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RECORDING MEDIUM AND INK-JET RECORDING METHOD EMPLOYING THE SAME
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- (57) Claim

1. A recording medium suitable for ink-jet printing, having on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a nonionic surfactant wherein the recording medium contains the surfactant in the range of from 0.05 to 2.0% by weight based on the basic magnesium carbonate.

7. An ink jet recording method in which ink is ejected through an orifice of an ink jet recording head onto a recording medium suitable for ink-jet recording in response to a recording signal, the recording medium containing basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant, wherein the recording medium contains the surfactant in the range of from 0.05 to 2.0 % by weight based on the basic magnesium carbonate, and the recording medium has on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title:

Recording Medium and Ink-Jet Recording Method Employing
the Same

The following statement is a full description of this invention, including the
best method of performing it known to me/us:-

- 1 -

1 Recording Medium and Ink-Jet Recording Method
 Employing the Same

BACKGROUND OF THE INVENTION

5 Field of the Invention

 The present invention relates to a recording medium useful for color recording, particularly for ink-jet color recording. The present invention also relates to a recording method employing the recording
10 medium.

Related Background Art

 Coated paper which has an ink-receiving layer which contains a porous inorganic pigment formed on an ink-absorbent paper base has been used for recording
15 mediums for ink-jet recording as described in Japanese Patent Application Laid-Open No. 56-148585. The porous inorganic pigment contained in the coating layer is exemplified by silica having superior color-developing properties as described in Japanese Patent
20 Application Laid-open No. 56-185690, and by many other materials including calcium carbonate, alumina, and so forth.

 The aforementioned coated paper is required to have performance of providing images in high density
25 and high sharpness with high resolution, and is further required to be responsive to high-speed print

1 output.

In serial type color ink-jet printers, in order to achieve high-speed print output, the increase of driving-frequency of the head is essential, and also important is the capability of the head to conduct printing both in the forward movement direction and in the backward movement direction. A color ink-jet system is considered as an example in which four ink heads respectively for the colors of black (Bk), yellow (Y), magenta (M) and cyan (C) are arranged in the order of Bk, Y, M, and C from the back side to the front side along the forward direction of the head movement. Here, the direction of the movement of the ink heads starting from the home position is defined to be "forward" direction, and the reversed direction to be "backward" direction. The order of the colors of dots plotted with the color inks to provide colors of red (R), green (G), and blue (B) in the forward movement of the head is reversed in the backward movement thereof. With the coated paper derived in the above cited prior art techniques, reversal of the dotting order of color inks results in change of color tone at mixed color portions, which hinders printing in back-and-forth directions.

25 The above prior art techniques have further disadvantages as mentioned below. For example, when

1 the silica having a large specific surface area as
disclosed in Japanese Patent Application Laid-Open No.
56-185690 is used for obtaining a sharp image with
high density, the dye applied on a recording medium
5 changes its color with lapse of time to deteriorate
the recorded image even when it is stored in an
ordinary environmental conditions, like posting on an
indoor wall. On the contrary, with a pigment such as
calcium carbonate, kaolin, and talc having a small
10 specific surface area, the above-mentioned indoor
discoloration is retarded, but disadvantageously the
derived image density is low without sharpness of the
image. Therefore, the suppression of the indoor
discoloration is not consistent with high image
15 density, and this inconsistency could not be removed
by prior techniques.

The inventors of the present invention became
aware of the fact that the indoor discoloration of the
recorded image results only when coated paper is used,
20 and does not result when non-coated paper such as
ordinary PPC paper is used, and also that this indoor
discoloration differs intrinsically from the dye
discoloration caused by projection of UV light or
visible light, and arises even in the absence of the
25 light.

The inventors considered that the indoor

1 discoloration results from oxidative decomposition of
the dye which is caused by interaction of the dye, the
pigment and an oxidative gas with each other.

Accordingly, it may be assumed that a larger specific
5 surface area of the used pigment causes more rapid
oxidative decomposition reaction. From this
assumption, the fact is understood that the higher
degree of indoor discoloration is caused on coated
paper having larger specific surface area of the
10 pigment used.

On the other hand, the image density will be
higher, if the active surface for dye absorption is
larger in the vicinity to the surface layer of the
coat layer.

15 The inventors of the present invention already
proposed a recording medium free from the
aforementioned problems of the indoor discoloration
and the insufficient image density, as shown in
EP405417A1, etc. This recording medium, however, does
20 not satisfactorily solve the problem of color tone
change in printing in the back and forth directions.

SUMMARY OF THE INVENTION

~~A primary object of the present invention is~~
25 to provide a recording medium which does not cause
~~changes in printed image quality even when the dotting~~



According to one aspect of the present invention there is disclosed a recording medium suitable for ink-jet printing, having on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a nonionic surfactant wherein the recording medium contains the surfactant in the range of from 0.05 to 2.0% by weight based on the basic magnesium carbonate.

According to another aspect of the present invention there is disclosed an ink jet recording method in which ink is ejected through an orifice of an ink jet recording head onto a recording medium suitable for ink-jet printing in response to a recording signal, the recording medium containing basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant, wherein the recording medium contains the surfactant in the range of from 0.05 to 2.0 % by weight based on the basic magnesium carbonate, and the recording medium has on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a longitudinal cross-section of a head portion of an ink-jet recording apparatus employed in the present invention.

