiO₂), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray
Co., Ltd.) as an adhesive and 100 parts of a 30% aqueous solution of a cationic resin (Sumirez Resin 1001; cationic
50 charge quantity 3.5 meq/g, manufactured by Sumitomo Chemical Co., Ltd.) as a dye fixer by a transfer roll coater so
that the dry solid content was 2 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was
obtained.

Example 11

55

On the base paper prepared in Example 6 was coated, as a composition of ink-receiving layer, an aqueous disper-
sion of 15% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar
cationic colloidal silica (particle size: 40 nm in width × 100-300 nm in length; cationic charge quantity: 1.90 meq/g) pre-

pared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601; cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by an air knife coater so that the dry solid content was 5 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Comparative Example 5

On the base paper prepared in Example 6 was coated, as a composition of ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 250 parts of a 40% aqueous dispersion of spherical colloidal silica (primary particle size: 300 ± 30 nm; cationic charge quantity: -0.01 meq/g), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601; cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 2 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Comparative Example 6

On the base paper prepared in Example 6 was coated, as a composition of ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 333 parts of a 30% aqueous dispersion of spherical colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) which was prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601; cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 2 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Comparative Example 7

On the base paper prepared in Example 1 was coated, as a composition of ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (agglomerate, particle size: 10-20 nm in width $\times$ 50-200 nm in length; cationic charge quantity: -0.02 meq/g), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 100 parts of a 30% aqueous solution of a cationic resin (Sumirez Resin 1001; cationic charge quantity 3.5 meq/g, manufactured by Sumitomo Chemical Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 2 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Comparative Example 8

On the base paper prepared in Example 6 was coated, as a composition of ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm ; cationic charge quantity: -0.09 meq/g), 300 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601; cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 2 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Comparative Example 9

An ink jet recording sheet was prepared in the same manner as in Comparative Example 7 except that the solid concentration of the aqueous dispersion was 15% and the coating was carried out using an air knife coater so that the dry solid content was 5 g/m², followed by drying and calendering.

The ink jet recording sheets obtained in Examples 6-11 and Comparative Examples 5-9 were evaluated and the results are shown in Table 2.

Table 2

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 6	A	1.38	A	81	1.12
Example 7	A	1.30	B	72	1.15
Example 8	A	1.40	A	84	1.10
Example 9	A	1.52	A	96	1.08
Example 10	A	1.41	A	85	1.13
Example 11	A	1.48	A	93	1.10
Comparative Example 5	B	1.08	C	64	1.24
Comparative Example 6	B	1.15	C	69	1.21
Comparative Example 7	A	1.17	C	85	1.21
Comparative Example 8	B	1.12	C	49	1.36
Comparative Example 9	C	1.18	B	68	1.31

As can be seen from the results of Table 2, as for the ink jet recording sheets of Examples 6-11 and Comparative Examples 5-9, the ink jet recording sheets of the Examples which used non-spherical colloidal silica and had a covering rate within the range of the present invention were superior in ink absorbability, image density and sharpness, and small in shape factor of dot which means shape of the recorded dot close to true circle.

On the other hand, in Comparative Examples 5 and 6, spherical colloidal silica was used and hence, the shape factor of the dot was great and shape of the recorded dot was inferior. In Comparative Example 7, acicular colloidal silica which was not cation-modified was used in place of the acicular colloidal silica of Example 10 which was cation-modified, and since the colloidal silica was not cation-modified, image density and sharpness were inferior. In Comparative Example 9, the coating amount was large, namely, 5 g/m², but the covering rate was low because particle size of the inorganic pigment used was great. In Comparative Example 8, the coating amount was 2 g/m² and the particle size of the inorganic pigment used was great and the covering rate was low.

[Examples 12-20 and Comparative Examples 10-15]

Example 12

To a pulp slurry comprising 90 parts of LBKP having a freeness of 450 ml csf and 10 parts of NBKP having a freeness of 480 ml csf were added 9 parts of kaolin, 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ketene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner machine and dried to obtain a base paper of 85 g/m² in basis weight. Subsequently, on the thus obtained base paper was coated, as a composition of ink-receiving layer, an aqueous dispersion of 4% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cation-modified colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length, cationic charge quantity: 0.41 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 6.2% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a size press so that the dry solid content was 0.5 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Example 13

An ink jet recording sheet was prepared in the same manner as in Example 12 except that the composition of ink-receiving layer had a solid concentration of 6% and was coated using a size press so that the dry solid content was 2 g/m².

Example 14

An ink jet recording sheet was prepared in the same manner as in Example 12 except that the composition of ink-receiving layer had a solid concentration of 10% and was coated using a size press so that the dry solid content was 4.5 g/m².

Comparative Example 10

An ink jet recording sheet was prepared in the same manner as in Example 12 except that the composition of ink-receiving layer had a solid concentration of 3% and was coated using a size press so that the dry solid content was 0.3 g/m².

Comparative Example 11

An ink jet recording sheet was prepared in the same manner as in Example 12 except that the composition of ink-receiving layer had a solid concentration of 12% and was coated using a size press so that the dry solid content was 5.5 g/m².

Example 15

An ink jet recording sheet was prepared in the same manner as in Example 12 except that as the composition of ink-receiving layer, there was used an aqueous dispersion of 6% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width × 100-300 nm in length, cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 100 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a size press so that the dry solid content was 2 g/m² and the coat was dried and finished by a machine calender to obtain an ink jet recording sheet.

Example 16

A paper was prepared in the same manner as in Example 12 and then, an oxidized starch was coated thereon by a size press at 0.5 g/m², dried and finished by a machine calender to obtain a sized base paper used in Example 16. Then, the 6% aqueous dispersion of Example 15 was coated thereon, dried and calendered under the same conditions as in Example 15 to prepare an ink jet recording sheet. The dry solid content in this case was 2.5 g/m².

Example 17

An ink jet recording sheet was prepared in the same manner as in Example 12 except that as the composition of ink-receiving layer, there was used an aqueous dispersion of 8% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 15 (particle size: 40 nm in width × 100-300 nm in length, cationic charge quantity: 1.90 meq/g), 150 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a size press and dried so that the dry solid content was 2 g/m² and finished by a machine calender to obtain an ink jet recording sheet.

