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(54) <b>Ink-jet</b> Tintens Feuille	recording sheet containing aluminiu strahlaufzeichnungsblatt, das Aluminiun pour l'enregistrement par jet d'encre co	n <b>m and magnesium salts</b> n- und Magnesiumsalze enthält ontenant des sels d'aluminium et de magnésium
<ul> <li>(84) Designa DE FR ( (30) Priority:</li> <li>(43) Date of 20.09.24</li> <li>(73) Propriet LTD. Tokyo (</li> <li>(72) Inventor</li> <li>Chatan Shinjuk</li> <li>Kondo, Nippon Shinjuk</li> </ul>	ated Contracting States: GB 15.03.1999 JP 6855399 31.03.1999 JP 9140399 publication of application: 000 Bulletin 2000/38 tor: NIPPON PAPER INDUSTRIES CO., (JP) rs: i, Akinobu, Nippon Paper Indust. Co., Ltd. cu-ku, Tokyo (JP) Noboru, Paper Industries Co., Ltd. cu-ku, Tokyo (JP)	<ul> <li>Ueno, Takashi, Nippon Paper Industries Co., Ltd. Shinjuku-ku, Tokyo (JP)</li> <li>Kuroyama, Yoshihiro, Nippon Paper Indust. Co., Ltd Shinjuku-ku, Tokyo (JP)</li> <li>(74) Representative: Bubb, Antony John Allen et al Wilson Gunn Gee, Chancery House, Chancery House, Chancery Lane London WC2A 1QU (GB)</li> <li>(56) References cited: EP-A- 0 391 308 EP-A- 0 436 230 US-A- 4 740 420</li> <li>PATENT ABSTRACTS OF JAPAN vol. 12, no. 257 (M-719), 20 July 1988 (1988-07-20) &amp; JP 63 039372 A (CANON INCORPORATED), 19 February 1988 (1988-02-19)</li> </ul>

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### Description

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**[0001]** The present invention relates to a recording material that can be printed with ink containing a water-soluble dye. In particular, the present invention relates to an ink jet recording sheet which provides a high quality image with superior resistance to light.

**[0002]** Ink jet recording is a method by which fine ink drops are jetted out using any kind of jetting method to form an image on a recording material. Since this method enables a recording apparatus to be operated at high speed and low noise and using generally inexpensive apparatus, the use of ink jet recording systems has been spreading rapidly. Moreover, the use of multicolor ink jet recording methods enables the formation of high resolution, high quality color

- <sup>10</sup> images comparable to silver-salt photography. Digital images, for example those obtained by a digital camera, are increasingly being printed using an ink jet printer. Because of the high image quality, these recorded materials are more frequently being displayed or stored for considerably long periods. Therefore, it is desirable that the ink jet recording material has good preservation characteristics, especially good light resistance, as well as high image quality. [0003] Ordinary ink jet recording sheets, printed using an ink jet printer, become discolored when exposed to UV
- <sup>15</sup> light from sunlight or fluorescent lamps. Therefore attempts have been made to improve the long-term preservation properties of the sheet. Although some attempts utilized a pigment ink system with a pigment resistant to discoloration, it has been desired to improve the light resistance by using a dye ink system because dye ink system provide sharper images.
- [0004] As examples of means to improve the light resistance by using a dye ink system, for example, a process to add benzotriazoles compounds and hindered phenol compounds in a dye ink (Japanese Tokkai (unexamined published patent application) Hei 9-132742), a process to add UV absorber such as benzophenones and benzotriazoles (Japanese Tokkai Sho 57-87988 and Japanese Tokkai Sho 63-222885), a process to add antioxidants such as hindered amines (Japanese Tokkai Sho 61-146591), a process to add zinc oxide and cationic resins concurrently (Japanese Tokkai Hei 7-32725) and the like have been disclosed. However, since these additives are difficult to disperse evenly in the materials, these attempts did not provide a satisfactory improvement.
- [0005] Japanese Tokkai Hei 9-1922 disclosed a process in which an phenol based antioxidants is used as an additive. This process improves the resistance of the image to light, but the paper itself has insufficient light resistance, so that exposure to light causes the paper to yellow.
- [0006] In order to improve preservation characteristics, such as water resistance, Japanese Tokkai Sho 61-43593 disclosed a method in which a cationic resin and magnesium sulfate are used, and Japanese Tokkai Sho 61-57379 disclosed a method in which a cationic resin and a water-soluble aluminum salt are used. However, the method using magnesium sulfate produce a paper having good image quality but the paper has poor light resistance. The method using a water-soluble aluminum salt produces a recording material with a poor image quality.
- **[0007]** The inventors of the present invention examined the above mentioned disadvantages and found that, when a ink-jet recording sheet in which the ink-receiving layer of the sheet contains only a water-soluble aluminum salt is printed, areas of the sheet that are printed with a heavy concentration of ink have a metallic gloss that degrades the image quality. This metallic gloss is often observed when images are printed with a photo quality ink-jet printer, which discharge relatively heavy concentration of ink. A sheet having a color developing layer comprising colloidal silica coated over an ink-receiving layer will show a metallic gloss, even when printed with a lower concentration of ink.
- 40 [0008] The cause of the metallic gloss is not well understood. One possible reason is that a complex between aluminum ion and dye is formed. Then the inventors found that the metallic gloss in question can be reduced by using a water-soluble aluminum salt and a specific amount of water-soluble magnesium salt together in the ink-receiving layer. [0009] The objective of this invention is to provide a recording material that can be printed by ink with water-soluble dye, particularly to provide a high quality ink jet recording sheet, which is superior in ink absorbency, ink coloration, light resistance and surface gloss.

