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Recording medium and recording method which makes use thereof

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RECORDING MEDIUM AND RECORDING METHOD WHICH MAKES USE THEREOF

BACKGROUND TO THE INVENTION

FIELD OF THE INVENTION

This invention relates to a recording medium and to a recording method using that medium. More particularly it relates to a recording medium that can give recorded images having good colour forming characteristics, ink dot shape, etc. and to the use of that recording medium in ink jet printing.

RELATED BACKGROUND ART

The method of ink jet recording works by generating small droplets of ink using various recording liquids (hereinafter referred to as ink) and various discharging systems. Such discharging systems include electrostatic attraction systems, systems where a mechanical vibration or displacement is imparted to the ink by means of a piezoelectric element, and a system where use is made of the pressure formed when a bubble is formed in the ink by the action of heat. The ink droplets are permitted to fly from the nozzle and become attached in part or in whole onto a

recording medium such as paper. This recording method is now attracting attention because it is quiet in use, can print at high speed, and can be used for multi-colour printing.

Various aqueous inks have been used for ink jet recording because they are safe and have good recording characteristics, while ordinary paper has generally been used as the recording medium. When an image is recorded on paper using a liquid ink, the printed letters or other image should not become blurred, and it is also desirable that the ink should dry as soon as possible after recording so as to avoid unexpected contamination of the paper surface.

In multi-colour ink jet recording systems where inks of two or more different colours are used, various requirements explained below need to be satisfied.

(1) Even where ink is absorbed rapidly into the recording medium, subsequently applied ink should not mix with the previously applied ink, should not disturb the existing pattern of ink dots, and should not flow outwardly.

(2) The spreading of the ink droplets on the recording medium should be such that the diameter of the ink dots does not increase more than is intended.

(3) The shape of the ink dots should approximate to a true circle, and the circumference of the circle should be smooth.

(4) The density of the ink dots should be high enough to retain a clear circumference.

(5) The whiteness of the recording medium should be high enough to give good contrast with the ink dots as printed.

(6) The colour of the ink should not be affected by the recording medium.

(7) Dimensional changes in the recording medium both before and after recording (e.g. wrinkling or elongation) should be minimised.

(8) The recorded image should be resistant to water, atmospheric oxidation and light.

(9) The amount of powder falling off from the coated layer of the recording medium or substrate should be minimised

In order to meet these needs, several previous proposals have been made. For example, Japanese Laid-open Patent Application No. 49113/1978 is concerned with the problem of improving ink absorption and reducing blurring of the ink dots. It discloses an ink jet recording paper comprising a sheet of wood pulp impregnated with a water soluble polymer. Japanese Laid-open Patent Application No. 5830/1980 discloses as an example of coated paper an ink jet recording sheet having an ink absorbing coating on a support. Japanese Laid-open Patent Application No.11829/1980 discloses an ink jet recording sheet of unsized paper having two or more layers of different ink absorptivities, Japanese Laid-open Patent Application No. 99693/1981 discloses an ink jet recording medium which is rendered water resistant by the presence of a quaternary ammonium halide.

There has also been proposed for use as an ink jet recording medium a paper containing synthetic amorphous silica. This recording medium when used in ink jet printing has excellent colour forming

characteristics. However, the shapes of the silica particles are non-uniform and there is a wide distribution in their particle sizes with the consequence that although ink absorptivity can be increased, the strength developed in the coated layer is reduced and powder tends to drop off from the coating layer of the recording medium or a substrate. This powder can clog the nozzle of the ink jet printer which results in a reduction in the reliability of the printer.

Japanese Laid-open Patent Application No. 146889/1984 discloses a non-coated ink jet recording paper internally loaded with synthetic amorphous silica. This recording paper has the advantages of improved dot shape and optical density compared with recording papers containing other conventional loading materials such as clay, talc or calcium carbonate. However, it cannot be used where high image quality is demanded.

The present invention is concerned with the production of a paper for use in multi-layer ink jet printing and it combines good coating strength with good colour forming characteristics, optical density and dot shape when used in multi-coloured ink jet printing.

In one aspect the invention provides a recording medium comprising a substrate and an ink receiving layer provided on the substrate, the ink receiving layer containing spherical silica, the ratio of the shortest diameter to the longest diameter of the spherical silica particles being 0.6 or more, and the ink receiving layer containing a silicon-containing water soluble polymer.

The present invention also provides a recording method that comprises ink jet printing using an ink having a surface tension of 28-68 dyne/cm at 25°C. onto the surface of a recording medium comprising a substrate and the ink receiving layer provided on the substrate, wherein the ink receiving layer contains spherical silica, the ratio of the shortest diameter to the longest diameter of the spherical silica being 0.6 or more, and the ink receiving layer containing a silicon-containing water-soluble polymer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Describing in detail about the present invention, the present inventors have found that, in recording on various recording media with an ink using a water-soluble dye as the recording agent, by incorporating spherical silica in the above recording media, the image formed with such ink can be improved in color forming characteristic, optical density and dot shape, and particularly that, in the papers for ink jet recording of the general paper type which could be made in the related art with excellent feel of touch, resistance to powder drop-off and at low cost, but could be improved in optical density and dot shape with

difficulty, the above mentioned color formation density and the dot shape were remarkably improved, based on which the objects of the present invention have been accomplished.

Describing about the recording medium which primarily characterizes the present invention, the feature of the recording medium of the present invention which is a sheet containing a fibrous material and a loading material resides in comprising spherical silica intermixed in said sheet, and the objects of the present invention could be accomplished by such a constitution and the constitution of ink as described below.

The fibrous material to be used in the present invention may be generally a wood pulp, typically LBKP and NBKP, and may be also mixed with various synthetic fibers, glass fibers, etc., if desired.

