

INK JET PRINTING METHOD

This invention relates to a method of thermal ink jet printing.

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Thermal ink jet recording systems comprise forming ink droplets by a system of heating an ink and utilizing the pressure developed thereby, and then depositing a portion or all of the ink droplets onto a recording material such as paper, etc., thereby making a recording. The known ink for use in ink jet recording systems includes solutions or dispersions of various water-soluble dyes or pigments in water or a liquid medium comprising water and a water-soluble organic solvent.

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1 It is needless to say that various properties are
required for the conventional ink as described above,
and the most important property is, among others, such
a liquid stability that neither clogging nor precipitation
5 takes place in a nozzle or orifice of the
recording apparatus during the recording with the ink,
or during interruptions of recording, or during a
prolonged intermission. In the ink jet system,
particularly an ink jet system based on a thermal energy,
10 the stability of the ink is particularly important,
because foreign matter is liable to deposit on the surface of
a thermal head due to changes in temperature. In the
case of the conventional ink, several additives are
required to satisfy various conditions such as ink
15 discharge conditions, a long term storage stability,
distinctness and density of an image during the recording,
surface tension, electrical properties, etc., or various
impurities are inevitably contained in the dyes. Thus,
there are various problems such as clogging in the
20 nozzle or orifice of an ink jet device, deposition on
the surface of a thermal head, precipitation during the
long term storage etc., which are reasons for delayed
spread of the ink jet recording system in spite of its

various distinguished characteristics.

5 An object of the present invention is to overcome the disadvantages of the prior art and provide a method of printing using in a thermal ink jet printer an ink with such stability that no clogging takes place in a nozzle, orifice, etc. during recording as well as during long term storage, or no deposition takes place particularly on the thermal head of an ink jet device
10 using thermal energy.

According to the present invention, there is provided a method of printing using in a thermal ink jet printer an ink comprising a water-soluble dye and
15 having a total concentration of iron and silicon at 9 ppm or less.

Preferably, the ink is prepared from a water-soluble dye having a total content of iron and silicon of 250
20 ppm or less.

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As a result of extensive studies to attain the said object, the present inventors have found that the commercially available dyes contain many impurities
5 (e.g. various organic and inorganic matters such as a dispersant, a levelling agent, etc.) beside the dyes themselves, and these impurities mainly cause the said problems. As a result of further studies of various influences by these impurities, the present inventors
10 have found that the largest cause for clogging in the nozzle or orifice, and precipitation during the preservation of ink, particularly deposition of foreign matter on the thermal head according to an ink jet system using thermal energy is iron and silicon
15 contained in the ink and the said various problems can be solved by using an ink free from such impurities, and have established the present invention.

The present invention will be described in detail below. The basic components of an ink for use in the
20 present invention are well known by themselves, and the dye is a water-soluble dye such as a direct dye, an acid dye, a basic dye, a reactive dye, etc. The dyes suitable as an ink for the ink jet recording system and satisfying the properties required for it, e.g. distinctness, water
25 solubility, stability, light fastness, etc. include, for example, C.I. Direct Black 17, 19, 32, 51, 71, 108, and 146; C.I. Direct Blue 6, 22, 25, 71, 86, 90, 106, and 199;

1 C.I. Direct Red 1, 4, 17, 28, and 83; C.I. Direct Yellow
12, 24, 26, 86, 98, and 142; C.I. Direct Orange 34, 39,
44, 46, and 60; C.I. Direct Violet 47, and 48; C.I.
Direct Brown 109; C.I. Direct Green 59; C.I. Acid Black
5 2, 7, 24, 26, 31, 52, 63, 112, and 118; C.I. Acid
Blue 9, 22, 40, 59, 93, 102, 104, 113, 117, 120, 167,
229, and 234; C.I. Acid Red 1, 6, 32, 37, 51, 52, 80,
85, 87, 92, 94, 115, 180, 256, 317, and 315; C.I. Acid
Yellow 11, 17, 23, 25, 29, 42, 61, and 71; C.I. Acid
10 Orange 7, and 19; C.I. Acid Violet 49; C.I. Basic Black
2; C.I. Basic Blue 1, 3, 5, 7, 9, 24, 25, 26, 28, and
29; C.I. Basic Red 1, 2, 9, 12, 13, 14, and 37; C.I.
Basic Violet 7, 14, and 27; C.I. Food Black 1, and 2,
etc. The foregoing examples of the dyes are particularly
15 preferable for the ink applicable to the present method
for recording, but the present invention will never be
limited to these dyes.

