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Recording Medium and Recording Method by Use
Thereof

5 Background of the invention

Field of the invention

This invention relates to a recording medium. An illustrative application of the medium is for ink jet recording method. The invention also relates to a recording method by use of the medium. An illustrative embodiment of the recording medium is excellent in ink receptivity, sharpness, storability, water resistance, and surface gloss of the recorded image, etc.

15 Related background art

Ink jet recording method performs recording by generating small droplets of ink by employing various ink (recording liquid) ejecting systems, such as electrostatic attraction system, the system of giving mechanical vibration or displacement to ink by use of a piezoelectric element, the system in which the pressure formed when ink is bubbled by heating is utilized, permitting them to fly and attaching a part or whole thereof onto a recording medium such as paper. This method is now attracting attention as a recording method which generates less noise and is capable of performing high speed printing and multi-color printing.

1 As inks for ink jet recording, there have been
used those composed mainly of water and a hydrophilic
solvent primarily for the reasons of safety and
recording characteristics, and in most cases, a poly-
5 hydric alcohol is added for prevention of clogging of
nozzles and improvement of ejection stability.

 As the recording medium to be used for the
ink jet recording method, there have been employed
recording media comprising a porous ink-receiving
10 layer provided on a conventional paper or a substrate
called as the ink jet recording paper.

 However, as the ink jet recording is improved
in performance such as speed-up or multi-coloration
of recording and is popularized, the recording medium
15 also is required to have a higher level of character-
istics.

 More specifically, it is required that ink
should be absorbed as rapid as possible, and that
spread of ink droplets should be adequate.

20 Further, for carrying out color jet recording
method by use of color inks, a recording medium is
required which is particularly excellent in color
forming property and sharpness of a recording dye and
can give high coloration characteristic.

25 Further, the recorded image by ink jet record-
ing is required to be excellent in storability,
durability and water resistance of the recorded image.

1 While the recorded images obtained by the ink
jet recording method have been employed exclusively
for surface image observation, recording media suited
for uses other than for surface image observation are
5 becoming demanded with improvement in performances
or wide popularization of the ink jet recording
device.

Uses of the recording medium other than for
surface image observation may include those in which
10 recorded images are projected onto a screen, etc. by
means of an optical instrument such as a slide or an
OHP (an overhead projector), etc. and those images
are observed; color resolution plates for preparation
of a positive plate for color printing; CMF (a color
15 mosaic filter), etc. to be used for color display such
as liquid crystal, etc.

When the recording medium is to be used for
surface image observation, the diffused light of the
recorded image is observed, while the transmitted
20 light through the recorded images becomes a problem
in the recording medium in the uses other than surface
observation. Accordingly, light transmissivity,
particularly excellent linear transmittance is
required in addition to the requisite performances
25 in general of the recording medium for ink jet
recording.

However, prior to the present invention, no

1 recording medium satisfying all of these requisite
performances has yet been known.

Also, most of the recording media for obser-
vation of the surface image of the prior art have
5 used a system in which a porous ink-receiving layer
is provided on the surface to fix the recording agent
by receiving ink in the porous void, and therefore,
the surface of the recording medium had no gloss
based on the fact that it is porous.

10 On the other hand, when the surface of the
ink receiving layer is non-porous, volatile components
such as polyhydric alcohol, etc., in the ink will
remain on the surface of the recording medium after
practice of recording. Thus it will take a long time
15 for drying and fixing of the ink, whereby there are
involved the drawbacks such that clothing may be soiled
by contact with a recorded image or that the recorded
image may be damaged.

However, as described above, a recording
20 medium has been demanded strongly which has a record-
ing medium having light transmissivity or a recording
medium having gloss on the surface. In the case of
recording media of such embodiments, it is essentially
required that the surface of the recording medium
25 should be non-porous. For such demands, in order to
enhance affinity for ink and ink receptivity, it has
been practiced in the prior art to use a recording

1 medium comprising a non-porous ink-receiving layer
formed by use of a water-soluble polymer.

For example, U.S. Patent 4503111 (Tektronics)
proposes a recording medium having a non-porous ink-
5 receiving layer formed by using primarily a poly-
vinylpyrrolidone.

However, such a recording medium has the
problems such that the recorded image is low in light
fastness, or that due to strong stickiness of the
10 surface of the ink receiving layer having received
the ink, blocking is liable to occur when the printed
matters are placed one upon another, or when a paper,
etc., is superposed on the recorded surface. Thus,
even in such a recording medium, when the recording
15 medium is placed under high humid condition, attachment
of water droplets, etc., on the surface of the record-
ing medium will cause the surface of the ink receiving
layer to have stickiness, whereby troubles may be
caused such as mutual blocking between recording
20 media or sticking of the recording medium mounted on
the recording device to the conveying system of a
printer, etc. In the recording medium after recording,
there is also the problem that the recorded image may
be damaged by migration or flowing-out, etc., of the
25 dye at the printed portion.

In one aspect the invention provides a recording medium comprising a substrate and a non-porous ink receiving layer provided thereon, said ink receiving layer comprising as a main constituent a hydrophilic and water-insoluble polymer and 2 to 30% by weight of a cationic resin based on the water-insoluble polymer.