## Summary of the Invention

[0010] The subject of the invention is an ink jet recording sheet having on at least one side of a support an inkreceiving layer comprising pigment and binder, wherein said ink-receiving layer contains a water-soluble aluminum salt and a water-soluble magnesium salt, the combined content of aluminum ion and magnesium ion being about 3 to 5 milli-mol (mmol) per 100g of said pigment and the content of aluminum ion being about 1 to 2 mmol per 100g of said pigment. In another aspect of the invention, the ink jet recording sheet further includes a color-developing layer that is formed over said ink-receiving layer, wherein said color-developing layer comprises colloidal silica.

<sup>55</sup> **[0011]** The content of aluminum ion and/or magnesium ion is the amount of aluminum ion and/or magnesium ion based on the amount of a pigment contained in a ink-receiving layer, expressed by milli-mol (mmol) of the aluminum ion and/or magnesium ion based on 100 g of the pigment. For example, when W grams of aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, molecular weight of 342.17) is contained per 100 grams of pigment, the content (A mmol per 100g of pigment) of the

aluminum ion is expressed by the following formula:

#### A = W x 2 / 342.17 x 1000

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#### Detailed Description of the Invention

**[0012]** The support of the present invention can be selected appropriately from well-known sheet-type supports. The support is preferably a paper made from wood pulps. The paper comprises a pulp suitable for use in making paper. Examples of the pulp for paper include chemical pulp such as LBKP (hardwood bleached pulp) and NBKP (softwood bleached pulp), mechanical pulp such as GP(groundwood pulp) and TMP(thermo mechanical pulp), waste paper pulp and mixture thereof, but the pulp is not limited to those. The support can be a so-called laminate paper, which is made by laminating a resin film on a paper or by processing a paper with a molten resin.

- [0013] The ink-receiving layer is a coated layer, which absorbs ink, and comprises pigment and a binder. For pigment, white pigment, such as precipitated and ground calcium carbonate, kaolin, clay, talc, titanium dioxide, zinc oxide, satin white, magnesium silicate, calcium silicate, aluminum silicate, aluminum hydroxide, alumina, quasi-boehmite, magnesium carbonate, synthetic silica, zeolite, are preferred. Among these, synthetic silica is more preferred, but most preferred are white carbon and anhydrous silica, as described in Kagaku Binran (Chemical Reference Guide) page 256, published by Maruzen, Oct.15, 1986.
- 20 [0014] The binder used for the ink-receiving layer can be selected from any binders that can bond strongly to the support paper and can form films when coated and dried. It is desirable to use water-soluble polymers, such as starches, for example oxidized starch, esterified starch, enzyme-modified starch and cationic starch, polyvinyl alcohol with various degrees of saponification and derivatives thereof, casein, soy proteins, cellulose derivatives such as carboxyme-thyl cellulose and hydroxymethyl cellulose, and isobutylene-maleic anhydride resin; or water-dispersible polymers,
- <sup>25</sup> such as acrylic emulsion, vinyl acetate emulsion, vinylidene chloride emulsion, 5 polyester emulsion, styrene-butadiene latex, acrylonitrile-butadiene latex and the like.

**[0015]** The ink-receiving layer also contains a water-soluble aluminum salt and a water-soluble magnesium salt, in which the combined content of aluminum ion and magnesium ion is about 3 to 5 mmol based on 100g of the pigment and the content of aluminum ion being about 1 to 2 mmol based on 100g of said pigment. Preferably, the ink-receiving

<sup>30</sup> layer contains a water-soluble aluminum salt and a water-soluble magnesium salt, in which the combined content of aluminum ion and magnesium ion is about 3.5 to 4.5 mmol based on 100g of the pigment and the content of aluminum ion being about 1.5 to 2.0 mmol based on 100g of said pigment.

