

COLOUR IMAGE FORMING METHOD AND INK USED THEREFORField of the Invention

5 This invention relates to an ink, to a combination of
inks for use in forming a colour image and to method
for forming a colour image. The ink can be used to
produce colour images having good light fastness even
where the colour image to be produced includes on the
recording medium regions of overlapping inks of
10 different colours which are required to produce a
mixed colour region of the image. Colour printing can
be carried out reproducably using the ink over
extended periods of time without difficulties arising
such as clogging of the nozzle or other parts of the
15 ink flow path in the printer, even in the case of an
ink jet printer in which the images are formed using
thermal energy.

Related Background Art

20 In an ink jet printer an image is formed from ink
droplets which become attached to a part or the whole
of a recording medium such as paper, various ink
ejecting systems being used to form the ink droplets.
As the ink to be used for forming colour images in
25 such an ink jet printing system, there can be used
inks prepared by dissolving or dispersing

water-soluble dyes of various hues, such as cyan, magenta, yellow, black etc in water or a liquid medium comprising water and a water-soluble solvent. Colour images are formed using at least two inks of different hues.

Also a plurality of inks of different hues as described above have been used to form colour images by the use of writing implements such as a fountain pen, a felt tipped pen, a ball point pen etc.

In the above mentioned inks various performance requirements are routine, amongst which the most commonly demanded requirement concerns the light fastness of the colour images formed. If the ink contains a dye of insufficient light fastness the problem often arises that after the image has been formed it will discolour or fade over a period of time so that its quality is reduced. Particularly where a colour image is formed by superposition of several dyes of different hues onto the paper, although the dyes may individually exhibit excellent light fastness, a new problem arises which is that the light fastness of the coloured image as a whole can be significantly reduced by interaction between the dyes.

For example a copper phthalocyanine dye widely used as a dye for a cyan ink in an ink jet printing system, or a phthalocyanine dye as described in Japanese Laid Open Patent Publication No 179569/1984 exhibits excellent light fastness individually. However, when it is superimposed on other dyes on a paper sheet as described above, it is frequently liable to promote fading of such other dyes, and in particular it can have a significant effect on magenta dyes and black dyes, particularly magenta dyes of the monoazo type. Preventing the fading of dyes in mixed colour regions where a number of dyes are superimposed one upon the other is a problem in the formulation of ink jet printing inks.

15 A further problem which arises in the formation of colour images as described above is to provide inks of each hue which are stable and do not clog or generate sediment at the nozzle of the printer, at an orifice of the printer or at a pen tip, such sediments can form during recording using the ink by various systems, during interruptions between periods of recording or during extended periods during which no recording is carried out.

25 In particular in ink jet systems that works using heat

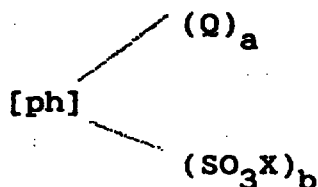
energy, foreign matter is liable to be deposited on the surface of the thermal printing head as a result of temperature change and this problem is particularly significant. Since a plurality of inks is needed to form a colour image, all of the inks used must have the appropriate liquid stability. However, in the case of the inks of the prior art various additives are needed to satisfy requirements such as the ability of the ink to be ejected, its long term storage stability, the sharpness and density of the recorded images produced, the surface tension, the electrical properties etc, and also because of various impurities present in the dyes used. Problems have arisen, for example that clogging occurred at a nozzle or orifice of an ink jet device, or deposited matter was generated on the surface of the heater, or sediment was generated during long term storage. Thus in spite of the various excellent characteristics of the ink jet system, this is one reason why its popularity has so far been limited.

SUMMARY OF THE INVENTION

The present invention provides an ink comprising a dye and a liquid medium for dissolving or dispersing the dye therein, wherein the dye is a

metallophthalocyanine dye represented by the formula:

5



wherein:

10

[ph] represents a phthalocyanine skeleton having at its centre a metal of group II, IV, VII or VIII of the Periodic Table at its centre;

Q represents $-\text{SO}_2\text{OR}_1$ or $-\text{SO}_2\text{NR}_2\text{R}_3$, wherein:

15

R_1 represents a straight or branched or cyclic alkyl or aralkyl group;

R_2 and R_3 independently represent $-\text{H}$, $-(\text{CH}_2\text{CH}_2\text{O})_n$, $-\text{R}_4$, $-(\text{CH}_2\text{CHOH})_n - \text{R}_4$, $-(\text{CHCH}_3\text{CH}_2\text{O})_n - \text{R}_4$, or a straight, branched or cyclic alkyl or aralkyl group, or $-\text{NR}_2\text{R}_3$ represents an amino acid salt

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residue, n represents an integer of 0 to 12, and R_4 represents H , CH_3 or CH_2OH ;

a and b independently represent an integer from 0 to 4 provided that the relationship $2 < a + b < 4$ is satisfied; and

X represents an alkali metal or NH_4 ;

and wherein the ink contains free ions of the metal at a concentration of 15 ppm or less.

5 The invention further comprises the combination for use in forming a colour image of a cyan ink as aforesaid with at least one of a magenta and a black ink.

10 The invention further provides a method for forming a colour image which comprises applying imagewise to a substrate a combination of inks as aforesaid.

15 The invention further comprises a method for forming a colour image which comprises applying imagewise to a substrate a plurality of inks including an ink as aforesaid, wherein the colour image is coated with a transparent protective member containing at least a UV- ray absorber.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present inventors have intensively studied
in order to accomplish the objects as described above
5 and consequently found that by using a specific
phthalocyanine dye as the dye for cyan ink and by
defining the amount of divalent or higher metal ions
in the ink, the fading prevention effect of other hues
to which the cyan ink is imparted overlappingly,
10 particularly magenta and/or black dyes, can be

1 obtained, thus giving color images with excellent
lightfastness.

Also, concerning the problem of liquid
stability of ink, it has been found that much
5 impurities are contained in commercially available
dyes, and that if they are utilized as such for
preparation of ink, these impurities, particularly
divalent or higher metal ions, mainly cause the
problems of clogging of a nozzle and lowering of ink
stability as described above.
10

A commercially available cyan dye, as it is,
contains a large amount of unreacted free metal ions
entrained during its synthesis. Accordingly, when such
commercially available cyan dye is used for an ink in
the present invention, these free metal ions or their
15 compounds cause, e.g., clogging of a nozzle or an
orifice and formation of sediment during the storage
of in the ink.

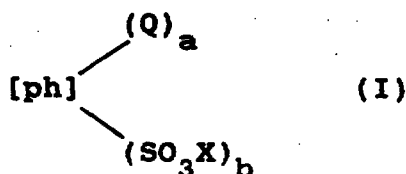
Particularly, this is the greatest cause for
deposition of foreign matters on the heating head in
20 the ink jet system utilizing heat energy. Thus, it
has been found that a cyan ink with high liquid
stability can be obtained by suppressing such
impurities at a certain value or less, and
consequently a color image with excellent
25 lightfastness can be stably formed.

1 Next, to describe in more detail about the
present invention, the principal specific feature of
the present invention is to use a phthalocyanine dye
having a coordination metal of the group II, IV, VII or
5 VIII or a metal-free phthalocyanine dye as the dye for
cyan ink in formation of a color image by use of ink,
and to obtain a color image with excellent
lightfastness by use of such cyan ink.

 In the prior art, it has been known to use a
10 copper phthalocyanine dye as the cyan dye in formation
of a color image by use of a plurality of inks with
different hues, for example, the three primary colors
of cyan, magenta and yellow or the four primary colors
containing black in addition to the three colors .
15 While such copper phthalocyanine dye itself shows
high lightfastness, the problem has issued that
lightfastness of dyes of other hues, for example,
magenta dye or black dye is remarkably lowered by
using such copper phthalocyanine dye. By use of the
20 phthalocyanine dye as mentioned above in place of the
copper phthalocyanine dye, the color image having
excellent lightfastness as a whole can be provided
without lowering in lightfastness of dyes of other
hues as described above.

