

Description

This invention relates to a recording medium suitable for use in ink jet recording, and, in particular, to a recording medium which has excellent absorptivity, has good colour forming characteristics with aqueous ink and can give rise to a recorded image of good print quality. The recorded image is also durable and exhibits little "indoor discoloration" of the image.

The following examples of recording media for ink jet printing are already known:

1. non-coated media formed of sheets resembling filter paper or blotting paper, the paper being, in general, made mainly from pulp having a low degree of sizing; and
2. media having a coated layer containing a pigment (e.g. silica or zeolite) the pigment being porous and capable of adsorbing components of the ink and showing a large oil absorption. Such a medium is disclosed in Japanese Laid-Open Patent Application No 148585/1981.

While the first recording medium (1) is inexpensive to manufacture and has excellent ink absorptivity, the ink penetrates deep into the fibre layer of the paper giving a poor colour forming characteristic with the pigment in the ink. Also, since the ink travels along the fibres on the paper surface, a phenomenon called feathering occurs in which a dot of ink applied to the medium does not remain circular but becomes ragged, giving reduced resolution and a poor quality image. Thus, papers of this non-coated type have been used only where a relatively low resolution is required and the images formed do not need to be of a high density. An example of such use is in monochromatic recording at personal computer terminals and the like.

In the second recording medium (2) because the ink absorbing layer is porous and uniform, it gives rise to excellent dot shape in the recorded image so that high resolution can be obtained while the medium maintains adequate ink absorptivity.

However, recording systems which require high quality images and high resolution also place further requirements on the recording medium. These are:

- (1) The medium should have sufficient capacity to absorb ink that a dot will not flow out and will not expand more than is necessary even when the dot is formed from ink droplets of different colours superimposed at the same position; and
- (2) absorption and drying of the ink should be fast enough that individual ink droplets do not become feathered even if something brushes and tends to smear them immediately after they have become attached to the paper;
- (3) when an ink is received in an ink absorbing layer it should exhibit good colour forming characteristics; and
- (4) the ink dots formed on the recording medium should have smooth peripheries and be of approximately spherical shape.

In addition, a recorded image should be durable, that is it should be water-resistant, light resistant etc.

US Patent 4478910 and Japanese Laid Open Patent Application No 230787/1984 are concerned with the physical properties of a pigment in an ink absorbing layer and disclose a recording medium using silica having a specific area of 200 m²/g or more, or silica having an acid value of 240 mg.mol/kg or more, to obtain a better dye colour forming characteristic.

In Japanese Laid Open Patent Application No 84992/1981 there is disclosed a method for improving the water resistance of an ink jet recorded image in which recording is performed using an ink containing acid/direct dyes and a recording medium having a polycationic polymeric electrolyte present in its ink absorbing layer. The dyes become attached to the ink absorbing layer and do not flow out even when the recorded image is dipped in water.

The light resistance of the image is considered to be the ability of the image to withstand discoloration and fading of the recorded image caused by photolysis of the dye. It was thought that this discoloration and fading was due to the inherent properties of the dye, but it has become known that an agent which imparts water-resistance (e.g. a poly cationic material) promotes photolysis of the dye. Japanese Laid Open Patent Applications Nos 11389/1985 and 49990/1985 describe a recording medium containing a polycation which exhibits little promotion of dye photolysis. Japanese Laid-open Patent Application No 72785/1985 describes a recording medium which contains a polycation together with the UV-absorber and an antioxidant.

However, recently, a new problem concerning the durability of the image, and in particular the so-called "indoor discoloration" of the recorded image has been highlighted. This problem of indoor discoloration has been considered to be caused by dye decomposition, but the problem has not been solved by the recording media known in the art.

Sunlight induced fading of a recorded image is a phenomenon which is brought about by the decomposition of a dye within a recorded image, the decomposition being brought about by visible light, or

UV radiation, and does not occur where the recording medium is not directly irradiated with sunlight. Where an image recorded on a recording medium is irradiated with sunlight, fading occurs with all recording media, including normal ppc paper and the recording media (1) and (2) described above. It is known that fading is promoted when the recording medium contains a polycationic substance. Fading as herein mentioned, refers to the phenomenon in which chromaticity of printed matter is lowered while discoloration refers to the phenomenon in which chromaticity is not lowered but hue is primarily changed.

"Indoor discoloration" occurs even when the recording medium is not directly radiated by sunlight, but does not occur on normal or non-coated paper. Also, discoloration occurs even when a polycation which has little influence on the light resistance of the image is used, or even when a UV-radiation absorber is used. As described, above the problem of indoor discoloration as mentioned in the present invention is a phenomenon inherent in a coated paper having an ink absorbing layer, but no clear cause or solution to the problem have yet been found. In addition, where such a coated paper is stored, unused, in a binder made of polypropylene or polyethylene for a number of months, discoloration to yellow occurs at the periphery of the paper and contact of the paper with adhesive tape or with the rubber roller of a printer results in discoloration to yellow around the contact portions. Like indoor discoloration, the problems of such discoloration to yellow is inherent in the coated paper. No solutions to these problems having yet been found.

According to one aspect of the present invention, there is provided a recording medium, comprising a substrate and an ink receiving layer on the substrate, the ink-receiving layer containing a silicon-containing pigment and a binder, wherein the recording medium exhibits discoloration E*ab of C.I. Food Black 2 being 20 or less according to the ozone test.

In a second aspect of the invention, there is provided a recording method, which comprises impelling droplets of an ink containing a water-soluble dye onto a recording medium as defined above.

The above recording medium can exhibit excellent durability in storage and can be resistant to discoloration to yellow upon being stored in a file or binder. It can exhibit good ink absorption and color forming characteristics with dyes and it can give a recorded image of high quality at high resolution.

The ink receiving layer may contain a silicon-containing pigment with a surface area in the range of 10 to 200 m²/g together with aluminium oxide particles. In an alternative form, the ink receiving layer may comprise an upper layer containing a silicon-containing pigment, aluminium oxide and a binder and an underlayer containing a pigment with a greater particle size than the above pigment. In a third form, the ink receiving layer may comprise a silicon-containing pigment which has been subjected to a surface treatment with one or a mixture of two or more materials selected from soaps, hydroxides, salts or oxides of metals selected from the group consisting of K, Ca, Mg, Al, Zn, Ba, Sr and Sn.

The present inventors have made numerous investigations concerning indoor discoloration and as a result have reached the following conclusion:

- (1) indoor discoloration occurs as a result of decomposition of dye with light and oxygen;
- (2) an ink receiving layer containing a pigment and a binder (hereinafter called a coated layer) catalyses this decomposition, and in particular a coated paper which has suitable properties for use in ink jet recording is likely to strongly catalyse decomposition. The reasons why this catalytic effect arises are believed to be that:

(a) indoor discoloration does not occur with non-coated paper but only with paper having a coated layer. It occurs particularly with coated paper having properties that are beneficial in ink jet recording, for example good color forming characteristics with a recording agent and good ink absorptivity;

(b) while fading occurs under irradiation with strong light such as sunlight, discoloration occurs under so-called indoor discoloration conditions, and is believed to happen as a result of dye decomposition by a different mechanism;

(c) the tendencies (a) and (b) set up above do not change even where the recording agent employed is changed to an acid dye, a basic dye, a direct dye or a food dye, etc.

On the basis of such conclusions, an ozone test as described below was devised as a method for measuring a catalytic activity of a coated layer for indoor discoloration.

The ozone test may be considered to be a method for expressing the catalytic activity of a coated layer when a dye is decomposed with oxygen, which is a method for expressing the novel physical property which could not be measured according to a variety of methods known in the art.

The ozone test is practiced according to the following procedure in the present invention.

(a) Preparation of test sample:

- (1) As a test solution, a solution having 2 parts by weight of C.I. Food Black 2 dissolved as a dye in a

solvent comprising 70 parts by weight of deionized water and 30 parts by weight of diethylene glycol is used.