**[0016]** When the combined content of aluminum ion and magnesium ion or the content of aluminum ion alone is less than the lower end of the respective ranges above, the light resistance becomes insufficient. On the contrary, when either of these contents exceeds the upper end of the respective ranges above, the printed paper exhibits a metallic,

uneven gloss in the areas printed with a high concentration of ink. This degrades the overall image quality. **[0017]** The water-soluble aluminum salt of the present invention is, for example, aluminum sulfate, ammonium aluminum sulfate, potassium aluminum sulfate, sodium aluminum sulfate, aluminum nitrate, aluminum chloride or a mixture thereof and aluminum sulfate is preferred among these. The water-soluble magnesium salt of the present invention is,

<sup>40</sup> for example, magnesium sulfate, magnesium chloride, magnesium acetate or a mixture thereof and magnesium sulfate is preferred among these.

**[0018]** Further, the ink-receiving layer may comprise hindered amine compounds of amino ether type having alkoxyl groups in order to impart light resistance. Suitable hindered amine compounds are represented by formula (1) below:

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 $\begin{bmatrix} R_5 & H \\ R_1O - N & O \\ R_4 & R_3 \end{bmatrix} = \begin{bmatrix} R_2 \\ R_2 \end{bmatrix}$ (1)

<sup>55</sup> wherein  $R_1$  is  $C_nH_{2n+1}$  (n= 1 to 14),  $R_2$  is  $C_nH_{2n}$  (n= 1 to 14) and  $R_3$  to  $R_6$  are each an alkyl group or carbonyl group. Benzotriazole compounds may be used together to improve the light resistance further. **[0019]** The n in  $R_1$  and  $R_2$  of the formula (1) is preferably 6 to 10, and the alkyl group or carbonyl group of  $R_3$  to  $R_6$  is preferably a lower alkyl group with 1 to 4 carbons, more preferably methyl group.

**[0020]** The hindered amine compound of the amino ether type having alkoxyl groups is preferably bis- (2, 2, 6, 6-tetramethyl-1-(octyloxy)-4-piperidinyl)sebacate wherein  $R_1$  is  $C_8H_{17}$ ,  $R_2$  is  $C_8H_{16}$  and  $R_3$  to  $R_6$  are methyl groups in the formula (1) (Tinuvin 123, manufactured by Ciba Specialty Chemicals, Inc.).

- **[0021]** Hindered amine compounds generally generate nitroxy radicals by reacting with hydroperoxide or triplet oxygen in the air, which further react to form aminoethers by capturing polymer radicals generated by photodegradation of dyes contained in ink. Then the generated aminoethers react with peroxy radicals generated by a reaction between polymer radicals and oxygen in the air to regenerate nitroxy radicals. The aminoether also releases olefins, simultaneously generating hydroxylamine that reacts with the peroxy radicals to regenerate nitroxy radicals. This process is repeated to capture the radicals and hamper a chain reaction, thereby preventing the image from photodegrading.
- <sup>10</sup> **[0022]** Since the hindered amine compounds of the present invention have an amino ether as part of their chemical structure, it is considered that peroxy radicals are immediately captured when generated. Thus the hindered amine compound is very effective in preventing photodegradation of the printed image. In the case of conventional hindered amine compounds unsubstituted or substituted by alkyl or acetyl groups, it is considered that there is a large energy barrier to producing aminoethers, which inhibits the effective prevention of photodegradation.
- 15 [0023] The content of the hindered amine compounds in the ink-receiving layer is desired to be about 0.5 to 15 wt%, preferably about 2 to 8 wt%. When the content of the compounds is less than 0.5 wt%, the addition of the compounds is not effective, and when the content is larger than 15 wt%, the applicability in manufacturing becomes worse.
  [0024] The ink-receiving layer may also include a benzotriazole compound preferably including, for example, 2-(2-hy-
- droxy-3,5-di-t- amylphenyl-2H-benzotriazole, iso-octyl-3,3-(2H-benzotriazole-2-yl)-5-t-butyl-4-hydroxyphenylpropion ate, 2-[2-hydroxy-3,5-di(1,1-dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl) 5-chlorobenzotriazole, and the like.

**[0025]** The content of the benzotriazole compound in the ink-receiving layer is desired to be about 0.5 to 12 wt%, preferably about 2.5 to 8 wt%. When the content of the benzotriazole compound is less than 0.5 wt%, the addition of the compounds would is not effective, and when the content is larger than 12 wt%, it causes significant coloring in the applied layer.

25 applied layer.