The loading material to be used in the present invention may be the spherical silica alone as described hereinafter. It is also possible to use, in combination with such spherical silica, inorganic pigments such as talc, clay, kaolin, diatomeceous earth, calcium carbonate, calcium sulfate, barium sulfate, titanium oxide, zinc oxide, zinc carbonate, aluminum silicate, calcium silicate, magnesium silicate, aluminum hydroxide, aluminum oxide, synthetic amorphous silica, colloidal silica, etc., and/or organic pigments

such as urea resin pigments, plastic pigments, etc., if desired.

As the spherical silica to be used in the present invention, synthetic spherical silica having inner surface area can be used. The spherical shape as mentioned in the present invention means that the ratio of the shortest diameter to the longest diameter in the same secondary particles is 0.6 or more, particularly preferably 0.8 or more.

The spherical silica to be used in the present invention can be prepared by, for example, forming silica gel and porous silica in the form of spherical shapes as described below.

Silica gel is a three-dimensionally polymerized product of high-reactive orthosilicic acid $Si(OH)_4$, and it may be structurally considered as a polymer of silicon dioxide $SiO_2 \cdot nH_2O$.

As a method for preparation of orthosilicic acid, there is the method in which silicon tetrachloride or sodium silicate is used. Also, silica gel can be produced by neutralizing alkaline content in water-glass (of which main components are Na_2SiO_3 and $Na_2Si_2O_5$) to effect gelation, followed by dehydration.

According to any method, the particle diameter and fine pore size of silica gel can be controlled by varying the concentration of orthosilicic acid, pH of the reaction mixture, solvent composition, stirring

speed during polymerization reaction. The spherical silica gel can be produced according to a method in which the polymerized reaction mixture is dispersed into an oil layer to effect gelation, or a method in which the polymerized reaction mixture is sprayed into dry air to effect gelation, etc.

According to the above operations, only ordinary gel can be obtained. A porous silica can be prepared by effecting gelation with addition of a pore forming agent such as dextran, long chain fatty acid, soluble starch, MgO, etc., into the sodium silicate solution, and then removing such agents by extraction with solvent or hydrolysis.

As another method for preparation of porous silica, there is a method in which silica sol with a narrow particle size distribution is gelled.

Porous silica having various pore sizes can be prepared according to the methods as mentioned above.

In the present invention, for improvement of storability of the ink jet recorded image, etc., in any of the steps in the methods for preparation as described above, a metal such as Al, Mg, Zn, Ca, etc., may be also included in the form of a complex silicate, etc.

The spherical silica prepared according to the above preparation method is more smooth in shape of particles and also higher in uniformity of the particle size as compared with synthetic amorphous silica

prepared by the processes of pulverization and classification. Accordingly, when the spherical silica is applied to a paper for ink jet recording, there are the advantage of reduced light scattering at an ink attached portion as well as improvement of optical density and dot shape of a recorded image through improvement of uniformity of capillary diameters. Further, due to the spherical shape, there is also the advantage of little wire abrasion of a paper machine.

The spherical silica to be used in the present invention should preferably have an average diameter of the secondary particles within the range of from 0.5 μm to 150 μm, particularly preferably from 1 μm to 30 μm, as measured by the Coulter method, which is a porous synthetic spherical silica with the particle proportion within the particle size range of average diameter ±1.5 μm being 60% or more, more preferably 80% or more (based on number of the particles). If the average diameter is greater than the above range, the image will become greater in coarse feeling due to lowering in resolution and deterioration of the dot shape.

As the particle diameter is smaller, the number of the particles of spherical silica being present in the surface and in the inside of the recording paper is increased, whereby probability of ink droplets being in contact with and being absorbed by spherical silica particles becomes greater. Accordingly, with respect

to the dot shape, the particle diameter should be preferably as small as possible, but in the case of a particle diameter smaller than 0.5 μm, above all when it is 0.2 to 0.4 μm, the scattering coefficient becomes greater to bring about undesirably lowering in optical density.

Also, in the case of sheet formation of a recording medium with spherical silica internally added, too fine particles pose a problem in production that it is difficult to retain them within the wet web on the wire of a paper machine even when used in combination with a yield enhancer, etc.

On the other hand, as to the average fine pore size (fine pore: voids between primary particles) in the inside of the spherical silica, there is an optimum range, and in the present invention, spherical silica with an average fine pore size within the range from 30 Å to 400 Å is preferred. As the fine pore size is greater, the fine pore volume in the inside of the secondary particles of the spherical silica becomes greater to make the ink absorbing capacity greater. However, when the fine pore size is greater than 400 Å, capillary condensation of the dye molecules near the surface layer of the secondary particles will occur with difficulty, whereby the optical density will be lowered. When the fine pore size is smaller than 30 Å, the ink absorbing capacity is undesirably small.

In the present invention, as the method for incorporating the above spherical silica and optionally other loading materials in the recording medium, there may be employed the so-called internal addition method in which the spherical silica is added to the slurry containing fibrous material in the paper making step, or the so-called after-treatment method in which it is impregnated or coated by means of a size press device or a spray device, etc., or alternatively both methods may be used in combination.

In the case of the internal addition method, paper strength enhancers, yield enhancers, colorant, etc., may be added if desired. As the yield enhancer, there may be employed cationic yield enhancers such as cationized starch, dicyandiamideformalin condensate, etc., or anionic yield enhancers such as anionic polyacrylamide, anionic colloidal silica, etc., either individually or in combination.