In another aspect the invention provides a recording method performing recording by attaching droplets of a recording liquid on a recording medium, said recording liquid containing a water soluble dye, water and an organic solvent, said recording medium comprising a non-porous ink receiving layer provided on a substrate, and the ink receiving layer comprising a hydrophilic and water-insoluble polymer and a cationic resin.

1 An embodiment of the present invention
provides a recording medium for ink jet recording
which is particularly excellent in ink receptivity,
and sharpness and surface gloss of the recorded
5 images, particularly suitable for obtaining a highly
precise image and a recording method by use thereof.

Another embodiment of the present invention
provides a recording medium for full color ink jet
recording which is excellent in water resistance,
10 free from stickiness or blocking on the surface even
under highly humid condition, and also free from
migration or flowing-out of the dye when water
droplets may be attached on the surface of the
recorded image, or even when left to stand under
15 highly humid condition, and a recording method by use
thereof.

Still another embodiment of the present invention
provides a recording medium for use in ink jet
recording, which can be used for observation by
20 projection of recorded imaged onto a screen, etc.,
by an optical instrument such as slide, OHP, etc.,
or for observation of transmitted light such as color
resolution plate in preparation of a positive plate
for color printing or CMF, etc., to be used for color
25 display such as liquid crystal, etc., and a recording
method by use thereof.

1 Detailed Description of the Preferred Embodiments

The recording medium of the present invention is characterized primarily by its ink receiving layer which comprises a water-insoluble polymer and contains
5 a cationic resin therein, and the objects of the present invention are accomplished primarily by this feature.

The recording medium of the present invention generally comprises a substrate as a supporting member
10 and a recording face provided on its surface, namely an ink receiving layer, including, for example, the particularly preferable embodiments as follows:

(1) The embodiment in which both the substrate and the ink receiving layer are light-transmissive,
15 and the recording medium as a whole is light-transmissive;

(2) The embodiment in which the surface of the ink receiving layer is smooth and has gloss.

In each embodiment, the ink receiving layer
20 may also function as the supporting member simultaneously.

The present invention is described in more detail by referring to some preferable embodiments as mentioned above as typical examples.

25 More specifically, according to the detailed study by the present inventors, it has been found that a recording medium satisfying the various requirements

1 mentioned above, particularly water resistance and anti-
blocking property, etc., under highly humid conditions
can be obtained first by forming its ink receiving layer
of water-insoluble polymer, and secondly by including
5 a specific amount of a cationic resin in the ink receiving
layer. Although an ink receiving layer comprising a
water-insoluble polymer can overcome various problems
under highly humid conditions such as water resistance,
stickiness, and blocking, it may not be able to overcome
10 such problems as ink receptivity, fixing characteristic
for aqueous ink, water resistance of the printed portion.
However, the inclusion of a specific amount of cationic
resin in the ink receiving layer can solve the problems
of ink receptivity, fixing characteristic, color forming
15 property of dye, water resistance of printed portion,
sharpness, preciseness of recorded images, etc., while
retaining various excellent performances obtained by
water-insoluble polymer.

20 The water-insoluble polymer which characterises
first the present invention is not a general hydrophobic
polymer having no hydrophilic property at all, but it
is a polymer which is insoluble in water but is suffic-
iently hydrophilic. Specific examples of such hydro-
25 philic and water-insoluble polymers are shown below.

(1) Block copolymer or graft copolymer having
hydrophilic segments and hydrophobic segments in the

1 molecule:

Such a block copolymer or graft copolymer is water-insoluble as a whole, but hydrophilic. The hydrophilic segment of such a polymer is a segment of
5 a polymer of two or more vinyl monomers having hydrophilic groups such as carboxylic group, sulfonic acid group, hydroxyl group, ether group, acid amide group, methylolated groups thereof, primary to tertiary amino groups, quaternary ammonium group, etc., and
10 examples of such hydrophilic monomer may include (meth)acrylic acid, maleic anhydride, vinylsulfonic acid, sulfonated styrene, vinyl acetate, mono(meth)acrylate or monomaleate of a polyol such as ethylene glycol, (meth)acrylic acid amide, methylolated
15 products thereof, mono- or di-alkylaminoethyl (meth)-acrylate, quaternarized products thereof, vinyl pyrrolidone, vinyl pyridine, etc.

The hydrophobic polymer segment is a polymer of two or more monomers, including olefins such as
20 ethylene, propylene, butylene, etc.; aromatic vinyl compound such as styrene, methyl styrene, vinyl naphthalene, etc.; halogenated olefins such as vinyl chloride, vinylidene chloride, vinylidene fluoride, etc.; various alcohol esters of unsaturated carboxylic
25 acids such as (meth)acrylic acid, crotonic acid and others; etc.