Generally, about 0.1 to about 20 % by weight of the
water-soluble dye is used in the conventional ink on the
20 basis of the total weight of ink. In the present invention,
the water-soluble dye can be used, of course, within the
said range, but it has been found by the present inventor
that even use of the water-soluble dye in an amount
over the said conventional range gives a better liquid
25 stability without any precipitation than that of the
conventional ink.

The solvent

1 for use in the ink according to the method of the present
invention is water or a mixture of water and a water-
soluble organic solvent. A particularly preferable
solvent in a mixture of water and a water-soluble organic
5 solvent, where the water-soluble organic solvent includes
a polyhydric alcohol having an effect on prevention of
an ink from drying, and the water is not the ordinary
water containing various ions, but preferably deionized
water. Examples of the water-soluble organic solvent
10 for use together with water includes alkyl alcohols having
1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol,
n-propyl alcohol, isopropyl alcohol, n-butyl alcohol,
sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol,
etc.; amides such as dimethyl formamide, dimethyl acetamide,
15 etc.; ketones or ketoalcohol such as acetone, diacetone
alcohol, etc.; ethers such as tetrahydrofuran, dioxane,
etc.; polyalkylene glycols such as polyethylene glycol,
polypropylene glycol, etc.; alkylene glycols whose
alkylene group has 2 to 6 carbon atoms, such as ethylene
20 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 glycol methyl (or
25 ethyl) ether, triethylene glycol monomethyl (or ethyl)
ether, etc.; N-methyl-2-pyrrolidone, 1,3-dimethyl-2-
imidazolidinone, etc. Among these many water-soluble

1 organic solvents, polyhydric alcohols such as diethylene glycol, etc., and lower alkyl ethers of polyhydric alcohols such as triethylene glycol monomethyl (or ethyl) ether, etc. are preferable.

5 Generally, the content of the water-soluble organic solvent in the ink is 0 to 95 % by weight, preferably 10 to 80 % by weight, and more preferably 20 to 50 % by weight on the basis of the total weight of ink.

10 The content of water depends on the species of the said solvent component, its composition or desired ink characteristics, and can be selected in a wide range, but is generally 10 to 100 % by weight, preferably 10 to 70 % by weight, and more preferably 20 to 70 % by weight on the basis of the total weight of ink.

15 The basic ink components used in the present invention are as described above, and the present invention is characterized in that the total content of iron and silicon contained in the ink is adjusted to 9 ppm or less. It is desirable that the iron content is
20 controlled to 4 ppm or less in the total content of iron and silicon.

25 As a result of extensive studies of the ink stability on the basis of the knowledge that, since the dyes so far used in the conventional ink are prepared for ^edyeing of fibers, the dyes contain various additives, such as a surfactant and a levelling agent as well as very many impurities such as sodium chloride, sodium sulfate, salts

1 of alkaline earth metals, etc., and these impurities
cause various troubles in the ink jet recording and
writing instruments, the present inventors have found
that the troubles can be solved to a considerable
5 degree by intensively removing these impurities from the
dyes to make the dyes of high purity for the ink, but
the deposition of foreign matters on a thermal head
cannot be fully prevented in the ink jet system,
particularly in the ink jet system using a thermal energy.
10 As a result of further detailed studies, the present
inventors have found by analysis of depositions that
the main components of the depositions are iron and
silicon, and further that the amount of depositions is
in good correlation with the total amount of iron and
15 silicon in the ink, and has established the present
invention. It is known that the commercially available
dyes contain a considerable amount (several tens to
several hundreds ppm) of iron and silicon.

A procedure for adjusting the content of iron and
20 silicon in the ink will be described in detail below.

First of all, sodium sulfate is added to an aqueous
dye solution at a desired concentration to salt out
the dye. Then, the deposited precipitates are recovered
by filtration, washed with a saturated solution of
25 sodium sulfate in pure water, and then dried. A
predetermined amount of the thus obtained dried solid
matters is dissolved in a water-soluble organic solvent,

1 and the resulting solution is filtered to obtain a
filtrate. In that case, any water-soluble organic
solvent can be used, so long as it can serve as a
poor solvent for sodium sulfate and as a good solvent
5 for the dye. A most suitable solvent can be selected
in view of the structure of a dye to be treated.
Usually, alcohols, glycols, and glycol ethers can
be preferably used as a solvent. The thus obtained
filtrate is left for 1 to 3 days, and then refiltered.