In the case of the after-treatment method, a surface treating agent such as modified starch or polyvinyl alcohol can be also used in combination with the spherical silica. Also, if desired, water resistance improvers of images, flowing property improvers, thickeners, pigment dispersing agents, foaming inhibitors, defoaming agents, foaming agents, penetrating agents, surfactants, colorants, fluorescent brightening agents, UV-ray absorbers, antioxidants,

etc., can be also formulated.

The content of the spherical silica in the recording medium in the present invention should be preferably 3 wt.% to 30 wt.% as the ash content in the paper, more preferably 8 to 30 wt.%, particularly preferably 15 to 25 wt.%.

As another embodiment of the present invention, there is a recording medium, comprising at least an ink receiving layer provided on a substrate, said ink receiving layer containing spherical silica.

As the binder forming the ink-receiving layer, there may be included water-soluble polymers such as starch, gelatin, casein, gum arabic, sodium alginate, carboxymethyl cellulose, polyvinyl alcohol and derivatives thereof, polyvinylpyrrolidone, sodium polyacrylate, etc.; polymeric emulsions such as synthetic rubber latex, etc.; organic solvent soluble resins such as polyvinylbutyral, polyvinyl chloride, etc.

Among the water-soluble polymers, particularly preferable are silicon-containing water-soluble polymers, for example, silicon-containing modified polyvinyl alcohols, etc., and any of those as disclosed in Japanese Laid-open Patent Application No. 59203/1983, No. 79003/1983 and No. 164604/1983 can be preferably used.

Examples of the silicon-containing modified polyvinyl alcohol to be used in the present invention

are shown below.

1) A product obtained by copolymerizing a vinyl ester and an olefinic unsaturated monomer containing silicon in the molecule represented by the formula (A) in the presence of alcohol under the conditions where the concentration ratio of these two kinds of monomers is kept constant throughout the polymerization period and saponifying the copolymer obtained:

$$CH_2 = CH\text{-}(CH_2)_n\text{-}Si(R^1)_m(R^2)_{3-m} \qquad (A)$$

wherein n is 0 to 1, m is 0 to 2, R^1 is a lower alkyl group, an allyl group or a lower alkyl having an allyl group, R^2 is a saturated branched or non-branched alkoxyl group having 1 to 40 carbon atoms, and said alkoxyl group may also have a substituent containing oxygen;

2) A product obtained by copolymerizing a vinyl ester and a silicon-containing polymerizable monomer represented by the formula (B) in the presence of alcohol by use of a radical polymerization initiator and saponifying the copolymer obtained;

$$CH_2=CR^3\text{-}CON(R^4)\text{-}R^5\text{-}Si(R^6)_n(R^7)_{3-n} \qquad (B)$$

wherein, R^3 is hydrogen or a methyl group, R^4 is

hydrogen or a lower alkyl group, R^5 is an alkylene group or a divalent organic residue of which chain carbon atoms are mutually bonded with oxygen or nitrogen, R^6 is hydrogen, halogen, a lower alkyl group, an allyl group or a lower alkyl group having an allyl group, R^7 is an alkoxyl group or an acyloxyl group where the alkoxyl group or the acyloxyl group may also have a substituent containing oxygen or nitrogen, n represents 0 to 2;

3) A product obtained by copolymerizing a vinyl ester and a silicon-containing polymerizable polymer represented by the formula (C) in the presence of alcohol by use of a radial polymerization initiator and saponifying the copolymer obtained;

$$CH_2=\overset{R^8}{\overset{|}{C}}-\overset{R^9_n}{\overset{|}{Si}}\cdot(O\underset{\underset{O}{\|}}{C}R^{10})_{3-n} \qquad (C)$$

wherein R^8 is a hydrogen atom or a methyl group, R^9 is a hydrogen atom, a halogen atom, a lower alkyl group, an allyl group or a lower alkyl group having allyl group, R^{10} is lower alkyl group, and n is 0 to 2.

As the modified polyvinyl alcohol to be used in the present invention, its modification degree should preferably be 35 mol% or less, preferably 0.05 to 20 mol%, more preferably 0.05 to 10 mol%. Also, as the modified polyvinyl alcohol to be used, its polymerization degree may be 100 to 10000, preferably 500 to 2000.

Further, the modified polyvinyl alcohol to be used should have a saponification degree of 80 mol% or higher, preferably 85 mol% or higher.

The silicon-containing water-soluble polymer forms a chemically bound product with various inorganic materials and therefore can form an ink-receiving layer which is much firmer as compared with the polyvinyl alcohol which has been generally used in the prior art, whereby it becomes possible to obtain both ink absorptivity and coated layer strength which could be effected with difficulty in the prior art.

As the polymeric emulsion, there may be included not only the polymeric emulsions in narrow sense of which dispersed phase and dispersing medium are both liquid, but also emulsions of synthetic polymers where the polymer in the dispersed phase should be properly considered as the solid at a temperature below the glass transition temperature as in the case of polystyrene emulsion.

Specific examples of the polymeric emulsion to be used in the present invention may include synthetic polymeric latices such as styrene-butadiene type latex, acrylonitrile-butadiene type latex, methyl methacrylate-butadiene type latex, vinyl acetate type latex, ethylene-vinyl acetate type latex, etc., as well as polyethylene emulsion, polystyrene emulsion, ionomer emulsion, etc.

In the related art, when a polymeric emulsion is used as the binder for a coated layer comprising a porous inorganic pigment as the main component, it had a drawback of low optical density of the image, although excellent in ink absorptivity. However, by simultaneously using a polymeric emulsion and particularly a silicon-containing water-soluble polymer as in the constitution of the recording medium of the present invention, it becomes possible to improve ink absorptivity, coated layer strength and optical density of image at the same time.