Also, other water-soluble polymers than those

1 mentioned above, namely hydrophilic natural or
synthetic polymers, including, for example, natural
resins such as albumin, gelatin, casein, starch,
cationic starch, gum arabic, sodium alginate, etc.,
5 polyvinyl alcohol, polyamide, polyacrylamide, poly-
vinyl pyrrolidone, polyethyleneimine, polyvinyl-
pyridinium halide, melamine resin, polyurethane,
polyester, sodium polyacrylate, etc., or hydrophobic
natural or synthetic polymers obtained by modifying
10 these to water-insoluble can be used as the hydro-
philic polymer segments or hydrophobic polymer
segments as a matter of course.

(2) Crosslinked product of water-soluble
polymer:

15 This is obtained by crosslinking various
water-soluble polymers, etc., as mentioned above and
described below with an appropriate crosslinking
agent or radiation to the extent that they can
become water-insoluble without losing hydrophilic
20 property.

(3) Polymer complex comprising acidic polymer
and basic polymer:

Such a polymer complex comprises a basic
polymer and an acidic polymer, and it is known per se
25 as disclosed in Japanese Patent Publications Nos.
37017/1976 and 42744/1980.

Preferable basic polymers for formation of

1 such a polymer complex are inclusive of those as
shown below.

Homopolymers of N-vinylpyrrolidone, N-vinyl-3-
methylopyrrolidone, N-vinyl-5-methylpyrrolidone,
5 N-vinyl-3,3,5-trimethylpyrrolidone, N-vinyl-3-
benzylpyrrolidone, N-vinylpiperidone, N-vinyl-4-
methylpiperidone, N-vinyl-caprolactam, N-vinylcapryl-
lactam, N-vinyl-3-morpholine, N-vinylthiopyrrolidone,
N-vinyl-2-pyrrolidone, or random co-
10 polymers, block copolymers, graft copolymers thereof
with other monomers in general;

homopolymers of N-vinyl-2-oxazolidone, N-
vinyl-5-methyl-2-oxazolidone, N-vinyl-5-ethyl-2-
oxazolidone, N-vinyl-4-methyl-2-oxazolidone, N-vinyl-
15 2-thioxazolidone, N-vinyl-2-mercaptobenzothiazole,
or random copolymers, block copolymers,
graft copolymers thereof with other monomers in general;

homopolymers of N-vinylimidazole, N-vinyl-2-
methylimidazole, N-vinyl-4-methylimidazole,
20 or random copolymers, block copolymers, graft
copolymers thereof with other monomers in general;

homopolymers of 2- or 4-vinylpyridine, etc.,
or random copolymers, block copolymers, graft co-
polymers thereof with other monomers in general; and
25 so on. Other copolymerizable monomers which may used
in the above copolymers may include monomers in
general such as methacrylate, acrylate, acrylamide,

1 acrylonitrile, vinyl ether, vinyl acetate, vinyl
imidazole, ethylene, styrene and others.

Particularly useful are homopolymers and
copolymers of N-vinylpyrrolidone, N-vinylpiperidone,
5 N-vinylcaprolactam, N-vinylmorpholine, N-vinyl-2-
oxazolidone and N-vinyl-5-methyl-2-oxazolidone. In
the case of copolymers, it is preferred that the
nitrogen containing monomer as mentioned above should
be contained at a proportion of 50 mol% or more.

10 On the other hand, the acidic polymer capable
of forming a polymer complex with the above basic
polymer (here, the "acidic polymer" in the present
invention is inclusive of those having alcoholic
hydroxyl group in the molecule, in addition to those
15 having sulfonic acid group, carboxylic acid group,
sulfate ester group, phosphate ester group, phenolic
hydroxyl group) may include those as shown below.

1. Polymer having carboxylic acid group

Terminal carboxylic group polyesters obtained
20 by the reaction of polycarboxylic acids such as citric
acid, tartaric acid, phthalic acid, etc., and poly-
hydric alcohols such as ethylene glycol, 1,4-butanediol,
diethylene glycol, etc., in acid excess;

acidic cellulose derivatives modified with
25 various polycarboxylic acids (see Japanese Patent
Publication No. 5093/1960);

homopolymers of polycarboxylic acid vinyl ether

1 ester monomers, etc., or random copolymers, block
copolymers, graft copolymers thereof with other
monomers in general (see Japanese Patent Publication
No. 8495/1960);

5 homopolymers of monomers such as acrylic acid
or methacrylic acid, random copolymers, block co-
polymers, graft copolymers thereof with other monomers
in general;

homopolymers of α, β -unsaturated vinyl monomers
10 such as maleic anhydride, itaconic acid, etc., random
copolymers, block copolymers, graft copolymers
thereof with other monomers in general (see Murahashi,
Inoue, Tani ed., "Gosei Kobunshi (Synthetic Polymer)
(III)", P. 250-257 and P. 374-380, Asakura Shoten,
15 1971).

2. Polymer having sulfonic acid group:

Cellulose derivatives such as O-ethyl cellulose
acetate hydrogen sulfate hydrogen phthalate,
cellulose acetate hydrogen sulfate hydrogen phthalate,
20 ethyl cellulose hydrogen-O-sulfobenzoate, O-P-sulfo-
benzyl cellulose acetate, O-ethyl-O-P-sulfoethyl
cellulose acetate, etc. (see Japanese Patent Publication
No. 5093/1960);

sulfonic acid modified polymers of polyvinyl
25 alcohol or vinyl alcohol copolymers with sulfonic
acid compounds (e.g. O-sulfobenzoic acid, sulfo-
propionic acid, sulfovaleric acid, sulfobenzoaldehyde,

1 sulfophthalic acid, etc.).

