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Recording Liquid and Recording Method Using
the Same

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a recording liquid (hereinafter referred to as an ink) for recording on a recording medium (e.g. a paper, a resin film) by means of ink jet recording or a writing tool (e.g. a fountain pen, a felt pen), as well as to a recording method using the recording liquid.

Description of the Invention

Ink jet recording is a recording method wherein an ink is ejected by an appropriate ejecting mechanism to form ink droplets and a part or all of the droplets are allowed to deposit on a recording medium such as a paper or the like to conduct recording. As the ink used in ink jet recording, there are known and being used inks obtained by dissolving or dispersing various water-soluble dyes or pigments in water or a liquid medium consisting of water and a water-soluble organic solvent.

Similar inks may be used for writing tools such as fountain pens, felt pens, ball pens and the like.

As the recording medium on which recording is

1 made with the above inks, there are being used paper,
converted paper, surface-treated plastic films, etc.

Such inks should have properties of water
resistance, light resistance, storage stability (no
5 precipitate formation during storage) and the like.

A number of water-soluble dyes for these
inks are known. Two or more of water-soluble dyes
are used in combination when desired ink properties
cannot be achieved with a single dye.

10 The use of at least two water-soluble dyes in
combination gives desired properties to the ink.
However, it has happened frequently that when such an
ink is used for recording on general office use paper
such as a notebook, a reporting paper, a copying
15 paper, a letter paper and the like, as compared with
the case where an ink containing a single dye is
used, the peripheral areas of ink dots get blurred and
the recorded image becomes unclear as a whole.

The present inventor made extensive research
20 on the cause of the above phenomenon, and found that
the recorded image becomes unclear as a whole when a
plurality of dyes used in combination exhibit
different tones and moreover have the different
affinity for cellulose fiber of recording paper from
25 each other.

That is, when a dye with higher affinity and
a dye with lower affinity is used in combination,

1 they cause fine separation from each other on the
cellulose of the paper and the different tones of
individual dyes appear separately on the paper, making
the image unclear.

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SUMMARY OF THE INVENTION

An object of the present invention is to
provide a recording liquid which has remedied the
above mentioned drawbacks of the prior art and can give
10 a recorded image of fine color and excellent clearness
particularly on papers whose fibers are exposed at the
surface (e.g. a reporting paper, a copying paper), as
well as a recording method using said recording liquid.

According to one aspect of the present
15 invention, there is provided a recording liquid
containing a plurality of water-soluble dyes, character-
ized in that said water-soluble dyes give a tone
satisfying the following formula (I) and have a
chromatographic characteristic satisfying the following
20 formula (II):

$$0 \leq \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2} \leq 10 \quad (I)$$

$$0 \leq \Delta R_f \leq 0.2 \quad (II)$$

In the formula (I), Δa^* and Δb^* represent
respectively a difference of a^* or b^* between any two
25 dyes selected from said plurality of dyes in
CIE- $L^*a^*b^*$, and ΔR_f represents a difference
of flow rate R_f in paper chromatography between

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the two dyes when the recording liquid contains only two dyes or between the dyes having the highest and the lowest flow rates when the recording liquid contains three or more dyes. The term "CIE 1976 (L*a*b*)" is an abbreviation of CIE (Commission Internationale de L'Eclairage) 1976 (L*a*b*) colour space.

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According to another aspect of the present invention, there is also provided a recording method wherein recording is conducted by depositing droplets of a recording liquid onto a recording medium, the recording liquid contains a plurality of water-soluble dyes; that the water-soluble dyes give a tone satisfying the following formula (I) and have a chromatographic characteristic satisfying the following formula (II); and that the recording material contains a cellulose fiber exposed at the surface of the recording medium.

$$0 \leq \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2} \leq 10 \quad (I)$$

$$0 \leq \Delta R_f \leq 0.2 \quad (II)$$

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be described in more detail.

The ink of the present invention generally comprises at least two water-soluble dyes, a liquid medium for dissolving or dispersing these dyes and, as necessary, appropriate additives. The water-soluble dyes are required to have similar tones and similar chromatographic characteristics.