Fig. 2 illustrates a transverse cross-section



1 of a head portion of an ink-jet recording apparatus
employed in the present invention.

Fig. 3 is a perspective illustration of the
appearance of a head having a multiple set of the
5 heads as shown in Fig. 1 and Fig. 2.

Fig. 4 is a perspective illustration of an
example of an ink-jet recording apparatus.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 The surfactant in the present invention
functions to control the dynamic ink permeability of a
recording medium, especially of the one containing
basic magnesium carbonate.

Usually, a coating layer composed of a
15 particulate pigment, a binder, and an additive such as
a waterproofing (dye fixing) agent tends to vary
remarkably in permeation characteristics including the
permeation rate and the running of ink depending on
whether the layer is wet or dry. The wet and dry
20 states give significant influence when paper having
ink-absorbency is used as the base material; much more
significant where pigment light coated paper pigment
or internal additive type paper having fiber of the
base paper exposed at the surface of a recording
25 medium is used as the recording medium. This is
considered to be due to the relative change of the

1 surface tension of the ink to the recording medium
between a dry state and a wet state. This difference
is assumed to be caused mainly by the characteristics
of the materials constituting the coating layer
5 including a pigment, a water-soluble resin, a binder,
and the like, or the characteristics of pulp fiber, a
sizing agent, and the like of the base paper.

In particular, the permeation rate and the
permeation characteristics are liable to vary in the
10 case where basic magnesium carbonate is used as the
pigment. Such variation can be controlled highly
effectively by combinedly using the specified
surfactant.

In the present invention, the incorporation
15 into the recording medium of a cationic surfactant
and/or a nonionic surfactant selected from among a
variety of surfactants is assumed to lower the surface
tension of the ink to suppress the variation of
dynamic permeability of the ink to the recording
20 medium between a dry state and a wet state, especially
of the recording medium containing basic magnesium
carbonate.

The effect of the addition of surfactant of
the present invention is particularly remarkable in
25 the case where basic magnesium carbonate is used as
the particulate pigment. More preferably, spherical

1 basic magnesium carbonate particles are used for
achieving a high image density. This is considered to
be due to the fact that the spherical agglomerate of
the basic magnesium carbonate leads to a denser packed
5 state in the formation of the coating layer in
comparison with the usual plate-shaped or column-
shaped agglomerate of basic magnesium carbonate, and
consequently the dye is caught nearer to the surface
of the coating layer when compared at the same ink
10 permeation rate. In other words, the active surface
of the basic magnesium carbonate particles is
considered to be more effectively utilized in the case
where they are sphere-shaped than in the case where
they are in other shapes.

15 Known spherical basic magnesium carbonate
materials are however constituted of agglomerates
having an average particle diameter ranging from about
3 to about 20 μm with broad particle-size
distribution. Therefore, in a recording medium formed
20 by applying a known spherical basic magnesium
carbonate on a substrate, the void formed by the basic
magnesium carbonate on the surface of the recording
medium is not so uniform as that formed by fine
particles of silica or alumina (having an average
25 particle diameter of less than 3 μm). Accordingly,
the variation of dynamic permeating property of ink

1 may affect image qualities such as optical density,
feathering, ink-running, etc. more greatly in the
former recording medium. Chiefly by the reason above,
the difference in image quality caused by the change
5 of the dotting order of the color inks can be
decreased particularly effectively by combined use of
a cationic surfactant and/or a nonionic surfactant
with basic magnesium carbonate as the main pigment in
the present invention.

10 The present invention is described below in
more detail by reference to preferred embodiment.

In the recording medium of the present
invention, the surfactant and the pigment may be
contained in the substrate (base material), or may be
15 contained in a coating layer formed on the substrate.
The content of the surfactant in the present invention
is preferably in the range of from 0.05 to 2.0 % by
weight, more preferably from 0.1 to 1.5 % by weight
based on the basic magnesium carbonate in order to
20 achieve the above-mentioned effect more sufficiently.
The content of the basic magnesium carbonate in the
recording medium of the present invention is
preferably in the range of from 0.2 to 50 g/m², more
preferably from 0.2 to 20 g/m² to achieve the above-
25 mentioned effect more sufficiently.

The substrate employed in the present

- 1 invention is preferably ink-absorbent base paper, but
is not limited thereto. For example, a film of a
polymer such as polyester may be used as the substrate
material. Preferred embodiment of the present
5 invention is described below by taking the cases
employing an ink-absorbent paper as the substrate.

The recording medium of the present invention
is constituted from a substrate, basic magnesium
carbonate, a cationic surfactant and/or a nonionic
10 surfactant, and preferable other additives such as a
binder, a dye fixing agent, and a fluorescent
whitener.

The basic magnesium carbonate for use in the
present invention is not specially restricted. The
15 object of the present invention can be achieved
satisfactorily with a commercially available magnesium
carbonate. However, use of spherical basic magnesium
carbonate is more preferable.

The spherical basic magnesium carbonate in the
20 present invention is the one having a shape disclosed
in Japanese Patent Application Laid-Open Nos. 60-
54915, 61-63526, and 63-89418, but the process
of its production is not limited to the process
described therein.