The recording medium of the present invention is prepared by adding a spherical silica and a binder into a coating solution for a substrate such as paper, etc., applying the coating solution on the substrate and drying the coated product. As other components contained in the coating solution in this case, there may be included organic pigments such as styrene type plastic pigments, acrylic type pigments, microcapsules, urea resin pigments, etc.; water-soluble polymers such as starch, gelatin, casein, gum arabic, sodium alginate, carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, sodium polyacrylate, etc.; organic solvent soluble resins such as polyvinylbutyral, polyvinyl chloride, etc.; further various additives such as dispersing agents, fluorescent dyes, pH controllers, defoaming agents, lubricants, preservatives, surfactants,

water resistant agents, etc.

Of the above components, water-soluble polymers, polymeric emulsions and organic solvent soluble resins used as the binders may be employed in an amount of 3 to 100 parts, preferably 10 parts to 80 parts based on 100 parts of spherical silica, but their amounts are not particularly limited if sufficient for binding spherical silica. However, use of more than 100 parts of the binder will undesirably make the void of the ink-receiving layer smaller.

The solid content in the coating solution should preferably an amount of about 1 to 50 wt.%, and said coating solution is applied by a method known in the art such as the roll coater method, the blade coater method, the air knife coater method, etc., to the substrate, generally in an amount of about 1 to 50 g/m^2 (dry coated amount), preferably, in an amount of about 2 to 30 g/m^2 (dry coated amount).

Such recording medium as has only the ink-receiving layer provided on the substrate, as it stands, can be used as the recording medium of the present invention, and it is also possible to give smoothness of the surface by super-calendering.

Next, the ink to be used in the recording method of the present invention is a recording liquid comprising a water-soluble dye and a liquid medium, together with other additives, the ink having a surface

tension at 25 °C within the range of 28 to 68 dyn/cm, preferably 30 to 65 dyn/cm, more preferably 40 to 60 dyn/cm. When printing is performed by use of an ink having lower surface tension than this range, its wettability to the recording medium is good, but spreading of the printed dot becomes greater. On the other hand, when an ink having higher surface tension than the above range is used, its wettability to the recording medium becomes bad, whereby ink absorptivity of the recording medium and dot density will be undesirably lowered.

As the water-soluble dye (recording agent) which is the essential component of the ink to be used in the recording method of the present invention, water-soluble dyes such as direct dyes, acidic dyes or dyes for foods, etc., may be preferably used.

Such water-soluble dyes may be generally used as a solution dissolved in a liquid medium comprising water and an organic solvent, and as such liquid medium components, mixtures of water and various water-soluble organic solvents may be preferably used, with the water content in the ink being preferably controlled within the range of from 20 to 90 wt.%.

Examples of the above water-soluble organic solvents may include alkyl alcohols having 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, isobutyl alcohol, etc.; amides such as dimethylformamide, dimethylacetamide, etc.; ketone or ketone alcohols such as acetone, diacetone alcohol, etc.; ethers such as tetrahydrofuran, dioxane, etc.; polyalkylene glycols such as polyethylene glycol, polypropylene glycol, etc.; alkylene glycols containing alkylene groups with 2 to 6 carbon atoms such as ethylene glycol, propylene glycol, 1,2,6-hexane triol, thioglycol, hexylene glycol, diethylene glycol, etc.; glycerine; lower alkyl ethers of polyhydric alcohols such as ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, triethylene glycol monomethyl (or ethyl) ether, etc. Of these many water-soluble organic solvents, polyhydric alcohols such as diethylene glycol, etc., lower alkyl ethers of polyhydric alcohol such as triethylene glycol monomethyl (or ethyl) ether, etc., are preferred. Polyhydric alcohols are particularly preferred, since they have the great effect as the wetting agent which prevents the phenomenon of clogging of nozzles caused by precipitation of the water-soluble dye through evaporation of water in the ink.

A solubilizing agent can be also added in the ink. Typical solubilizing agents are nitrogen-containing heterocyclic ketones, and their intended action is to improve dramatically the solubility of the water-soluble dye in the liquid medium. For example,

N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone may be preferably used.

The ink prepared from such components is itself excellent in recording characteristics (signal response, stability of liquid droplet formation, discharging stability, continuous recording performance over a long time, discharging stability after recording stopping over a long time), storage stability, fixability onto a recording medium, and various additives may be further added thereto for improvement of these characteristics. For example, there may be employed viscosity controllers of water-soluble resins, etc., such as polyvinyl alcohol, celluloses, etc.; various surfactants such as cationic, anionic or nonionic surfactants; surface tension controllers such as diethanolamine, triethanolamine, etc.; pH controllers with buffer solutions, etc.

Also, for formulation of an ink to be used for the ink jet recording method of the type in which ink is charged, specific resistance controllers of inorganic salts such as lithium chloride, ammonium chloride, sodium chloride, etc., may be added. Further, when ink is applied for the ink jet recording system of the type in which ink is discharged by the action of heat energy, thermal physical properties (e.g. specific heat, coefficient of thermal expansion, thermal conductivity, etc.) may be sometimes controlled.

In the present invention, it can be considered, as mentioned below, how color forming characteristic of image, optical density and dot shape can be improved.

That is, in the case of a recording paper with little content of loading material or small ink absorbing capacity of loading materials, the ink collided with the paper surface is blurred along the fibers to disturb the dot shapes, and at the same time the dye is penetrated deep into the inner portion of the paper, whereby the optical density of image will be lowered.

On the other hand, since the recording medium of the present invention contains spherical silica with appropriate particle diameters in the surface layer and in the inside of the medium (in large amount), the probability of the ink droplets being captured and absorbed by the spherical silica is high, whereby blurring and diffusion of the ink may be considered to be inhibited to improve the dot shapes. Further, in the case of spherical silica, since uniformity in shape and size of the voids between the secondary particles is high, the improvement effect of the dot shape may be considered to become greater as compared with the case of amorphous silica.