(2) The above test solution is applied to a coated layer at a proportion of $0.4 \mu\text{l}$ to $0.5 \mu\text{l}/\text{cm}^2$. As a method for the application of the test solution, there may be employed the method in which the solution is directly attached as the droplets by a fountain pen filler or a pipette, the method in which ink is transferred by use of a stamp, etc., the method in which ink is applied by use of a bar coater, etc., the method in which it is attached as small droplets by use of the ink jet recording system, etc.

(b) Test conditions:

(1) With the test tank being shielded from light, fresh ozone is constantly fed within the tank from the outside thereof, and set so that its concentration may be maintained constantly in the range of 0.1 ± 0.05 vol. %.

Also, the air inside of the tank is set so as to be circulated constantly by convection by means of a fan.

(2) The environmental conditions within the tank are set so that the temperature may be maintained in the range of $20^\circ\text{C} \pm 2^\circ\text{C}$, and the humidity in the range of $65\% \pm 3\%$ RH. For further making the absorbed water content within the test sample constant after completion of evaporation of volatiles in the ink, the test sample is used after storage under the above environment for 2 days after preparation.

(3) After set under the conditions of (1) and (2), the sample is exposed to ozone in the test tank for 15 minutes.

(c) Determination of measured value:

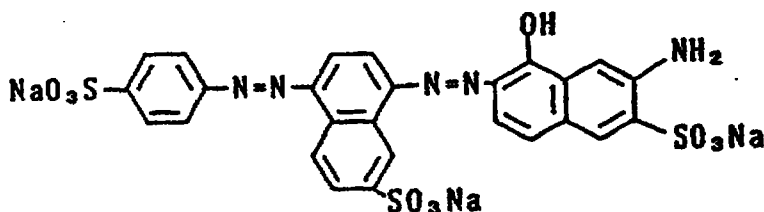
(1) The color difference ΔE^*_{ab} of the test sample between before and after the ozone exposure in the above test tank for 15 minutes is determined according to JIS Z 8730, and defined as the discoloration ΔE^*_{ab} of C.I. Food Black 2.

By use of a recording medium with a color difference (ΔE^*_{ab}) of the test sample obtained of 20 or less measured according to the ozone test as described above, the recording medium which can provide an image without any indoor discoloration as intended by the present invention can be obtained.

That the discoloration of C.I. Food Black 2 by the ozone test is over 20 is not preferable because the effect for indoor discoloration is poor. More preferably, the discoloration may be 10 or less.

C.I. Food Black 2 has the function of an indicator similar to a pH indicator or a redox indicator, and makes it possible to evaluate and measure the catalytic activity in the ozone test.

C.I. Food Black as herein mentioned is a commercially available dye represented by the formula shown below:



and it is readily available from the market.

C.I. Food Black 2 to be used in the present invention has a purity of 90% or higher. In general, commercially available dye has a purity of about 50 to 60%, containing much inorganic salts, particularly NaCl and Na_2SO_4 , etc. as impurities. If this is used as such, the effect of C.I. Food Black 2 as the indicator is lowered and further the influence by impurities is included in the test result. For this reason, C.I. Food Black 2 as herein mentioned is purified to enhance its purity to 90% or higher, with the concentration of NaCl and Na_2SO_4 being reduced to 1% or less. As the purification method in this case, any of the methods known in the art can be used. As such method, there may be included the method in which the dye is salted out with sodium sulfate, then dissolved in a solvent and filtered; the treatment method with a cation exchange resin technique; the aeration method; the agglomeration precipitation method by use of an agglomerating agent; the filtration method; the electrolytic method; etc.

It is well known in the art that a dye is decomposed with oxygen, and there is, for example, a literature

such as J. Soc. Dyers. Colors, Vol. 100 (1984), No. 4, P. 125 to 127 (M. Matsui et al), etc.

However, in a non-coated paper, no remarkable discoloration occurs even when the ozone test may be practiced, while remarkable discoloration occurs in a coated paper, and therefore it may be considered that the coated layer plays some catalytic action for indoor discoloration. Also, decomposition of a dye with ozone may be considered to be greatly varied depending on pH, ionic strength, etc., surrounding environment, adsorbed situation of the dye in the coated layer such as Van der Waals force, hydrogen bonding, etc., and it may be estimated that decomposition of the dye will be directed toward suppression, if ozone is decomposed before attacking the dye or the dye is absorbed by the coated layer so as to be protected from attack, etc.

The recording medium of the present invention with the discoloration of C.I. Food Black 2 being 20 or less according to the ozone test may be also considered to be a recording medium having such special coated layer.

On the other hand, the ozone concentration in practically accessible air is several ppm, with its lethal amount being 50 ppm, and therefore it can be hardly thought that only ozone contributes directly to indoor discoloration. Even if oxygen molecules in general may contribute to such discoloration, the decomposition mechanism by oxygen molecules is different from that by ozone because oxygen of oxygen molecules in general is in the triplet state while oxygen of ozone in singlet state. Thus, it may be estimated to be difficult to connect the results of the ozone test directly with indoor discoloration.

Having introduced above some presumptions about the relationship between the ozone test and indoor discoloration, it is not relevant to the present invention at all whether these presumptions are correct or not.

Additionally, it has been found that even when the recording medium of the Present invention is stored in a file or a binder made of polypropylene or polyethylene for one to several months, coloration (discoloration to yellow) of a white portion as observed in a conventional coated paper does not occur. According to the present inventors' presumptions, such discoloration to yellow may be considered to occur on the ground that an antioxidative agent contained in polypropylene or polyethylene is adsorbed by a porous pigment for forming a coated layer and is oxidized on the coated paper, whereby the coated layer is colored to yellow. Most of products made of polypropylene or polyethylene contains as an adduct an antioxidative agent such as BHT which has a phenol group in its molecular structure. It has been known that such phenolic antioxidative agent is colored to yellow by oxidation.

Discoloration to yellow as well as indoor coloration is a phenomenon inherent only in a coated paper and is considered to be promoted by catalytic property of a coated layer.

Thus, it has been found that a recording medium having a particular coated layer as in the present invention.

Anyway, according to the knowledge by the present inventors, the recording medium having a coated layer with the discoloration ΔE^*_{ab} of C.I. Food Black 2 of 20 or less according to the ozone test is free from any indoor discoloration even when attached on the wall in office or home for one to several months or stored in a drawer of a desk, and is also free from discoloration to yellow if stored in a file or a binder for one to several months is also excellent in ink jet recording adaptability such as ink absorptivity and color forming characteristic of recording agent, etc. as the recording medium having a coated layer.

In the following, description is made about a preferably construction for obtaining the recording medium of the present invention, and the recording medium obtained must have the discoloration ΔE^*_{ab} of C.I. Food Black 2 being 20 or less according to the above ozone test, as a matter of course.

The substrate to be used in the recording medium of the present invention may include, for example, papers, synthetic papers, plastic films, etc., and particularly a paper with a basis weight ranging from 50 to 250 g/m² and a Stöckigt sizing degree of 0 to 100 sec. is suitable. A paper with a basis weight less than 50 g/m² does not have firmness and involves a problem in paper feeding and discharging characteristic in printer. On the other hand, if the basis weight exceeds 250 g/m², there is the problem that powder drop-off of the coated layer will become excessive. If the sizing degree of the paper exceeds 100 sec., adhesive force between the coated layer and the base paper will be lowered, whereby powder drop-off will similarly occur.

The paper to be used in the present invention is a sheet containing a fibrous material and, if necessary, a filler, and any of the papers prepared by sheet-making into the range as specified above with an appropriate sizing agent according to the acidic or neutral sheet making method known in the art can be used.

The fibrous material constituting the above paper to be used in the present invention is composed mainly of a wood pulp, typically LBKP and NBKP, but it may be mixed with various synthetic fibers, glass fibers, etc., if desired.

The coated layer is formed on the above substrate by use of a coating liquid prepared by mixing a

pigment and a binder, and further various additives, if necessary.