25 The term "spherical" in the present invention
concerns with the shape of agglomerate of the primary

1 particles, and does not necessarily mean a complete
sphere shape. The preferred shape of the sphere is
the one having the ratio of the major axis length (a)
to the minor axis length (b) in the range of $0.7 \leq b/a$
5 ≤ 1.0 .

However, in the production of such spherical
basic magnesium carbonate, the complete spherical
shape of the product cannot always be obtained,
depending on the reaction conditions modified for
10 controlling the particle diameter, the specific
surface area, the oil absorption, and other pigment
properties. For example, particles lacking a portion
of the sphere, or particles agglomerating in a flower-
petal shape may be formed. In the present invention,
15 the particle with a lacking portion less than 1/4 in
volume of the assumed complete sphere is included also
in the sphere.

In the case where the primary particles
constructing the agglomerate are relatively large and
20 consequently the peripheral line tracing the outermost
particles is remarkably rugged, the peripheral line is
drawn so as to form a shape of a circle or an ellipse
having the largest ratio of the aforementioned b/a
within the allowable b/a ratio defined above.

25 Further, in the present invention, the basic
magnesium carbonate containing the above-defined

1 spherical particles in an amount of not less than 85 %
of the total particles is included in the spherical
basic magnesium carbonate. A particle, which looks as
if glued with another particle but more than half of
5 the outline is discerned, is regarded as one
agglomerated particle.

The average particle diameter of the spherical
basic magnesium carbonate is in the range of from 0.5
to 20 μm , preferably from 1 to 12 μm . An excessively
10 fine particle size causes lower ink absorbency, while
an excessively large particle size may cause falling-
off of the particles from the recording medium.

Here, the particle diameter means the major
axis length "a" described above. The average particle
15 diameter means a simple average of 100 or more of the
major axis diameters "a" measured by electron
microscopy. In the particle size distribution of the
spherical basic magnesium carbonate, 95 % or more in
number of the particles have preferably a size of not
20 larger than 25 μm , more preferably not larger than 15
 μm , still more preferably not larger than 10 μm .

An excessively large ratio in number of
particles having larger size is undesirable because
the dispersibility of particles is lowered to result
25 in formation of larger agglomerate in slurry
preparation, which affect adversely the coating

1 suitability and printing suitability.

The specific surface area is measured by the BET method. The particles have the surface area particularly preferably in the range of from 10 m²/g
5 to 70 m²/g. With an excessively small specific surface area, the image density cannot be high, while with an excessively large specific surface area, resistance to indoor discoloration of the recording medium is low.

10 The surfactant for use in the present invention is exemplified below without limiting the invention in any way. The cationic surfactant is the one having a primary to quaternary ammonium group, a pyridinium group, or the like as the hydrophilic
15 group, specific examples including:

cetyltrimethylammonium chloride,
stearyltrimethylammonium chloride,
behenyltrimethylammonium chloride,
octadecyltrimethylammonium chloride,
20 hexadecyltrimethylammonium chloride,
dodecyltrimethylammonium chloride,
dioctyldimethylammonium chloride,
distearyldimethylammonium chloride,
lauryldimethylbenzylammonium chloride,
25 myristyldimethylbenzylammonium chloride,
stearyldimethylbenzylammonium chloride,

1 tetradecyldimethylbenzylammonium chloride,
octadecyldimethylbenzylammonium chloride,
oxyethyldodecylamine, and the like.

The nonionic surfactant includes:

5 polyoxyethylene alkyl ether,
polyoxyethylene alkylphenol ether,
polyoxyethylene alkylphenyl ether,
polyoxyethylene aliphatic ester,
sorbitan ester ether,
10 sorbitan ester; and the like, but is not limited
thereto.

In the present invention, other conventionally
used inorganic or organic pigments may be used in
combination with the spherical basic magnesium
15 carbonate within the range in which the object of the
present invention is achievable.

The inorganic pigment includes silica,
alumina, aluminum silicate, magnesium silicate,
hydrotalcite, calcium carbonate, titanium oxide, clay,
20 talc, and the like, but is not limited thereto. The
organic pigment is exemplified by plastic pigments
such as urea resins, urea-formalin resins,
polyethylene resins, polystyrene resins, and the like,
but is not limited thereto. The mixing ratio of the
25 pigment is preferably in the range of from 10 to 60 %
by weight based on the basic magnesium carbonate.

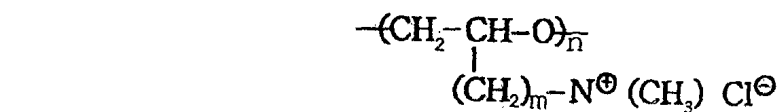
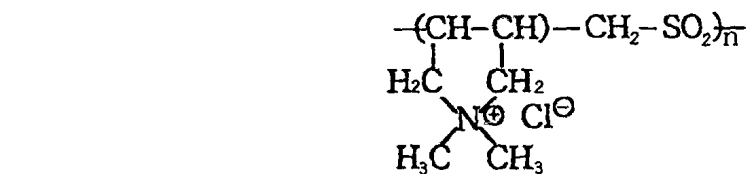
1 The binder for use in the present invention
includes, for example, water-soluble polymers such as
polyvinyl alcohol, starch, oxidized starch, cationic
starch, casein, carboxymethylcellulose, gelatin,
5 hydroxyethylcellulose, acrylic resins, and the like;
water-dispersible polymers such as SBR latex,
polyvinyl acetate emulsion, and the like; and
combination of two or more thereof.