**[0026]** A cationic resin dye fixing agent can be added to ink-receiving layer in order to impart water resistance to the image. Examples of such agents include dicyandiamide-alkylamine polycondensed material, dicyanodiamide-formal-dehyde polycondensed material, polyethylene-imine derivatives, alkylamine-epichlorohydrin polycondensed material, polymethacrylic acid quaternary ammonium salt derivatives, polydiallyl-dimethyl-ammonium chloride, and other com-

- <sup>30</sup> mercially available dye fixing agents. Mixtures of these can also be used without the loss of the advantage of the present invention. The coating compositions for the ink-receiving layers may contain various additives, such as an antifoaming agent, a surface-sizing agent, a water-proofing agent, a pH-adjusting agent, other UV absorber, an antioxidant, a dye or coloring pigment for adjusting color phase, a fluorescent dye or mixtures thereof without the loss of the effect of the present invention.
- <sup>35</sup> **[0027]** It is desirable that the coverage of the ink-receiving layer formed on the support be about 5 to 25 g/m<sup>2</sup>, preferably about 7 to 20 g/m<sup>2</sup>, on a dry solids basis. When the coverage of the ink-receiving layer is less than 5 g/m<sup>2</sup>, the ink absorbency of the layer becomes poor which will cause the ink to bleed. On the other hand, when the coverage is larger than 25 g/m<sup>2</sup>, the amount of absorbed ink becomes excessive, thereby reducing the recording density and therefore degrading the quality of the image.
- <sup>40</sup> **[0028]** It is desirable that the content of the pigment in the ink-receiving layer be more than 40 wt%, preferably more than 60 wt%.

**[0029]** The applied coating solution forms an ink-receiving layer, which usually forms a layer clearly distinguishable from the base paper, but the coating solution sometimes impregnates the base paper to form an area where the components of the coating solution and paper fibers are mixed. In the latter case, the ink-receiving layer is defined as

<sup>45</sup> including the mixed area and the weight percentage in the ink-receiving layer used in this specification does not include the weight of the paper. Therefore, it should be noted that all components of the coating solution except water remain in the ink-receiving layer.

**[0030]** It is desirable to form a color-developing layer comprising colloidal silica onto the ink-receiving layer. The colloidal silica has a chain and non-spherical from, which means that the colloidal silica is in the form of small primary

- <sup>50</sup> particles that are connected together to form a chain. The chain of silica particles can be linear, or the ends of the chain can be connected together to form a ring, or a combination of linear chain with one or more rings can be formed. This type of colloidal silica improves the ink-absorbing property of the sheet. The coating compositions for the color-developing layers may contain various additives, such as an antifoaming agent or a cationic resin without the loss of the effect of the present invention.
- <sup>55</sup> **[0031]** It is desirable that the coverage of the color-developing layer be about 1 to 6 g/m<sup>2</sup>, preferably about 1.5 to 5 g/m<sup>2</sup>, on a dry solids basis. When the coverage of the color-developing layer is less than 1 g/m<sup>2</sup>, superior recorded density and surface gloss cannot be attained. On the other hand, when the coverage is larger than 6 g/m<sup>2</sup>, the ink absorbency of the layer becomes poor. In order to get a reproducibility of images comparable to silver salt photography,

the 75 degree specular glossiness of the ink jet recording sheet is desirably at least about 30%, preferably at least about 35% at the surface.

**[0032]** The ink-receiving layers and color-developing layers may be coated onto the support using conventional coaters of various kinds, e.g., a blade coater, an air knife coater, a roll coater, a curtain coater, a bar coater, a gate roll coater and a gravure coater and the like. Further various calendering treatments such as a machine calender, a soft calender, and a super calender can be used solely or in combination for finishing the surface.

**[0033]** The ink-jet recording sheet of the present invention does not have a metallic gloss in the printed area and has a superior resistance of the image to light and sufficient gloss. These properties are particularly important and unexpected when the sheet includes a color developing layer, because previous recording sheets that included a color

<sup>10</sup> developing layer were likely to exhibit a metallic gloss. Further, when the ink-receiving layer comprises a hindered amine compound of amino ether type, such as the one represented by formula (1) mentioned above, especially when used in connection with a benzotriazole compound, light resistance is increased even more.

**[0034]** The present invention will now be illustrated in more detail by reference to the following examples, but it should be understood that these examples are not to be construed as limiting the scope of the present invention in any way.

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### Examples

**[0035]** The average primary particle size of colloidal silica is measured by BET method, the average secondary particle length of non-spherical colloidal silica is measured by laser scattering method. The ink jet recording sheets in the following examples and comparative examples are evaluated by the following method. Unless otherwise noted, all "parts" are by weight in the following examples and comparative examples. The weight in the coating solution is based on dry basis, excluding water.

(1) 75 degree specular glossiness

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**[0036]** The 75 degree specular glossiness is determined by using a glossimeter, GM-26D (trade name, a product of Murakami Shikisai Kenkyujo), in accordance to JIS P8142.

(2) ink jet recording properties

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**[0037]** A predetermined solid or image pattern is printed on the test sheet using an ink jet printer, Model PM750C (trade name, a product of Seiko Epson Corp.) and the various properties of the recorded sheet is evaluated by the following method:

35 <u>a. light resistance</u>

**[0038]** The recorded density of magenta ink is measured after being treated for 25 hours by Xenon Weather Meter SC700-WN (trade name, a product of Suga Test Machinery Limited), compared with the density before the test. The results are rated as follows;

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AA: Light resistance is better than rank A below.