In the present invention, the tone of a dye is represented by the a^* and b^* of the dye defined by the CIE 1976 (L^* , a^* , b^*) space.

1 In the present invention, the chromatographic
characteristic of a dye is represented by a flow rate
of the dye measured using the following paper
chromatography procedure. The object of the present
5 invention can be achieved by combined use of dyes
which are similar to each other in this flow rate.

The flow rate of a water-soluble dye is
measured as follows.

A dye is dissolved in a water/diethylene glycol
10 (55/45 by volume) mixed solvent at a concentration of
5 % by weight to prepare a test solution. 2 μ l of
this test solution is charged to the lower end of a
piece of filter paper [Toyo Filter Paper No. 50
(trade name), manufactured by Toyo Roshi K.K.]. Then,
15 development is effected for a predetermined length of
time according to an ordinary method by using the above
mixed solvent as a developer. Thereafter, the
development distance A of the developer from the
charge point as well as the flow distance B of the dye
20 from the charge point is measured, and their ratio
B/A (= Rf) is calculated. This Rf is defined as the
flow rate of the dye.

The present inventor investigated the
chromatographic characteristics of various water-
25 soluble dyes on the basis of the flow rate defined
above, and found that when two or more water-soluble
dyes having a difference of flow rate of greater than

1 0.2 are used in combination to prepare an ink and
 recording is made with the ink on a recording material
 of paper type, the image obtained is always blurred at
 the peripheries and accordingly unclear.

5 The afore-mentioned difference of flow rates
 refers to the one between the two dyes used or the
 ones between the highest and the lowest flow rates
 among three or more dyes used in combination.

10 The study by the present inventor on various
 combinations of a number of dyes revealed that a
 clear image having a desired tone can be formed only
 when the dyes having similar tones and similar
 chromatographic characteristics, i.e., the dyes
 satisfying both of the formulas (I) and (II) shown
 15 above are used in combination.

A combination of dyes which are similar to
 each other only in tone or in chromatographic character-
 istic is incapable of giving a fully satisfactory
 image.

20 A plurality of water-soluble dyes used in
 combination in the present invention may be any water-
 soluble dyes used in conventional inks. The examples
 are acid dyes such as

	C.I. Acid Black 24	(a*=2.0, b*=2.0, Rf=0.93)
25	C.I. Acid Black 26	(2.3 4.8 0.90)
	C.I. Acid Black 52:1	(4.2 4.7 0.97)
	C.I. Acid Black 107	(0.6 3.4 0.85)

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1	C.I. Acid Black 110	(a*=4.4, b*=11.9, Rf=0.86)
	" 139	(4.1 5.3 0.90)
	C.I. Acid Yellow 23	(-4.2 42.7 0.90)
	" 29	(2.0 42.4 0.82)
5	" 38	(3.7 43.4 0.85)
	" 65	(0.4 49.2 0.85)
	C.I. Acid Red 27	(31.0 5.0 0.91)
	" 35	(51.4 8.0 0.95)
	" 42	(40.1 7.6 0.93)
10	" 106	(43.9 5.2 0.99)
	" 122	(53.3 8.7 0.98)
	" 131	(37.8 19.8 0.96)
	" 145	(39.2 21.0 0.92)
	" 161	(40.7 3.7 0.86)
15	" 276	(51.8 9.5 0.74)
	" 128	(33.8 1.6 0.68),

and direct dyes such as

	C.I. Direct Black 19	(a*=0.6, b*=-0.8, Rf=0.77)
	" 154	(0.7 1.1 0.72)
20	C.I. Direct yellow	
	" 12	(15.2 31.8 0.87)
	" 86	(-4.6 59.7 0.82)
	" 142	(-10.4 57.4 0.76)
	C.I. Direct Blue 86	(-17.8 -28.5 0.86)
25	" 199	(-15.94 -32.97 0.84)

The dyes for combination is selected from the above dyes and mixed such that the tones and

1 chromatographic characteristics of the combined dyes
satisfy the Formula (I) and (II). The water-soluble
dyes used in the present invention are not limited to
those enumerated above, but any dyes may be used as
5 long as their color tones and the chromatographic
characteristics are close to each other.