Comparative Example 12

An ink jet recording sheet was prepared in the same manner as in Example 17 except that in place of the columnar cationic colloidal silica used in Example 17 there was used 333 parts of a 30% aqueous dispersion of spherical cationic

colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2). The dry solid content was 2.0 g/m².

5 Comparative Example 13

An ink jet recording sheet was prepared in the same manner as in Example 17 except that in place of the columnar cationic colloidal silica used in Example 17 there was used 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (agglomerate, particle size: 10-20 nm in width $\times$ 50-200 nm in length; cationic charge quantity: -0.02 meq/g). The dry solid content was 2.0 g/m².

Comparative Example 14

An ink jet recording sheet was prepared in the same manner as in Example 6 except that in place of the columnar cationic colloidal silica used in Example 17 there was used 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm ; cationic charge quantity: -0.09 meq/g). The dry solid content was 2.0 g/m².

Example 18

An ink jet recording sheet was prepared in the same manner as in Example 12 except that as the composition of ink-receiving layer, there was used an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 15 (particle size: 40 nm in width $\times$ 100-300 nm in length, cationic charge quantity: 1.90 meq/g), 200 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a size press and dried so that the dry solid content was 4.0 g/m² and finished by a calender to obtain an ink jet recording sheet.

30 Comparative Example 15

An ink jet recording sheet was prepared by coating the 10% aqueous dispersion used in Example 18 by an air knife coater, drying the coat and calendering the dried coat. The dry solid content was 6.0 g/m².

The ink jet recording sheets prepared in Examples 12-18 and Comparative Examples 10-15 were evaluated and the results are shown in Table 3.

Table 3

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 12	A	1.33	B	74	1.14
Example 13	A	1.40	A	86	1.09
Example 14	A	1.55	A	96	1.07
Comparative Example 10	C	1.26	C	66	1.28
Comparative Example 11	A	1.50	A	98	1.09
Example 15	A	1.38	A	85	1.10
Example 16	A	1.41	A	90	1.09
Example 17	A	1.36	A	83	1.12
Comparative Example 12	B	1.32	C	71	1.24

Table 3 (continued)

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Comparative Example 13	A	1.35	C	82	1.25
Comparative Example 14	B	1.11	C	44	1.46
Example 18	A	1.34	A	78	1.08
Comparative Example 15	A	1.32	A	92	1.08

As can be seen from the results of Table 3, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer and superior in ink absorbability, image density and sharpness, and small in shape factor of dot which means shape of recorded dot close to true circle.

In Examples 12-14 and Comparative Examples 10-11, the binder was used in the same amount. In Comparative Example 10, the desired amount could not be coated because the concentration of the coating solution was low. On the other hand, Comparative Example 11 gave good results, but since the concentration of the coating solution was high, the layer was coated in an amount more than needed and the sheet was not preferred to be handled as a plain paper.

Example 15 and Example 16 compared unsized base paper and sized base paper and when sized base paper was used, a larger amount of layer could be coated with the same concentration of coating liquid and the sheet was superior in various characteristics.

[Examples 19-25 and Comparative Examples 16-21]

Example 19

[Preparation of base paper]

To a pulp slurry comprising 90 parts of LBKP having a freeness of 450 ml csf and 10 parts of NBKP having a freeness of 480 ml csf were added 9 parts of kaolin, 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ketene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner machine and size pressed with 0.5 g/m² of oxidized starch, thereafter, dried and finished by a machine calender to obtain a base paper of 85 g/m² in basis weight.

[Preparation of ink jet recording sheet]

On the thus obtained base paper was coated, as a composition for ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cation-modified colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length, cationic charge quantity: 0.41 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 6.2% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 1.5 g/m² and the coat was dried and calendered. Thus, an ink jet recording sheet was obtained.

Example 20

An ink jet recording sheet was prepared in the same manner as in Example 19 except that the composition for ink-receiving layer had a solid concentration of 15% and was coated using a rod coater so that the dry solid content was 2.5 g/m².

Example 21

An ink jet recording sheet was prepared in the same manner as in Example 19 except that the composition for ink-

receiving layer had a solid concentration of 20% and was coated using a rod coater so that the dry solid content was 5.0 g/m².

Comparative Example 16

An ink jet recording sheet was prepared in the same manner as in Example 19 except that the composition for ink-receiving layer had a solid concentration of 5% and was coated using a rod coater so that the dry solid content was 0.3 g/m².

Comparative Example 17

An ink jet recording sheet was prepared in the same manner as in Example 19 except that the composition for ink-receiving layer had a solid concentration of 25% and was coated using a rod coater so that the dry solid content was 6.5 g/m².

Example 22

On the base paper prepared in Example 19 was coated an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width × 100-300 nm in length, cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 100 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 2.1 g/m², dried and finished by a calender to obtain an ink jet recording sheet.

Example 23

A base paper prepared in Example 19 without size pressing was used in Example 23 as a base paper. Then, the 10% aqueous dispersion of Example 22 was coated, dried and calendered under the same conditions to obtain an ink jet recording sheet. The dry solid content was 1.3 g/m².

Example 24

On the base paper prepared in Example 19 was coated an aqueous dispersion of 15% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 22 (particle size: 40 nm in width × 100-300 nm in length, cationic charge quantity: 1.90 meq/g), 150 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 2.0 g/m², dried and finished by a calender to obtain an ink jet recording sheet.

Comparative Example 18

An ink jet recording sheet was prepared in the same manner as in Example 26 except that in place of the columnar cationic colloidal silica used in Example 24 there was used 333 parts of a 30% aqueous dispersion of spherical cationic colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂). The dry solid content was 2.0 g/m².

Comparative Example 19

An ink jet recording sheet was prepared in the same manner as in Example 6 except that in place of the columnar cationic colloidal silica used in Example 24 there was used 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (agglomerate, particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: -0.02 meq/g). The dry solid content was 2.0 g/m².