Also, in the recording medium of the present invention containing spherical silica, since the ink absorbing capacity of the spherical silica is high, the ink remains near the surface of the printed surface,

and further capillary condensation of the dye is liable to occur near the surface layer of the secondary particles, the silica having fine pore sizes with small scattering coefficient, whereby excellent color forming characteristic and optical density may be considered to be exhibited.

In the present invention, it may be considered as follows how ink absorptivity and coated layer strength can be improved while maintaining excellent color forming characteristic of the image by using particularly a silicon-containing water-soluble polymer as the binder in the receiving layer.

That is, when a water-soluble polymer is used as a binder for spherical silica, the amount of the water-soluble polymer must be increased in order to impart sufficient coated layer strength, whereby the interparticulate voids between and the inner surface area of the pigment particles become smaller and ink absorptivity is liable to be lowered.

On the other hand, the silicon-containing water-soluble polymer to be used in the present invention forms a chemically bound product with spherical silica to have a strong binding force, and therefore the amount of the silicon-containing water-soluble polymer formulated for imparting sufficient coated layer strength may be smaller as compared with the case of a water-soluble polymer of the related art.

Accordingly, in the particular case fusing the silicon-containing water-soluble polymer, it becomes possible to obtain both of good ink absorptivity and coated layer strength.

Also, when a polymeric emulsion is used alone in a small amount as the binder for the porous inorganic pigment, a recording medium having sufficient coated layer strength and excellent ink absorptivity can be obtained, but due to small affinity between the water-soluble dye and the binder, there is the drawback that optical density of the image is low.

Accordingly, by using as the binder a silicon-containing water-soluble polymer and a polymeric emulsion in combination, it becomes possible to improve ink absorptivity and coated layer strength at the same time while maintaining more excellent optical density of the image.

According to the present invention, ink can be absorbed rapidly into the inner portion of the recording medium, without the phenomenon of flow-out or blurring of the ink even when inks with different colors may be attached on the same site within short time, to give a recorded image of high resolution with excellent color forming characteristic. Also, because of strong coated layer strength, powder drop-off will occur with difficulty, whereby the problems such as clogging of nozzle, etc., will hardly occur. Accordingly, the

recording medium of the present invention is suitable not only for recording in general, but also particularly for ink jet recording method. Above all, when the surface tension of the recording liquid is from 40 to 60 dyn/cm, excellent effect can be obtained which can satisfy color characteristic, optical density, ink absorptivity at the same time.

The present invention is described in more detail by referring to the following Examples and Comparative examples, by which the present invention is not limited. In the description, parts or % are based on weight, unless otherwise particularly noted.

Examples 1-5, Comparative Examples 1-3

As the starting material pulps, 80 parts of LBKP with a freeness (C.S.F.) of 370 ml and 20 parts of NBKP with a freeness of 410 ml were employed, and a synthetic spherical silica was internally added as the loading material in an amount of 35 wt.% based on the pulp solid content, and a cationized starch (CATOF, produced by Oji National) as the yield enhancer in an amount of 0.3 wt.% based similarly on the pulp solid, and further a polyacrylamide type yield enhancer (Pearlfrock FR-X, produced by Seiko Kagaku Kogyo) was added in an amount of 0.05 wt.% immediately before paper-making, followed by paper-making at a basis weight of 70 $9/m^2$ by use of a TAPPI standard sheet former.

Then, an oxidized starch (MS3800, produced by

Nippon Shokuhin) solution with a concentration of 2% was attached by a size press device to give recording media of the present invention and for comparative purpose.

The synthetic spherical silicas employed were as shown below.

Example 1

Hipersil-3
(trade name, produced by Shandon Co.; average diameter, 3.2 μm; fine pore size, 120 Å; proportion of the particles in the particle size range of average diameter ±1.5 μm, 97%)

Example 2

Wakogel LC-10K
(trade name; produced by Wako Junyaku Kogyo; average diameter, 10 μm; fine pore size, 90 Å)

Example 3

Hipersil-5
(trade name; produced by Shandon Co.; average diameter, 5 μm; fine pore size, 120 Å; proportion of the particles in the particle size range of average diameter ±1.5 μm, 94%)

Example 4

TSK gel silica 60
(trade name; produced by Toyo Soda Kogyo; average diameter, 5 μm; fine pore size, 60 Å)

Example 5

Unisil Q30

(trade name; produced by Gaskuro Kogyo; average diameter, 10 μm; fine pore size, 35 Å)

For comparative purpose, the above spherical silicas were replaced with the loading materials shown below to give Comparative examples.

Comparative example 1

Synthetic amorphous silica

(Syloid 72, produced by Fuji Devison Kagaku; average diameter, 4.3 μm; fine pore size, 170 Å)

Comparative example 2

Heavy calcium carbonate

(Escaron #200, produced by Sankyo Seifun)

Comparative example 3

Talc

(LM-S1, produced by Fuji Talc Kogyo; average diameter, 2.3 μm)

For the above recording media ink jet recording was performed by an ink jet printer (produced by Canon, PJ-1080), and ink jet recording aptitude was evaluated.

(1) Dot size

Diameters of 20 printed dots were measured by a stereoscopic microscope, and shown as an average value.

(2) Dot shape

Printed dot was observed by a stereoscopic microscope, and a shape which is substantially circular is rated as o, a shape which is slightly deformed in

circular diameter as Δ, and an amorphous shape as x.