As preferable embodiments for forming the coated layer according to the present invention, there may be included:

- 5 (1) the embodiment in which a silicon-containing type pigment and aluminum oxide are used in combination;
- (2) the embodiment in which an upper layer containing a silicon-containing type pigment used in the above embodiment (1) and an under layer containing a pigment with a greater secondary particle size than the above pigment are provided;
- 10 (3) the embodiment in which a silicon-containing type pigment subjected to the surface treatment with one or a mixture of two or more of soaps, hydroxides, salts or oxides of metals selected from the group consisting of Na, K, Ca, Mg, Al, Zn, Ba, Sr and Sn is incorporated;
- (4) the embodiment in which a silicon-containing pigment subjected to thermal treatment at a high temperature of 400 °C or higher is incorporated, etc.

In addition, a ratio of a pigment to a binder in an ink-receiving layer comprising mainly such pigment is preferably 1/3 - 5/1, more preferably 1/2 - 3/1 when the ink-receiving layer is a monolayer. The ratio range is such that the coated layer may become porous. If the ratio is less than 1/3 (the amount of the binder is too large), porosity will be lowered, resulting in lowering of ink absorptivity. On the other hand, if the ratio exceeds 5/1 (the amount of the colorant is too large), powder drop off in the coated layer will become remarkable, in some cases, resulting in that indoor discoloration, discoloration to yellow, etc., become 20 outstanding even when the above preferable pigment is used.

As the silicon-containing pigment to be used in the embodiment (1), (a) those with low specific surface area and (b) those with high pH of the pigment itself, etc. may be suitable. Specific examples of (a) with suitable range may be pigments having a specific surface area according to the BET method in the range of 10 to 200 m²/g, preferably 10 to 100 m²/g. As such pigments, silica, synthetic silicate, silicate mineral, etc. 25 are preferred in aspect of dye color forming characteristic. No such pigment has been generally used in the coated paper for ink jet, but they are commercially sold for use in paints or agricultural medicines, and pigments of various grades are readily available. If the specific surface area exceeds 200 m²/g, indoor discoloration occurs remarkably. On the other hand, although the catalytic activity is lowered as the specific surface area is smaller, a specific surface area smaller than 10 m²/g will result undesirably in lowering of color forming characteristic of the recording agent. 30

As the above pigment (b), one with its pH of 7 or higher may be suitably used, more preferably one with pH of 8 or higher.

In the present invention, pH of the pigment refers to the pH when measured by sampling 100 ml of ion-exchanged water (pH 5.8 to 6.4) in a beaker of 200 cc, adding 10 g of a pigment thereto, stirring the mixture with a stirrer for 5 minutes and measuring the pH by means of a pH meter under the state where 35 the pigment is suspended. Ordinarily, the pigment of the silica type has a pH of about 5.5 to 6.5 depending on the manufacturing method. For example, the silica produced by the dry process becomes weakly acidic due to the minutely adsorbed HCl produced as a by-product.

As the method for making thus the pH of the pigment 7 or higher, there are:

- 40 (i) the method for producing silica by the reaction between sodium silicate and a salt in an aqueous solution, wherein pH is enhanced by maintaining higher the concentration of a basic oxide and unreacted salt during purification of the silica by salting out;
- (ii) the method in which the silanol groups on the surface of a pigment are coated in the form of salt by adding metal salt or metal soap of Mg, Ba, Zn, etc. into a suspension of a pigment such as purified silica, etc.; 45
- (iii) the method in which a basic oxide such as MgO, CaO, BaO, etc. is incorporated in the crystal structure of the pigment; etc. According to these methods, a silicon-containing type pigment with a pH of 7 or higher can be obtained.

When a silicon-containing pigment with a pH less than 7 is used, a recorded image obtained is 50 subjected to great discoloration and fading, particularly remarkable indoor discoloration. The cause is not clear, but it may be considered that the dye (particularly the azo type pigment) adsorbed onto the pigment may be oxidized with oxygen in the air to become a decomposed product and effect discoloration, namely the active sites on the pigment surfaces promote catalytically the oxidative decomposition of the dye. This catalytic action is greatly changed depending on the pH of the pigment, and promotes oxidative decomposition at less than pH 7, while the catalytic action is lowered at pH 7 or higher to become inactive, whereby 55 discoloration or brown discoloration of a black dye may be considered to be prevented. In this case, a suitable pigment has a specific surface area in the range of 10 to 650 m²/g, more preferably 10 to 200 m²/g.

However, while the recording medium by use of such pigment may be ameliorated in indoor

discoloration, color forming characteristic of the dye including the pigment according to the method (i) is not necessarily satisfactory, and it was impossible to satisfy both of the indoor discoloration inhibiting effect and the image density only by use of these silica type pigments.

In the embodiment (1), the above problem is solved by using in combination the above silicon-containing pigment and aluminum oxide. More specifically, for the first time by using in combination the above silicon-containing pigment and aluminum oxide, further excellent dye color forming characteristic can be obtained while maintaining the excellent brown discoloration inhibiting effect, whereby an image of high density can be provided.

In the embodiment of (1), the amount of the aluminum oxide contained in the coated layer may preferably comprise 10 to 80% by weight of the total pigment, more preferably 25 to 65%. At a level less than 10%, the effect is not sufficient as compared with the case when no aluminum oxide is contained, while at a level exceeding 80%, the ink absorptivity of the coated layer will be undesirably lowered to great extent. Although the mechanism how the aluminum oxide inhibits indoor discoloration of the dye in the coated layer to exhibit the effect of enhancing dye color forming characteristic is not clarified, according to the knowledge of the present inventors, it may be considered that incorporation of aluminum oxide may result in improvement of dye trappability in the coated layer to trap the dye in the ink, which is attached on the surface, at nearer to the surface without penetration into the inner portion, because of its strong dye absorptivity owing to having a positive surface potential in spite of relative lower specific surface area.

The aluminum oxide as herein mentioned may be obtained industrially by calcining aluminum hydroxide obtained by arc discharging of metallic aluminum pellets in pure water, or obtained by hot caustic soda treatment of bauxite which is a naturally occurring mineral, and the method for preparation thereof is known per se, and various products having various crystal types (α form, γ form, δ form, η form, θ form) and various particle sizes, bulk densities, specific surface areas are commercially available, and the present invention is inclusive of all of these.

For example, there can be used any of alumina powder, molten alumina, spherical alumina particles or α -alumina, γ -alumina which are materials for ceramics, porcelains, grinding agents, etc., and otherwise ultrafine particulate alumina by the gas phase method (produced by Aerosil), active alumina for use in catalyst or adsorbent (produced by Iwatani Sangyo), colloidal aqueous dispersion of alumina hydrate (Alumina: produced by Nissan Kagaku), etc.

Although a composite of alumina and silica (activated clay, etc.) may be available as aluminum oxide, double salts of alumina containing basic oxides such as MgO, CaO, ZnO, CuO, NiO, MnO, Fe₂O₃, etc. cannot be used, because the color forming characteristic of the dye is undesirably lowered.

The aluminum oxide to be used in the present invention has more preferably physical properties of a particle size ranging from 0.001 μ m to 10 μ m and a specific surface area ranging from 1 to 500 m²/g, more preferably 10 to 200 m²/g. If the particle size is too small, powder drop-off will occur at the coated layer, while the dot shape will be worsened if it is too large. On the other hand, with a specific surface area less than 1 m²/g, ink absorptivity will be remarkably lowered, while if it is over 500 m²/g, indoor discoloration cannot be improved even when the alumina oxide is combined with the above silicon-containing pigment.

Examples of the binder to be used in the embodiment (1) may include water-soluble polymers such as polyvinyl alcohol, starch, oxidized starch, cationized starch, casein, carboxymethyl cellulose, gelatin, hydroxyethyl cellulose, etc. and water-dispersed type polymers such as SBR latex, MBR latex, vinyl acetate emulsion, acrylic type emulsion, etc., which may be used either singly or as a mixture of two or more kinds.