25 The phthalocyanine dye to be used in the
present invention is represented by the following

1 formula (I):



5 In the above formula, [ph] represents a phthalocyanine skeleton having a coordination metal atom of the group II, IV, VII or VIII or no coordination metal atom at its center; Q represents any desired substituent; a is an integer of 0 to 4; X represents an alkali metal or NH₄; and b represents an integer of 1 to 4.

The phthalocyanine dye to be used in the present invention may be any phthalocyanine dye, provided that it is included within the above formula. The phthalocyanine dye which can give still better color images in respect of tone, lightfastness, water resistance, relationship with dyes of other hues, liquid stability of the ink formed, and other various performances is represented by the above formula, wherein Q represents a -SO₂OR₁ group or a -SO₂NR₂R₃ group; a and b independently represent an integer of 0 to 4, provided that the relationship of $2 \leq a + b \leq 4$ is satisfied; the above R₁ represents a straight or cyclic alkyl or aralkyl group which may also have branching; R₂ and R₃ independently represent a -(CH₂CH₂O)_n - R₄, -(CH₂CHOH)_n - R₄, or -(CHCH₃CH₂O)_n - R₄

1 group, a straight or cyclic alkyl or aralkyl group
which may also have a branch, or an amino acid salt
residue; n represents an integer of 0 to 12; and R_4
represents H, CH_3 or CH_2OH .

5 The above preferable phthalocyanine dye may be
any dye, provided that it is included within the above
definition. Specific examples thereof include those
as mentioned below. Among these phthalocyanine dyes,
particularly preferable are those with their center
10 metal being Ni, Co, V, particularly Ni. In the
following formulae, ph represents the phthalocyanine
skeleton, and the respective substituents Q and
sulfonic acid salt residue are bound to the benzene
ring of phthalocyanine.

15 1-1 a=1, $Q=SO_2NH_2$
b=1, X=Na
center metal=Ni

1-2 a=0,
b=2, X=Na
center metal=Ni

20 1-3 a=0,
b=3, X=Na
center metal=Ni

1-4 a=1, $Q=SO_2NH_2$
25 b=3, X=Na
center metal=Ni

- 1 1-5 $a=2$, $Q=SO_2NH_2$
 $b=2$, $X=Na$
center metal=Ni
- 5 1-6 $a=3$, $Q=SO_2NH_2$
 $b=1$, $X=Na$
center metal=Ni
- 1-7 $a=2$, $Q=SO_2NH(CH_2)_3CH_3$
 $b=1$, $X=Na$
center metal=Ni
- 10 1-8 $a=2$, $Q=SO_2NHC_2H_5$
 $b=2$, $X=K$
center metal=Ni
- 1-9 $a=2$, $Q=SO_2NH(CH_2CH_2O)_2CH_3$
 $b=1$, $X=K$
center metal=Ni
- 15 1-10 $a=2$, $Q=SO_2NHCH_2CH_3$
 $b=1$, $X=Li$
center metal=Ni
- 1-11 $a=3$, $Q=SO_2OC_2H_5$
 $b=1$, $X=Na$
center metal=Co
- 20 1-12 $a=2$, $Q=SO_2OCH(CH_3)_2$
 $b=1$, $X=Na$
center metal=Co
- 25 1-13 $a=1$, $Q=SO_2NH_2$
 $b=2$, $X=Na$

1 center metal=Co

1-14 a=1, Q=SO₂O(CH₂)₃CH₃

b=3, X=K

cente metal=V

5 1-15 a=1, Q=SO₂NH₂

b=2, X=Na

center metal=V

1-16 a=1, Q=SO₂(CH₂)₂CH₃

b=2, X=Na

10 center metal=V

The phthalocyanine dyes as described above are commercially available with ease, and any of such commercially available phthalocyanine dyes can be used in the present invention, and these cyan dyes can be used of course alone or as a combination of two or more kinds thereof, or can be used as the essential component in combination with other various dyes such as direct dyes, acidic dyes, etc. These commercially available phthalocyanine dyes are produced primarily for dyeing of fibers, therefore containing much impurities.

The present inventors have studied also about these impurities and found that a considerable amount of divalent or higher free metal ions (e.g. several decades to several hundreds ppm) are contained together with much inorganic salts, and these metal

ions cause many problems during formation of color
image, particularly during color formation according
to the ink jet system. That is, it has been found that
these metal ions mixed in the cyan ink, when the cyan
ink is overlapped with inks of other hues, particularly
a magenta and/or a black ink during formation of color
image, will promote lightfastness deterioration of the
dyes in these other hues.

Also, it has been found that these metal ions
deposit foreign matters on the thermal head of the ink
jet device, when the ink jet system is particularly
utilizing heat energy, thereby causing also prevention
of smooth ejection of ink to obstruct stable formation
of satisfactory color images.

Fading of magenta and black dyes with metal
ions in color images and deposition of foreign matters
on the thermal head as described above depend greatly
on the concentration of metal ions in the ink, and
these problems can be sufficiently solved by
controlling the free metal ions in the ink to 15 ppm
or less, preferably 3 ppm or less.

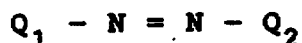
The method of controlling the concentration of
the metal ions in the ink to 15 ppm or less may be the
method in which the phthalocyanine dye is purified before the
preparation of the ink or the method in
which the cyan ink during or after the preparation of the

1 ink is purified. As the method
for the purification of dye or ink, there may be
employed any of the methods known in the art such as
the salting out method, washing with an organic
5 solvent, precipitation, recrystallization, the ion
exchange method, the aeration method, the
agglomeration precipitation method with an
agglomeration agent, the filtration method, the lime
softening method, the electrolytic method or a
10 combination of these methods.

In the method for forming a color image of the
present invention, there is used the cyan ink
containing the phthalocyanine dye as described above
and also inks of hues other than cyan, and the effect
15 of the present invention can be most exhibited when
the ink used in combination is magenta and/or a black
dye. To describe in detail, in the prior art, when a
phthalocyanine type dye which is itself excellent in
lightfastness is used as the cyan dye, fading of much
20 magenta and black dyes was promoted. However, in the
present invention, magenta and black dyes having other
excellent performances which could not be used due to
promotion of such fading in the prior art can be
satisfactorily used, whereby further excellent color
25 image can be formed.

For example, as the magenta dye, xanthene type

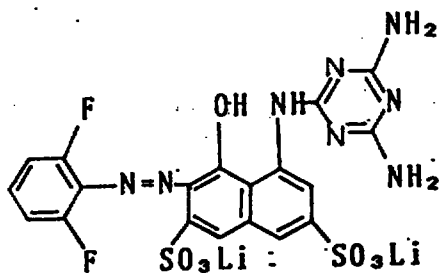
1 dyes such as C.I. Acid Red 50, 51, 52, 87, 91, 92, 93,
94, 95, 98, etc. and anthraquinone type dyes such as
C.I. Acid Red 80, 81, 82, 83, etc. can be preferably
used not depending on their structures, and those
5 which can preferably bring about the effects of the
present invention are monoazo dyes represented by the
following formula:



wherein Q_1 represents a substituted or unsubstituted
10 phenyl or naphthyl group and Q_2 represents a substituted
naphthyl group.