(3) Color forming characteristic

Sharpness of the color of the ink jet recorded image was compared by visual observation, and evaluated at the ranks of ●, o, Δ, x with the best one being ● and the worst one x.

(4) Optical density

The solid printed portion was measured by a Macbeth densitometer TR-534 model.

The results are shown in Table 1.

(Ink composition)

C.I. Direct Blue 86	3 parts
Diethylene glycol	30 parts
N-methyl-2-pyrrolidone	10 parts
Pure water	60 parts

(Surface tension at 25°C 54 dyn/cm)

Table 1

	Item			
	Dot diameter (μm)	Dot shape	Color forming characteristic	Optical density (O.D.)
Recording paper:				
Example 1	385	o	◉	0.68
Example 2	392	o	◉	0.71
Example 3	390	o	◉	0.70
Example 4	388	o	◉	0.71
Example 5	394	o	◉	0.72
Comparative example 1	403	Δ	o	0.59
Comparative example 2	442	x	x	0.56
Comparative example 3	418	x	Δ	0.52

Example 6

By use of LBKP with a freeness (C.S.F.) of 400 ml, talc (LM-S1, produced by Fuji Talc Kogyo) was added internally thereto as the loading material in an amount of 20 wt.% based on the pulp solid content, and a cationized starch (CATOF, produced Oji National) as the yield enhancer in an amount of 0.2 wt.% based similarly on the pulp solid, followed by paper-making at a basis weight of 70 g/m^2 by use of a TAPPI standard sheet former to provide an original paper.

Then, the above paper was subjected to impregnating coating treatment with a solution having the following composition by means of a size press device to a dried coating amount of 4.0 g/m^2, followed by drying in a conventional manner, to obtain the recording paper of the present invention.

Polyvinyl alcohol (PVA105; produced by Kuraray)	4 parts
Synthetic spherical silica (Deverosil 100-3; produced by Nomura Kagaku; average diameter, 3.3 μm; the proportion of particles within the particle size range of average diameter ±1.5 μm, 80%)	4 parts
Water	92 parts

On the above recording medium, ink jet recording was performed with the use of the ink shown below, and the ink jet recording characteristics were evaluated similarly as in Examples 1 to 5. The results are shown in Table 2.

Ink A: surface tension 68 dyn/cm	(Composition)
Glycerine	10 parts
Pure water	90 parts
C.I. Acid Red 87	2 parts
Ink B: surface tension 64 dyn/cm	(Composition)
Diethylene glycol	5 parts
Glycerine	10 parts
Pure water	85 parts

C.I. Acid Red 87	2 parts
Ink C: surface tension 58 dyn/cm	(Composition)
Diethylene glycol	30 parts
Pure water	70 parts
C.I. Acid Red 87	2 parts
Ink D: surface tension 44 dyn/cm	(Composition)
Ethylene glycol	15 parts
Diethylene glycol	15 parts
Pure water	70 parts
Acetynol EH	0.2 parts
C.I. Acid Red 87	2 parts
Ink E: surface tension 33 dyn/cm	(Composition)
Ethylene glycol	15 parts
Diethylene glycol	15 parts
Pure water	70 parts
Acetynol EH	0.7 parts
C.I. Acid Red 87	2 parts
Ink F: surface tension 28 dyn/cm	(Composition)
Ethylcellosolve	10 parts
Diethylene glycol	10 parts
Ethylene glycol	10 parts
Pure water	60 parts
Florade FC430	1.5 parts
C.I. Acid Red 87	2 parts

Table 2

	Ink					
	A	B	C	D	E	F
Surface tension:	68	64	58	44	33	28
Evaluation Item:						
Dot diameter (μm)	321	337	363	378	395	401
Dot shape	Δ	o	o	o	o	Δ
Color forming characteristic	Δ	o	◉	◉	o	o
Optical density	0.51	0.69	0.76	0.74	0.67	0.60

Example 7

On the recording media of the present invention obtained in Examples 1-6, by use of the four kinds of inks as shown below, an ink jet recording was practiced by use of a recording device having on-demand type ink jet recording head (orifice size 50 x 40 μm; the number of nozzle, 24; driving voltage, 24.5 V; frequency 2 KHz) in which bubbles are generated by a heat generating resistor and ink is discharged by the pressure of the bubbles.

Yellow ink

C.I. Direct yellow 86	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts

Water	55 parts
Magenta ink	
C.I. Acid Red 35	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts
Cyan ink	
C.I. Direct Blue 86	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts
Black ink	
C.I. Food Black 2	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts

As a result, in every recording medium, sharp color images with excellent color forming characteristic and high optical density were obtained.

Examples 8-11, Comparative examples 4,5

As the substrate, a general fine paper with the size degree of 35 sec. based on JISP8122 (Ginwa (trade name); basis weight 64 g/m^2; produced by Sanyo Kokusaku K.K.) was used and a coating solution having a

composition shown below was coated on the substrate at a dried coating amount of 15 g/m^2 by a blade coater, followed by drying in a conventional manner, to obtain the recording medium to be used in the present invention.

Synthetic spherical silica	100 parts
Polyvinyl alcohol (PVA117; produced by Kuraray)	50 parts
Water	380 parts

The synthetic spherical silica employed are shown below.

(Example 8)

Hipersil-3 (as described above)

(Example 9)

Hipersil-5 (as described above)

(Example 10)

Hipersil-10 (trade name; produced by Shandon Co.; average diameter, 9.8 μm; proportion of the particles within the particle size range of average diameter ±1.5 μm, 84%)

(Example 11)

Deverosil 100-3 (as described above)

Also, for comparative purpose, the above spherical silica was replaced with the wet process synthetic amorphous silica shown below to give Comparative examples.