- A : The recorded density after treatment is more than 90% of the recorded density of the untreated sheet.
- B : The recorded density after treatment is 70 to 90% of the recorded density of the untreated sheet.
- C : The recorded density after treatment is 50 to 70% of the recorded density of the untreated sheet.
- D : The recorded density after treatment is less than 50% of the recorded density of the untreated sheet.

### b. metallic gloss

[0039] The metallic gloss is evaluated by a visual inspection of printed black solid areas, and rated as follows;

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- A : No metallic gloss is observed.
- B : Almost no metallic gloss is observed.
- C : Some metallic gloss is observed.
- D : Significant metallic gloss is observed.

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c. recorded density

[0040] Densities of recorded images are reflection densities of the printed solid areas as measured with a Macbeth

densitometer, RD 915 (trade name, a product of Macbeth Limited).

#### d. ink absorbency

- <sup>5</sup> **[0041]** Ink absorbency is evaluated by observing the extent of bleeding at the boundary between printed areas of solid magenta and solid green (mixture of cyan and yellow). Results are rated as follows;
  - A : No bleeding is observed at the boundaries.
  - B : Almost no bleeding is observed at the boundaries.
  - C : Some bleeding is observed at the boundaries.
    - D : Significant bleeding is observed at the boundaries.

### Example 1

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- 15 [0042] A slurry consisting of 93 parts of LBKP (hardwood bleached pulp) with a freeness of 440 ml, 7 parts of NBKP (softwood bleached pulp) with a freeness of 520 ml, 7 parts of talc, 1.5 parts of aluminum sulfate, 0.4 parts of sizing agent and 0.02 parts of yield improver is prepared. Paper is manufactured from the slurry using a twin wire machine and pre-dried using a cylinder drier. Then oxidized starch is applied to the paper with a two roll sizing press to have a combined solid coverage of 4 g/m<sup>2</sup> of both sides and is subjected to a machine calender treatment. A base paper with a dry coverage of 160 g/m<sup>2</sup> and a smoothness of 35 seconds is obtained.
- a dry coverage of 160 g/m<sup>2</sup> and a smoothness of 35 seconds is obtained.
   [0043] To form an ink-receiving layer, coating solution 1 below is coated onto one surface of the obtained base paper by means of a Mayer bar so as to have a dry coverage of 13 g/m<sup>2</sup>. The paper is then subjected to a calendering machine with a linear pressure of 78 kN/m (80 Kg/cm). Then, a color-developing layer is formed by coating coating solution 2 below onto the ink-receiving layer by means of a Mayer bar so as to have a dry coverage of a Mayer bar so as to have a dry coverage of 2 g/m<sup>2</sup> and calendering
- <sup>25</sup> at a linear pressure of 98 kN/m (100 Kg/cm). An ink jet recording sheet with a dry weight of 175 g/m<sup>2</sup> is obtained. The formulation of the coating solutions 1 and 2 are shown below. All parts are on a solid basis except water. It is designed that the coated solutions 1 and 2 are kept on the base paper and never flow out or bleed out from the paper.

Coating solution 1

# [0044]

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- Synthetic amorphous silica: Fineseal X-37B (an average secondary particle size of 4 micron, Tokuyama) 100 parts
- <sup>35</sup> Water-soluble polymer: PVA-117(Polyvinyl alcohol, Kurarey Co., Ltd.) 15 parts
  - water-soluble aluminum salt (aluminum sulfate 18H<sub>2</sub>O, weight given on an anhydride basis)
     0.34 parts (corresponding to 2.0 mmol of aluminum ion per 100 g of pigment)
  - water-soluble magnesium salt (magnesium sulfate 7H<sub>2</sub>O, weight given on an anhydride basis)
     0.20 parts (corresponding to 1.7 mmol of magnesium ion per 100 g of pigment)
- 40 Dye fixing agent: PAS-H-10L(quaternary ammonium salt type polymer, Nitto Boseki) 5 parts
  - Water 550 parts

#### Coating solution 2

## 45 **[0045]**

- Non-spherical (beads type) colloidal silica: Snowtex OUP with an average primary particle size of 10 to 20 nm and secondary particle length of 50 to 300 nm (Nissan Chemical)
   100 parts
- Water 420 parts
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# Example 2

**[0046]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the amount of magnesium sulfate 7H<sub>2</sub>O (as an anhydride) in coating solution 1 is increased to 0.30 parts (corresponding to 2.5 mmol of magnesium ion per 100 g of pigment).

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### Example 3

**[0047]** An ink jet recording sheet is obtained in the same manner as in Example 2, except that the amount of aluminum sulfate  $18H_2O$  (as an anhydride) in the coating solution 1 is decreased to 0.21 parts (corresponding to 1.2 mmol of aluminum ion per 100 g of pigment).