Comparative Example 20

An ink jet recording sheet was prepared in the same manner as in Example 24 except that in place of the columnar cationic colloidal silica used in Example 24, there was used 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm ; cationic charge quantity: -0.09 meq/g). The dry solid content was 1.8 g/m².

Example 25

On the base paper prepared in Example 19 was coated an aqueous dispersion of 20% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 24 (particle size: 40 nm in width $\times$ 100-300 nm in length; cationic charge quantity: 1.90 meq/g), 200 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity: 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 4.5 g/m², the coat was dried and finished by a calender to obtain an ink jet recording sheet.

Comparative Example 21

An ink jet recording sheet was prepared by coating the 20% aqueous dispersion used in Example 25, drying and calendering the coat. The dry solid content was 7.0 g/m².

The ink jet recording sheets prepared in Examples 19-25 and Comparative Examples 16-21 were evaluated and the results are shown in Table 4.

Table 4

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 19	A	1.45	A	82	1.10
Example 20	A	1.48	A	88	1.08
Example 21	A	1.57	A	98	1.06
Comparative Example 16	C	1.20	C	63	1.30
Comparative Example 17	A	1.52	A	98	1.07
Example 22	A	1.44	A	91	1.10
Example 23	A	1.33	A	82	1.11
Example 24	A	1.38	A	85	1.10
Comparative Example 18	B	1.32	C	69	1.22
Comparative Example 19	A	1.34	C	81	1.23
Comparative Example 20	B	1.09	C	42	1.48
Example 25	A	1.50	A	93	1.10
Comparative Example 21	A	1.41	A	95	1.08

As can be seen from Table 4, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer and superior in ink absorbability, image density and sharpness, and small in shape factor of dot which means that the shape of recorded dot was close to a true circle.

In Examples 19-21 and Comparative Examples 16-17, the binder was used in the same amount. In Comparative Example 16, the desired amount of the layer could not be coated because the concentration of the coating liquid was low. On the other hand, Comparative Example 17 gave good results, but since the concentration of the coating liquid was high, the layer was coated in an amount more than needed and the sheet was not preferred to be handled as a plain paper.

Example 22 and Example 23 compared unsized base paper and sized base paper and when sized base paper was used, a larger amount of layer could be coated with the same concentration of coating solution and the sheet was superior in various characteristics.

In Example 24 and Comparative Examples 18-20, the material used was changed. When materials other than those of the present invention were used, the results were inferior.

In Example 25 and Comparative Example 21, the coater was changed. When the sheet was prepared using the air knife coater of Comparative Example 21, good evaluation results were obtained, but since the concentration of the coating liquid was high, the layer was coated in an amount more than needed and the sheet was not preferred to be handled as a plain paper.

[Examples 26-32 and Comparative Examples 22-27]

Example 26

To a pulp slurry comprising 90 parts of LBKP having a freeness of 450 ml csf and 10 parts of NBKP having a freeness of 480 ml csf were added 9 parts of kaolin, 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ketene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner machine and dried to obtain a base paper of 85 g/m² in basis weight. Subsequently, on the thus obtained base paper was coated, as a composition for ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cation-modified colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.41 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 6.2% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 1.5 g/m² and the coat was dried and finished by a machine calender. Thus, an ink jet recording sheet was obtained.

Example 27

An ink jet recording sheet was prepared in the same manner as in Example 26 except that the composition for ink-receiving layer had a solid concentration of 15% and was coated using a transfer roll coater so that the dry solid content was 2.5 g/m².

Example 28

An ink jet recording sheet was prepared in the same manner as in Example 26 except that the composition for ink-receiving layer had a solid concentration of 20% and was coated using a transfer roll coater so that the dry solid content was 5.0 g/m².

Comparative Example 22

An ink jet recording sheet was prepared in the same manner as in Example 26 except that the composition for ink-receiving layer had a solid concentration of 5% and was coated using a transfer roll coater so that the dry solid content was 0.3 g/m².

Comparative Example 23

An ink jet recording sheet was prepared in the same manner as in Example 26 except that the composition for ink-receiving layer had a solid concentration of 25% and was coated using a transfer roll coater so that the dry solid content was 6.5 g/m².

Example 29

An ink jet recording sheet was prepared in the same manner as in Example 26 except that as the composition for ink-receiving layer, there was used an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width $\times$ 100-300 nm in length; cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2), 100 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a transfer roll coater so that the dry solid content was 1.3 g/m² and the coat was dried and finished by a machine calender to obtain an ink jet recording sheet.

Example 30

A paper was prepared in the same manner as in Example 26 and then, 0.5 g/m² of an oxidized starch was coated thereon by a size press, dried and finished by a calender to obtain a sized base paper used in Example 30. Then, the 10% aqueous dispersion of Example 29 was coated thereon, dried and calendered under the same conditions to prepare an ink jet recording sheet. The dry solid content was 2.1 g/m².

Example 31

An ink jet recording sheet was prepared in the same manner as in Example 26 except that in place of the composition for ink-receiving layer of Example 26, there was used an aqueous dispersion of 15% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 29 (particle size: 40 nm in width $\times$ 100-300 nm in length; cationic charge quantity: 1.90 meq/g), 150 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a transfer roll coater so that the dry solid content was 2.0 g/m², dried and finished by a machine calender to obtain an ink jet recording sheet.

Comparative Example 24

An ink jet recording sheet was prepared in the same manner as in Example 31 except that in place of the columnar cationic colloidal silica used in Example 31, there was used 333 parts of a 30% aqueous dispersion of spherical cationic colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2). The dry solid content was 2.0 g/m².

Comparative Example 25

An ink jet recording sheet was prepared in the same manner as in Example 31 except that in place of the columnar cationic colloidal silica used in Example 31, there was used 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (particle size: 10-20 nm in width $\times$ 50-200 nm in length); cationic charge quantity: -0.02 meq/g). The dry solid content was 2.0 g/m².

Comparative Example 26

An ink jet recording sheet was prepared in the same manner as in Example 31 except that in place of the columnar cationic colloidal silica used in Example 31, there was used 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm ; cationic charge quantity: -0.09 meq/g). The dry solid content was 1.8 g/m².