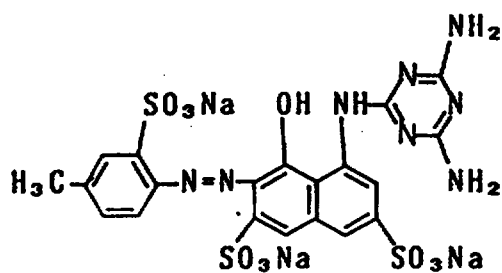
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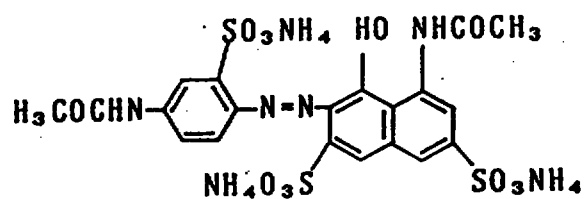
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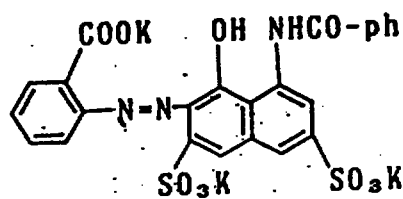
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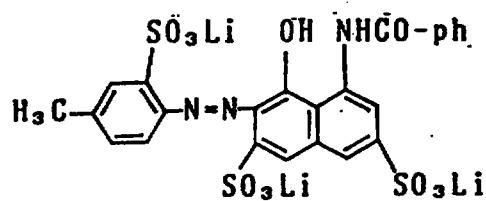
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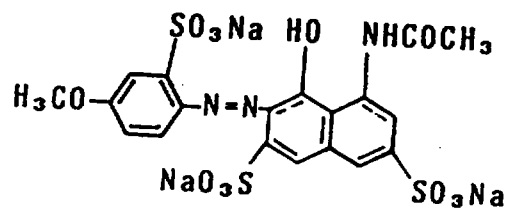
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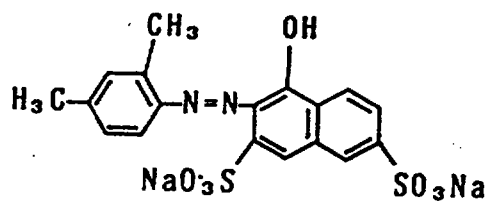
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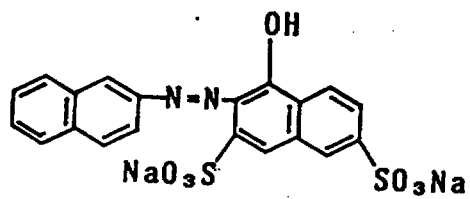
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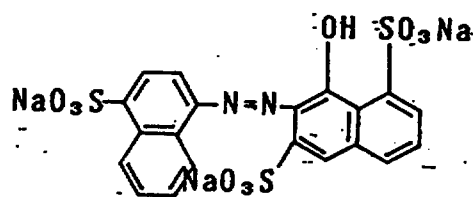
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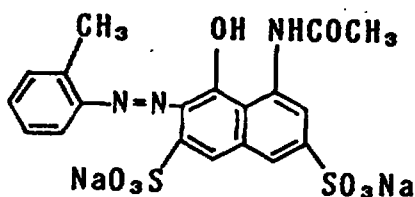


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The black dye to be used in the present invention may be any black dye known in the art. The black dyes which well can bring about the effects of the present invention is represented by the following general formula:

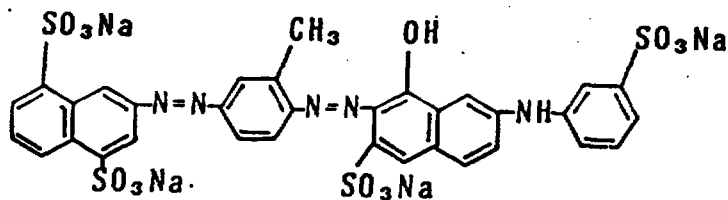


wherein Q_3 represents a substituted phenyl or naphthyl group, Q_4 represents a substituted phenylene or naphthylene group and Q_5 represents a substituted naphthyl group.

Examples of the black dyes include those represented by the following formulae.

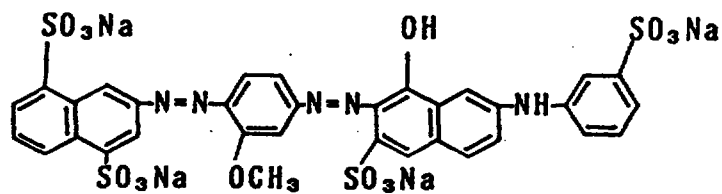
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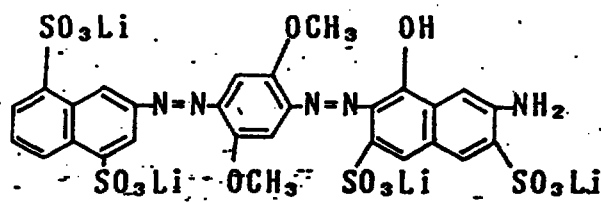
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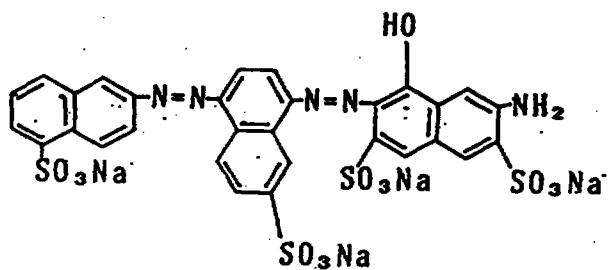
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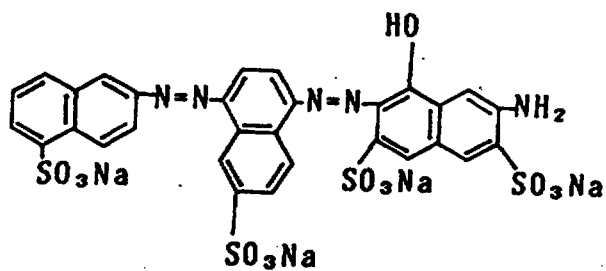
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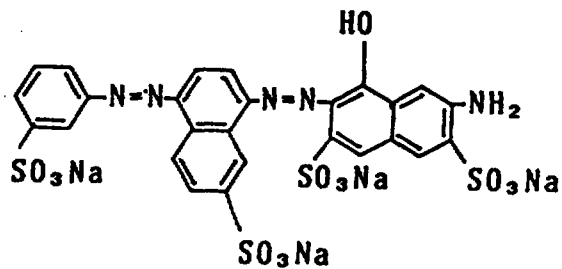
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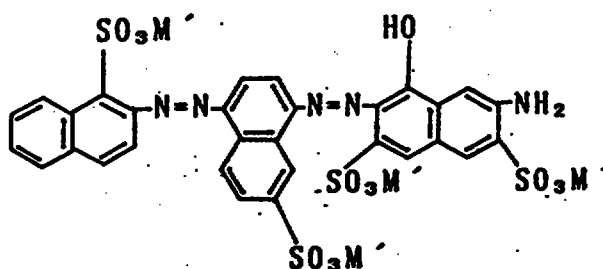
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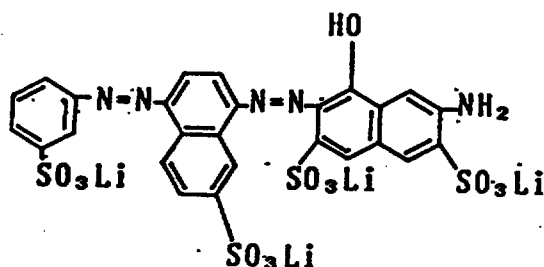


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Also, in the present invention, other than magenta and/or black inks as described above, yellow inks can be used, and all of the yellow inks used in the ink jet system, etc. can be used without any limitation for the ink to be used in these yellow inks.

In the method of the present invention, other than the cyan ink prepared from the phthalocyanine dye as described above, ink of at least one color other than cyan is used in combination. The ink to be used in combination may be prepared from any dye, but concerning magenta color and black color, the respective dyes as mentioned above are preferred, and concerning yellow dye, any yellow dye may be employed.

1 The method itself for the preparation of these aqueous
inks of these respective colors may be practiced
according to the prior art technique.

As described above, by use of the above ink as
5 the cyan ink in formation of color images,
lightfastness of the image can be remarkably improved.
In addition, for exhibiting its effect fully, it is
preferable to incorporate a UV-ray absorber in at
least one ink of the plural inks to be used.