In the present invention, the coated layer is formed by use of a coating liquid with a suitable concentration and viscosity by mixing the materials as described above.

The coating amount of the aqueous coating liquid may be suitably in the range of 2 to 50 g²/m on drying. If it is less than 2 g²/m, the ink absorptivity of the coated layer is lowered, and there is the problem of feathering that the ink is blurred along with fibers exposed on the surface. When it is excesses 50 g/m², the coated layer becomes fragile to result in the problem of powder drop-off.

As a modification example of the embodiment (1), there is the embodiment (2) in which a layer containing the silicon-containing pigment (a) or (b) as mentioned above is made as an upper layer and a layer containing a pigment with a particle size greater than the silicon-containing pigment is made an under layer.

In the present invention, by forming the under layer with a pigment having greater particle size and embedding the fine unevenness on the surface of the under layer with the pigment having smaller particle size in the upper layer, the advantage in using a pigment with greater particle size is utilized to give an image without occurrence of powder drop-off, and further with good dot shape and without feeling of roughness.

The specific surface area of the pigment for forming the under layer should preferably be not less than

that of the pigment for forming primarily the upper layer, more preferably 200 m²/g or higher, also in aspect of ink absorptivity. According to the knowledge of the present inventors, so long as the dye in the ink droplets is trapped in the upper layer, the specific surface area of the pigment for forming the under layer will contribute little to indoor discoloration.

5 In aspect of color forming characteristic and ink absorptivity, the construction such that the ink absorptivity of the upper layer is so slow as to cause feathering of the ink droplets attached on the surface to appropriate sizes and such that the ink absorptivity of the under layer is great is preferred, and for this purpose the ratio of the pigment to the binder in the upper layer is preferably in the range of 1/3 to 5/1, more preferably 1/2 - 3/1, and such ration in the coated layer as a whole is preferably in the range of 1/1 to 10/1.

10 Since the ink receiving layer is constituted of the two layers as described above, the coated amount of the upper layer may be preferably 1 to 20 g/m², more preferably 5 to 15 g/m², and that of the under layer is preferably greater than that of the upper layer within the range such that the total coated amount in the ink receiving layer may be 2 to 50 g/m², preferably 8 to 30g/m².

15 If the amount of the upper layer is less than 1 g/m², there is no noticeable effect as compared with the case that no upper layer is provided, while with an amount over 20 g/m², the effect of the under layer cannot be exhibited, whereby ink absorption speed, dye color forming characteristic, indoor discoloration, etc. will be lowered.

In addition, in order to further improve ink absorptivity of the recording medium, there can preferably be 20 used, as a pigment for forming an under layer, porous silica particles in the form of a spherical particulate shape as disclosed in Japanese Laid-Open Patent Application No. 183382/1987.

In particular, when the spherical silica having a particle size of 10 to 30 μm is used for formation of an under layer, there can be provided a coated layer which have a large amount of void and excellent ink-absorptivity, as compared with that using a conventional amorphous silica.

25 When such particles is used for formation of a coated layer being a monolayer, there have been posed the problems that dots obtained get to be in the form of star shapes, that high adhesive strength can be obtained with difficulty, that powder drop-off occurs with ease, and that images obtained becomes rough.

Concerning specific metal compounds characterized in the embodiments (3), as the metal soap, there may be included the reaction products with stearic acid, lauric acid or other fatty acids or aromatic acids; as 30 the salt, chlorides, sulfates, nitrates, ammonium salts, acetates, carbonates, oxalates, silicates, etc. thereof. Also, double salts of the above metals and those having crystal water may be also included. As the metal, above all, Ca, Mg, Al and Zn are preferred with respect to bonding force with silica, absence of toxicity and non-coloring property, etc.

The metal compound to be used in the present invention may be used either singly or a combination of 35 two or more kinds, preferably in an amount of 0.1 to 30 parts by weight, particularly 0.5 to 20 parts by weight, per 100 parts by weight of silica. If the amount used is less than 0.1 part by weight, the advantageous effect of the present invention is insufficient, while if it is more than 30 parts by weight, undesirable results will occur such as lowering in ink absorptivity of the recording medium or lowering in color characteristic.

40 As the method for treating silica with the above metal compound, there may be employed preferably a dry process and a wet process. The dry process is a method in which the metal compound is attached uniformly onto silica by mixing silica with the metal compound, or by adding the powder of the metal compound, its aqueous solution or dispersion, etc. to silica under stirring by spraying method, etc.

On the other hand, the wet process is a method in which silica is dipped in a treating liquid containing 45 the metal compound during the steps of producing silica, in which gellation, aging and precipitation are conducted with the metal compound being added to the silica dispersion, in which the metal compound is added at the initial state of reaction, or in which the surface is treated by spraying the metal compound during the drying step. Among them, particularly preferred are the method in which the metal compound is added at the initial or later stage of the aging reaction or gellation or the method in which it is added at the 50 initial stage of the reaction, whereby the silica surface can be covered with good efficiency.

The above methods are not limited, but any method may be employed, provided that silica can be previously treated on the surface thereof with the metal compound prior to inclusion in the coated layer.

As the silica before treatment to be used in the recording medium of the present invention, any of 55 natural or synthetic silica may be available, but particularly preferably is synthetic fine particulate silica with a specific surface area having preferably 200 to 700 g/m² according to the BET method, and by use of the silica with such specific surface area, excellent color forming characteristic of the water-soluble dye in ink, optimum shape and size of ink dots can be accomplished.

As the silicon-containing type pigment before thermal treatment to be used in (4), any of natural or

synthetic silica may be available, but particularly preferably is synthetic fine particulate silica with a specific surface area of preferably 200 to 700 g/m² according to the BET method, and by use of the silica with such specific surface area, excellent color forming characteristic of the water-soluble dye in ink, optimum shape and size of ink dots can be accomplished.

5 The silica to be used in the present invention is a silica obtained by subjecting the silica as mentioned above to thermal treatment at a temperature of 400 °C or higher, preferably 600 °C to 1200 °C, further preferably for about 10 minutes to about 10 hours, and by thermal treatment of the silica under the above conditions, the problem of the prior art occurred when silica is included in the recording medium, namely the problem of indoor discoloration and discoloration to yellow of the recorded image has been solved, while
10 retaining the advantage possessed by silica such as excellent color forming characteristic, etc. There is also an example in which a silica treated with a silane coupling agent, etc. is used, but such silica is made remarkably hydrophobic on its surface, thereby involving problems such as difficult preparation of a coating liquid, lowering in coating workability, etc. However, in the present invention, there is not such problem as mentioned above, since the surface of the silica particles is not made hydrophobic.

15 In any of the above embodiments (1) to (4), after coating with an aqueous coating liquid comprising a pigment and a binder, drying is performed by drying methods known in the art, for example, by use of a hot air drying furnace, a hot drum, etc. to give the recording medium of the present invention.

Also, for smoothening of the coated layer surface, or for enhancing the surface strength of the coated layer, super calendering may be also used in the steps.

20 Further, in the present invention, the coated layer may also contain dye fixing agents (water-resistant agents), fluorescent whitener, surfactants, deforming agents, pH controllers, antifungal agents, UV-absorbers, antioxidants, etc.

Particularly, an antioxidant known in the art such as thioether tends to inhibit indoor discoloration, and even when it is contained in the coated layer, discoloration to yellow will not occur. Thus it may be
25 contained in the range such that the coated layer is not colored or the coated layer strength is not lowered.

According to the knowledge of the present inventors, particularly when a polycationic substance is contained as the dye fixing agent, water resistance of the recorded image can be strengthened simultaneously with exhibition of the effect to inhibit indoor discoloration, and therefore it may be more preferably contained in the coated layer.

30 As such cationic substance, any of water-resistant agents for paper for ink jet known in the art having quaternized amine within the structure may be available. Such water-resistant agent (dye fixing agent) may be desirably used in an amount of about 0.5 to 15% by weight based on the pigment. It is not preferable to contain 15% or more by weight thereof, because light resistance will be remarkably lowered, although there might be the effect against indoor discoloration of the image.