(Comparative example 4)

Nipsil E200A (trade name; produced by Nippon

silica Kogyo K.K.; average diameter, 1.5 μm; proportion of the particles within the particle size range of average diameter ±1.5 μm, 99%)

(Comparative example 5)

Nipsil E150K (trade name; produced by Nippon Silica Kogyo K.K.; average diameter, 4.6 μm; proportion of the particles within the particle size range of average diameter ±1.5 μm, 8%)

On the above recording media, ink jet recording was performed by an ink jet printer (PJ-1080; produced by Canon), and the ink jet recording aptitude was evaluated.

Evaluation was conducted for optical density (O.D.), color forming characteristic, dot diameter, ink absorptivity, coated layer strength.

The ink absorptivity is represented by the amount of ink absorbed within one second after solid printing of cyan. Ink absorptivity is better, as the numerical value is greater.

The coated layer strength was measured by writing on the ink receiving layer surface of the recording medium with three pencils of 2H, H, HB, and the medium which gave powder drop-off with the use of any pencil was rated as x, the medium which gave no powder drop-off with the use of any pencil as ●, and the medium which gave no powder drop-off with the use of HB pencil but which gave powder drop-off with H and

2H pencils, respectively, as o.

The results are shown in Table 3.

(Ink composition)

C.I. Direct Blue 86	3 parts
Diethylene glycol	30 parts
N-methyl-2-pyrrolidone	10 parts
Pure water	60 parts

(Surface tension at 25 °C 54 dyn/cm)

Comparative example 6

A recording medium of Comparative example 6 was prepared in entirely the same manner as in Comparative example 5 except for changing the amount of the polyvinyl alcohol formulated to 70 parts, and its ink jet recording aptitude was evaluated. The results are shown in Table 3.

Table 3

	Item				
	Optical density (O.D.)	Color forming characteristic	Dot diameter (μm)	Ink absorptivity cc/cm^2	Coated layer strength
Recording medium:					
Example 8	1.40	◎	235	2.92×10^{-3}	○
Example 9	1.35	◎	218	3.74×10^{-3}	○
Example 10	1.18	○	224	3.45×10^{-3}	○
Example 11	1.33	◎	230	2.88×10^{-3}	○
Comparative example 4	1.25	◎	232	2.84×10^{-3}	x
Comparative example 5	1.02	○	220	3.10×10^{-3}	x
Comparative example 6	1.36	○	252	2.30×10^{-3}	○

Example 12

As the substrate, a general fine paper (Ginwa: trade name, basis weight 64 g/m^2) was used and a coating solution having a composition shown below was coated on the substrate at a proportion of dried coating amount of 12 g/m^2 by an air knife coater, followed by drying in a conventional manner, to obtain a recording medium.

Spherical silica (Hipersil-5) 100 parts

Polyvinyl alcohol (PVA117; produced by Kuraray) 20 parts

Polyvinyl alcohol (PVA105; produced by Kuraray)	40 parts
Cationic resin (Polyfix601; produced by Showa Kobunshi)	5 parts
Water	750 parts

On the recording medium, ink jet recording was performed similarly as in Example 6 and its recording characteristics were evaluated. The results are shown in Table 4.

Table 4

	Ink					
	A	B	C	D	E	F
Surface tension:	68	64	58	44	33	28
Evaluation item: Dot diameter (μm)	280	310	342	360	366	381
Dot shape	Δ	o	o	o	o	Δ
Color forming characteristic	Δ	o	◎	◎	◎	o
Optical density (O.D.)	0.76	0.87	0.92	0.89	0.82	0.69
Ink absorptivity cc/cm^2	0.86×10^{-3}	1.15×10^{-3}	2.01×10^{-3}	2.15×10^{-3}	2.30×10^{-3}	2.88×10^{-3}

Examples 13-17

As the substrate, a general fine paper with the size degree of 35 sec. based on JISP8122 (Ginwa; trade name; basis weight 64 g/m^2; produced by Sanyo Kokusaku Pulp K.K.) was used and a coating solution having a

composition shown below was coated on the substrate at a dried coating amount of 15 g/m^2 by a bar coater, followed by drying in a conventional manner, to obtain the recording medium to be used in the present invention.

Example 13

Spherical silica (Wakogel LC-10K, as described above)	100 parts
Silicon-containing water-soluble polymer (R-2105; produced by Kuraray K.K)	40 parts
Cationic resin (Polyfix601; produced by Showa Kobunshi K.K.)	5 parts
Water	660 parts

Example 14

Spherical silica (Hipersil-3, as described above)	100 parts
Silicon-containing water-soluble polymer (R-1130; produced by Kuraray K.K.)	40 parts
Cationic resin (Polyfix601; produced by Showa Kobunshi K.K.)	5 parts
Water	660 parts

Example 15

Spherical silica (UnisilQ30, as described above)	100 parts

Silicon-containing water-soluble polymer (R-2130; produced by Kuraray K.K.)	40 parts
Cationic resin (Polyfix601; produced by Showa Kobunshi K.K.)	5 parts
Water	660 parts

Example 16

Spherical silica (UnisilQ30, as described above)	100 parts
Silicon-containing water-soluble polymer (R-1130; produced by Kuraray K.K.)	20 parts
Styrene-butadiene type latex (L-1876; produced by Asahi Kasei K.K.)	20 parts
Cationic resin (Polyfix601; produced by Showa Kobunshi K.K.)	5 parts
Water	660 parts

Example 17

Spherical silica (Hipersil-5, as described above)	100 parts
Ethylene-acetic acid vinyl type latex	20 parts
Silicon-containing water-soluble polymer (R-1130; produced by kuraray K.K.)	20 parts

Cationic resin		
(Polyfix601; produced by		
Showa Kobunshi K.K.)		5 parts
Water		660 parts

On the recording media obtained, ink jet recording was performed by use of an ink jet printer (PJ-1080; produced by Canon) and ink jet recording aptitude was evaluated. The results are shown in Table 5.