3. Polymer having hydroxyl group:

Ethyl cellulose, benzyl cellulose, hydroxyethyl
cellulose, hydroxyethyl/ethyl cellulose, hydroxyethyl/
5 benzyl cellulose;

homopolymers of monomers having sulfonic acid
or phenol groups, or random copolymers, block co-
polymers and graft copolymers thereof with other
monomers in general;

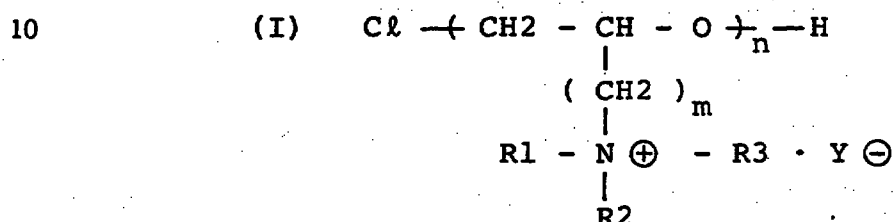
10 otherwise acid modified products of various
polymers with compounds containing carboxylic groups
or sulfonic acid groups or phenolic groups.

Preferable basic polymers and acidic polymers
for forming the polymer complex as described above
15 should have molecular weights of 500 or more, prefer-
ably 1000 or more, respectively and by use of the
both polymers with these molecular weights, an ink
receiving layer excellent in ink receptivity, sharpness
of image, and water resistance can be formed.

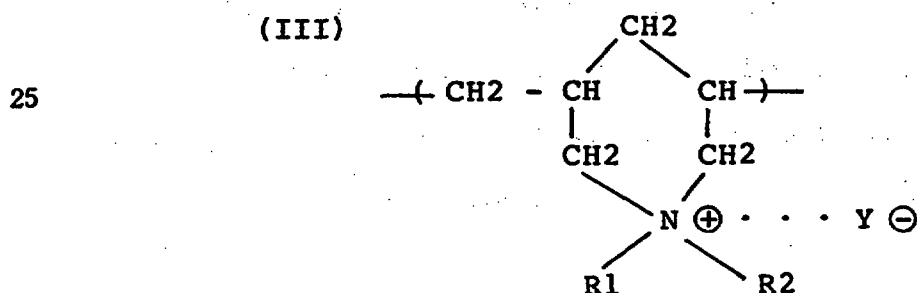
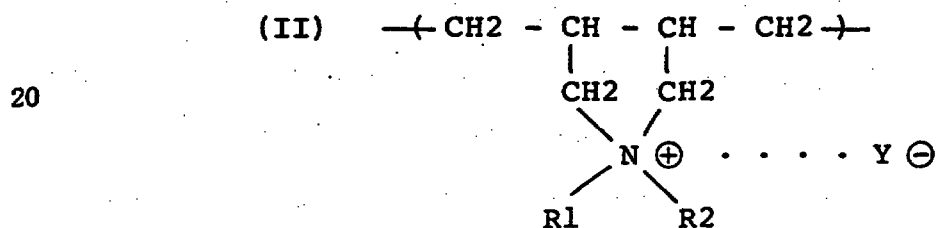
20 The proportions of both polymers used may
be within the range of from 20/1 to 1/10 in terms of
the weight ratio of the basic polymer/acidic polymer.

The second specific feature of the recording
medium of the present invention resides in that a
25 specific amount of a cationic resin is included during
formation of the ink receiving layer from the hydro-
philic and water-insoluble polymer as described above.

1 As such a cationic resin, any of the polymers
known in the art having ionic cationic group can be
used in the present invention, preferably having
quaternary ammonium groups, particularly preferably
5 the compounds represented by the formula (I) shown
below and polydiallylamine derivatives or acrylamides,
etc., having the monomers represented by the formulae
(II)-(IV) shown below.



15 wherein R1, R2, R3 each represent hydrogen or an alkyl
group, m is 1 to 7, n is 2 to 20, and Y represents an
acid group.



(IV)



In the formulae (II)-(IV), R1 and R2 each represent -CH₃, -CH₂-CH₃, -CH₂CH₂OH, Y represents an acid group.

10 Examples of the compound represented by the
formula (I) may include Narpoly-607 (produced by
Narcochemical Co.), Polyfix^(Registered Trade Mark) 601 (produced by Showa
Highpolymer Co., Ltd.), etc.

The compounds represented by the formulae
15 (II)-(IV) are polydiallylamine derivatives, which can
be obtained by cyclic polymerization of diallylamine
compounds, and may be exemplified by Percol 1697
(produced by Allied Colloid Co.), Cat Flocc C
(produced by Calgon Corp), PAS (produced by Nitto
20 Boseki Co., Ltd.), Neofix RPD (produced by Nikka
Kagaku Co., Ltd.).