35 According to the recording method in which recording is performed with multi-color aqueous inks of, for example, yellow (Y), magenta (M), cyan (C), black (Bk), etc., by use of the ink jet recording system on the recording medium with the construction as described above, the image obtained is free from indoor discoloration and the recorded image with excellent storability can be obtained.

40 The recording medium of the present invention contains a large amount of a pigment with high dye trapping ability in its surface layer, and therefore the probability that the dye in the ink droplets is trapped and absorbed by the pigment is high, whereby feathering or diffusion of ink can be inhibited, with the results that the dot shape can be improved to exhibit excellent ink absorptivity, resolution, color forming characteristic, color forming density, etc.

45 Further, the present invention exhibits the ink jet recording adaptability for the coated paper as above, particularly excellent image density, and has little problem of image storability inherent in the coated paper and of discoloration to yellow upon storing the paper in a file or a binder. Thus, in the recording method according to the ink jet recording system by use of the recording medium of the present invention and multi-color inks, the obtained image can be stored on the wall or in a drawer in an office which is not directly irradiated with sunlight for 1 to several months without ensuing the problem of indoor discoloration
50 or the problem of coloration (discoloration to yellow) of a white portion in the coated paper or the recorded image during storage thereof in a file or a binder made of polyethylene, polypropylene, etc., for one to several months.

The present invention is described below in more detail by referring to Examples and Comparative examples. In the sentences, parts and % are based on weight, unless otherwise particularly noted.

55 Examples 1 - 8 and Comparative examples 1 - 4

Pure papers with a basic weight of 100 g/m² and a sizing degree of 22 sec. as a substrate were coated

with coating compositions shown below to a coated amount on drying of 20 g/m² by the bar coater method, followed by hot air drying at 100 °C for 5 minutes to obtain recording media of the present invention and recording media for comparative purpose.

5

(Coating liquid composition)

10	Pigment	25 parts
	Polyvinyl alcohol (PVA,	
	produced by Kuraray)	5 parts
15	Cation-modified polyvinyl alcohol	
	(PVA-C-118-2A, produced by Kuraray)	5 parts
20	Polyamine type water-resistant agent	
	(Polyfix 601, produced by Showa	
25	Kobunshi) (60% aqueous solution)	3 parts
30	Fluorescent whitener (Kaycoll BRAL	
	produced by Shinnisso Kako)	0.3 parts
35	Water	200 parts

40

As the pigments in the above coating liquid compositions, those shown below in Table 1 were employed.

45

50

55

Table 1

		Pigment	Parts	Specific Surface Area (m ² /g)
5	Example 1	Finesil SP-20 (Tokuyama Soda)*1	16	18
		Aerosil aluminum oxide-C (Nippon Aerosil)*2	9	100
10	" 2	Finesil SP-20 (the same as above)	16	
		Active alumina 2R-30 (Iwatani Kagaku Kogyo)	9	48
15	" 3	Finesil SP-20 (the same as above)	7	
		Alumina sol 520 (Nissan Kagaku)*3	17	300
	" 4	Mizukanite P-1 (Mizusawa Kagaku)*4	16	600
		Activated clay (Tsuchiya Kaonlin Kogyo)	9	
20	" 5	Mizukanite P-1 (the same as above)	20	
		Active alumina 2R-30 (the same as above)	5	
25	" 6	Mizukanite P-1 (the same as above)	16	
		Alumina spherical particles AX-10 (Micron)	9	1 or less
	" 7	Tokusil CM (Tokuyama Soda)*1	16	80
30		Aerosil aluminum oxide-C (the same as above)	9	
	" 8	Mizukasil P-527 (Mizusawa Kagaku)*5	16	40
		Activated clay (the same as above)	9	10 or less
35	Comparative example 1	Siloid 620 (Fuji Davidson)*1	25	300
	" 2	Mizukasil P-78D (Mizusawa Kagaku)*1	25	384
40	" 3	Finesil X-37(b) (Tokuyama Soda)*1	16	360
		Active alumina RK-30	9	282
	" 4	Nipsil HD-2 (Nippon Silica Kogyo)*5	16	264
		Aerosil aluminum oxide C	9	

Note) *1: fine powdery silicic acid; *2: ultra-fine particulate alumina; *3: 20% colloidal dispersion of alumina hydrate; *4: synthetic silicate mineral; *5: fine powdery silica.

Comparative examples 5 and 6

A commercially available coated paper NM for ink jet (produced by Mitsubishi Paper Mills, Ltd.) (Comparative example 5) and FC-9 (produced by Jujo Paper Mfg. Co., Ltd.) (Comparative example 6) were employed as the recording media for comparative purpose.

Ink jet recording adaptability of the above recording media was evaluated by performing ink jet

recording with an ink having the composition shown below by use of (a) an ink jet printer having ink jet heads each equipped with 128 nozzles at nozzle intervals of 16 nozzles/1 mm for four colors of Y, M, C and Bk and (b) an ink jet printer having 24 nozzles at intervals of 8 nozzles/1 mm for the four colors.

5

Ink composition (I)

Dye 3 parts
 Diethylene glycol 20 parts
 10 Water 7 parts

Dye (Ink I)

Y: C.I. Direct Yellow 86
 15 M: C.I. Acid Red 35
 C: C.I. Direct Blue 199.
 Bk: C.I. Direct Black 17

Ink composition (II)

20

Dye 2 parts
 Polyethylene glycol 20 parts
 Polyethylene glycol #200 15 parts
 25 Water 63 parts

Dye (Ink II)

Y: C.I. Acid Yellow 42
 M: C.I. Acid Red 92
 30 C: C.I. Direct Blue 86
 Bk: C.I. Direct Black 51

Ink composition (III)

35 C.I. acid black 26 was used as the dye in the ink composition (II).
 Evaluation was performed with respect to the following items. The results are shown below in Table 2.

Measurement and evaluation methods

- 40 (1) Discoloration ΔE^*_{ab} of Food Black 2 by the ozone test was measured according to the method as described above.
- (2) For measurement of indoor storability (1), a color image was formed by use of the ink (I), (II) and the printer (a), attached on the wall in an office and left to stand for 6 months. The image with no discoloration recognized as compared with the same image stored similarly in a clear pocket file for 6 months was rated as o, that with excessive discoloration as x, and that with medium discoloration therebetween as Δ .
- 45 (3) For measurement of indoor storability (2), a solid pattern of Bk was printed by use of the ink (III) and the printer (b), attached similarly on the wall in an office as in (2) and left to stand for one month. The difference ΔE^*_{ab} between the chromaticity of this image and the chromaticity of the image immediately after printing was determined for evaluation of indoor discoloration.
- 50 (4) For color characteristic, chroma of the printed matter by solid printing (Y, M, C) with the use of the ink (I) and the printer (a) was measured by use of a high speed color analyzer CA-35 (produced by Murakami Shikisai Kagaku).
- (5) For image density, O.D. of the printed matter with solid printing with the use of the ink (III) and the printer (a) was measured by use of Macbeth Densitometer RD-914.
- 55 (6) For evaluation of discoloration to yellow, the following test was done. Recording mediums were stored in a clear pocket file (produced by Lion) for 6 months in a dark place. Thereafter, the recording medium with no discoloration to yellow at its coated surface was ranked as o, and that with discoloration to yellow

was ranked as x.