Example 32

An ink jet recording sheet was prepared in the same manner as in Example 26 except that in place of the composition for ink-receiving layer of Example 26, there was used an aqueous dispersion of 20% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica used in Example 29 (particle size: 40 nm in width $\times$ 100-300 nm in length; cationic charge quantity: 1.90 meq/g), 200 parts of a 10%

aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer and this was coated by a transfer roll coater so that the dry solid content was 4.5 g/m² and dried and finished by a machine calender to obtain an ink jet recording sheet.

Comparative Example 27

An ink jet recording sheet was prepared by coating the 20% aqueous dispersion used in Example 32 by an air knife coater, drying the coat and calendering the dried coat. The dry solid content was 5.5 g/m².

The ink jet recording sheets prepared in Examples 26-32 and Comparative Examples 22-27 were evaluated and the results are shown in Table 5.

Table 5

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 26	A	1.42	A	81	1.12
Example 27	A	1.46	A	86	1.09
Example 28	A	1.55	A	97	1.05
Comparative Example 22	C	1.17	C	61	1.34
Comparative Example 23	A	1.50	A	96	1.08
Example 29	A	1.32	A	80	1.13
Example 30	A	1.43	A	89	1.11
Example 31	A	1.37	A	84	1.11
Comparative Example 24	B	1.30	C	66	1.24
Comparative Example 25	A	1.32	C	79	1.25
Comparative Example 26	B	1.06	C	41	1.50
Example 32	A	1.48	A	92	1.10
Comparative Example 27	A	1.45	A	93	1.09

As can be seen from the results of Table 5, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer and superior in ink absorbability, image density and sharpness and small in shape factor of dot which means that the shape of recorded dot was close to true circle.

In Examples 26-28 and Comparative Examples 22-23, the binder was used in the same amount. In Comparative Example 22, the desired amount of the layer could not be coated because the concentration of the coating liquid was low. On the other hand, Comparative Example 23 gave good results, but since the concentration of the coating liquid was high, the layer was coated in an amount more than desired and the sheet was not preferred to be handled as a plain paper.

Example 29 and Example 30 compared unsized base paper and sized base paper and when sized base paper was used, a larger amount of layer could be coated with the same concentration of coating liquid and the sheet was superior in various characteristics.

In Example 31 and Comparative Examples 24-26, the material used was changed. When materials other than those of the present invention were used, the results were inferior.

In Example 32 and Comparative Example 27, the coater was changed. When the sheet was prepared using the air knife coater of Comparative Example 27, good evaluation results were obtained, but since the concentration of the coat-

ing solution was high, the layer was coated in an amount more than desired and the sheet was not preferred to be handled as a plain paper.

[Examples 33-39 and Comparative Examples 28-34]

Example 33

[Preparation of base paper]

To a pulp slurry comprising 90 parts of LBKP having a freeness of 450 ml csf and 10 parts of NBKP having a freeness of 480 ml csf were added 9 parts of kaolin, 0.8 part of cationized starch, 0.4 part of aluminum sulfate and 0.10 part of an alkyl ketene dimer, thereby adjusting the pH of the pulp slurry to 8.2. A paper was prepared using the pulp slurry by Fourdriner machine and dried to obtain a base paper of 85 g/m² in basis weight. The cationic charge quantity of the resulting base paper was previously measured to obtain 0.02 meq/100 g.

[Preparation of ink jet recording sheet]

On the thus obtained base paper was coated, as a composition for ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cationic colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.46 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 7.0% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 0.5 g/m² and the coat was dried and finished by a machine calender. Thus, an ink jet recording sheet was obtained. The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 0.57 meq/100 g.

Example 34

An ink jet recording sheet was prepared in the same manner as in Example 33 except that the ink-receiving layer was coated so that the dry solid content thereof was 2.0 g/m². The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 2.30 meq/100 g.

Example 35

An ink jet recording sheet was prepared in the same manner as in Example 33 except that the ink-receiving layer was coated so that the dry solid content thereof was 4.5 g/m². The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 5.00 meq/100 g.

Comparative Example 28

An ink jet recording sheet was prepared in the same manner as in Example 33 except that the ink-receiving layer was coated so that the dry solid content thereof was 0.3 g/m². The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 0.35 meq/100 g.

Comparative Example 29

An ink jet recording sheet was prepared in the same manner as in Example 33 except that in place of the acicular cationic colloidal silica used in Example 33, there was used 333 parts of a 30% aqueous dispersion of spherical cationic colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂). The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 0.75 meq/100 g.

Comparative Example 30

An ink jet recording sheet was prepared in the same manner as in Example 34 except that in place of the acicular

cationic colloidal silica used in Example 34, there was used 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (agglomerate, particle size: 10-20 nm in width $\times$ 50-200 nm in length; cationic charge quantity: -0.02 meq/g). The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 1.30 meq/100 g.

Example 36

On the base paper prepared in Example 33 was coated an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width $\times$ 100-300 nm in length, cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 50 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a rod coater so that the dry solid content was 1.0 g/m^2 , dried and finished by a machine calender to obtain an ink jet recording sheet. The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 3.40 meq/100 g.

Comparative Example 31

An ink jet recording sheet was prepared in the same manner as in Example 36 except that in place of the columnar cationic colloidal silica used in Example 36 there was used 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: $1.0 \mu\text{m}$; cationic charge quantity: -0.09 meq/g). The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 1.70 meq/100 g.

Comparative Example 32

A base paper as prepared and dried in Example 33 was used as the ink jet recording sheet of Comparative Example 32 as it was. The total cationic charge quantity of the ink jet recording sheet was measured by colloidal titration to obtain 0.02 meq/100 g.