Evaluation was conducted in the same manner as the above Examples.

Table 5

	Item				
	Optical density (O.D.)	Color forming characteristic	Dot diameter (μm)	Ink adsorptivity cc/cm^2	Coated layer strength
Recording medium:					
Example 13	1.22	◎	228	3.23×10^{-3}	◎
Example 14	1.28	◎	233	3.18×10^{-3}	◎
Example 15	1.27	◎	222	3.22×10^{-3}	◎
Example 16	1.34	◎	220	3.45×10^{-3}	◎
Example 17	1.39	◎	229	3.48×10^{-3}	◎

CLAIMS

1. A recording medium comprising a substrate and an ink receiving layer provided on said substrate, wherein said ink receiving layer contains spherical silica, the ratio of the shortest diameter to the longest diameter of the spherical silica being 0.6 or more, and the ink receiving layer containing a silicon-containing water soluble polymer.

2. A recording medium according to Claim 1 wherein the secondary particles of the spherical silica have an average diameter in the range of from 0.5 to 150μm.

3. A recording medium according to Claim 1 wherein the secondary particles of the spherical silica have an average size of voids between the primary particles in the range of from 30 to 400 Å.

4. A recording medium according to any preceding claim wherein said ink receiving layer contains a silicon-containing modified polyvinyl alcohol.

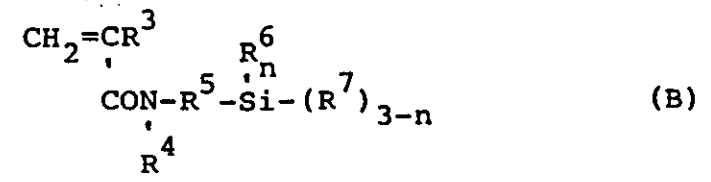
5. A recording medium according to Claim 4, wherein the silicon-containing modified polyvinyl alcohol is a product obtained by copolymerizing a vinyl ester and an olefinic unsaturated monomer containing silicon in the molecule represented by the formula (A) in the presence of alcohol under the conditions where the concentration ratio of these two kinds of monomers is kept constant throughout the polymerization period and saponifying the copolymer obtained:

$$CH_2 = CH\text{-}(CH_2)_n\text{-}Si(R^1)_m(R^2)_{3-m} \qquad (A)$$

wherein n is 0 to 1, m is 0 to 2, R^1 is a lower alkyl group, an allyl group or a lower alkyl having an allyl group, R^2 is a saturated branched or non-branched alkoxyl group having 1 to 40 carbon atoms and said alkoxyl group may also have a substitutent containing oxygen.

6. A recording medium according to Claim 4, wherein the silicon containing modified polyvinyl alcohol is a product obtained by copolymerizing a vinyl ester

and a silicon containing polymerizable monomer represented by the formula (B) in the presence of alcohol by use of a radical polymerization initiator and saponifying the copolymer obtained;



(B)

wherein, R^3 is hydrogen or a methyl group, R^4 is hydrogen or a lower alkyl group, R5 is an alkylene group or a divalent organic residue of which chain carbon atoms are mutually bonded with oxygen or nitrogen, R^6 is hydrogen, halogen, a lower alkyl group, an allyl group or a lower alkyl group having an allyl group, R7 is an alkoxyl group or an acyloxyl group where the alkoxyl group or the acyloxyl group may also have a substituent containing oxygen or nitrogen, and n represents 0 to 2.

7. A recording medium according to Claim 4 wherein the silicon containing modified polyvinyl alcohol is a product of copolymerizing a vinyl ester and a silicon-containing polymerizable polymer represented by the formula (C) in the presence of alcohol by use

of a radial polymerization initiator and saponifying the copolymer obtained;

$$CH_2=C(R^8)-Si(R^9)_n(OCR^{10})_{3-n} \quad (C)$$

wherein R^8 is a hydrogen atom or a methyl group, R^9 is a hydrogen atom, a halogen atom, a lower alkyl group, an allyl group or a lower alkyl group having an allyl group, R^{10} is lower alkyl group, and n is 0 to 2.

8. A recording medium according to any of Claims 4 to 7, wherein the degree of modification of the modified polyvinyl alcohol is less than 35 mole %.

9. A recording medium according to any of Claims 4 to 8 wherein the degree of polymerization of the modified polyvinyl alcohol is 100 to 10,000.

10. A recording medium according to any of Claims 5 to 9 wherein the degree of said saponification of the modified polymeric alcohol is 18 mole % or above.

11. A recording medium substantially as described in any of examples 13 to 17.

12. A method for making a recording medium which comprises coating a substrate with an aqueous coating composition comprising spherical silicia having a ratio of the shortest to the largest diameter of 0.6 or more, a silicon-containing water-soluble polymer and a solid or liquid polymer as a dispersed phase.

13. A recording method which comprises ink jet printing using an ink having a surface tension of 28-68 dyne/cm at 25°C onto the surface of a recording medium comprising a substrate and an ink receiving layer provided on the substrate wherein said ink receiving layer contains spherical silica, the ratio of the shortest diameter to the longest diameter of the spherical silica being 0.6 or more, and the ink receiving layer containing a silicon-containing water-soluble polymer.

14. A recording method according to Claim 13 wherein the surface tension of the ink is 30 to 65 dyne/cm at 25°C.

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**** END OF REGISTER ENTRY ****