Table 2

5

Example

10

ΔE^*ab

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
2.9	4.7	6.3	5.6	7.8	3.4	10.3	5.1

Indoor
storability (1)

15

(I)

0 0 0 0 0 0 0 0

(II)

0 0 0 0 0 0 0 0

20

Indoor
storability (2)

1.7 2.8 3.6 3.8 4.1 1.8 7.3 3.6

Color
characteristic

25

Y

81.5 83.9 78.3 80.2 85.6 77.1 81.0 80.3

M

70.4 74.0 70.6 71.1 74.2 66.3 70.4 69.4

C

58.8 50.1 57.0 59.2 59.7 54.5 56.7 59.1

30

Image density

Bk

0.72 0.76 0.83 0.71 0.84 0.70 0.83 0.75

35

Discoloration
to yellow

0 0 0 0 0 0 0 0

40

45

50

55

Table 2

	<u>Comparative example</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
<u>ΔE^{*ab}</u>	28.0	26.7	25.2	23.5	32.0	34.0
<u>Indoor storability (1)</u>						
(I)	X	X	X	X	X	X
(II)	X	X	X	X	X	X
<u>Indoor storability (2)</u>	17.6	14.3	15.2	15.7	21.0	20.0
<u>Color characteristic</u>						
Y	80.8	82.7	80.4	82.3	-	-
M	67.7	73.6	69.8	71.4	-	-
C	56.7	59.1	59.7	60.0	-	-
<u>Image density</u>						
Bk	0.79	0.77	0.76	0.75	-	-
<u>Discoloration to yellow</u>	X	X	X	X	X	X

Examples 9 - 14, Comparative examples 7 - 9

A pure paper with a basis weight of 100 g/m² and a sizing degree of 22 sec. as the substrate was coated with a coating composition shown below to a coated amount on drying of 15 g/m² by the bar coater method, followed by hot air drying at 110 °C for 5 minutes, to form an under layer.

Pigment	24 parts
Polyvinyl alcohol (PVA-117, produced by Kuraray)	4 parts
Polyvinyl alcohol (PVA-105, produced by Kuraray)	4 parts
Water	200 parts

The under layer thus formed was coated with a coating composition shown below to a coated amount on drying of 8 gm/m² by the bar coater method, followed by drying at 110 °C for 5 minutes, to form a upper

layer to obtain the recording medium of the present invention and the recording medium for comparative purpose.

5	Pigment	25 parts
	Polyvinyl alcohol (PVA-117, produced by Kuraray)	6 parts
10	Polyvinyl alcohol (PVA-105, produced by Kuraray)	6 parts
	Polyamine type water-resistant agent (28% aqueous solution) (PASH-10L, produced by Nittobo)	4 parts
15	Water	200 parts

20 The pigments used for formation of the upper layer in Examples 9 - 14 and Comparative examples 7 - 9 are shown in Table 3.

25

30

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Table 3

	Pigment (Manufacturer)	Average particle size (μm)	Specific surface area (m^2/g)	Parts used
(Upper layer) Example 9	Finesil SP-20 (Tokuyama Soda)	9.1	18	13
	Spherical alumina AX-O (produced by Micron)	3.0	0.5	12
10	Mizukasil P-527 (Mizusawa Kagaku)	2.9	40	16
	Aerosil aluminum oxide-C	0.02	100	9
11	Kyoward 600 (Kyowa Kagaku) 1	5.4	30	13
	Active alumina RG-30 (Iwatani Kagaku Kogyo)	0.5	48	12
12	Nipsil E-150J (Nippon Silica Kogyo)	4.2	95	7
	Alumina sol 520 (Nissan Kagaku)	0.1 or less	300	18
13	Finesil SP-20	9.1	18	16
	Aerosil aluminum oxide-C	0.02	100	9
14	Finesil SP-20	9.1	18	13
	Aerosil aluminum oxide-C	0.02	100	12

Table 3

	Pigment (Manufacturer)	Average particle size (μm)	Specific surface area (m^2/g)	Parts used
(Under layer) Examples 9-11	Sailoid 620 (Fuji Davidson)	12.0	300	24
12-14	Spherical Silica (Asahi Grass)	15.0	700	24
(Upper layer) Comparative Example 7	Sailoid 72 (Fuji Davidson)	2.5	300	25
8	Finesil X-37 (B) (Tokuyama Soda)	3.7	260	25
9	Nipsil HD-2 (Nippon Silica Kogyo)	3.2	264	13
	Aerosil aluminum oxide-C	0.02	100	12
(Under layer) Comparative Examples 7-9	Sailoid 620 (Fuji Davidson)	12.0	300	24

1 Magnesium silicate

2 Synthetic silicate mineral: the colorants other than alumina are all silica.

For each of the above recording media, recording was performed and evaluated in the same manner as in Example 1. The results are shown in Table 4.

Table 4

	Ink absorptivity	Indoor storability		Indoor storability	Color characteristic			Image density	Ozone test
		(I)	(II)		ΔE^{*ab}	Y	M	C	
Example 9	O	O	O	O	5.2	86.7	74.2	53.2	0.75
10	O	O	O	O	2.3	87.3	74.2	51.9	0.82
11	Δ	O	Δ	Δ	7.8	87.8	75.7	54.2	0.81
12	O	O	O	O	5.6	76.4	68.1	51.9	0.88
13	O	O	O	O	2.1	75.0	64.8	48.2	0.71
14	O	O	O	O	2.4	87.1	74.4	51.1	0.82
Comparative 7	O	X	X	X	21.6	88.7	75.9	56.0	0.75
8	O	X	X	X	21.2	83.9	74.3	55.2	0.73
9	O	X	X	X	21.4	93.0	75.8	56.0	0.89

Examples 15 - 19

As shown below in Remarks, a variety of silica to be used in the present invention were prepared. Next, by use of silica shown in Remarks respectively, the coating liquids with the compositions shown

below were prepared.

Next, pure paper in general (Ginkan; basis weight 64 g/m², produced by Sanyo Kokusaku Pulp K.K.) were coated with the respective coated liquids by bar coater at a coated amount on drying of 12 g/m², followed by drying in a conventional manner to obtain recording media of the present invention.

5

Silica in Remarks

100 parts

10

Polyvinyl alcohol (PVA 117,

produced by Kuraray)

70 parts

Water

100 parts

15

Comparative example 10

For comparison, in place of the surface treated silica B in Example 15, an untreated silica A was used, following otherwise the same procedure as in Example 15, to prepare a recording medium of comparative example.

Comparative example 11

For comparison, in place of the surface treated silica B in Example 15, a coating solution was prepared by merely blending the silica A and calcium chloride which is the treating agent compound at normal temperature during preparation of the coating liquid, following otherwise the same procedure as in Example 15, to prepare a recording medium of comparative example.

30 Remarks

(Examples 15 - 19, Comparative examples 10, 11)

Example 15

35

Silica B: Immediately after aging for 40 minutes in the reaction of silica A as described below, 5% of magnesium chloride was added based on silica, followed further by aging for 20 minutes, and otherwise the same procedure as for silica A was repeated to obtain silica B.

40 Example 16

Silica C: Immediately before drying by spray dryer in the reaction of silica A as described below, 10% of aluminum hydroxide was added based on silica, and otherwise the same procedure as for silica A was repeated to obtain silica C.

45

Example 17

Silica D: Immediately after alkali neutralization in the reaction of silica A as described below, 6% of zinc oxide was added based on silica, and otherwise the same procedure as for silica A was repeated to obtain silica D.

50

Example 18

Silica E: During drying by spray dryer in the reaction of silica A as described below, 15% of magnesium laurate was added based on silica, and otherwise the same procedure as for silica A was repeated to obtain silica E.

55

Example 19

Silica F: Silica A as described below was subjected to thermal treatment at 700 °C for one hour to obtain silica F.

Comparative example 10

5 Silica A: Into a reactor were charged 10 m³ of commercially available sodium silicate, and 35 m³ of water, and under stirring of the mixture, 3.2 m² of sulfuric acid (200 g/ml) was added over about 15 minutes. Under stirring of this liquid, steam was blown there into to elevate the temperature within 60 minutes to 90 °C. Then, aging was effected at the same temperature for 40 minutes, and the alkali was neutralized with
10 sulfuric acid to complete the reaction. Next, the solution was filtered, washed with water and pulverized after drying by a spray dryer to obtain silica A with a specific surface area of 350 g/m².