Example 37

[Preparation of base paper]

To a pulp slurry comprising 90 parts of LBKP having a freeness of 450 ml csf and 10 parts of NBKP having a freeness of 480 ml csf were added 10 parts of precipitated calcium carbonate (TP-121 manufactured by Okutama Kogyo Co., Ltd.) as a loading material, 0.8 part of cationized starch (Cato 3210 manufactured by Oji National Co., Ltd.), 0.4 part of aluminum sulfate and 0.1 part of an alkyl ketene dimer (SPK-903 manufactured by Arakawa Kagaku Co., Ltd.). Using the pulp slurry, a paper was prepared by Fourdriner machine, dried and finished by a machine calender to obtain a base paper of 85 g/m^2 in basis weight. The cationic charge quantity of the resulting base paper was previously measured to obtain 3.50 meq/100 g.

[Preparation of ink jet recording sheet]

Using the thus obtained base paper, an ink jet recording sheet was prepared in the same manner as in Example 42 except that the ink-receiving layer was coated so that the dry solid content thereof was 5.0 g/m^2 . The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 19.50 meq/100 g.

Comparative Example 33

An ink jet recording sheet was prepared in the same manner as in Example 36 except that the ink-receiving layer was coated so that the dry solid content thereof was 5.5 g/m^2 . The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 21.10 meq/100 g.

Example 38

On the base paper prepared in Example 37 was coated an aqueous dispersion of 10% in solid concentration which

was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width $\times$ 100-300 nm in length, cationic charge quantity: 1.13 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 17.5% by weight in terms of Al_2O_3 based on silica (in terms of SiO_2), 200 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 33 parts of a 30% aqueous solution of a cationic resin (Sumirez Resin 1001, cationic charge quantity 3.5 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by an air knife coater so that the dry solid content was 3.0 g/m², and the coat was dried and finished by a machine calender to obtain an ink jet recording sheet. The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 7.25 meq/100 g.

Example 39

The same composition for ink-receiving layer as of Example 38 except that the solid concentration of the aqueous dispersion was 4% was coated by a size press so that the dry solid content thereof was 0.5 g/m² and the coat was dried and finished by a machine calender to prepare an ink jet recording sheet. The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 4.05 meq/100 g.

Comparative Example 34

A base paper as prepared and dried in Example 37 was used, as it was, as the ink jet recording sheet of Comparative Example 34. The total cationic charge quantity of the resulting ink jet recording sheet was measured by colloidal titration to obtain 3.50 meq/100 g.

The ink jet recording sheets prepared in Examples 33-39 and Comparative Examples 28-34 were evaluated and the results are shown in Table 6.

Table 6

Examples or Comparative Examples	Total cationic charge quantity (meq./100 g)	Ink absorability	Image density	Sharpness	Covering rate (%)	Shape factor of dot
Example 33	0.57	A	1.33	B	75	1.14
Example 34	2.30	A	1.41	A	86	1.09
Example 35	5.00	A	1.56	A	96	1.06
Comparative Example 28	0.35	C	1.24	C	65	1.27
Comparative Example 29	0.75	B	1.26	C	73	1.21
Comparative Example 30	1.30	C	1.29	C	84	1.28
Example 36	3.40	A	1.38	A	79	1.12
Comparative Example 31	1.70	C	1.08	C	40	1.48
Comparative Example 32	0.02	D	1.02	D	0	1.98
Example 37	19.50	A	1.56	A	99	1.05
Comparative Example 33	21.10	A	1.55	A	100	1.06
Example 38	7.25	A	1.32	A	91	1.10
Example 39	4.05	A	1.30	A	75	1.13
Comparative Example 34	3.50	C	1.06	D	0	1.76

As can be seen from the results of Table 6, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer and superior in ink absorbability, image density and sharpness and small in shape factor of dot which means that the shape of the recorded dot was close to true circle.

In Examples 33-35 and Comparative Example 28, comparison was made using the same acicular cationic colloidal silica. As for the ink jet recording sheet of Comparative Example 28 which was small in the coating amount, the total cationic charge quantity was outside the range of the present invention, the shape factor of dot was great and both the ink absorbability and the sharpness were inferior. In Example 33 and Comparative Example 29, the same coating amount was employed, but in the ink jet recording sheet of Comparative Example 29 where the material used was outside the scope of the present invention, the shape factor of dot was great and sharpness was inferior.

In Example 34 and Comparative Example 30, the same coating amount was employed, but in the ink jet recording sheet of Comparative Example 30 where the material used was outside the scope of the present invention, the shape factor of dot was great and both the ink absorbability and the sharpness were inferior. The ink jet recording sheet of Comparative Example 31 where powdered silica which was outside the present invention was used was inferior in all of the characteristics.

Regarding Example 37 and Comparative Example 33, the total cationic charge quantity of the ink jet recording sheet of Example 37 was within the range of the present invention and the sheet was superior in all of the characteristics. On the other hand, in Comparative Example 33 the coating amount was increased and the total cationic charge quantity of the ink jet recording sheet was also outside the range of the present invention. The results of evaluation on the characteristics were good, but the sheet was not preferable to be handled as a plain paper.

In Comparative Examples 32 and 34, the base paper was handled, as it was, as the ink jet recording sheet and the sheet was inferior in all of the characteristics.

[Examples 40-44 and Comparative Examples 35-42]

Preparation Example 1

A polyvinylamine copolymer was synthesized by a known process, for example, by the process in accordance with Japanese Patent Kokai No.4-11094. In a reaction apparatus provided with a stirrer, a nitrogen-introducing pipe and a cooling pipe were charged 4 g of a starting material consisting of N-vinylformamide and acrylonitrile at a molar ratio of 45/55 and 35.9 g of desalted water. After the content was heated to 60°C with stirring in a nitrogen gas stream, thereto was added 0.12 g of 10 wt% aqueous solution of 2,2'-azobis-2-amidinopropane dihydrochloride. The content was kept at 60°C for 3 hours with stirring to obtain a copolymer. The reaction rate of the monomers at this time was about 93%. Furthermore, concentrated hydrochloric acid in an amount equivalent to the formyl group in the copolymer was added to the copolymer, followed by keeping at 75°C for 8 hours with stirring to hydrolyze the copolymer. The resulting copolymer solution was added to acetone and the precipitated polyvinylamine copolymer was vacuum dried and dissolved in desalted water. The polyvinylamine copolymer had a weight-average molecular weight of about 80,000. The molar ratio of vinylamine measured by the method of determination of the amount of primary amine with copper-(ethylenedinitro)tetraacetic acid described in "Bunseki Kagaku Binran" was about 40 mol%.