The ink receiving layer of the recording medium of the present invention is preferably formed in non-porous state from the hydrophilic and water-insoluble polymer and the cationic resin as described above, and the cationic resin added is controlled to within the range of from 2 to 30 wt.%, preferably 3

1 to 20 wt.% based on the water-insoluble polymer. For
formation of a non-porous ink-receiving layer, during
formation of the ink receiving layer, without use of
an excessive amount of fillers, etc., a solution of
5 the materials as described above may be applied and
dried on the substrate to form the layer.

In the prior art, for example, in Japanese
Laid-open Patent Publications Nos. 84992/1981 and
20696/1984, etc., recording media containing cationic
10 resins such as polyvinylpyridinium bromide, dimethyl-
ammonium chloride, etc., in a porous ink-receiving
layer have been known. In the case of such a record-
ing medium having a porous surface, since the cationic
resin contained in the ink receiving layer is adsorbed
15 by the porous pigment or cellulose fiber elements at
the outermost portion of the ink receiving layer, its
preferable amount added was about 0.01 to 2 wt.% of
the coated layer in the case of a coated paper.

In the case of a recording medium having an
20 ink receiving layer with porous surface, since the
dye in the ink received is captured by the porous
layer near the surface of the recording medium and
also similarly forms some kinds of bonding with the
cationic resin existing on the outermost surface, the
25 amount of the cationic resin may be sufficiently about
0.01 to 0.1 wt.%. If the amount is increased to more
than that range, for example, 2-3 wt.% or more, there

1 may be caused problems such as decoloration or stick-
ing of the recording medium surface due to lowering
in ink absorbing capacity of the ink receiving layer
or a bleed of the cationic resin.

5 However, in the case when the ink receiving
layer contains a cationic resin in the recording
medium with non-porous surface as in the recording
medium of the present invention, the ink absorbing
mechanism is different from that of the porous ink
10 receiving layer (in the case of non-porous ink receiving
layer, according to swelling of ink receiving layer),
and therefore effect of the cationic resin added is
different.

 In the case of a recording medium with non-
15 porous surface, the dye received at the surface
reaches the innermost portion of the ink receiving
layer, and the cationic resin is uniformly dispersed
in the resin forming primarily the ink receiving layer.
For sufficient water resistance of the printed portion
20 in this case, 2 wt.% or more of a cationic resin is
required, and, on the contrary, neither lowering in
ink absorbency nor bleed of cationic resin as in the
case of porous ink-receiving layer will occur even if
2 wt.% or more of a cationic resin may be contained.
25 However, in the case of a non-porous surface, if a
cationic resin is contained in excess of 30 wt.%, the
film forming property of the ink receiving layer will

1 be deteriorated or lowered and otherwise water re-
sistance of the ink receiving layer itself will be
undesirably lowered, whereby the surface of the ink
receiving layer becomes sticky due to the cationic
5 resin under highly humid conditions.

Thus, the present inventors have found that
the preferable content of a cationic resin when
added in a recording medium with non-porous surface
is about 2 to 30 wt.%, preferably 3 to 20 wt.%,
10 which is not suitable in the porous case, and therefore
it is one of the specific features of the present
invention to contain a cationic resin at a proportion
as specified above.

In the present invention, in addition to the
15 water-insoluble polymer and the cationic resin as
described above, other water-soluble to hydrophilic
polymers may be employed in combination within the
range which does not impair the objects of the
present invention.

20 Further, for strengthening the ink receiving
layer and/or adhesion to the substrate, if desired,
hydrophobic resins such as SBR latex, NBR latex,
polyvinylformal, polymethyl methacrylate, polyvinyl
butyral, polyacrylonitrile, polyvinyl chloride, poly-
25 vinyl acetate, phenol resin, alkyd resin, etc., may be
used in combination within the range which does not
impair the objects of the present invention.

Also, for improvement of ink absorbency of the ink receiving layer, it is possible to disperse fillers such as silica, clay, talc, diatomaceous earth, calcium carbonate, calcium sulfate, barium sulfate, aluminum silicate, synthetic zeolite, alumina, zinc oxide, lithopon, satin white, etc. in the ink receiving layer, within the range which does not make the ink receiving layer porous.

As for the substrate to be used as the supporting material for the ink receiving layer in the present invention, it may be any transparent or opaque substrate known in the art. Preferable examples of transparent substrates may include films or plates such as of polyester resins, diacetate resins, polycarbonate resins, polyvinyl chloride resins, (Registered Trade Mark) polyimide resins, cellophane, celluloid, etc. and glass plates. Preferable opaque substrates may include, for example, paper, cloth, wood, metal plate, synthetic paper in general, or otherwise the above transparent substrates which have been subjected to opacifying treatment according to known means.

The recording medium of the present invention is formed by use of the principal materials as described above, and in the preferable embodiment of the above (1), both the substrate and the ink receiving layer are light transmissive with linear transmittance being 10% or higher, and the recording

1 medium as a whole is light-transmissive.

The recording medium according to this embodiment is particularly excellent in light-transmissivity and therefore used primarily in the case of OHP, etc., for projecting recorded images by an optical instrument onto a screen, etc., and it is useful as the recording medium for observation of transmitted light.