10 As the UV-ray absorber to be used in the
present invention, there have been known in the art
those which prevent material from deterioration by UV-
ray by absorbing primarily the rays at UV-wavelength
portion in the sunlight to convert them, into, e.g.,
15 heat energy, and which have been utilized widely in
the field of synthetic resins and foods of the prior
art. All of these known UV-ray absorbers can be used
in the present invention, and they may not be
necessarily water-soluble. They may be also insoluble
20 in ink medium if they can be stably dispersed in ink
medium. However, particularly preferable ones in the
present invention are soluble in ink medium, namely
water or water and a hydrophilic solvent, including a
benzophenone type, a benzotriazole type, a
25 cyanoacrylate type, and a salicylic acid type UV-ray
absorber which have hydrophilic group such as sulfonic

1 acid group, a carboxylic acid group, a phenolic
hydroxyl group, an amino group or a soluble salt
thereof and derivatives thereof. More specifically,
there may be included 2,2'-dihydroxy-4,4'-
5 dimethoxybenzophenone-5-sulfonic acid, salts thereof
with sodium, potassium, lithium, etc.; 2-hydroxy-4-
methoxybenzophenone-5-sulfonic acid and salts thereof
with sodium, potassium, lithium, etc.; (2'-hydroxy-5'-
methylphenyl)benzotriazole; (2'-hydroxy-
10 phenyl)benzotriazole; and the like.

These UV-ray absorbers may be added to at
least one of plural inks with different hues for
forming color image in the present invention to
accomplish the objects of the present invention.
15 However, since the color image is not necessarily
prepared by overlapping used ink droplets with each
other and there may also exist the region of only one
color or only two overlapping colors, it is
practically preferable that at least the three primary
20 colors of the inks used should contain UV-ray
absorber.

The amount of the UV-ray absorber in the ink
may be preferably in the range from 0.1 to 5 wt.%,
more preferably from 0.5 to 3 wt.%, in the ink, since
25 the effect of the present invention is insufficient if
it is too small, while liquid stability, etc. of the

1 ink may be impaired if it is too large.

As described above, by using an ink containing a UV-absorber, and also using the above specific cyan dye as the dye for cyan ink, lightfastness of the full color image can be remarkably improved.

The content of the above dye in the ink according to the present invention may be determined depending on the kind of the liquid medium component, the characteristics demanded for the ink and the like. It may be generally made within the range from 0.1 to 20% in weight %, preferably from 0.5 to 15%, more preferably from 1 to 10%, based on the total weight of ink.

The solvent suitably used in the present invention is water or a solvent mixture of water with a water-soluble organic solvent. Particularly suitable is a solvent mixture of water and a water-soluble organic solvent, and the water-soluble organic solvent may include those containing polyhydric alcohol having the drying prevention effect of ink. Also, as water, it is preferable to use deionized water rather than water in general containing various ions, particularly divalent or higher metal ions.

Examples of the water-soluble organic solvent to be used in mixture with water may include alkyl alcohols having 1 to 4 carbon atoms such as methyl

1 alcohol, ethyl alcohol, n-propyl alcohol, isopropyl
alcohol, n-butyl alcohol, sec-butyl alcohol, tert-
butyl alcohol, isobutyl alcohol, etc.; amides such as
dimethylformamide, dimethylacetamide, etc.; ketones or
5 ketoalcohols such as acetone, diacetone alcohol, etc.;
ethers such as tetrahydrofuran, dioxane, etc.;
polyalkylene glycols such as polyethylene glycol,
polypropylene glycol, etc.; alkylene glycols with
alkylene group having 2 to 6 carbon atoms such as
10 ethylene glycol, propylene glycol, butylene glycol,
triethylene glycol, 1,2,6-hexanetriol, thiodiglycol,
hexylene glycol, diethylene glycol, etc.; glycerine;
lower alkyl ethers of polyhydric alcohols such as
ethylene glycol methyl (or ethyl) ether, diethylene
15 glycol methyl (or ethyl) ether, triethylene glycol
monomethyl (or ethyl) ether, etc.; N-methyl-2-
pyrrolidone, 1,3-dimethyl-2-imidazolidinone, etc.
Among these many water-soluble organic solvents,
polyhydric alcohols such as ethylene glycol, etc.,
20 lower alkyl ethers of polyhydric alcohols such as
triethylene glycol monomethyl (or ether) ether, etc.
are preferred.

The content of the above water-soluble organic
solvent in the ink may be 5 to 95% by weight,
preferably 10 to 80% by weight, more preferably 20 to
25 50 % by weight, based on the total weight of ink. At

1 this time, the content of water may be determined
within a broad range depending on the kind of the
above solvent component, its composition or the
desired characteristics of ink. It is generally made
5 within the range from 10 to 90%, preferably from 10 to
70%, more preferably from 20 to 70%, based on the
total weight of ink.

The ink of the present invention comprising
such components is itself excellent in all of
10 recording characteristics (signal response
characteristic, stability of droplet formation,
ejecting stability, continuous recordability for long
time, ejecting stability after stopping of recording
for long time), storage stability, fixability onto
15 recording medium or lightfastness, weathering
resistance, water resistance of recorded images, etc.

For further improvement of such
characteristics, various additives known in the prior
art may be further added. For example, there may be
20 included viscosity controllers such as polyvinyl
alcohol, celluloses, water-soluble resins, etc.;
surface tension controllers such as various cationic,
anionic or nonionic surfactants, diethanolamine,
triethanolamine, etc.; pH controllers by use of
25 buffers; antifungal agent, etc.

Also, for preparing an ink to be used for the

1 ink jet system of the type in which ink is charged,
specific resistivity controllers of inorganic salts
such as lithium chloride, ammonium chloride, sodium
chloride, etc. may be added. Further, when such ink
5 is applied to the ink jet system of the type in which
ink is ejected by the action of heat energy, thermal
physical properties (e.g. specific heat, thermal
expansion coefficient, thermal conductivity, etc.) may
be often controlled.

10 As described above, improvement of
lightfastness in color image formation is effected by
incorporating a UV-absorber in at least one of plural
inks. As another means, there is the method in which
the color image is coated with a transparent
15 protective member containing a UV-absorber after
recording of images.

The transparent protective member (laminate)
which can be used in the present invention is
described in detail below.

20 The transparent protective member to be used
in the present invention is a laminate material for
treating the image surface of a color image (print)
formed on paper, plastic sheet, etc. by ink jet
recording, etc., and can readily impart water
25 resistance, solvent resistance, abrasion resistance,
gloss, etc. to the recorded image. Further, by

1 incorporating a UV-ray absorber in the transparent
protective member, lightfastness of the color image
can be also improved to great extent.

Specific examples of the UV-ray absorber
5 suitably used in the present invention may include
benzophenone type compounds, for example, 2-hydroxy-
4-methoxy-5-sulfobenzophenone such as Cyasorb UV-284
(trade name, produced by ACC Co.), 2,2'-dihydroxy-
4,4'-dimethoxybenzophenone such as Uvinul D-49 (trade
10 name, produced by BASF Co.), 2,4-dihydroxybenzophenon
such as Uvinul 400 (trade name, produced by BASF Co.);
benzotriazole type compounds, for example, 2-(2'-
hydroxy-3',5'-di-tert-butylphenyl)triazole such as
Tinuvin 320 (trade name, produced by Ciba Geigy Co.),
15 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chloro-
benzotriazole such as Tinuvin 326 (trade name,
produced by Ciba Geigy Co.), 2-(2'-hydroxy-3',5'-di-
tert-butyl-phenyl)-5-chlorobenzotriazole such as
Tinuvin 327 (trade name, produced by Ciba Geigy Co.),
20 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole
such as Tinuvin 328 (trade name, produced by Ciba
Geigy Co.), 5-tert-butyl-3-(5-chloro-2H-benzotriazol-2-
yl)-4-hydroxybenzopropionic acid octyl ester such as
Tinuvin 109 (trade name, produced by Ciba Geigy Co.),
25 etc.