 The preferred mixing ratio of the pigment and
10 the binder (P/B) in the present invention is not lower
than 1/4 by weight in view of further improvement of
ink absorbency of the ink-receiving layer, and not
higher than 10/1 by weight in view of prevention of
pigment-falling-off of the ink-receiving layer, more
15 preferably being in the range of from 6/1 to 1/1.

 Further in the present invention, the ink
receiving layer may contain an additive, if necessary,
such as a dye-fixing agent (waterproofing agent), a
fluorescent whitener, a surfactant, an anti-foaming
20 agent, a pH controlling agent, a mildewproofing agent,
a UV absorbing agent, an anti-oxidizing agent, a
dispersing agent, a viscosity-reducing agent, and the
like. Such additives are arbitrarily selected from
known compounds depending on the object.

25 The dye-fixing agent is explained as an
example of the additives. The additional use of the

- 1 following dye-fixing agent improves the water-
resistance of the formed image.



25 The above compounds are merely examples, and do not
limit the present invention. The waterproofing effect
of the dye-fixing agent depends on the kind of the dye
used for ink-jet recording. Accordingly, the
combination with the dye for recording have to be
sufficiently examined.

The recording medium of the present invention
is prepared by applying an aqueous coating liquid
containing a pigment, a binder, and other additives by
a known method such as a roll-coater method, a blade-

1 coater method, an air-knife-coater method, a gate-roll-
coater method, a size-press method, and the like onto
the surface of a substrate, and then drying the coated
matter by means of a hot-air drying oven, a hot drum,
5 or the like. The recording medium may be further
subjected to a supercalender treatment for the purpose
of smoothing the surface of the ink-receiving layer or
raising the surface strength of the ink-receiving
layer.

10 The total amount of the coating of the pigment
in the ink-receiving layer is preferably in the range
of from 0.2 to 50 g/m², more preferably from 0.2 to 20
g/m². At a small amount of the coating, a part of the
substrate may be exposed on the surface. At the
15 coating amount of less than 0.2 g/m², no effect is
achieved in color development of the dye in comparison
with the case of mediums having no ink-receiving
layer, while at the coating amount of more than 50
g/m², pigment-falling-off occurs at the coating layer,
20 which are not desirable. Meanwhile, the amount of the
coating is in the range of from 0.5 to 100 μm in terms
of the layer thickness.

The ink itself for the ink-jet recording on
the recording medium described above may be any known
25 ink, which can be used without any inconvenience. The
recording agent therefor may be a water-soluble dye

1 such as direct dyes, acidic dyes, basic dyes, reactive
dyes, and food dyes. Any dye for ink-jet recording
use may be employed without any particular limitation,

The particularly preferred embodiment of the
5 recording method of the present invention is an ink-
jet recording which employs a direct dye and/or an
acidic dye as the recording agent. Although the
relation thereof with the recording medium is not
exactly known, the effect is assumed to be due to a
10 chemical reaction with the basic magnesium carbonate
contained or the cationic and/or nonionic surfactant
in the recording medium, thereby removing sufficiently
the difference in color tone between the image formed
by forward movement of head and the one formed by
15 backward movement of the head, and yet retaining
sufficient recording image density and sufficient
resistance against the indoor discoloration.

The aforementioned water-soluble dye is used
conventionally in an amount ranging from about 0.1 to
20 20 % by weight in an ink. In the present invention
also, the dye may be used in an amount in the same
range.

The solvent for the aqueous ink of the present
invention is water, or a mixed solvent of water and a
25 water-soluble organic solvent. Particularly suitable
is a mixed solvent of water and a water-soluble

1 organic solvent, the water-soluble organic solvent
containing a polyhydric alcohol which is effective to
prevent drying of ink.

The method of recording by applying the ink on
5 the aforementioned recording medium is preferably any
ink-jet recording method, in which the ink is ejected
through a nozzle to apply the ink onto the recording
medium as an ejected-ink-receiving body.

In particular, the recording medium of the
10 present invention is effectively used in the recording
method in which an ink receives thermal energy to
change its volume abruptly by phase transition and is
ejected by the action caused by this volume change, as
described in Japanese Patent Application Laid-Open No.
15 54-59936.

A recording apparatus is described below which
is suitable for recording on the recording medium of
the present invention.

An example of the constitution of the heads,
20 which is a main portion of the apparatus, is shown in
Fig. 1, Fig. 2, and Fig. 3.

A head 13 is formed by bonding a plate of
glass, ceramics, or plastics having a groove 14 for
ink passage with a heat-generating head 15. (The type
25 of the head is not limited to the one shown in the
drawing.) The heat-generating head 15 is constituted

1 of a protection layer 16 formed of silicon oxide or
the like, aluminum electrodes 17-1 and 17-2, a heat-
generating resistance layer 18 formed of nichrome or
the like, a heat accumulation layer 19, and a
5 substrate plate 20 having a high heat-releasing
property made of alumina or the like.

Ink 21 reaches the ejection orifice 22 (a fine
pore), forming a meniscus by action of pressure P not
shown in the figure.