10 Then, a predetermined amount of water is added
to the filtrate, and the resulting mixture is stirred
and passed through a cation exchange resin layer.
Then, an additive is added thereto, if required, and the
mixture is stirred to prepare an ink. Then the
15 contents of iron and silicon in the ink are determined
by an atomic absorption spectrometer or an inductively
coupled plasma emission spectrometer to confirm
whether the total content of iron and silicon contained
is 9 ppm or less, and whether preferably the content
of iron is 4 ppm or less. The ink can be placed at
20 practical use, if the contents of iron and silicon are
satisfactory.

In the foregoing procedure, the initial salting-out
treatment is mainly to remove sodium chloride which is
25 a typical impurity contained in most of the commercially
available ordinary dyes, and the next treatment with the

1 water-soluble organic solvent is to remove sodium sulfate
originally contained as an impurity in the dye and the
sodium sulfate much added in the salting-out treatment.
The refiltration after the standing of the filtrate for
5 a long term is mainly to remove colloidal matters
containing iron and silicon in the solution. The
subsequent treatment with the cation exchange resin is
to remove the iron ions contained.

In the foregoing, one procedure for adjusting the
10 contents of iron and silicon in the ink has been described,
but the adjustment is not restricted thereto. That is,
any procedure can be effectively utilized, so long as
it can remove ionized iron or colloidal iron compounds,
silicon compounds, etc. For example, an procedure of
15 exposure to air, a coagulation-precipitation procedure
using a coagulant, a filtration procedure, a lime-
softening procedure, an electrolytic procedure, etc. can
be used.

As a contamination source of iron and silicon as
20 impurities, water to be used can be mentioned beside the
dye to be used. Contamination of iron and silicon can
be prevented by using treated water such as distilled
water, ion-exchanged water, or a mixture thereof as
water for the ink. Most contamination source of iron
25 and silicon is the dye to be used. Particularly when
the dye to be used is a commercially available product,
their contents are very high in the most cases.

1 In the foregoing, removal of iron and silicon
contained in the ink has been mainly described, but
actually it is the ordinary expedient to remove
various inorganic salts such as sodium chloride, sodium
5 sulfate, etc., or calcium, etc. together with the
removal of iron and silicon.

 The above embodiment of the treatment is described
referring to commercial dyes which contain a considerable
quantity of impurity. When the dye itself is highly
10 pure resulting from a pure starting material or when
synthesized dye product is purified, not all of the
above-mentioned treatments is needed, thus the treating
process may be advantageously simplified.

 A powder or water solution of the dye of high
15 purity may be used for ink without or optionally with
addition of an extra component as long as it satisfies
the requirement of the invention as to the concentration
of silicon and iron in the solution. For example: 5-30
weight % aqueous solution of the above-mentioned dye of
20 high purity will contain only approximately 10-75 ppm
of impurity, and is very useful as a constituent for
an aqueous dye solution for ink.

 The aqueous dye solution mentioned above may be
employed as it is without adding a solvent, provided that
25 the solution satisfies requirement for an ink such as
concentrations of a dye, iron and silicon, etc.

 The basic ink composition

1 used in the method of the present invention is as described above.

In addition, various so far known dispersants, surfactants, viscosity-controlling agents, surface
5 tension-controlling agents, etc. can be added thereto, if required, and for example, viscosity-controlling agents such as polyvinyl alcohol, cellulose, water-soluble resin, etc.; various cationic, anionic or non-ionic surfactants; surface tension-controlling agents
10 such as diethanolamine, triethanolamine, etc.; pH-controlling agents such as buffer solution; antifungal, etc. can be used.

To prepare an ink for use in ink jet system of a type of injecting the ink under an action of thermal
15 energy, thermal properties, for example, specific heat, coefficient of thermal expansion, thermal conductivity, etc. of the ink may be adjusted.