Preparation Example 2

A polyvinylamine copolymer was obtained in the same manner as in Preparation Example 1 except that the molar ratio of N-vinylformamide and acrylonitrile was changed to 24/78. The weight-average molecular weight of the polyvinylamine copolymer was about 80,000 and the molar ratio of vinylamine was 20 mol%.

Preparation Example 3

A polyvinylamine copolymer was obtained in the same manner as in Preparation Example 1 except that the molar ratio of N-vinylformamide and acrylonitrile was changed to 24/78 and polymerization time was 1 hour. The weight-average molecular weight of the polyvinylamine copolymer was about 30,000 and the molar ratio of vinylamine was 20 mol%.

Preparation Example 4

A polyvinylamine copolymer was obtained in the same manner as in Preparation Example 1 except that the molar ratio of N-vinylformamide and acrylonitrile was changed to 12/88. The weight-average molecular weight of the polyvinylamine copolymer was about 70,000 and the molar ratio of vinylamine was about 10 mol%.

[Preparation of base paper]

To a pulp slurry comprising 70 parts of LBKP having a freeness of 380 ml csf and 30 parts of NBKP having a freeness of 450 ml csf were added 10 parts of precipitated calcium carbonate (TP 121 manufactured by Okutama Kogyo Co., Ltd.) as a loading material, 0.6 part of aluminum sulfate, 0.1 part of an alkyl ketene dimer (Sizepine K903 manufactured by Arakawa Kagaku Co., Ltd.) and 0.8 part of amphoteric starch (Cato 3210 manufactured by Oji National Co., Ltd.). Using the pulp slurry, a paper was prepared by Fourdriner machine, dried and finished by a machine calender to obtain a base paper of 85 g/m² in basis weight.

[Base paper prepared using polyvinylamine copolymer]

Base papers were prepared using polyvinylamine copolymers in the above formulation of the base paper with changing the kind and the amount of the polyvinylamine copolymers as shown in Table 7.

Table 7

Base paper	Polyvinylamine copolymer	Molecular weight	Molar ratio (%)	Amount (Part)
Base paper 1	No	-	-	-
Base paper 2	Preparation Example 1	About 80,000	40	1
Base paper 3	Preparation Example 1	About 80,000	40	3
Base paper 4	Preparation Example 2	About 80,000	20	3
Base paper 5	Preparation Example 3	About 30,000	20	3
Base paper 6	Preparation Example 4	About 70,000	10	3

Example 40

An ink jet recording sheet was prepared using the base paper 2 obtained above and an ink-receiving layer was coated thereon.

On the base paper was coated, as a composition for ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of acicular cationic colloidal silica (particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: 0.46 meq/g) prepared by modifying acicular colloidal silica with aluminum oxide hydrate in an amount of about 7.0% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 16.7 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a transfer roll coater so that the dry solid content was 3.0 g/m² and dried and finished by a machine calender. Thus, an ink jet recording sheet was obtained.

Example 41

An ink jet recording sheet was prepared by coating an ink-receiving layer on the base paper 3 obtained above.

On the base paper was coated, as a composition for ink-receiving layer, an aqueous dispersion of 10% in solid concentration which was mainly composed of 1000 parts of a 10% aqueous dispersion of columnar cationic colloidal silica (particle size: 40 nm in width × 100-300 nm in length, cationic charge quantity: 1.90 meq/g) prepared by modifying columnar colloidal silica with aluminum oxide hydrate in an amount of 29.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) as an adhesive and 34 parts of a 60% aqueous solution of a cationic resin (Polyfix 601, cationic charge quantity 6.9 meq/g, manufactured by Showa Kobunshi Co., Ltd.) as a dye fixer by a size press so that the dry solid content was 0.5 g/m², and the coat was dried and finished by a machine calender to obtain an ink jet recording sheet.

Example 42

An ink jet recording sheet was prepared in the same manner as in Example 41 except that a rod coater is used in place of the size press and the coating amount was 1.0 g/m².

Example 43

An ink jet recording sheet was prepared in the same manner as in Example 41 except that an air knife coater was used in place of the size press, the concentration of the coating liquid for ink-receiving layer was 15% and the coating amount was 5.0 g/m².

Comparative Example 35

An ink jet recording sheet was prepared in the same manner as in Example 41 except that the coating amount was 0.3 g/m².

Comparative Example 36

An ink jet recording sheet was prepared in the same manner as in Example 41 except that an air knife coater was used in place of the size press, the concentration of the coating liquid for ink-receiving layer was 15% and the coating amount was 5.5 g/m².

Example 44

An ink jet recording sheet was prepared in the same manner as in Example 40 except that the base paper 4 was used and a rod coater was used in place of the transfer roll coater.

Comparative Example 37

An ink jet recording sheet was prepared in the same manner as in Example 44 except that in place of the acicular cationic colloidal silica used in Example 44, there was used 333 parts of a 30% aqueous dispersion of spherical cationic colloidal silica (primary particle size: 80 nm; cationic charge quantity: 0.80 meq/g) prepared by modifying spherical colloidal silica with aluminum oxide hydrate in an amount of 12.5% by weight in terms of Al₂O₃ based on silica (in terms of SiO₂).

Comparative Example 38

An ink jet recording sheet was prepared in the same manner as in Example 44 except that in place of the acicular cationic colloidal silica used in Example 44, there was used 1000 parts of a 10% aqueous dispersion of acicular colloidal silica (an agglomerate, particle size: 10-20 nm in width × 50-200 nm in length; cationic charge quantity: -0.02 meq/g).

Comparative Example 39

An ink jet recording sheet was prepared in the same manner as in Example 44 except that in place of the acicular cationic colloidal silica used in Example 44, there was used 333 parts of a 30% aqueous dispersion of powdered silica (Nipsil E220A manufactured by Japan Silica Kogyo Co., Ltd.; average particle size: 1.0 μm; cationic charge quantity: -0.09 meq/g).