10 On application of an electric signal to the
electrodes 17-1 and 17-2, the region designated by a
symbol "n" of the heat-generation head 15 generates
abruptly heat to form a bubble in the ink 21 at the
position adjacent thereto. The pressure generated by
15 the bubble pushes out the meniscus 23 and ejects the
ink 21 from the orifice 22, as a recording droplets
24, and the droplets are propelled to a recording
medium 25. Fig. 3 illustrates exterior appearance of
a multi-head constructed by juxtaposing a multiplicity
20 of heads shown in Fig. 1. The multi-head is prepared
by bonding a glass plate 27 having multi-grooves 26
with a heat-generation head 28 similar to the one
described in Fig. 1.

Incidentally, Fig. 1 is a cross-sectional view
25 of the head 13 along an ink flow path, and Fig. 2 is a
cross-sectional view of the head at the line A-B in

1 Fig. 1.

Fig 4 illustrates an example of the ink-jet recording apparatus having such a head mounted therein.

5 In Fig. 4, a blade 61 as a wiping member is held at one end by a blade-holding member, forming a fixed end in a shape of a cantilever. The blade 61 is placed at a position adjacent to the recording region of the recording head, and in this example, is held so
10 as to protrude into the moving path of the recording head. A cap 62 is placed at a home position adjacent to the blade 61, and is constituted such that it moves in the direction perpendicular to the moving direction of the recording head to come into contact with the
15 ejection nozzle face to cap the nozzles. An ink absorption member 63 is provided at a position adjacent to the blade 61, and is held so as to protrude into the moving path of the recording head in a manner similar to that of the blade 61. The
20 aforementioned blade 61, the cap 62, and the absorption member 63 constitute an ejection-recovery section 64, the blade 61 and the absorption member 63 removing off water, dust, and the like from the ink ejecting nozzle face.

25 A recording head 65 has an ejection energy generation means, and conducts recording by ejecting

1 ink toward a recording medium opposing to the ejection
nozzle face. A carriage 66 is provided for supporting
and moving the recording head 65. The carriage 66 is
engaged slideably with a guide rod 67. A portion of
5 the carriage 66 is connected (not shown in the
drawing) to a belt 69 driven by a motor 68, so that
the carriage 66 is movable along the guide rod 67 to
the recording region of the recording head and the
adjacent region thereto.

10 The constitution of a paper delivery portion
51 for delivery of a recording medium and a paper
delivery roller 52 driven by a motor not shown in the
figure delivers the recording medium to the position
opposing to the ejecting nozzle face of the recording
15 head, and the recording medium is discharged with the
progress of the recording to paper discharge portion
provided with paper-discharge rollers 53.

In the above constitution, the cap 62 of the
ejection-recovery portion 64 is out of the moving path
20 of the recording head 65 during returning of the head
to the home position at the end of the recording,
etc., while the blade 61 is made to protrude into the
moving path. Therefore, the ejecting nozzle face of
the recording head 65 is wiped therewith. The cap 62
25 moves to protrude toward the moving path of the
recording head 65 when the cap 62 comes into contact

1 for capping with the ejecting nozzle face of the
recording head 65.

At the time when the recording head 65 moves
from the home position to the record-starting
5 position, the cap 62 and the blade 61 are at the same
position as in the above-mentioned wiping time, so
that the ejection nozzle face of the recording head is
wiped also in this movement.

The recording head moves to the home position
10 not only at the end of the recording and at the time
of ejection recovery, but also at a predetermined
interval during movement for recording in the
recording region. By such movement, the wiping is
conducted.

15 The present invention is described in more
detail by reference to examples. In the examples, the
terms "part" and "%" are based on weight unless
otherwise mentioned.

20 Example 1 and Comparative Example 1

< Method for Preparing Recording Medium >

The constitutional elements in the Example and
Comparative Example are listed below:

Substrate material:

25 Wood-free paper (Ginwa, made by Sanyo Kokusaku Pulp
Co., Ltd.)

1 Coating material:

(1) Basic magnesium carbonate (dense magnesium carbonate, made by Konoshima Kagaku K.K., average primary particle diameter: 0.47 μm , specific surface area: 27 m^2/g , bulk density: 0.44 g/cc, oil absorption: 79 ml/100 g),

(2) Binder (PVA-217, made by Kuraray Co., Ltd., saponification degree: 89 mol%, polymerization degree: 1700),

10 (3) Waterproofing agent (polyallylamine hydrochloride, PAA-HCl-3L, made by Nitto Boseki Co., Ltd., average molecular weight: 10,000),
(4) Cationic surfactant (Coatamine 24P, made by Kao Corporation, lauryltrimethylammonium chloride).

15 The recording medium was prepared in the manner described below.

Firstly, 15 parts of the Pigment (1), basic magnesium carbonate, was mixed with 85 parts of water, and the mixture was stirred for 15 minutes by means of
20 a commercial homogenizer at stirring rate of 10,000 rpm. To the mixture, a separately prepared binder solution (aqueous 10% polyvinyl alcohol solution) was added in an amount to give a pigment/binder ratio (solid ratio) of 2/1, and stirred for 5 minutes. The
25 aforementioned Additive (3) was added thereto in a ratio of 10 % (solid ratio) based on the Pigment (1),

1 and stirred for 5 minutes. Further thereto, the
Surfactant (4) was added at a ratio (solid ratio) of
0.5 % based on the Pigment (1), and stirred further
for 5 minutes to provide a coating liquid.