Such a light-transmissive recording medium can be prepared by forming a light-transmissive ink receiving layer from a mixture of the water-insoluble polymer and the cationic resin as described above on the light-transmissive substrate as described above.

As the method for forming such an ink receiving layer, there may preferably be employed a method in which a coating solution is prepared by dissolving or dispersing a mixture of the water-insoluble polymer and the cationic resin as described above and said coating solution is coated on the light transmissive substrate according to the known method such as roll coating, rod bar coating, spray coating, air knife coating, etc., followed by rapid drying, or a method in which a solution of the water-insoluble polymer is applied and then a solution of the cationic resin is applied. It is also possible to use the method in which a mixture of the above water-insoluble polymer and the cationic resin is subjected to hot

1 melt coating or the method in which a single film for
ink receiving layer is once formed from the materials
as described above, and said film is laminated on the
above substance.

5 The recording medium of the present invention
according to the embodiment (1) formed as described
above is a light-transmissive recording medium having
sufficient light transmissivity.

The sufficient light transmissivity as herein
10 mentioned means that the linear transmittance of the
recording medium should desirably exhibit at least 2%,
preferably at least 10%.

If the linear transmittance is 2% or higher,
the recorded image can be observed by projection by
15 OHP, for example, onto a screen. Further, in order
for the fine portion of the recorded image to be
observed sharply, the linear transmittance should
desirably be 10% or higher.

The linear transmittance T (%) as herein
20 mentioned is a value which is determined by measuring
the spectral transmittance of the linear light which
enters a sample perpendicularly, transmits through
the sample, passes through a slit on the light
receiving side which is located at least 8 cm apart
25 from the sample on the line extended from the incident
light pathway and is received on a detector, for
example, by means of 323 Model Hitachi Automatic

1 Recording Spectrophotometer (produced by Hitachi
Seisakusho), further determining the Y value of
tristimulus values of color and calculating from the
following formula:

5
$$T = Y/Y_o \times 100 \quad (1)$$

T: linear transmittance

Y: Y value of a sample

Y_o: Y value of a blank

Thus, the linear transmittance as mentioned in
10 the present invention is relative to linear light, and
it is different from diffuse transmittance (determined
so as to be inclusive of diffused light by providing
an integrating sphere at the rear of a sample) or
opacity (determined from the ratio of values when
15 white and black backings are applied on the back of a
sample) according to the method in which light trans-
missivity is evaluated with diffused light.

Since what becomes a problem in an instrument
utilizing optical techniques is the behavior of linear
20 light, it is particularly important to determine the
linear transmittance of a recording medium in evalu-
ation of the light transmissivity of the recording
medium to be used in such an instrument.

For example, in the case of observing a
25 projected image by OHP, in order to obtain an image
which is high in contrast between the recorded portion
and the non-recorded portion and which is sharp and

1 easy to observe, it is demanded that the non-recorded
portion in the projected image should be light, namely
that the linear transmittance of the recording medium
should be at a certain level or higher. In the test
5 by use of a test chart in OHP, for obtaining an image
suited for the above purpose, the linear transmittance
of the recording medium is required to be 2% or higher,
preferably 10% or higher in order to obtain a sharper
image. Therefore, the recording medium suited for
10 this purpose is required to have a linear transmittance
which is at least 10%.

The preferable embodiment of the above (2) is
also a kind of the above embodiment (1) and is
characterized in that its ink receiving layer has a
15 smooth surface, with the 45° specular gloss based on
the JIS Z 8741 being 30% or higher.

The recording medium of this type is particu-
larly excellent in surface gloss, and particularly
useful as the recording medium for observation of
20 surface images of full color excellent in sharpness.
The recording medium in this embodiment may be either
transparent or opaque, and any of the transparent
and opaque substrates as described above can be used.
Also, the ink receiving layer formed on these substrates
25 may be either transparent or opaque. The materials and
the methods, etc., to be used for formation of the
ink receiving layer may be the same as in the above

1 embodiment (1), but the fillers, etc., as mentioned
above may be used to the extent that the ink receiving
layer becomes opaque, so long as the smoothness of the
surface of ink receiving layer can be maintained.

5 If necessary, in addition to the coating methods
as mentioned above, the cast coating method may be
employed, or gloss may be imparted by means of calender
rolls.

In the present invention as described above,
10 the ink receiving layer to be formed on the substrate
may have a thickness, which is generally 1 to 200 μm ,
preferably 3 to 100 μm , more preferably 5 to 30 μm .

Further, in the present invention, by imparting
organic or inorganic fine powder in an amount of
15 0.01 to about 1.0 g/m^2 on the recording surface of the
light-transmissive recording medium of various em-
bodiments as described above, the conveying character-
istic within the printer, antiblocking characteristic
during piling, fingerprint resistance, etc. of the
20 recording medium obtained can be further improved.

Having described above by referring to
examples of typical embodiments of the light-trans-
missive recording medium of the present invention, the
light-transmissive recording medium of the present
25 invention will not of course be limited to these
embodiments. In either of these embodiments, it can
further incorporate various known additives, including

1 dispersing agents, fluorescent dyes, pH controllers,
defoaming agents, lubricants, preservatives, surfactants,
etc.