### Example 4

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**[0048]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the dry coverage of coating solution 2 is increased to 5  $g/m^2$ .

### Example 5

**[0049]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the dry coverage of coating solution 2 is increased to 9  $g/m^2$ .

#### Example 6

**[0050]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the dry coverage of coating solution 2 is decreased to  $0.8 \text{ g/m}^2$ .

#### Example 7

[0051] An ink jet recording sheet is obtained in the same manner as in Example 1, except that coating solution 2 is omitted.

#### Example 8

[0052] An ink jet recording sheet is obtained in the same manner as in Example 1, except that 3 parts of Tinuvin 123
 <sup>30</sup> (Hindered amine compound, (bis-(2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl)sebacate, manufactured by Ciba Specialty Chemicals, Inc.) are added to coating solution 1.

#### Example 9

<sup>35</sup> **[0053]** An ink jet recording sheet is obtained in the same manner as in Example 8, except that 10 parts of Tinuvin 900(Benzotriazole compound, manufactured by Ciba Specialty Chemicals Inc.) are further added to coating solution 1.

#### Comparative example 1

40 [0054] An ink jet recording sheet is obtained in the same manner as in Example 1, except that the amount of magnesium sulfate 7H<sub>2</sub>O (as an anhydride) in coating solution 1 is increased to 0.40 parts (corresponding to 3.3 mmol of magnesium ion per 100 g of pigment).

#### Comparative example 2

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**[0055]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the amount of magnesium sulfate  $7H_2O$  (as an anhydride) in coating solution 1 is decreased to 0.10 parts (corresponding to 0.8 mmol of magnesium ion per 100 g of pigment).

50 Comparative example 3

**[0056]** An ink jet recording sheet is obtained in the same manner as in Example 2, except that the amount of aluminum sulfate  $18H_2O$  (as an anhydride) in coating solution 1 is increased to 0.41 parts (corresponding to 2.4 mmol of aluminum ion per 100 g of pigment).

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#### Comparative example 4

[0057] An ink jet recording sheet is obtained in the same manner as in Example 2, except that the amount of aluminum

sulfate 18H<sub>2</sub>O (as an anhydride) in coating solution 1 is decreased to 0.14 parts (corresponding to 0.8 mmol of aluminum ion per 100 g of pigment).

### Comparative Example 5

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**[0058]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the magnesium sulfate  $7H_2O$  is omitted from coating solution 1.

Comparative example 6

**[0059]** An ink jet recording sheet is obtained in the same manner as in Example 1, except that the aluminum sulfate 18 hydrate is omitted from coating solution 1, and the amount of magnesium sulfate  $7H_2O$  (as an anhydride) is increased to 0.48 parts (corresponding to 4.0 mmol of magnesium ion per 100 g of pigment).

[0060] The evaluation results for Examples 1 to 7 and Comparative examples 1 to 6 are summarized in Table 1 below. The ink jet recording sheets having a light resistance rating of AA, A or B and a metallic gloss and an ink absorbency ratings of A or B can be used without causing any problem.

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Table 1

	Al ion (mmol/ 100g of pigment)	Mg ion (mmol/ 100g of pigment)	AI + Mg ion (mmol/100g of pigment)	light resistance	Metallic gloss	75 degree specular glossiness	recorded density	ink absorbency
Example 1	2.0	1.7	3.7	А	В	36.1	2.30	А
Example 2	2.0	2.5	4.5	A	В	35.9	2.26	A
Example 3	1.2	2.5	3.7	В	В	35.9	2.30	A
Example 4	2.0	1.7	3.7	A	В	42.0	2.35	A
Example 5	2.0	1.7	3.7	A	В	43.9	2.37	В
Example 6	2.0	1.7	3.7	A	В	27.9	2.12	A
Example 7	2.0	1.7	3.7	A	A	7.8	1.84	A
Example 8	2.0	1.7	3.7	AA	В	36.0	2.25	A
Example 9	2.0	1.7	3.7	AA	В	36.1	2.23	A
Comparative example 1	2.0	3.3	5.3	A	С	36.2	2.23	A
Comparative example 2	2.0	0.8	2.8	С	В	35.8	2.32	A
Comparative example 3	2.4	2.5	4.9	A	D	35.9	2.24	A
Comparative example 4	0.8	2.5	3.3	D	В	36.2	2.31	A
Comparative example 5	2.0	0.0	2.0	С	В	36.0	2.32	A
Comparative example 6	0.0	4.0	4.0	С	С	35.9	2.28	A