Comparative example 11

15 Silica A

Treating method: no treatment (during preparation of coating solution, 3% of calcium chloride was merely mixed with silica).

For the above recording media, recording was performed and evaluated in the same manner as in
20 Example 1. The results are shown in Table 5.

Table 5

	<u>Example</u>					<u>Comparative example</u>	
	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>10</u>	<u>11</u>
25 <u>ΔE*ab</u>	15.2	16.1	16.2	14.2	17.6	25.6	23.1
<u>Indoor storability (1)</u>							
35 (I)	○	○	○	○	○	X	Δ
(II)	Δ	Δ	Δ	Δ	Δ	X	X
40 <u>Indoor storability (2)</u>	9.7	10.1	11.1	9.2	10.5	20.3	17.2
<u>Color characteristic</u>							
45 Y	82.3	84.6	80.3	82.1	83.9	84.2	81.7
M	70.3	72.0	70.1	71.0	71.5	71.6	70.0
50 C	51.0	51.8	51.6	50.8	52.0	52.2	51.3
<u>Image density</u>							
Bk	0.71	0.73	0.69	0.70	0.72	0.73	0.71
55 <u>Discoloration to yellow</u>	○	○	○	○	○	X	X

**Claims**

1. A recording medium, comprising a substrate, a ink receiving layer on the substrate, the ink-receiving layer containing a silicon-containing pigment and a binder, wherein the recording medium exhibits discoloration ΔE^*_{ab} of C.I. Food Black 2 of 20 or less according to the ozone test.
2. A recording medium according to claim 1, wherein the ink-receiving layer is porous.
3. A recording medium according to claim 1, wherein the discoloration E^*_{ab} of C.I. Food Black according to the ozone test is 10 or less.
4. A recording medium according to claim 1, wherein the ratio of the pigment to the binder is in the range of 1/3 to 5/1 in terms of weight ratio.
5. A recording medium according to claim 4, wherein the ratio is in the range of 1/2 to 3/1.
6. A recording medium according to any preceding claim, wherein the pigment has a specific surface area of 10 to 200 m²/g, and the ink-receiving layer also contains aluminium oxide particles.
7. A recording medium according to claim 6, wherein the aluminium oxide particles comprise 10 to 80% by weight of the total pigment.
8. A recording medium according to claim 6 or 7, wherein the aluminium oxide particles have particle sizes in the range of 0.001 to 10 μ m.
9. A recording medium, according to any of claims 1 to 5, wherein the ink-receiving layer comprises an upper layer containing the pigment, aluminium oxide and the binder, and an under layer containing a pigment with greater particle size than the pigment in the upper layer.
10. A recording medium according to claim 9, wherein the pigment contained in the under layer is spherical silica.
11. A recording medium according to claim 9 or 10, wherein the specific surface area of the silicon-containing type pigment is in the range of 10 to 200 m²/g.
12. A recording medium according to any of claims 6, 7, 8 or 11, wherein the specific surface area is in the range of 10 to 100 m²/g.
13. A recording medium according to any of claims 6 to 12, wherein the aluminium oxide particles have a specific surface area in the range of 1 to 500 m²/g.
14. A recording medium according to claim 13, wherein the aluminium oxide particles have a specific surface area in the range of 10 to 200 m²/g.
15. A recording medium according to any of claims 9 to 11, wherein the pigment contained in the under layer has a specific surface area of 200 m²/g or higher.
16. A recording medium according to claim 15, wherein the pigment has a specific surface area of 200 to 700 m²/g.
17. A recording medium according to claim 9, wherein the ratio of the pigment to the binder used in the ink-receiving layer is 1/1 to 10/1 in terms of weight ratio.
18. A recording medium according to claim 9, wherein the coated amount of the upper layer is in the range of 1 to 20 g/m².
19. A recording medium according to claim 9, wherein the coated amount of the lower layer is larger than that of the upper layer.



20. A recording medium according to any of claims 1 to 5, wherein the silicon-containing type pigment has been subjected to a surface treatment with one or a mixture of two or more selected from soaps, hydroxides, salts or oxides of metals selected from K, Ca, Mg, Al, Zn, Ba, Sr and Sn.
- 5 21. A recording medium according to claim 20, wherein the silicon-containing type pigment before the treatment has a specific surface area of 60 m²/g.
22. A recording medium according to claim 20 or 21, wherein the silicon-containing type pigment is a synthetic fine particulate silica.
- 10 23. A recording medium according to any of claims 20 to 22, wherein the silicon-containing type pigment has a specific surface area in the range of 1 to 200 m²/g.
24. A recording method, which comprises impelling droplets of ink containing a water-soluble dye on to a recording medium according to any preceding claim.
- 15 25. A recording method according to claim 24, wherein said recording method is ink jet recording method.
26. A recording method according to claim 24 or 25, wherein recording is performed by use of at least two colors of inks of yellow, magenta, cyan and black.
- 20

Revendications

- 25 1. Support d'enregistrement comprenant un substrat, une couche réceptrice d'encre sur le substrat, la couche réceptrice d'encre contenant un pigment renfermant du silicium et un liant, le support d'enregistrement présentant un changement de couleur ΔE^* ab du colorant noir C.I. Food Black 2 égal ou inférieur à 20, suivant le test à l'ozone.
- 30 2. Support d'enregistrement suivant la revendication 1, dans lequel la couche réceptrice d'encre est poreuse.
3. Support d'enregistrement suivant la revendication 1, dans lequel le changement de couleur ΔE^* ab du colorant noir C.I. Food Black 2 est égal ou inférieur à 10, suivant le test à l'ozone.
- 35 4. Support d'enregistrement suivant la revendication 1, dans lequel le rapport du pigment au liant est compris dans l'intervalle de 1/3 à 5/1, en rapport pondéral.
5. Support d'enregistrement suivant la revendication 4, dans lequel le rapport est compris dans l'intervalle de 1/2 à 3/1.
- 40 6. Support d'enregistrement suivant l'une quelconque des revendications précédentes, dans lequel le pigment possède une surface spécifique de 10 à 200 m²/g et la couche réceptrice d'encre contient également des particules d'oxyde d'aluminium.
- 45 7. Support d'enregistrement suivant la revendication 6, dans lequel les particules d'oxyde d'aluminium représentent 10 à 80 % en poids du pigment total.
8. Support d'enregistrement suivant la revendication 6 ou 7, dans lequel les particules d'oxyde d'aluminium possèdent des diamètres de particules compris dans l'intervalle de 0,001 à 10 μ m.
- 50 9. Support d'enregistrement suivant l'une quelconque des revendications 1 à 5, dans lequel la couche réceptrice d'encre comprend une couche supérieure contenant le pigment, de l'oxyde d'aluminium et le liant, et une couche sous-jacente contenant un pigment ayant un diamètre de particules supérieur à celui du pigment présent dans la couche supérieure.
- 55 10. Support d'enregistrement suivant la revendication 9, dans lequel le pigment présent dans la couche sous-jacente consiste en silice sphérique.