The thus obtained ink for use in the method of the present invention is completely free from the troubles
20 of the prior art and is distinguished and well balanced, as such, in the recording characteristics in the ink jet system (signal response, stability of liquid droplet

1 formation, discharging stability, continuous and prolonged
recordability, and stability of ink discharging after
prolonged interruption in working), storage stability,
fixing property to a recording material, light
5 fastness of recorded image, resistance to weathering,
etc. and is also useful as an ink for ink jet recording
of various other types or as an ink for writing
instruments.

10

The present invention will be described in detail
15 below, referring to Examples, where parts or % is by
weight.

Example 1

Preparation of ink

At first, an aqueous 10 % solution of commercially
20 available dye, "Special Black 7984" (made by Bayer Co.)
was prepared, and sodium sulfate was added to the
aqueous solution. The solution was stirred to salt out
the dye. The precipitates were recovered by filtration,
washed with a saturated solution of sodium sulfate in
25 pure water, and dried. The dried solid matters were
weighed out to make the dye concentration of 3 % in
the resulting ink, and dissolved in a 3 : 1 mixture of

1 ethylene glycol and N-methyl-2-pyrrolidone. Then, the
resulting solution was filtered under pressure through
a Teflon^(RTM) filter having an average pore size of 1 μm , and
the filtrate was sealed in a plastic container and left
5 in a cold dark place for three days. Then, the filtrate
was refiltered through the Teflon filter having an
average pore size of 1 μm . Then, 60 parts of water
was added to 40 parts of the thus obtained filtrate
with stirring to make an ink. Then, the ink was passed
10 through a layer of cation exchange resin C-464 made by
Sumitomo Kagaku Kogyo K.K., Japan, and then the ink was
adjusted to pH 9.8 with an aqueous 1N sodium hydroxide
solution. Total content of iron and silicon in the ink
was determined by an inductively coupled plasma emission
15 spectrometer and found to be 8.6 ppm (iron content: 3.6
ppm). The following items T1 - T5 of the thus prepared
ink were investigated in a recording apparatus with a
multi-head of on-demand type of giving a thermal
energy to an ink in the recording head to generate liquid
20 droplets and to conduct recording (discharging orifice
diameter: 35 μm ; resistance of exothermic resistor:
150 ohms, driving voltage: 30 volts, frequency: 2KHz),
and were found good throughout.

(T1) Long term storage stability: The ink was
25 sealed in a plastic film bag and preserved at -30°C and
 60°C for 6 months, separately. No insoluble precipitates
were found and no changes in the physical properties and

1 color tone of the ink were found even thereafter.

(T2) Discharging stability: Discharging was carried out continuously for 24 hours in the respective atmospheres at room temperature, 5°C and 40°C, and
5 high quality stable recording was obtained in any of the atmospheres.

(T3) Discharge response: Intermitted discharging of the ink at intervals of 2 second and discharging of the ink 2 month after standing were investigated. Stable
10 uniform recording was obtained without any clogging at the orifice edge in any of the dischargings.

(T4) Quality of recorded image: The images recorded on the recording materials listed in Table 1 had a high optical density and a good distinctness. The percent
15 decrease in the density was less than 1 % 6 months after the exposure to room light.

(T5) Fixing property on various recording materials: After 15 seconds from printing on the recording materials in Table 1, the prints were rubbed with fingers to
20 determine the presence of image aberration, spread, etc. Distinguished fixing property was obtained on any of the recording materials without image aberration, spreading, etc.

Examples 2 - 5

25 Inks were prepared with the commercially available dyes given in Table 2 in the same manner as in Example 1, and T1 to T5 of the inks were investigated in the same

1 manner as in Example 1. All the inks had good results
as in Example 1.

Example 6

With the ink of Example 2 as yellow ink, the ink
5 of Example 3 as Magenta ink, the ink of Example 4 as cyan
ink, and the ink of Example 5 as black ink, full color
photographs were reproduced in the same ink jet recording
apparatus as used in Examples 2 to 5. The resulting
images were very distinct in the individual colors and
10 had a good color reproduction.