5 The resulting coating solution was applied on
the aforementioned substrate material with a wire bar
coater. The coated matter was dried at 110°C for 5
minutes, and treated with a supercalender. Thus the
recording medium of the present invention was
10 prepared.

The recording medium employed in Comparative
Example 1 was prepared in the same manner as in
Example 1 except that the cationic surfactant (5) was
not used.

15 The recording mediums for Examples 2 to 5 and
Comparative Example 2 to 6 were prepared in the same
manner as above.

Table 1 summarizes the constitutional elements
and their mixing ratio used in Examples 2 to 5 and
20 Comparative Examples 2 to 6. As the substrate
material, ink-absorbent paper was consistently used
which had a basis weight of 100 g/m², thickness of 100
μm, and a sizing degree of 2 seconds, and contained
calcium carbonate as a filler at a content of 6.5 % in
25 terms of ash according to JIS-P-8128. The amount of
coating was adjusted to be 6 g/m² as dry coating

1 matter.

Table 1

Example 2

5 Pigment: Spherical basic magnesium carbonate (average
particle diameter: 5.0 μm , bulk density: 0.3 g/cc,
specific surface area: 30 m^2/g , oil absorption: 70
ml/100 g): 15 parts

Binder: PVA-217: 6 parts

10 Waterproofing agent: Dimethyldiallylammonium chloride-
acrylamide copolymer (PAS-J41, made by Nitto
Boseki Co. Ltd., average molecular weight:
10,000): 3 parts

Surfactant: Cation BB (dodecyltrimethylammonium
15 chloride, made by Nippon Oil and Fat Co., Ltd.):
0.075 part

Example 3

Pigment: The same as in Example 2

Binder: The same as in Example 2

20 Waterproofing agent: The same as in Example 2

Surfactant: Nonion T-208.5 (polyoxyethylene tridecyl
ether, made by Nippon Oil and Fat Co., Ltd.):
0.070 part

Example 4

25 Pigment: The same pigment as in Example 2: 10 parts,
and Silica (Fine Sil K-40, made by Tokuyama Soda

- 1 Co, Ltd., average particle diameter: 1.5 μm ,
specific surface area: 300 g/m^2): 5 parts

Binder: The same as in Example 2

Waterproofing agent: PAA-HCl-3L: 1.5 parts

- 5 Surfactant: The same as in Example 3

Example 5

Pigment: The same pigment as in Example 2: 10 parts,
and alumina (Aluminum oxide C, made by Degussa

Co.,

- 10 average particle diameter: 20 nm, specific surface
area: 100 g/m^2): 5 parts

Binder: The same as in Example 2

Waterproofing agent: The same as in Example 4

Surfactant: Electrostripper QN (made by Kao

- 15 Corporation): 0.05 part

Comparative Example 2

Pigment: The same as in Example 2

Binder: The same as in Example 2

Waterproofing agent: The same as in Example 4

- 20 Surfactant: Not used

Comparative Example 3

Pigment: The same as in Example 4

Binder: The same as in Example 2

Waterproofing agent: The same as in Example 4

- 25 Surfactant: Not used

Comparative Example 4

1 Pigment: The same as in Example 5

Binder: The same as in Example 2

Waterproofing agent: The same as in Example 4

Surfactant: Not used

5 Comparative Example 5

Pigment: Silica (Finesil K-40, made by Tokuyama Soda Co., Ltd.)

Binder: The same as in Example 2

Waterproofing agent: The same as in Example 4

10 Surfactant: Sanisol (alkylbenzylmethyllummonium chloride, made by Kao Corporation): 0.075 part

Comparative Example 6

Pigment: The same as in Comparative Example 5

Binder: The same as in Example 2

15 Waterproofing agent: The same as in Example 4

Surfactant: Not used

Comparative Examples 7 - 9

The recording mediums for comparison were prepared in the same manner as in Example 1 except
20 that the anionic surfactants below were used respectively in place of the cationic surfactant of Example 1.

Comparative Example 7:

25 Polyoxyethylene octylphenol ether sulfate (made by Matsumoto Yushi K.K.)

Comparative Example 8:

- 1 Sodium dicetylsulfosuccinate (made by Matsumoto
Yushi K.K.)

Comparative Example 9:

- Potassium alkylphosphate (made by Matsumito
5 Yushi K.K.)

With the above recording mediums, color ink-
jet recording was conducted by use of the inks having
the compositions below in an amount of 8 nL/mm^2 for
10 single color ink dot in the two ink-dotting orders of
 $C \rightarrow M \rightarrow Y \rightarrow Bk$ and $Bk \rightarrow Y \rightarrow M \rightarrow C \rightarrow Bk$.