Comparative Examples 40-42

Ink jet recording sheets of Comparative Example 40, Comparative Example 41 and Comparative Example 42 were prepared in the same manner as in Example 44 except that the base paper 5, the base paper 6 and the base paper 1 were used, respectively.

The ink jet recording sheets prepared in Examples 40-44 and Comparative Examples 35-42 were evaluated and the results are shown in Table 8. Evaluation of the water resistance was conducted in the following manner.

[Water resistance]

One drop of distilled water was dripped on a letter portion and a ruled line portion printed with magenta ink and the letter and the line were left to stand to dry and then, the degree of spreading was visually judged. The criteria for evaluation are as follows:

A: The characteristics are good.

B: The characteristics are practically acceptable.

C: The characteristics are bad.

Table 8

Examples or Comparative Examples	Ink absorbability	Image density	Sharpness	Covering rate (%)	Shape factor of dot	Sharpness
Example 40	A	1.44	B	89	1.08	A
Example 41	A	1.34	A	77	1.13	A
Example 42	A	1.35	A	83	1.11	A
Example 43	A	1.46	A	95	1.09	A
Comparative Example 35	B	1.23	C	69	1.25	A
Comparative Example 36	A	1.48	A	98	1.10	A
Example 44	A	1.46	A	88	1.09	A
Comparative Example 37	B	1.30	C	72	1.20	A
Comparative Example 38	C	1.23	C	81	1.25	B
Comparative Example 39	C	1.12	C	46	1.46	B
Comparative Example 40	A	1.45	A	87	1.10	C
Comparative Example 41	A	1.44	A	85	1.12	C
Comparative Example 42	A	1.43	A	86	1.11	C

As can be seen from the results of Table 8, the ink jet recording sheets of the present invention were high in covering rate of the contour-coated layer and superior in ink absorbability, image density and sharpness and small in shape factor of dot which means that the shape of the recorded dot was close to a true circle, and were excellent in water resistance.

In Examples 41-43 and Comparative Examples 35-36, comparison was made using the same columnar cationic colloidal silica. As for the ink jet recording sheet of Comparative Example 35 which was small in the coating amount, the shape factor of dot was great and the sharpness was inferior. In the ink jet recording sheet of Comparative Example 36, a large coating amount was employed and the results of evaluation on the characteristics were good, but the sheet was not preferred to be handled as a plain paper.

In Example 44 and Comparative Examples 37-39, the same coating amount was employed, but in the ink jet recording sheets of Comparative Examples where the material used was outside the scope of the present invention, the shape factor of dot was great and the sharpness was inferior.

As for the ink jet recording sheets of Comparative Examples 40-42, the base paper used was outside the present invention and they were inferior in water resistance, though superior in other characteristics.

[Industrial Applicability]

The slightly coated type ink jet recording sheet of the present invention comprises a support and an ink-receiving layer which is contour-coated on the support and mainly composed of a non-spherical cationic colloidal silica and further, the total cationic charge quantity is specified and the support used contains a specific polyvinylamine copolymer,

whereby no uneven spread of ink occurs, ink absorbability is excellent, density and sharpness of the recorded image are high, the recorded dot is close to true circle and water resistance is excellent.

Claims

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1. An ink jet recording sheet comprising a support and an ink-receiving layer coated thereon, characterized in that the ink-receiving layer is a coated layer which is mainly composed of non-spherical cationic colloidal silica and which is contour-coated along the surface of the support at a coating amount of 0.5-5.0 g/m².
- 10 2. An ink jet recording sheet according to claim 1, wherein the support contains a polyvinylamine copolymer which is obtainable by copolymerization reaction of N-vinylformamide with acrylonitrile and which has a molecular weight of 50,000 or more and a molar ratio of vinylamine of 20 mol% or more.
- 15 3. An ink jet recording sheet according to claim 1 or 2, wherein total cationic charge quantity of the recording sheet is 0.5-20 meq/100 g.
4. An ink jet recording sheet according to any of the claims 1 to 3, wherein the contour-coated layer is a layer coated at a covering rate of at least 70% on the surface of the support.
- 20 5. An ink jet recording sheet according to anyone of the preceding claims, wherein the ink-receiving layer comprises a composition mainly composed of a non-spherical cationic colloidal silica and a binder.
6. An ink jet recording sheet according to claim 5, wherein the ink-receiving layer comprises 100 parts by weight of a non-spherical cationic colloidal silica and 5-20 parts by weight of a binder.
- 25 7. An ink jet recording sheet according to anyone of the preceding claims, wherein the ink-receiving layer is obtainable by coating on the support an ink-receiving layer composition of 4-20% by weight in coating liquid concentration.
8. An ink jet recording sheet according to claim 7, wherein the ink-receiving layer is obtainable by coating an ink-receiving layer composition of 4-10% by weight in coating liquid concentration on the support by a size press.
- 30 9. An ink jet recording sheet according to claim 7, wherein the ink-receiving layer is obtainable by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on the support by a rod coater.
- 35 10. An ink jet recording sheet according to claim 7, wherein the ink-receiving layer is obtainable by coating an ink-receiving layer composition of 10-20% by weight in coating liquid concentration on the support by a transfer roll coater.
- 40 11. An ink jet recording sheet according to anyone of the preceding claims, wherein the non-spherical cationic colloidal silica is acicular or columnar.