Comparative Example

An aqueous 10% solution of dye "Special Black 7984"

1 shown in Example 1 was prepared, and sodium sulfate was
added to the aqueous solution with stirring to salt out
the dye. Then, the precipitates were recovered by
filtration, washed with a solution of sodium sulfate in
5 pure water, and dued. A predetermined amount of the
dried solid matters were weighed out to make the dye
concentration of 3 % in the resulting ink, and dissolved
in a 3 : 1 mixture of ethylene glycol and N-methyl-2-
pyrrolidone. Then, the solution was filtered under
10 pressure through a Teflon filter having an average pore
size of 1 μ m, and 60 % of water was added to 40 % of the
filtrate with stirring to make a sample ink.

The iron content of the ink was determined by an
atomic absorption spectrometer and found to be 6.1 ppm.
15 The silicon content was determined by an inductively
coupled plasma emission spectrometer and found to be
4.5 ppm. T1 to T4 of the ink were determined in the
same manner as in Example 1. Precipitation of insoluble
matters was observed one month after the ink storage.
20 In T2, the ink often failed to be discharged, and
the driving voltage was forced to be changed (to increase
the voltage). Observation of the thermal head surface
by a microscope revealed deposition of brown precipitates.

In T3, the orifice was clogged after being left
25 standing for one month, and the ink discharging was
found unstable. Ink of the same dye obtained in the
same manner as in Example 1, excluding only the standing

1 treatment, and ink of the same dye obtained in the same
manner as in Example 1 excluding only the cation exchange
resin treatment were subjected to determination of total
content of iron and silicon in the individual inks, and
5 it was found that the total content of the former was
9.4 ppm, and that of the latter was 9.9 ppm. T1 to T5
of these inks were likewise investigated. Poor results
were obtained, as compared with those of Example 1 with
full treatments.

10 Table 1

<u>Recording material</u> (Trade Name)	<u>Classification</u>	<u>Manufacturer</u>
Ginkan	High quality paper	Sanyo-Kokusaku Pulp K.K.
Seven-Star	High quality paper	Hokuetsu Seishi K.K.
15 Hakubotan	Medium quality paper	Honshu Seishi K.K.
Toyo Filter Paper No.4	No-sized Paper	Toyo Filter Paper K.K.

Table 2

<u>Ex.No</u>	<u>Dye</u>	<u>Content of iron & silicon in ink</u>
20 2	Water Yellow 6 (made by Orient Kagaku Kogyo K.K.)	7.2 ppm (Fe: 3.5 ppm)
3	Chuganol Fast Red 3B (made by Chugai Kasei K.K.)	6.8 ppm (Fe: 3.1 ppm)
4	Kayarus Turquoise Blue GL (made by Nihon Kayaku K.K.)	8.4 ppm (Fe: 4.0 ppm)
25 5	Supranol Fast Black VLG (made by Bayer Co.) ("Supranol" is a Trade Mark)	7.9 ppm (Fe: 3.8 ppm)

1 Example 87

1. Purification of amines as a starting material:

173 g of sulfanilic acid was added into 1.7 l of distilled water, and heated to 80°C to make a solution. Then the solution was filtered at that temperature. The filtrate was left stand to cool to room temperature and the resulting precipitate was collected by filtration and washed with 0.3 l of distilled water to obtain 152 g of purified sulfanilic acid (in terms of the pure compound).

233 g of 1-aminonaphthalene-7-sulfonic acid was added to 2.2 l of distilled water, and the solution was treated in the same manner as described above to obtain 200 g of purified cake (in terms of a pure product).

319 g of 1-hydroxy-7-aminonaphthalene-3,6-disulfonic acid was added to 3.2 l of distilled water, and the solution was treated in the same manner as described above to obtain 255 g of purified cake (in terms of a pure product).

20

2. Synthesis of dyes:

(1) Preparation of first diazo solution:

17.3 g of the aforementioned purified sulfanilic acid and 25 ml of 35 % hydrochloric acid were added to 340 ml of distilled water, and agitated for 3 hours to obtain a homogeneous slurry. Thereto 250 g of ice prepared from distilled water was added and cooled to 3°C. To the slurry,

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1 an aqueous solution of 7.3 g of sodium nitrite in 73 ml of
distilled water was added. The solution was stirred
at 3°C for one hour to be diazotized, followed by
addition of 2 g of sulfamic acid to decompose the
5 remaining sodium nitrite, thus giving first diazo
solution.