Selection of the substance having absorption

1 at the UV-region as described above and determination
of the concentration added may be suitably controlled
depending on the solubility in the resin forming the
transparent protective member, its thickness, etc.

5 As the resin component forming the transparent
protective member containing a substance having
absorption at UV-region, there may be included those
mainly composed of thermoplastic resins such as ethyl
cellulose, vinyl acetate resins and derivative
10 thereof, polyethylene, ethylene-vinyl acetate
copolymer, acrylic resin and derivatives thereof,
polystyrene and copolymers thereof, polyisobutylene,
hydrocarbon resin, polypropylene, polyamide resins,
polyester resins, etc. Such transparent protective
15 member can be used as a single layer or a multi-layer,
and may be used as laminated generally on one surface
of a color image, or in some cases on both surfaces
thereof. The essential components of the above
transparent protective member are as described above,
20 but various kinds of resins, an additive known in the
art such as plasticizers, lubricants, antioxidants,
light stabilizers, antistatic agents, swelling agents,
heat stabilizers, dyes, pigments, etc. can be added
optionally to such an extent that does not impair its
25 transparency.

The transparent protective member to be used

1 in the present invention is formed of the essential or
necessary components as described above, and its
thickness can be set at a broad range, depending on
its uses. For exhibiting effectively the effect of the
5 present invention, its thickness may be most
preferably within the range of from 5 to 50 μm . If
the thickness exceeds 50 μm , there will ensue the
problem of curl. In addition, and the problem of
lowering in transparency by coloration is liable to
10 occur. On the other hand, if the thickness is less
than 5 μm , it becomes difficult to incorporate a
substance having sufficient absorption at the UV-
region.

From the components and the constitution as
15 described above, the transparent protective member to
be used in the method of the present invention can be
obtained. And the transparent protective member
laminated on the colour image should preferably have an
absorption distribution which is preferable to be 1 or
20 more in the whole region of wavelength 300 to 350 nm
and to be 0.1 or less in the whole region of the
wavelength 400 to 800 nm. Such absorbance
distribution can be controlled by selection of the UV-
ray absorber and setting of its concentration,
25 combination with selection of the resin, addition of

1 various additives, control of layer thickness.

5 If the absorbance distribution of the transparent protective member does not become 1 or higher in the whole region of the wavelength 300 to 350 nm, the effect of preventing the reaction, in which the dye forming the color image is decomposed by the UV-ray to fade or discolor, becomes insufficient. On the other hand, if the absorbance in the whole region of the wavelength of 400 to 800 nm is not 0.1 or lower, it is unsuitable as the transparent protective member due to coloration or lowering in transparency. The above values of absorbance were measured by U-3200 Model autographic spectrophotometer (produced by Hitachi Seisakusho).

15 The transparent protective member containing at least a UV-ray absorber as described above is suitable for formation of a protective layer for a color print having images formed on paper, plastic sheet, etc. according to the recording method particularly by use of dyes, above all the ink jet recording method. Accordingly, the above transparent protective member may be used for any system, provided that a uniform layer having a specific absorbance distribution can be imparted to the color image surface. As the representative imparting system, the following two systems broadly classified are

20

25

1 particularly important.

As the first system, there is the system in which the transparent protective member is adhered to the color image surface by pressure.

5 This system can easily perform lamination by merely superposing the transparent member on the color image surface and permitting them to pass through pressurizing rollers.

10 The second system is the same as in the above adhesion method by pressure in superposing the transparent protective member or the color image surface and permitting them to pass through pressurizing rollers, but it is of the type which heat is applied simultaneously while pressurization, and it is characterized by use of a hot melt type resin at
15 the contacted surface between the transparent protective member and the color image.

20 The above two systems are particularly effective in the present invention, and therefore the transparent protective member should preferably consist of the form of film or sheet so as to be convenient for these systems.

Also, for providing a single layer or a multi-layer having a specific absorbance distribution as the protective layer on the color image, the transparent
25 protective member may sometimes take a form which can

1 be used more effectively for the above two systems,
and may also have a peelable substrate to be used in
the transfer system in some cases. The transparent
protective member to be used for the constitution in
5 such a case has a transfer layer (protective layer) to
be finally laminated on the color image surface and a
substrate to be removed after transfer; and the
transparent protective member can be formed by
laminating the material for formation of the transfer
10 layer on the so selected substrate by use of known
methods such as bar coating, blade coating, reverse
roll coating and gravure roll coating, etc., the
substrate and the transfer layer being selected in
view of, e.g., peelability between the substrate and
15 the transfer layer and matching of the transfer layer
to the surface of the color image to be protected by
the transfer layer.

As the material to be used for the substrate,
there may be employed, for example, paper, cloth,
20 plastic film, etc. to the surface of which there is
applied various peel-off treating agents having
peeling performance such as silicone resin, or Mylar (Registered
Trade Mark) film, polypropylene film, etc.

By applying lamination treatment of the
transparent protective member as described above to
25 the image surface obtained by the recording method by

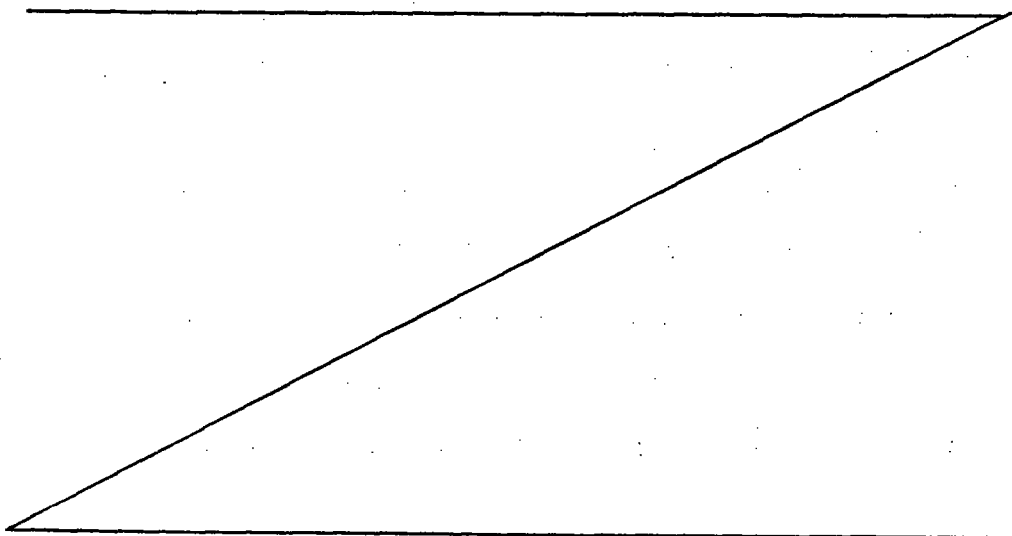
1 use of a dye, particularly by the ink jet recording
method, and further by use of a specific cyan dye as
described above as the cyan ink, its lightfastness is
remarkably improved other than improvements of water
5 resistance, solvent resistance, abrasion resistance,
gloss, etc. which effects could also be obtained by
utilizing the laminate members of the prior art.

As the recording medium available in the
present invention, there can be used as a matter of
10 course, a large number of various ink jet recording
papers proposed in the prior art or plastic sheets for
OHP to effect excellent recording, or papers for
copying, report papers, bond papers, slip papers,
continuous slip papers, printout papers for computer,
15 etc. widely used for business in general can be all
used, and these papers may be low or highly sized.

According to the present invention, as
described above, the cyan dye in the cyan ink to be

20

25



1 used in the present invention does not promote fading
of the dyes of other hues, particularly magenta and
black dyes, and therefore various excellent dyes which
could be used with the cyan ink with difficulty in the
5 prior art can be used, whereby color images with
extremely excellent lightfastness, etc. can be formed.