Ink composition

	Dye	5 parts
	Diethylene glycol	20 parts
15	Water	80 parts

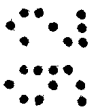
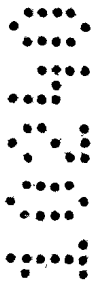
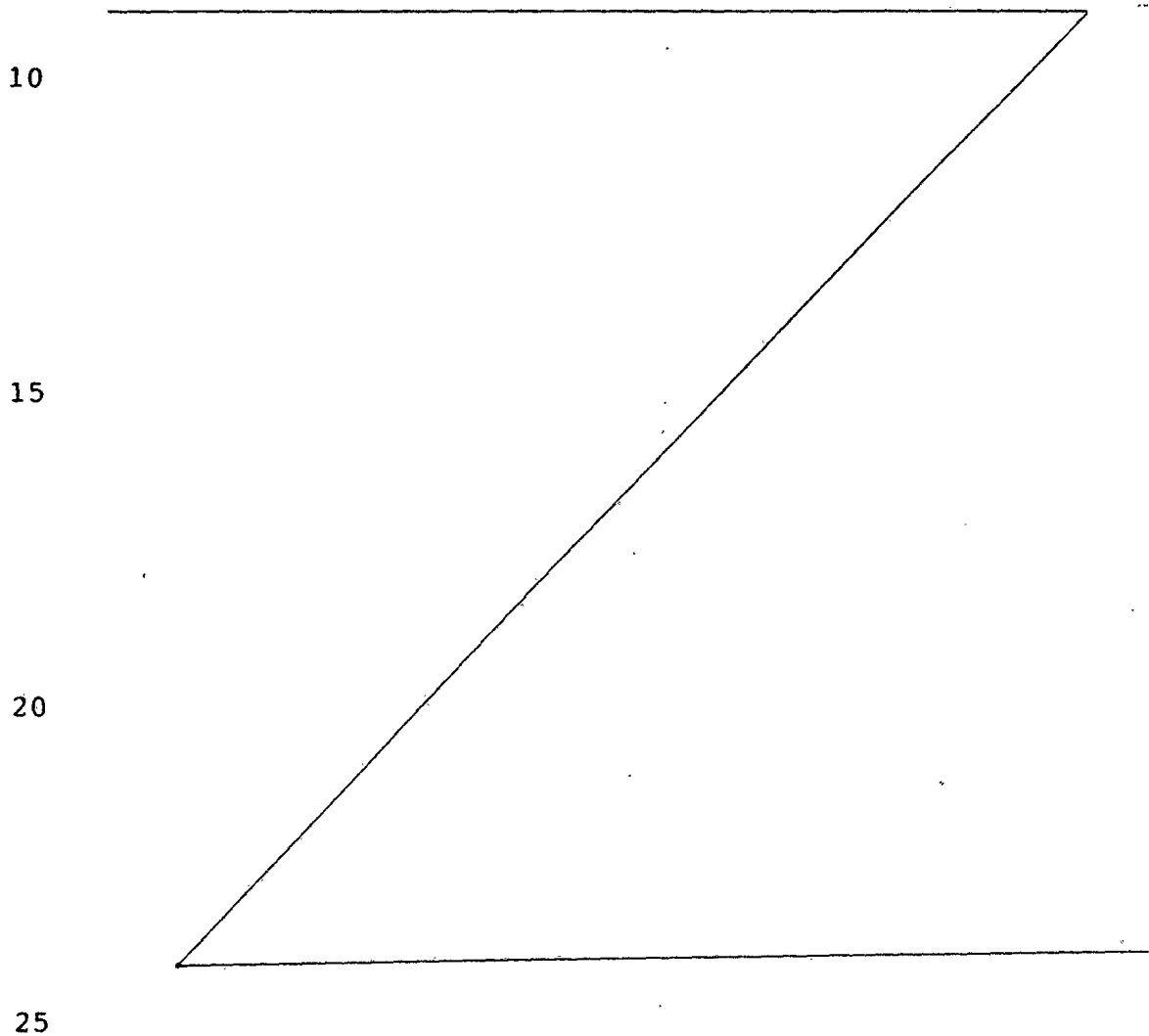
Dyes

- Y: C.I. Direct Yellow 86
M: C.I. Acid Red 35
C: C.I. Direct Blue 199
20 Bk: C.I. Food Black 2

The image density of the solid-print portions
of the single colors and the mixed colors were
evaluated.

- 25 Solid printing was conducted with black color
ink and the combinations of two color inks of yellow

1 and magenta, magenta and cyan, and cyan and yellow
with the head movement in the forward direction and in
the backward direction, thus changing the order of the
dotting of the ink colors. The reflective optical
5 densities of each of the colors of the solid prints
were measured by means of MacBeth Reflectodensitometer
RD-918. The results of the measurement are shown in
Table 2.