11. Support d'enregistrement suivant la revendication 9 ou 10, dans lequel la surface spécifique du pigment contenant du silicium est comprise dans l'intervalle de 10 à 200 m²/g.
12. Support d'enregistrement suivant l'une quelconque des revendications 6, 7, 8 et 11, dans lequel la surface spécifique est comprise dans l'intervalle de 10 à 100 m²/g.
13. Support d'enregistrement suivant l'une quelconque des revendications 6 à 12, dans lequel les particules d'oxyde d'aluminium possèdent une surface spécifique comprise dans l'intervalle de 1 à 500 m²/g.
14. Support d'enregistrement suivant la revendication 13, dans lequel les particules d'oxyde d'aluminium possèdent une surface spécifique comprise dans l'intervalle de 10 à 200 m²/g.
15. Support d'enregistrement suivant l'une quelconque des revendications 9 à 11, dans lequel le pigment présent dans la couche sous-jacente possède une surface spécifique égale ou supérieure à 200 m²/g.
16. Support d'enregistrement suivant la revendication 15, dans lequel le pigment possède une surface spécifique de 200 à 700 m²/g.
17. Support d'enregistrement suivant la revendication 9, dans lequel le rapport du pigment au liant utilisé dans la couche réceptrice d'encre est compris dans l'intervalle de 1/1 à 10/1, en rapport pondéral.
18. Support d'enregistrement suivant la revendication 9, dans lequel la quantité de revêtement de la couche supérieure est comprise dans l'intervalle de 1 à 20 g/m².
19. Support d'enregistrement suivant la revendication 9, dans lequel la quantité de revêtement de la couche inférieure est supérieure à celle de la couche supérieure.
20. Support d'enregistrement suivant l'une quelconque des revendications 1 à 5, dans lequel le pigment contenant du silicium a été soumis à un traitement de surface avec un composé, ou un mélange de deux ou plus de deux composés choisis entre des savons, des hydroxydes, des sels ou des oxydes de métaux choisis entre K, Ca, Mg, Al, Zn, Ba, Sr et Sn.
21. Support d'enregistrement suivant la revendication 20, dans lequel le pigment contenant du silicium, avant traitement, possède une surface spécifique de 60 m²/g.
22. Support d'enregistrement suivant la revendication 20 ou 21, dans lequel le pigment contenant du silicium est une silice synthétique en particules fines.
23. Support d'enregistrement suivant l'une quelconque des revendications 20 à 22, dans lequel le pigment contenant du silicium possède une surface spécifique comprise dans l'intervalle de 1 à 200 m²/g.
24. Procédé d'enregistrement, qui consiste à chasser des gouttelettes d'une encre contenant un colorant hydrosoluble contre un support d'enregistrement suivant l'une quelconque des revendications précédentes.
25. Procédé d'enregistrement suivant la revendication 24, qui consiste en un procédé d'enregistrement par jet d'encre.
26. Procédé d'enregistrement suivant la revendication 24 ou 25, dans lequel l'enregistrement est effectué au moyen d'au moins deux couleurs d'encres choisies entre le jaune, le magenta, le cyan et le noir.

Patentansprüche

1. Aufzeichnungsmaterial mit einem Substrat und einer tintenaufnehmenden Schicht auf dem Substrat, die ein Silicium-haltiges Pigment, und ein Bindemittel enthält, wobei das Aufzeichnungsmaterial im Ozon-test eine Entfärbung ΔE^* ab von C.I. Food Black 2 von 20 oder weniger zeigt.



2. Aufzeichnungsmaterial nach Anspruch 1, wobei die tintenaufnehmende Schicht porös ist.
3. Aufzeichnungsmaterial nach Anspruch 1, wobei die Entfärbung ΔE^* ab von C.I. Food Black im Ozontest 10 oder weniger beträgt.
- 5 4. Aufzeichnungsmaterial nach Anspruch 1, wobei das Verhältnis des Pigments zu dem Bindemittel angegeben als Gewichtsverhältnis im Bereich von 1/3 bis 5/1 liegt.
- 10 5. Aufzeichnungsmaterial nach Anspruch 4, wobei das Verhältnis im Bereich von 1/2 bis 3/1 liegt.
6. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, wobei das Pigment eine spezifische Oberfläche von 10 bis 200 m²/g aufweist und die tintenaufnehmende Schicht ferner Aluminiumoxidteilchen enthält.
- 15 7. Aufzeichnungsmaterial nach Anspruch 6, wobei die Aluminiumoxidteilchen 10 bis 80 Gew.% des gesamten Pigmentes ausmachen.
8. Aufzeichnungsmaterial nach Anspruch 6 oder 7, wobei die Aluminiumoxidteilchen eine Teilchengröße im Bereich von 0,001 bis 10 µm aufweisen.
- 20 9. Aufzeichnungsmaterial nach Anspruch 1 bis 5, wobei die tintenaufnehmende Schicht eine obere Schicht mit dem Pigment, Aluminiumoxid und dem Bindemittel und eine untere Schicht mit einem Pigment mit einer Teilchengröße größer als diejenige des Pigments in der oberen Schicht aufweist.
- 25 10. Aufzeichnungsmaterial nach Anspruch 9, wobei es sich bei dem Pigment in der unteren Schicht um kugelförmiges Siliciumdioxid handelt.
11. Aufzeichnungsmaterial nach Anspruch 9 oder 10, wobei die spezifische Oberfläche des Silicium enthaltenden Schriftpigments im Bereich von 10 bis 200 m²/g liegt.
- 30 12. Aufzeichnungsmaterial nach Anspruch 6, 7, 8 oder 11, wobei die spezifische Oberfläche im Bereich von 10 bis 100 m²/g liegt.
13. Aufzeichnungsmaterial nach Anspruch 6 bis 12, wobei die Aluminiumoxidteilchen eine spezifische Oberfläche im Bereich von 1 bis 500 m²/g aufweisen.
- 35 14. Aufzeichnungsmaterial nach Anspruch 13, wobei die Aluminiumoxidteilchen eine spezifische Oberfläche im Bereich von 10 bis 200 m²/g aufweisen.
- 40 15. Aufzeichnungsmaterial nach Anspruch 9 bis 11, wobei das in der unteren Schicht enthaltene Pigment eine spezifische Oberfläche von 200 m²/g oder mehr aufweist.
16. Aufzeichnungsmaterial nach Anspruch 15, wobei das Pigment eine spezifische Oberfläche von 200 bis 700 m²/g aufweist.
- 45 17. Aufzeichnungsmaterial nach Anspruch 9, wobei das Verhältnis des Pigments zu dem Bindemittel in der tintenaufnehmenden Schicht im Bereich von 1/1 bis 10/1, angegeben als Gewichtsverhältnis, liegt.
18. Aufzeichnungsmaterial nach Anspruch 9, wobei die Beschichtungsmenge der oberen Schicht im Bereich von 1 bis 20 g/m² liegt.
- 50 19. Aufzeichnungsmaterial nach Anspruch 9, wobei die Beschichtungsmenge der unteren Schicht größer ist als diejenige der oberen Schicht.
- 55 20. Aufzeichnungsmaterial nach Anspruch 1 bis 5, wobei das Silicium enthaltende Schriftpigment einer Oberflächenbehandlung mit einem der folgenden Bestandteile oder mit einer Mischung aus zwei oder mehr dieser Bestandteile, ausgewählt aus Seifen, Hydroxiden, Salzen oder Oxiden der Metalle K, Ca, Mg, Al, Zn, Ba, Sr oder Sn, unterzogen wurde.



21. Aufzeichnungsmaterial nach Anspruch 20, wobei das Silicium enthaltende Schriftpigment vor der Behandlung eine spezifische Oberfläche von $60 \text{ m}^2/\text{g}$ aufweist.
- 5 22. Aufzeichnungsmaterial nach Anspruch 20 oder 21, wobei es sich bei dem Silicium enthaltenden Schriftpigment um synthetisches, feinteiliges Siliciumdioxid handelt.
23. Aufzeichnungsmaterial nach Anspruch 20 bis 22, wobei das Silicium enthaltende Schriftpigment eine spezifische Oberfläche im Bereich von 1 bis $200 \text{ m}^2/\text{g}$ aufweist.
- 10 24. Aufzeichnungsverfahren, umfassend das Aufbringen von Tröpfchen einer Tinte mit einem wasserlöslichen Farbstoff auf ein Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche.
25. Aufzeichnungsverfahren nach Anspruch 24, wobei es sich bei dem Aufzeichnungsverfahren um ein Tintenstrahlaufzeichnungsverfahren handelt.
- 15 26. Aufzeichnungsverfahren nach Anspruch 24 oder 25, wobei das Aufzeichnen unter Verwendung mindestens zweier Tintenfarben, ausgewählt aus der Gruppe Gelb, Magenta, Cyan und Schwarz, erfolgt.

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