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

Examples 1 - 6

The components shown below were thoroughly
mixed with stirring and filtered through a filter made
of Teflon (Registered Trade Mark) having a mean pore size of 0.45 μ m to
15 prepare 6 sets of cyan ink, magenta ink, and black ink
with their respective compositions. The dye used for
the cyan ink, before formed into an ink, was subjected
to sufficient purification treatment in order to
remove free metal ions (metal ions not forming the
20 metal phthalocyanine dye). Further, as the dye, there
was used a dye which contained no more than 80 ppm of
free metal ion content in the dye powder. As water
and the organic solvent, those containing no metal ion
25 were used.

1 Example 1

Ink composition:

	Dye	X parts
	Polyethylene glycol (M.W. 300)	10 parts
5	Diethylene glycol	15 parts
	1,3-Dimethyl-2-imidazolidinone	10 parts
	Water	65 parts

Cyan ink: 0.2 part of the dye of the above formula

(1-3) was used (free nickel ion in the ink=
1.2 ppm);

Magenta ink: 0.5 part of the dye of the above formula

(2-1) was used;

Black ink: 0.6 part of the dye of the above formula

(3-1) was used.

15 Example 2

Ink composition:

	Dye	X parts
	Diethylene glycol	30 parts
	N-methyl-2-pyrrolidone	15 parts
20	Water	55 parts

Cyan ink: 0.5 part of the dye of the above formula

(1-4) was used (free nickel ion in the ink=
2.1 ppm);

Magenta ink: 0.8 part of the dye of the above formula

(2-2) was used;

25

Black ink: 0.9 part of the dye of the above formula

1 (3-2) was used.

Example 3

Ink composition:

	Dye	X parts
5	Polyethylene glycol (M.W. 600)	5 parts
	Triethylene glycol	15 parts
	N-methyl-2-pyrrolidone	10 parts
	Water	70 parts

Cyan ink: 0.2 part of the dye of the above formula

10 (1-6) was used (free nickel ion in the ink=
1.0 ppm);

Magenta ink: 0.8 part of the dye of the above formula

(2-3) was used;

Black ink: 0.9 part of the dye of the above formula

15 (3-3) was used.

Example 4

Ink composition:

	Dye	X parts
	Diethylene glycol	20 parts
20	Polyethylene glycol (M.W. 300)	10 parts
	N-methyl-2-pyrrolidone	10 parts
	Water	60 parts

Cyan ink: 0.3 part of the dye of the above formula

(1-9) was used (free nickel ion in the ink=
1.5 ppm);

25 Magenta ink: 0.6 part of the dye of the above formula

1 (2-4) was used;

Black ink: 0.4 part of the dye of the above formula

(3-4) was used.

Example 5

5 Ink composition:

	Dye	X parts
	Polyethylene glycol (M.W. 200)	10 parts
	Ethylene glycol	20 parts
	Diethylene glycol	10 parts
10	Water	60 parts

Cyan ink: 0.3 part of the dye of the above formula

(1-13) was used (free cobalt ion in the ink=
1.7 ppm);

Magenta ink: 1.0 part of the dye of the above formula

15 (2-5) was used;

Black ink: 0.7 part of the dye of the above formula

(3-5) was used.

Example 6

Ink composition:

20	Dye	X parts
	Triethanolamine	10 parts
	Triethylene glycol	10 parts
	Diethylene glycol	15 parts
	Water	65 parts

25 Cyan ink: 0.2 part of the dye of the above formula

(1-15) was used (free vanadium ion in the

ink=0.9 ppm);

1

Magenta ink: 0.5 part of the dye of the above formula
(2-6) was used;

Black ink: 0.3 part of the dye of the above formula
(3-6) was used.

5

From the cyan inks and, the magenta inks, and
the cyan inks and the black inks as described above,
color charts were prepared and their lightfastness
were examined. The recording medium used was IJ
Mattecoat NM (produced by Mitsubishi Paper Mills,
10 Ltd).

Color chart was formed by means of a recording
device having an on-demand type multi-head (ejecting
orifice diameter 35 μ m, resistance value of heat-
generating resistor 50 ohm, driving voltage 30 V,
15 frequency 2 KHz) which performs recording by
generating liquid droplets by giving heat energy to
the ink in the recording head.

Lightfastness test was conducted as follows.
The color chart as prepared above was irradiated with
20 xenon light by a weather-o-meter Ci-35 produced by
Atlas Co. and the color difference (ΔE) before and
after irradiation was measured by use of CA-35
produced by Murakami Color Research Institute. The
results are shown below in Table 1.

25

Table 1

1 (Light resistance test results)

	Example	Cy + M	Cy + Bk
	1	⊙	⊙
	2	⊙	⊙
5	3	⊙	⊙
	4	⊙	⊙
	5	○	○
	6	○	○

Cy...cyan, M...magenta, Bk...black

10 Evaluation in the above formula was conducted according to the following standards:

⊙... $\Delta E \leq 10$, ○... $10 < \Delta E < 20$, △... $20 \leq \Delta E \leq 30$, x... $30 < \Delta E$

Comparative examples 1 - 6

15 Color charts of violet color were prepared and their lightfastness tests were conducted according to the same procedure as in Example 1, except that the coordination metal of the cyan dye used in Example 1 was replaced with copper. The results are shown in Table 2.

20

Table 2

(Lightfastness test results)

	Comparative example	Cy + M	Cy + Bk
25	1	x	x
	2	x	x

1	3	x	x
	4	x	x
	5	x	x
	6	x	x

5 As shown above, when copper phthalocyanine dyes were employed, remarkable fading tendency was observed.

Examples 7 - 10

10 Four kinds of cyan ink were prepared in the same manner as in Examples 1 - 6, and by use of the respective inks of yellow, magenta and black similarly prepared, full color images were formed according to the same ink jet system as in Examples 1 - 6.

15 For examination of the color images obtained, each color chart sample was irradiated with xenon light in Ci35 produced by Atlas Co. for 50 hours. As the result, sharpness of the color image substantially unchanged, with lowering in density being very slight.

Ink composition of Example 7

20	Dye	X parts
	Diethylene glycol	30 parts
	N-methyl-2-pyrrolidone	10 parts
	Water	60 parts

Cyan ink...2 parts of the dye of the above formula 1-2
25 Magenta ink...2 parts of the dye of the above formula
2-1;

1 Yellow ink...2 parts of Nyrosan Yellow C-3GL (produced
by Sand);

Black ink...3 parts of the dye of the above formula 3-

1

5 Ink composition of Example 8

Dye	X parts
Diethylene glycol	30 parts
Glycerine	7 parts
Water	63 parts

10 Cyan ink...2 parts of the dye of the above formula 1-3

Magenta ink...2 parts of the dye of the above formula

2-2 ;

Yellow ink...2 parts of Direct Fast Yellow-GC(produced
by Hodogaya Kagaku Kogyo);

15 Black ink...3 parts of the dye of the above formula 3-

2.

Ink composition of Example 9

Dye	X parts
Polyethylene glycol (M.W. 300)	20 parts
Ethylene glycol	10 parts
N-methyl-2-pyrrolidone	10 parts
Water	60 parts

Cyan ink...2 parts of the dye of the above formula 1-6

Magenta ink...2 parts of the dye of the above formula

2-3 ;

25

Yellow ink...1.5 parts of Chuganol Fast Yellow

1 (produced by by Chugai Kasei) ;

Black ink...3 parts of the dye of the above formula 3-
3 ;

Ink composition of Example 10

5	Dye	X parts
	Triethanolamine	10 parts
	Triethylene glycol	10 parts
	Diethylene glycol	15 parts
	Water	65 parts

10 Cyan ink...2 parts of the dye of the above formula 1-
13 ;

Magenta ink...2 parts of the dye of the above formula
2-5 ;

Yellow ink...2 parts of Supracen Yellow GR (produced
by Bayer) ;

15 Black ink...3 parts of the dye of the above formula 3-
4 .

Comparative examples 7 - 10

Inks of four primary colors were formed in the
same manner as in Examples 7 - 10 except for using
20 copper phthalocyanine dye in place of the cyan dyes in
Examples 7 - 10, and full color images were formed
similarly and lightfastness tests were conducted
similarly. As the result, sharpness of the color
25 image was remarkably lowered, particularly fading of
the magenta color was remarkable, and the skin color

1 portion of human image was observed to be discolored
into green, with reddish color of color image being
lowered as a whole.