Patentansprüche

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1. Tintenstrahl-Aufzeichnungsblatt, umfassend einen Träger und eine hierauf beschichtete Tintenaufnahmeschicht, dadurch **gekennzeichnet**, dass die Tintenaufnahmeschicht eine Schicht ist, die hauptsächlich aus nicht-kugelförmigem, kationischen, kolloidalen Siliciumdioxid zusammengesetzt ist und die entlang dem Profil der Oberfläche des Trägers in einer Beschichtungsmenge von 0,5 bis 5,0 g/m² beschichtet ist.
- 50 2. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 1, wobei der Träger ein Polyvinylamin-Copolymer enthält, welches durch Copolymerisation von N-Vinylformamid mit Acrylonitril erhältlich ist und ein Molekulargewicht von 50.000 oder mehr und ein Vinylamin-Molverhältnis von 20 mol-% oder mehr hat.
3. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 1 oder 2, wobei die gesamte kationische Beladungsmenge des Aufzeichnungsblattes 0,5 bis 20 mäg/100 g beträgt.
- 55 4. Tintenstrahl/Aufzeichnungsblatt gemäss einem der Ansprüche 1 bis 3, wobei die entlang dem Profil beschichtete Schicht eine Schicht ist, die zu einem Bedeckungsgrad von mindestens 70 % auf der Oberfläche des Trägers

beschichtet ist.

- 5 5. Tintenstrahl-Aufzeichnungsblatt gemäss einem der vorhergehenden Ansprüche, wobei die Tintenaufnahmeschicht eine Zusammensetzung umfasst, die sich hauptsächlich aus nicht-kugelförmigem, kationischen, kolloidalen Siliciumdioxid und einem Bindemittel zusammensetzt.
6. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 5, wobei die Tintenaufnahmeschicht 100 Gew.-Teile des nicht-kugelförmigen, kationischen, kolloidalen Siliciumdioxids und 5 bis 20 Gew.-Teile des Bindemittels umfasst.
- 10 7. Tintenstrahl-Aufzeichnungsblatt gemäss einem der vorhergehenden Ansprüche, wobei die Tintenaufnahmeschicht durch Beschichten einer Tintenaufnahmeschicht -Zusammensetzung mit einer Beschichtungsflüssigkeitskonzentration von 4 bis 20 Gew.% auf dem Träger erhältlich ist.
- 15 8. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 7, wobei die Tintenaufnahmeschicht durch Beschichten einer Tintenaufnahmeschicht -Zusammensetzung mit einer Beschichtungsflüssigkeitskonzentration von 4 bis 10 Gew.% auf dem Träger durch eine Leimpresse erhältlich ist.
- 20 9. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 7, wobei die Tintenaufnahmeschicht durch Beschichten einer Tintenaufnahmeschicht -Zusammensetzung mit einer Beschichtungsflüssigkeitskonzentration von 10 bis 20 Gew.% durch einen Stabbeschichter auf den Träger erhältlich ist.
- 25 10. Tintenstrahl-Aufzeichnungsblatt gemäss Anspruch 7, wobei die Tintenaufnahmeschicht durch Beschichten einer Tintenaufnahmeschicht -Zusammensetzung mit einer Beschichtungsflüssigkeitskonzentration von 10 bis 20 Gew.% durch einen Transferwalzenbeschichter auf den Träger erhältlich ist.
11. Tintenstrahl-Aufzeichnungsblatt gemäss einem der vorhergehenden Ansprüche, wobei das nichtkugelförmige, kationische, kolloidale Siliciumdioxid nadelförmig oder säulenförmig ist.

Revendications

- 30 1. Feuille permettant la reproduction par jet d'encre comprenant un support et une couche réceptrice d'encre appliquée sur celui-ci, caractérisée en ce que la couche réceptrice d'encre est une couche revêtue qui est principalement composée de silice colloïdale cationique non sphérique et qui est revêtue sur le contour de la surface du support d'un revêtement dans une quantité de 0,5-5,0 g/m².
- 35 2. Feuille permettant l'enregistrement par jet d'encre selon la revendication 1, dans laquelle le support contient un copolymère de polyvinylamine pouvant être obtenu par une réaction de copolymérisation de N-vinylformamide avec l'acrylonitrile et qui a un poids moléculaire de 50 000 ou davantage et un rapport molaire de vinylamine de 20 % molaire ou davantage.
- 40 3. Feuille permettant l'enregistrement par jet d'encre selon la revendication 1 ou 2, dans laquelle la quantité de charge cationique totale de la feuille d'enregistrement est de 0,5-20 meq/100 g.
- 45 4. Feuille permettant l'enregistrement par jet d'encre selon l'une quelconque des revendications 1 à 3, dans laquelle la couche revêtue sur le contour est une couche revêtue à raison d'un revêtement d'au moins 70 % de la surface du support.
- 50 5. Feuille permettant l'enregistrement par jet d'encre selon l'une quelconque des revendications précédentes, dans laquelle la couche réceptrice d'encre comprend une composition principalement composée d'une silice colloïdale cationique non sphérique et d'un liant.
- 55 6. Feuille permettant l'enregistrement par jet d'encre selon la revendication 5, dans laquelle la couche réceptrice d'encre comprend 100 parties en poids d'une silice colloïdale cationique non sphérique et 5-20 parties en poids d'un liant.
7. Feuille permettant l'enregistrement par jet d'encre selon l'une quelconque des revendications précédentes, dans laquelle la couche réceptrice d'encre peut être obtenue par revêtement sur le support d'une composition de couche réceptrice d'encre de 4-20 % en poids en concentration liquide de revêtement.

8. Feuille permettant l'enregistrement par jet d'encre selon la revendication 7, dans laquelle la couche réceptrice d'encre peut être obtenue par revêtement d'une composition de couche réceptrice d'encre de 4-10 % en poids en concentration liquide de revêtement sur le support par une presse encolleuse.

5 **9.** Feuille permettant l'enregistrement par jet d'encre selon la revendication 7, dans laquelle la couche réceptrice d'encre peut être obtenue par revêtement d'une composition de couche réceptrice d'encre de 10-20 % en poids en concentration liquide de revêtement sur le support par un revêtisseur à tige.

10 **10.** Feuille permettant l'enregistrement par jet d'encre selon la revendication 7, dans laquelle la couche réceptrice d'encre peut être obtenue par revêtement d'une composition de couche réceptrice d'encre de 10-20 % en poids en concentration liquide de revêtement sur le support par un revêtisseur à rouleau de transfert.

15 **11.** Feuille permettant l'enregistrement par jet d'encre selon l'une quelconque des revendications précédentes, dans laquelle la silice colloïdale cationique non sphérique est aciculaire ou colonnaire.

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