## Claims

- 1. An ink jet recording sheet having on at least one side of a support an ink-receiving layer comprising pigment and binder, wherein said ink-receiving layer contains a water-soluble aluminum salt and a water-soluble magnesium salt, the content of aluminum ion and magnesium ion being 3 to 5 milli-mol per 100g of said pigment and the content of aluminum ion being 1 to 2 milli-mol per 100g of said pigment.
- 2. An ink jet recording sheet as in claim 1, wherein said water-soluble aluminum salt is at least one salt selected from the group consisting of aluminum sulfate, ammonium aluminum sulfate, potassium aluminum sulfate, sodium aluminum sulfate, aluminum nitrate and aluminum chloride and said water-soluble magnesium salt is at least one salt selected from the group consisting of magnesium sulfate, magnesium chloride and magnesium acetate.
  - 3. An ink jet recording sheet as in claim 1, wherein said water-soluble aluminum salt is aluminum sulfate and said water-soluble magnesium salt is magnesium sulfate.
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- **4.** An ink jet recording sheet as in any one of claims 1 to 3, wherein the content of said pigment is more than 40 % by weight of said ink-receiving layer, the content of aluminum ion and magnesium ion being 3.5 to 4.5 milli-mol per 100g of said pigment and the content of aluminum ion being 1.5 to 2.0 milli-mol per 100g of said pigment.
- **5.** An ink jet recording sheet as in any one of claims 1 to 4, wherein a color-developing layer containing colloidal silica is formed onto said ink-receiving layer.
  - 6. An ink jet recording sheet as in claim 5, wherein said colloidal silica has a chain and non-spherical form having some limited number of small primary particles of spherical silica connected together to form a chain which may be linear or in the form of a ring, or to form a combination of a chain with one or more attached rings.
  - **7.** An ink jet recording sheet as in claim 5 or 6, wherein the coverage of said color-developing layer is 1 to 6 g/m<sup>2</sup> on a dry solids basis.
- An ink jet recording sheet as in any one of claims 1 to 7, which has a 75 degree specular glossiness is at least 30% at the surface.
  - **9.** An ink jet recording sheet as in any one of claims 1 to 8, wherein said ink-receiving layer further comprises a hindered amine compound of amino ether type having alkoxyl groups of the formula:
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- wherein  $R_1$  is  $C_n H_{2n+1}$  (n= 1 to 14),  $R_2$  is  $C_n H_{2n}$  (n= 1 to 14), and  $R_3$  to  $R_6$  are alkyl or carbonyl groups.
  - **10.** An ink jet recording sheet as in claim 9, wherein said ink-receiving layer further comprises a benzotriazole compound.

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#### Patentansprüche

 Tintenstrahlaufzeichnungsblatt das auf wenigstens einer Seite eines Trägers eine Tinten aufnehmende Schicht, umfassend Pigment und ein Bindemittel, aufweist, wobei die genannte Tinte aufnehmende Schicht wasserlösliche Aluminiumsalze und wasserlösliche Magnesiumsalze enthält und wobei der kombinierte Gehalt an Aluminiumionen und an Magnesiumionen 3 bis 5 Millimol pro 100 g des genannten Pigments und der Gehalt an Aluminiumionen 1 bis 2 Millimol pro 100 g des genannten Pigments beträgt.

- 2. Tintenstrahlaufzeichnungsblatt nach Anspruch 1, wobei das wasserlösliche Aluminiumsalz wenigstens ein Salz ist, das ausgewählt ist aus der Gruppe bestehend aus Aluminiumsulfat, Ammoniumaluminiumsulfat, Kaliumaluminiumsulfat, Natriumaluminiumsulfat, Aluminiumnitrat und Aluminiumchlorid und das wasserlösliche Magnesiumsalz wenigstens ein Salz der Gruppe ist, bestehend aus Magnesiumsulfat, Magnesiumchlorid und Magnesiumacetat.
- 3. Tintenstrahlaufzeichnungsblatt nach Anspruch 1, bei dem das genannte wasserlösliche Aluminiumsalz Aluminiumsulfat ist und das genannte wasserlösliche Magnesiumsalz Magnesiumsulfat ist.
- 10 4. Tintenstrahlaufzeichnungsblatt nach einem der Ansprüche 1 bis 3, bei dem der Gehalt des genannten Pigments größer ist als 40 Gewichtsprozent der genannten Tinte aufnehmenden Schicht, der Gehalt an Aluminiumionen und Magnesiumionen zwischen 3,5 und 4,5 Millimol pro 100 g des genannten Pigments und der Gehalt an Aluminiumionen 1,5 bis 2 Millimol pro 100 g des genannten Pigments beträgt.
- Tintenstrahlaufzeichnungsblatt nach einem der Ansprüche 1 bis 4, bei dem eine Farbentwicklungsschicht, die kolloidales Siliziumdioxid enthält, auf der genannten Tinte aufnehmenden Schicht gebildet ist.
  - 6. Tintenstrahlaufzeichnungsblatt nach Anspruch 5, bei dem das genannte kolloidale Siliziumdioxid eine ketten- und nichtsphärische Form aufweist mit einer begrenzten Anzahl von kleinen Primärpartikeln von kugelförmigen Siliziumdioxid die miteinander verbunden sind zur Bildung einer Kette, die linear oder in Form eines Rings ausgebildet sein kann oder zur Bildung einer Kombination aus einer Kette mit einem oder mehreren daran befestigten Ringen.
  - 7. Tintenstrahlaufzeichnungsblatt nach Anspruch 5 oder 6, bei dem die Bedeckungsrate der genannten Farbentwicklungsschicht 1 bis 6 g/m<sup>2</sup> auf trockener Feststoffbasis beträgt.
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- 8. Tintenstrahlaufzeichnungsblatt nach einem der Ansprüche 1 bis 7, welches einen 75 Grad Spiegelglanz auf wenigstens 30 % der Oberfläche aufweist.
- **9.** Tintenstrahlaufzeichnungsblatt nach einem der Ansprüche 1 bis 8, bei dem die genannte Tinte aufnehmende Schicht eine behinderte Aminverbindung vom Aminoethertyp umfasst mit Alkoxygruppen der Formel:
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Dabei steht  $R_1$  für  $C_nH_{2n+1}$  (n = 1 bis 14),  $R_2$  steht für  $C_nH_{2n+2}$  (n = 1 bis 14) und  $R_3$  bis  $R_6$  Alkyl- oder Carbonyl-gruppen sind.