Example 11

5 By use of the four kinds of cyan ink used in
the above Examples 7 - 10, the following tests 1 - 3
were conducted giving good results in all of the
tests.

Test 1

10 Storability of ink for long term: when ink was
sealed in a glass vessel and stored at -30°C and 60°C
for 6 months, no precipitation of insoluble matter
was observed and there was also no change in physical
properties and tone of the solution.

15 Test 2

Ejecting stability: when continuous ejection
was performed at room temperature of 5°C and 40°C ,
respectively, recording of high quality could be
performed stably from the beginning to the end.

20 Test 3

Ejecting response: concerning intermittent
ejection at an interval of 2 seconds and ejection
after standing for 2 months, ejecting response was
examined, and the resulting recording was stable and
25 uniform without clogging at the orifice tip in
both cases.

1 Comparative example 11

Cyan inks were prepared according to the same method as in Example 1, except for performing particularly no purification treatment of free metals in the cyan dyes as described in Examples 7 - 10, and the above tests 1 - 3 were conducted. As the result, in test 1, precipitation of insoluble matter was observed after one month ink storage. Also, in test 2, it was frequently observed that the ink was not ejected, and the driving voltage was forced to be changed (voltage up). When the surface of the heat-generating head was observed by a microscope, brown precipitate was found to be deposited. Further, in test 3, clogging of the orifice occurred after standing for one month, whereby ejecting of ink was observed to be unstable.

The results of the above Example 11 and Comparative example 11 are shown in the following Tables.

20 Table 3

Cyan ink	I	<u>Example 11</u>		
		II1	II2	II3
Example 7	1.2	○	○	○
Example 8	0.5	◎	◎	◎
Example 9	0.8	◎	○	◎
Example 10	3.0	○	○	○

1

Comparative example 11

	<u>Cyan ink</u>	<u>I</u>	<u>II1</u>	<u>II2</u>	<u>II3</u>
	Example 7	50.3	x	x	△
	Example 8	23.0	△	△	x
5	Example 9	86.0	x	x	x
	Example 10	35.1	x	x	△

I...amount of free metals (ppm)

II...test results (test 1 - 3)

◎ : very good

10

○ : good

△ : slightly inferior

x : inferior.

The amount of free metal ions is measured by the following procedure: the ink was diluted with water to allow its concentration to be 1/10; the solution obtained was injected, together with an eluant (10 mM oxalic acid, 7.5 mM citric acid), into a column of ion chromatography for cation analysis; and then the quantitative analysis at a wavelength of 480 nm with the use of a color forming reagent was effected.

Examples 12 - 17

The following inks were prepared similarly as in Example 1.

Example 12

Ink composition:

25

Dye

X parts

1 Polyethylene glycol (M.W. 300) 10 parts
 Diethylene glycol 15 parts
 1,3-dimethyl-2-imidazolidinone 10 parts
 UV-ray absorber (sodium 2-hydroxy-4-
5 methoxybenzophenone-5-sulfonate) 2 parts
 Water 63 parts

Yellow ink: 2.5 parts of C.I. Acid Yellow 23 were used
 as the dye;

Cyan ink: 2 parts of the dye of the above formula (1)
10 were used as the dye (free nickel ion in
 the cyan ink=1.9 ppm);

Black ink: 3 parts of C.I. Direct Black 154 were used
 as the dye.

Example 13

15 Ink composition:

 Dye X parts
 Diethylene glycol 30 parts
 N-methyl-2-pyrrolidone 20 parts
 UV-ray absorber (potassium 2-hydroxy-4-
20 methoxybenzophenone-5-sulfonate) 1.5 parts
 Water 48.5 parts

Yellow ink: 2 parts of C.I. Acid Yellow 86 were used
 as the dye;

Magenta ink: 1.8 parts of C.I. Acid Red 32 were used
 the dye;

25 Cyan ink: 2.3 parts of the dye of the above formula

1 (3) were used as the dye (free nickel ion in
the cyan ink=0.5 ppm) ;

Black ink: 3.1 parts of C.I. Direct Black 19 were
used as the dye.

5 Example 14

Ink composition:

Dye	X parts
Triethylene glycol	30 parts
N-methyl-2-pyrrolidone	15 parts
UV-ray absorber (lithium 2-hydroxy-4- methoxybenzophenone-5-sulfonate)	2 parts
Water	53 parts

Yellow ink: 2.4 parts of C.I. Direct Yellow 98 were
used as the dye ;

15 Magenta ink: 2 parts of C.I. Acid Red 85 were used as
the dye ;

Cyan ink: 1.8 parts of the dye of the above formula
(6) were used as the dye (free nickel ion in
the cyan ink=0.8 ppm) ;

20 Black ink: 3.2 parts of C.I. Direct Black 17 were
used as the dye.

Example 15

Ink composition:

Dye	X parts
Polyethylene glycol (M.W. 200)	10 parts
Diethylene glycol	20 parts

1	Triethanolamine	10 parts
	UV-ray absorber (sodium 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sulfonate	2 parts
	Water	58 parts

Yellow ink: 2 parts of C.I. Direct Yellow 26 were used as the dye;

Magenta ink: 2.1 parts of C.I. Acid Red 115 were used as the dye;

10 Cyan ink: 1.9 parts of the dye of the above formula
(8) were used as the dye (free nickel ion in
the cyan ink=2.5 ppm);

Black ink: 3.2 parts of C.I. Food Black 2 were used
as the dye.

15 Example 16

Ink composition:

Dye	X parts
Diethylene glycol	30 parts
UV-ray absorber (potassium 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sulfonate	2.5 parts
Water	67.5 parts

**Yellow ink: 2 parts of C.I. Acid Yellow 61 were used
as the dye;**

25 **Magenta ink:** 2 parts of C.I. Acid Red 180 were used
as the dye;

1 Cyan ink: 1.8 parts of the dye of the above formula
(13) were used as the dye (free cobalt ion
in the cyan ink=2.9 ppm);

Black ink: 3 parts of C.I. Food Black 1 were used
5 as the dye.

Example 17

Ink composition:

Dye	X parts
Polyethylene glycol (M.W. 300)	20 parts
10 N-methyl-2-pyrrolidone	15 parts
UV-ray absorber (lithium 2,2'-dihydroxy- 4,4'-dimethoxybenzophenone-5- sulfonate	2 parts
Water	63 parts

15 Yellow ink: 2 parts of C.I. Acid Yellow 23 were used
as the dye;

Magenta ink: 2 parts of C.I. Acid Red 37 were used as
the dye;

Cyan ink: 2 parts of the dye of the above formula (14)
20 were used as the dye (free vanadium ion in
the cyan ink=1.5 ppm);

Black ink: 3.1 parts of C.I. Direct Black 32 were
used as the dye;

By use of the six sets of yellow, magenta,
25 cyan and black inks of the above Examples 12 - 17,
full color images were formed by means of a recording

1 device having an on-demand type multi-head (ejecting
orifice diameter 35 μ m, resistance value of heat-
generating resistor 50 ohm, driving voltage 30 V,
frequency 2 KHz) which performs recording by
5 generating liquid droplets by giving heat energy to
the ink in the recording head. For examination of
lightfastness, these images were irradiated with xenon
light in a weather-o-meter Ci-35 produced by Atlas Co
for 100 hrs. As the result, as is apparent from Table
10 4, sharpness of the full color images was found to be
substantially same as the original sharpness, with
lowering in density being also very slight.