The recording medium of the present invention
5 is not necessarily required to be colorless, but it
may also be a colored recording medium.

The recording medium of the present invention
as described above is a recording medium having an ink
receiving layer with non-porous surface and can ex-
10 hibit excellent ink receptivity and provide a recorded
image of excellent gloss, water resistance and sharp-
ness at the printed portion, and yet with its surface
being not becoming tacky or sticky.

Thus, to say nothing about mono-color, even
15 when inks with different colors in full-color image
recording may be attached on the same spot to overlap
each other within a short time, there is no such
phenomenon such as flow-out or ooze-out, whereby the
ink receiving layer will not be lowered in strength
20 and there can be obtained an image which is sharp with
high resolution.

Moreover, the recording medium of the present
invention, being different from the recording medium
by use of a water-soluble polymer of the prior art,
25 is excellent in water resistance and therefore, when
left to stand under highly humid conditions, the
surface of the ink receiving layer will not become

1 sticky or tacky when water droplets, etc., are adhered
on the surface. Also, in the recording medium after
recording, there occurs no migration or flowing-out of
the dye at the recorded portion, whereby recorded
5 images excellent in storability and water resistance
can be given.

In the present invention, it is also possible
to provide a recording medium which is excellent in
water resistance and also in surface gloss which
10 could not be seen in the recording medium for ink
jet recording of the prior art. Also, the recording
medium of the present invention is applicable for
uses other than for observation of surface images of
the prior art such as those used for observation of
15 the recorded image projected onto a screen, etc., by
an optical instrument such as slide or OHP, color
resolution plates during preparation of positive
plates for color printing or CMF used for color dis-
play such as liquid crystal, etc.

20 The present invention is described in more
detail by referring to Examples, Comparative examples
and Use examples. In the description, parts and %
are based on weight.

25 Example 1

88 parts of a 10% dimethylformamide (herein-
after called DMF) solution of a polyvinylpyrrolidone

1 (PVPK-90, produced by GAF) and 12 parts of 10% DMF
solution of a novolac type phenol resin (Resitop PSK-
2320, produced by Gun-ei Chemical Industries Co., Ltd.)
were mixed. The mixture was gelled to form a polymer
5 complex, but when the mixture is heated with stirring
to 90°C, it becomes a solution. To this solution were
added 2 parts of 50% ethanol solution of a cationic
resin (Elecond PQ-10, produced by Soken Chemical Co.,
Ltd.), and this was used as the coating solution.

10 As a light transmitting substrate, a polyethy-
lene terephthalate film with a thickness of 100 μ m
(produced by Toray) was used, and the above coating
solution was applied on this film according to the
bar coater method to a film thickness after drying of
15 8 μ m, followed by drying at 80°C for 10 minutes, to
obtain a light-transmitting recording medium of the
present invention.

The recording medium of the present invention
thus obtained was found to be colorless and transparent.

20

Example 2

In the same manner as in Example 1 except for
using a commercially available cast coated paper as
the substrate, a recording medium of the present
25 invention was obtained.

Example 3 and Comparative examples 1 - 2

15

20

50 parts

25

The same as the coating solution composition in Example 1 except for no cationic resin (Elecond PQ-

1 10) was added into the coating solution.

Example 4

Comb type polymer (produced by Soken
5 Chemical Co., Ltd.) <25% methyl-
(Registered Trade Mark)
cellosolve/solution> 60 parts
Methylvinyl ether/maleic acid mono-
(Registered Trade Mark)
n-butyl ester copolymer (GANTREZ)
ES-425, produced by GAF) <10% water/
10 ethanol solution> 38 parts
Cationic resin (Elecond PQ-10, produced
by Soken Chemical Co., Ltd.)
<50% ethanol solution> 2 parts

The above comb type polymer comprises 80 parts
15 of a copolymer (main chain) comprising 64 parts of 2-
hydroxyethyl methacrylate and 16 parts of dimethyl-
acrylamide, to which 20 parts of MMA macromer were
graft polymerized.

Coating solution composition of Example 5;

20 Polyvinylpyrrolidone (PVP K-90, produced
by GAF) <10% DMF solution> 100 parts
Isobutylene/maleic anhydride copolymer
(ISOBAM, Kuraray Isoprene Chemical)
<10% DMF solution> 30 parts
(Registered Trade Mark)
25 Cationic resin (POLYFIX 601, produced
by Showa Highpolymer Co., Ltd.)
<10% DMF solution> 25 parts

1 Coating solution composition of Comparative example 3;

The same as the coating solution composition
(Registered Trade Mark)
of Example 2 except that no cationic resin (POLYFIX 601)
was added into the coating solution.

5 For the recording media of the above Examples
and Comparative examples, by use of the four kinds of
inks shown below, ink jet recording was practiced by
use of an on-demand type ink jet printer (PJ 1080A,
produced by Canon K.K.) which discharges inks by
10 piezoelectric oscillators.