14 192 10240

Table 2

	OD (Bk)	Direction	OD R(M/Y)	OD G(C/Y)	OD B(C/M)
Example 1	1.38	forward	1.40/1.28	1.40/1.26	1.42/1.38
		backward	1.41/1.29	1.42/1.28	1.40/1.40
Comparative Example 1	1.38	forward	1.43/1.27	1.40/1.26	1.40/1.37
		backward	1.35/1.35	1.35/1.35	1.35/1.45
Example 2	1.35	forward	1.36/1.25	1.35/1.25	1.34/1.32
		backward	1.36/1.25	1.34/1.26	1.35/1.33
Example 3	1.35	forward	1.35/1.24	1.34/1.26	1.35/1.32
		backward	1.35/1.25	1.35/1.25	1.34/1.34
Comparative Example 2	1.34	forward	1.36/1.26	1.34/1.25	1.35/1.31
		backward	1.30/1.32	1.28/1.35	1.30/1.37
Example 4	1.40	forward	1.40/1.28	1.40/1.27	1.42/1.35
		backward	1.40/1.29	1.41/1.28	1.43/1.36
Comparative Example 3	1.40	forward	1.40/1.23	1.40/1.22	1.40/1.36
		backward	1.32/1.28	1.33/1.28	1.35/1.40
Example 5	1.42	forward	1.45/1.30	1.42/1.30	1.41/1.40
		backward	1.47/1.31	1.41/1.32	1.40/1.40
Comparative Example 4	1.43	forward	1.45/1.25	1.41/1.24	1.42/1.40
		backward	1.38/1.30	1.35/1.29	1.37/1.45
Comparative Example 5	1.45	forward	1.50/1.35	1.45/1.35	1.46/1.40
		backward	1.40/1.40	1.40/1.40	1.38/1.50
Comparative Example 6	1.45	forward	1.50/1.35	1.46/1.35	1.44/1.39
		backward	1.40/1.40	1.38/1.38	1.37/1.47
Comparative Example 7	1.33	forward	1.35/1.10	1.36/1.08	1.37/1.24
		backward	1.18/1.28	1.22/1.27	1.22/1.33
Comparative Example 8	1.32	forward	1.35/1.08	1.37/1.09	1.37/1.22
		backward	1.18/1.28	1.21/1.26	1.24/1.35
Comparative Example 9	1.32	forward	1.36/1.10	1.38/1.08	1.36/1.24
		backward	1.17/1.29	1.25/1.26	1.24/1.35

1 In Table 2, the term "OD R(M/Y)" means the
reflective optical densities of magenta color and
yellow color at the yellow/magenta solid print
portion, and the terms "OD G(Y/C)" and "OD B(C/M)"
5 have analogous meaning. The term "forward" means the
printing with the head moving in the forward
direction, and the term "backward" means the printing
with the head moving in the backward or reversed
direction.

10 As shown clearly in Table 2, the presence of
the basic magnesium carbonate and a cationic
surfactant and/or a nonionic surfactant resolves the
difference of color tone between the mixed color
portions dotted with different order of ink colors.

15 The present invention provides printed images
having consistent color tone by use of a serial type
color ink-jet printer regardless of the movement
direction of the head, thus enabling high-speed
printing.

20

25

The claims defining the invention are as follows:

1. A recording medium suitable for ink-jet printing, having on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a nonionic surfactant wherein the recording medium contains the surfactant in the range
5 of from 0.05 to 2.0% by weight based on the basic magnesium carbonate.
2. The recording medium of claim 1, wherein the basic magnesium carbonate is spherical or elliptical basic magnesium carbonate.
3. The recording medium of claim 2, wherein the spherical basic magnesium carbonate is in a shape of a sphere having the ratio of major axis length a to minor axis
10 length b in the range of $0.7 \leq b/a \leq 1.0$.
4. The recording medium of claim 1, wherein the recording medium contains the basic magnesium carbonate at a content in the range of from 0.2 to 50 g/m².
5. The recording medium of claim 1, wherein the recording medium further contains a dye fixing agent.
- 15 6. The recording medium of claim 1, wherein the substrate is paper.
7. An ink jet recording method in which ink is ejected through an orifice of an ink jet recording head onto a recording medium suitable for ink-jet recording in response to a recording signal, the recording medium containing basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant, wherein the
20 recording medium contains the surfactant in the range of from 0.05 to 2.0 % by weight based on the basic magnesium carbonate, and the recording medium has on a substrate a coat layer which contains basic magnesium carbonate, and a cationic surfactant and/or a non-ionic surfactant.
8. The ink jet recording method of claim 7, wherein the basic magnesium
25 carbonate is spherical or elliptical basic magnesium carbonate.
9. The ink jet recording method of claim 8, wherein the spherical basic magnesium carbonate is in a shape of a sphere having the ratio of major axis length a to minor axis length b in the range of $0.7 \leq b/a \leq 1.0$.
10. The ink jet recording method of claim 7, wherein the recording medium
30 contains the basic magnesium carbonate at a content in the range of from 0.2 to 50 g/m².
11. The ink jet recording method of claim 7, wherein the recording medium further contains a dye fixing agent.
12. The ink jet recording method of claim 7, wherein the ink contains a direct
35 dye and/or an acid dye.
13. A recording medium suitable for ink-jet printing containing basic magnesium carbonate, and a cationic surfactant and/or a nonionic surfactant



substantially as hereinbefore described with reference to any one of the examples excluding the comparative examples.

14. An ink jet recording method substantially as hereinbefore described with reference to any one of the examples excluding the comparative examples.

5

DATED this Seventeenth Day of January 1995

Canon Kabushiki Kaisha

Patent Attorneys for the Applicant

SPRUSON & FERGUSON



Recording Medium and Ink-Jet Recording
Method Employing the Same

ABSTRACT OF THE DISCLOSURE

A recording medium contains, within an ink
5 absorbent substrate per se or in an ink receiving
coat layer formed on a substrate, basic magnesium
carbonate together with a cationic surfactant and/or
a nonionic surfactant. The recording medium is
suitably used for color ink jet recording of the
10 both-ways serial printing type and eliminates
substantially the tone difference between forward
and backward printings and the discoloration during
indoor storage.

FIG. 4