Table 4

(Test results of lightfastness of Examples)

15	Example 12	◎
	Example 13	◎
	Example 14	◎
	Example 15	◎
	Example 16	○
20	Example 17	○
	◎ : very good, ○ : good, △ : slightly inferior, x : inferior	

Examples 18 - 23

By use of the six sets of yellow, magenta,
cyan and black inks of the above Examples 1 - 6, full
25 color images were formed by means of a recording

1 device having an on-demand type multi-head (ejecting
orifice diameter 35 μm , resistance value of heat-
generating resistor 50 ohm, driving voltage 30 V,
frequency 2 KHz) which performs recording by
5 generating liquid droplets by giving heat energy to
the ink in the recording head, and further the
respective full color images were coated respectively
according to the method as described below by use of
the six kinds of laminate samples (a - f) as shown
10 below in Table 5.

After a transparent paint with the composition
shown below was applied by use of a bar coater to a
PET (polyethyleneterephthalate) film having a
thickness of 100 μm to a dry film thickness of 15 to
15 50 μm , the coating was dried at 70 $^{\circ}\text{C}$ to form a
transfer layer on the PET film, thus giving transfer
peel type protective member (A - F). Next, the full
color image obtained as previously described was
laminated with the above protective member (A - F) by
20 means of a laminator (MS Lamipet L-230A, produced by
Meiko Shokai) so that the transfer layer may cover the
color image surface. Then, the PET film was peeled
off to obtain laminate color images of Examples 18 -
23.

25 Transparent paint (composition):

Dianal LR-216 (trade name, produced

1 by Mitsubishi Rayon, 40% toluene
 solution of an acrylic resin) 100 parts
 Tinuvin 328 (trade name, produced
 by Ciba-Geigy, UV-absorber) X parts

5 Table 5

Example	I	II	III	IV
18	A	a	1.6	15
19	B	b	1.2	15
10 20	C	c	1.2	30
21	D	d	1.2	50
22	E	e	1.6	30
23	F	f	3.3	10

15 I: protective member, II: laminate sample, III: amount
 of Tinuvin 328 added (parts), IV: dry film thickness
 (μm)

20 For examination of lightfastness of the
 laminate full color images of Examples 18 - 23, the
 images were irradiated with xenon light in a weather-o-
 meter Ci-35 produced by Atlas Co for 200 hrs. As the
 result, as is apparent from Table 6, sharpness of the
 full color images was found to be substantially same
 as the original sharpness, with lowering in density
 being also very slight.

25 Table 6

(Test results of light resistance of Examples)

- | | | |
|---|--------------------------------|---|
| 1 | Example 18 (Laminate sample a) | ◎ |
| | Example 19 (Laminate sample b) | ◎ |
| | Example 20 (Laminate sample c) | ◎ |
| | Example 21 (Laminate sample d) | ◎ |
| 5 | Example 22 (Laminate sample e) | ○ |
| | Example 23 (Laminate sample f) | ○ |

◎:very good, ○:good, △:slightly inferior, x:inferior

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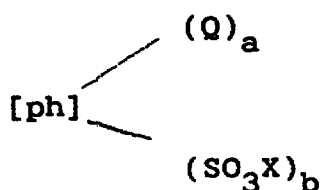
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CLAIMS:

1. An ink comprising a dye and a liquid medium for dissolving or dispersing the dye therein, wherein the dye is a metallophthalocyanine dye represented by the formula:



wherein:

[ph] represents a phthalocyanine skeleton having at its centre a metal of group II, IV, VII or VIII of the Periodic Table at its centre;

Q represents $-\text{SO}_2\text{OR}_1$ or $-\text{SO}_2\text{NR}_2\text{R}_3$, wherein:

R_1 represents a straight or branched or cyclic alkyl or aralkyl group;

R_2 and R_3 independently represent $-\text{H}$, $-(\text{CH}_2\text{CH}_2\text{O})_n$

$-\text{R}_4$, $-(\text{CH}_2\text{CHOH})_n - \text{R}_4$, $-(\text{CHCH}_3\text{CH}_2\text{O})_n - \text{R}_4$, or a

straight, branched or cyclic alkyl or aralkyl group, or $-\text{NR}_2\text{R}_3$ represents an amino acid salt

residue, n represents an integer of 0 to 12, and

R_4 represents H , CH_3 or CH_2OH ;



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a and b independently represent an integer from 0 to 4 provided that the relationship $2 < a + b < 4$ is satisfied; and

X represents an alkali metal or NH_4 ;

5 and wherein the ink contains free ions of the metal at a concentration of 15 ppm or less.

10 2. An ink according to claim 1, wherein the concentration of free metal ions in the ink is 3 ppm or less.

15 3. An ink according to claim 1 or 2, wherein the metallophthalocyanine is a nickel phthalocyanine, vanadium phthalocyanine or cobalt phthalocyanine.

4. An ink according to claim 1 or 2, wherein the metallophthalocyanine is any of the compounds of formula 1-1 to 1-16 mentioned in the description.

20 5. An ink according to any preceding claim, wherein the content of dye is 0.1 to 20 wt.% of the total weight of the ink.



6. An ink according to any preceding claim, wherein the ink is an aqueous ink.

5 7. An ink according to any preceding claim, further comprising a UV-absorber.

8. An ink according to claim 7, wherein the UV-absorber is a benzophenone, a benzotriazole, a cyanoacrylate, or a salicylic acid derivative.

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9. An ink according to claim 7 or 8, wherein the UV-absorber is dissolved in the ink.

15 10. An ink according to claim 9, wherein the UV-absorber is 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sulphonic acid, 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid or a salt of either of the above compounds with sodium, potassium or lithium, or is (2'-hydroxy-5'-methylphenyl) benzotriazole or (2'-hydroxyphenyl) benzotriazole.

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11. An ink according to any of claims 7 to 10, wherein the UV-absorber is present in an amount of 0.5 to 3 wt.% of the total weight of the ink.

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12. A cyan ink as claimed in any preceding claim.

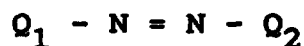


13. A cyan ink substantially as set forth in any of Examples 1 to 10 and 12 to 17.

5 14. The combination for use in forming a colour image of a cyan ink as claimed in claim 12 or 13 with at least one of a magenta ink and a black ink.

10 15. The combination of claim 14, wherein the magenta ink contains a monoazo dye.

16. The combination of claim 15, wherein the magenta ink contains a dye represented by the formula:



15 wherein Q_1 represents a substituted or unsubstituted phenyl or naphthyl group and Q_2 represents a substituted naphthyl group.

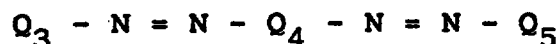
20 17. The combination of claim 16, wherein the magenta ink contains any of the dyes of formulae 2-1 to 2-10 mentioned in the description.

18. The combination of any of claims 14 to 17, wherein the magenta ink contains a UV-absorber.



19. The combination of any of claims 14 to 18, wherein the black ink contains a disazo dye.

20. The combination of claim 19, wherein the disazo dye is of the formula:



wherein Q_3 represents a substituted phenyl or naphthyl group, Q_4 represents a substituted phenylene or naphthylene group, and Q_5 represents a substituted naphthyl group.

21. The combination of claim 20, wherein the black ink contains any of the dyes of formulae 3-1 to 3-8 in the description.

22. The combination of any of claims 14 to 21, wherein the black ink contains a UV-absorber.

23. The combination of claims 18 or 22, wherein the UV-absorber is soluble in the ink.

24. The combination of claims 18, 22, or 23, wherein the UV-absorber is present in the magenta or in the black ink in an amount of 0.1 to 5% by weight based on the weight of the ink.



25. A method for forming a colour image which comprises applying imagewise to a substrate a combination of inks as claimed in any of claims 14 to 24.

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26. A method according to claim 25, wherein the inks are applied by ink jet printing.

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27. A method according to claim 25, wherein the inks are ejected by the action of heat.

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28. A method for forming a colour image which comprises applying imagewise to a substrate a plurality of inks including an ink as claimed in claim 12, wherein the colour image is coated with a transparent protective member containing at least a UV- ray absorber.