Yellow ink (composition)

	C.I. Direct Yellow 86	2 parts
	Diethylene glycol	20 parts
	Polyethylene glycol #200	10 parts
15	Water	70 parts

Red ink (composition)

	C.I. Acid Red 35	2 parts
	Diethylene glycol	20 parts
	Polyethylene glycol #200	10 parts
20	Water	70 parts

Blue ink (composition)

	C.I. Direct Blue 86	2 parts
	Diethylene glycol	20 parts
	Polyethylene glycol #200	10 parts
25	Water	70 parts

Black ink (composition)

	C.I. Food Black 2	2 parts
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1	Diethylene glycol	20 parts
	Polyethylene glycol #200	10 parts
	Water	70 parts

Evaluation results of the recording media of
5 Examples and Comparative examples are shown in Table 1.

The respective evaluation items in Table 1
were measured according to the methods shown below.

(1) Ink fixing time was measured by leaving
the recording medium after practice of recording to
10 stand under room temperature (20°C, 65 %RH) and
measuring the time before ink no longer attaches to
a finger when the recorded image is touched with the
finger.

(2) Dot density was measured for black dots
15 by use of Sakura microdensitometer PDM-5 (produced
by Konishiroku Photo Industry Co., Ltd.) by applying
JIS K 7505 for printed microdots.

(3) Linear transmittance was determined from
the above formula (1) by measuring spectral trans-
20 mittance by use of 323 model Hitachi automatic
recording spectrophotometer (produced by Hitachi
Seisakusho Co., Ltd.) by maintaining the distance
from the sample to the window on the light receiving
side at about 9 cm.

25 (4) For gloss, 45° specular gloss was measured
on the surface of recording medium based on JIS Z-
8741.

(5) Water resistance was evaluated by comparison of the optical density (O.D.) after immersion measured by use of a Macbeth densitometer when the recording medium was immersed in stationary water for 5 minutes with the O.D. value before immersion. The sample unmeasurable on account of dissolution of the ink receiving layer during immersion was rated as x.

Table 1

	Example					Comparative example		
	1	2	3	4	5	1	2	3
Ink fixing time	3 min.	3 min.	1 min.	3 min.	3 min.	1 min.	3 min.	1 min.
Dot density	1.1	1.0	1.1	1.1	1.1	1.1	1.1	1.1
Linear transmittance	79%	-	79%	78%	77%	80%	79%	79%
Gloss	-	70%	-	-	-	-	-	-
Water resistance	92%	91%	89%	87%	93%	x	34%	40%

CLAIMS

1. A recording medium comprising a substrate and a non-porous ink receiving layer provided thereon, said ink receiving layer comprising as a main constituent a hydrophilic and water-insoluble polymer and to 30% by weight of a cationic resin based on the water-insoluble polymer.
2. A recording medium according to claim 1, wherein said recording medium has a linear transmittance of not less than 2%.
3. A recording medium according to claim 1, wherein said recording medium has a linear transmittance of not less than 10%.
4. A recording medium according to claim 1, 2 or 3, wherein the ink receiving surface of said recording medium has a 45° specular gloss of 30% according to JIS Z 8741.
5. A recording medium according to any preceding claim, wherein said cationic resin is a polydiallylamine derivative or an acrylamide.



6. A recording medium according to any preceding claim, wherein said ink receiving layer contains a polymer complex of an acidic polymer and a basic polymer as said water-insoluble polymer.

5

7. A recording medium according to claim 6, wherein the weight ratio of the basic polymer and the acidic polymer is within the range of 20/1 to 1/10.

10

8. A recording medium according to claim 6 or 7, wherein each of the basic polymer and the acidic polymer has a molecular weight of not less than 500.

15

9. A recording medium according to any preceding claim, wherein the ink receiving layer has a thickness in the range of from 1 to 200 μm .

20

10. A recording medium according to any preceding claim, wherein the ink receiving layer has a thickness in the range of from 3 to 100 μm .

25

11. A recording medium according to any preceding claim, wherein the ink receiving layer has a thickness in the range of from 5 to 30 μm .

12. A recording medium according to any preceding



claim, wherein the cationic resin is contained in an amount of 3 to 20% by weight based on the water-insoluble polymer.

5 13. A recording medium according to any of claims 1 to 12, which is used for ink jet recording.

14. A recording method performing recording by attaching droplets of a recording liquid on a
10 recording medium, said recording liquid containing a water soluble dye, water and an organic solvent, said recording medium comprising a non-porous ink receiving layer provided on a substrate, and the ink receiving layer comprising a hydrophilic and water-insoluble
15 polymer and a cationic resin.

15. A recording method according to claim 14, wherein said recording method is an ink-jet recording method.

20 16. The recording method according to claim 14 or 15, wherein the content of the cationic resin is in the range of from 3 to 20% by weight based on the water-insoluble polymer.



17. The recording medium according to claim 14, 15 or 16, wherein said cationic resin is polydiallylamine derivative or an acrylamide.

5 18. A recording medium according to claim 1 and substantially as hereinbefore described in any of the examples.

10 19. A recording method according to claim 14 and substantially as hereinbefore described in any of the examples.



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