(2) First coupling:

22.3 g of the above-mentioned purified 1-amino-
naphthalene-7-sulfonic acid was added to 670 ml of
10 distilled water, and stirred for 2 hours to give a
homogeneous slurry. Thereto added were 300 g of ice
prepared from distilled water, the first diazo solution
described above and 20 ml of 25 % sodium hydroxide, and
the mixture was stirred at 0 - 3°C and at pH 2 - 3 for
15 15 hours to carry out coupling reaction. Then 200 g of
sodium chloride (Japanese pharmacopoeia grade) was added
to salt out the monoazo compound, which was collected by
filtration and washed with 500 ml of 10 % solution of
sodium chloride (Japanese pharmacopoeia grade), and
20 dried to give 35.6 g of monoazo compound shown below.

Hereinafter "water" means distilled water,
"ice" means ice prepared from distilled water, and
"sodium chloride" means the one of the Japanese pharma-
copoeia grade.

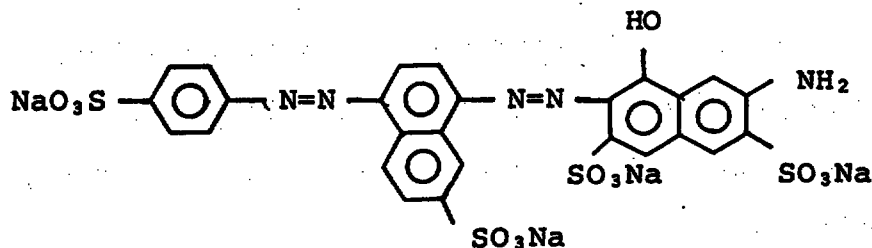
25 (3) Preparation of second diazo solution:

The entire monoazo compound obtained according to
item (2) above was added to 800 ml of 5 % hydrochloric

1 acid and stirred for 5 hours to give a homogeneous slurry,
800 g of ice was added thereto and cooled to 3°C. To this
slurry, a solution of 7.3 g of sodium nitrite in 73 ml
of water was added. Subsequently, it was diazotized with
5 stirring at 3°C for 10 hours and 2 g of sulfamic acid
was added to decompose the remaining sodium nitrite to
obtain second diazo solution.

(4) Second coupling:

31.9 g of purified 1-hydroxy-7-amino-naphthalene-
10 3.6-disulfonic acid prepared as above was added to 900
ml of water. To this solution, 1200 g of ice, the
second diazo solution obtained according to item (2)
above and 100 ml of 25 % sodium hydroxide solution were
added and subjected to coupling reaction at pH 8 - 10,
15 and at a temperature 2 - 5°C. After stirring for 5 hours
at the same temperature and pH, 400 g of sodium chloride
was added to salt out a compound, which was filtered and
washed with 300 ml of 10 % aqueous sodium chloride
solution, and dried to give 59.2 g of a disazo dye of the
20 formula below:



25 The contents of iron and silicon in the above disazo
dye were determined as being 35 ppm and 27 ppm respectively.

1 3. Preparation of ink:

The desired quantity of disazo dye prepared according to item (2) above was weighed out so as to give the dye concentration of 3 % in the ink, and dissolved in a mixed solution of ethylene glycol and N-methyl-2-pyrrolidone (mixing ratio: 3 to 1), and thereto 1.5 times weight of water based on this solution was added to obtain ink. The total content of iron and silicon was 1.96 ppm (1.15 ppm iron, and 0.81 ppm silicon). The test T1 to T5 were performed in the same manner as in Example 1 by using the ink prepared above. The results were all satisfactory as Example 1.

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CLAIMS:

1. A method of printing using in a thermal ink jet printer an ink comprising a water-soluble dye and having a total concentration of iron and silicon at 9 ppm or less.
2. A method according to claim 1, wherein the concentration of iron in the ink is 4 ppm or less.
3. A method according to claim 1, wherein the concentration of the water-soluble dye is from 0.1 to 20 % by weight.
4. A method according to any preceding claim, wherein the ink comprises water as a solvent.
5. A method according to claim 4, wherein the water is deionized water.
6. A method according to claim 4 or 5, wherein the ink also comprises a water-soluble organic solvent.
7. A method according to claim 6 wherein the water-soluble organic solvent is polyhydric alcohol.



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8. A method according to any preceding claim, wherein the ink is prepared from a water-soluble dye having a total content of iron and silicon of 250 ppm or less.

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9. A method according to Claim 1, using an ink substantially as described in any of the Examples.