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**10.** Tintenstrahlaufzeichnungsblatt nach Anspruch 9, bei dem die Tinte aufnehmende Schicht darüber hinaus eine Benzotriazolverbindung enthält.

## 50 Revendications

pigment.

- Feuille d'enregistrement pour jet d'encre ayant sur au moins une face d'un support une couche réceptrice d'encre comprenant pigment et liant, dans laquelle ladite couche réceptrice d'encre contient un sel d'aluminium soluble dans l'eau et un sel de magnésium soluble dans l'eau, la teneur en ion aluminium et en ion magnésium étant de 3 à 5 millimoles pour 100 g dudit pigment et la teneur en ion aluminium étant de 1 à 2 millimoles pour 100 g dudit
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- 2. Feuille d'enregistrement pour jet d'encre comme dans la revendication 1, dans laquelle ledit sel d'aluminium soluble

dans l'eau est au moins un sel choisi au sein du groupe constitué du sulfate d'aluminium, du sulfate d'ammonium aluminium, du sulfate de potassium aluminium, du sulfate de sodium aluminium, du nitrate d'aluminium et du chlorure d'aluminium et ledit sel de magnésium soluble dans l'eau est au moins un sel choisi au sein du groupe constitué de sulfate de magnésium, chlorure de magnésium et acétate de magnésium.

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- 3. Feuille d'enregistrement pour jet d'encre comme dans la revendication 1, dans laquelle ledit sel d'aluminium soluble dans l'eau est du sulfate d'aluminium et ledit sel de magnésium soluble dans l'eau est du sulfate de magnésium.
- 4. Feuille d'enregistrement pour jet d'encre selon l'une quelconque des revendications 1 à 3, dans laquelle la teneur dudit pigment est supérieure à 40 % en poids de ladite couche réceptrice d'encre, la teneur en ion aluminium et en ion magnésium étant de 3,5 à 4,5 millimoles pour 100 g dudit pigment et la teneur en ion aluminium étant de 1,5 à 2,0 millimoles pour 100 g dudit pigment.
- Feuille d'enregistrement pour jet d'encre selon l'une quelconque des revendications 1 à 4, dans laquelle une couche de développement de couleur contenant de la silice colloïdale est formée sur ladite couche réceptrice d'encre.
  - 6. Feuille d'enregistrement pour jet d'encre selon la revendication 5, dans laquelle ladite silice colloïdale a une forme de chaîne et n'est pas sphérique, ayant quelques quantités limitées de petites particules primaires de silice sphérique reliées ensemble pour former une chaîne qui peut être linéaire ou sous la forme d'un anneau, ou pour former une combinaison d'une chaîne avec un ou plusieurs anneaux fixés.
  - 7. Feuille d'enregistrement pour jet d'encre selon la revendication 5 ou 6, dans laquelle la surface de recouvrement de ladite couche de développement de couleur est de 1 à 6 g/m<sup>2</sup> sur la base de la teneur en matières solides sèches.
- <sup>25</sup> 8. Feuille d'enregistrement pour jet d'encre selon l'une quelconque des revendications 1 à 7, qui a un brillant spéculaire à 75° d'au moins 30 % à la surface.
  - **9.** Feuille d'enregistrement pour jet d'encre selon l'une quelconque des revendications 1 à 8, dans laquelle ladite couche réceptrice d'encre comprend en outre un composé à amine bloquée de type aminoéther ayant des groupes alkoxyle conformes à la formule générale :
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**10.** Feuille d'enregistrement pour jet d'encre selon la revendication 9, dans laquelle ladite couche réceptrice d'encre comprend en outre un composé benzotriazole.

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