These water-soluble dyes are used in the
present invention in a total amount of ordinarily
about 0.5 to 30 % by weight, more preferably about 1
10 to 10 % by weight based on the ink.

The solvent used in the ink of the present
invention is water or a mixed solvent comprising water
and a water-soluble organic solvent. A mixed solvent
is particularly preferred which contains, as the
15 water-soluble organic solvent, a polyhydric alcohol
effective for retarding the ink drying.

As water, deionized water is preferred to
ordinary water containing various ions.

As the water-soluble organic solvent used
20 together with water, there may be mentioned, for
example, alkyl alcohols of 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 and the like;
25 amides such as dimethylformamide, dimethylacetamide
and the like; ketones or ketoalcohols such as acetone,
diacetone alcohol and the like; ethers such as

1 tetrahydrofuran, dioxane and the like; polyalkylene
glycols such as a polyethylene glycol, a polypropylene
glycol and the like; alkylene glycols having 2 to 6
carbon atoms such as ethylene glycol, propylene
5 glycol, butylene glycol, triethylene glycol, 1,2,6-
hexanetriol, thiodiglycol, hexylene glycol, diethylene
glycol and the like; lower alkyl ethers of polyhydric
alcohols such as glycerine, ethylene glycol methyl (or
ethyl) ether, diethylene glycol methyl (or ethyl)
10 ether, triethylene glycol monomethyl (or monoethyl)
ether and the like; N-methyl-2-pyrrolidone; 1,3-
dimethyl-2-imidazolidinone; and so forth. Of these,
polyhydric alcohols (e.g. diethylene glycol) and
lower alkyl ethers of polyhydric alcohols [e.g.
15 triethylene glycol monomethyl (or monoethyl) ether]
are preferred.

The content of the water-soluble organic
solvent in the ink is ordinarily 0 to 95 % by weight,
preferably 10 to 80 % by weight, more preferably 20
20 to 50 % by weight based on the total weight of the
ink.

The content of water in the ink may vary
widely depending upon the type and composition of the
water-soluble organic solvent, and the properties of
25 the ink. It is ordinarily 10 to 90 % by weight,
preferably 10 to 70 % by weight, more preferably
20 to 70 % by weight based on the total weight of the

1 ink.

The ink of the present invention is basically constituted as described above. The ink may further contain, as necessary, conventionally known additives
5 such as a dispersant, a surfactant, a viscosity-controlling agent, a surface tension-controlling agent and the like.

These additives include, for example, viscosity-controlling agents such as a polyvinyl
10 alcohol, a cellulose, a water-soluble resin and the like; surfactants of cationic, anionic or nonionic type; surface tension-controlling agents such as diethanol amine, triethanol amine and the like; buffer solutions as a pH-controlling agent; and antiseptics.

15 Further, a resistivity-adjusting agent such as lithium chloride, ammonium chloride, sodium chloride and other inorganic salts may be added to an ink formulation which is electrified in the ink jet printing process. When the ink of the present
20 invention is used in such ink jet recording as the ink is ejected by the action of thermal energy, the ink may be controlled in thermal properties (e.g. specific heat, thermal expansion coefficient, thermal conductivity).

25 The drawbacks of the prior art are sufficiently remedied in the ink of the present invention as describes above. Therefore, when the present ink is

1 used for recording on various recording materials, for
example, those of paper type whose cellulose is
exposed at the surface, by means of ink jet recording
or an ordinary writing tool, a mixed tone of the two
5 or more water-soluble dyes contained in the ink can
be reproduced on the recording materials in such an
extent that the reproduced tone has no practical
problem. Hence, a clear, high contrast, high quality
image of excellent light resistance and water
10 resistance can be obtained not only in ordinary
recording using a black ink of the present invention
but also in full color recording using a plurality of
color inks of the present invention.

In preparation of conventional inks, attention
15 has been paid only to color mixing between the water-
soluble dyes to be jointly used in the inks. As a
result, a desired color tone of ink has been achieved
but it has been difficult to reproduce it on recording
materials, particularly those whose cellulose are
20 exposed at the surface. In contrast, in preparation
of the present ink, in addition to the color mixing
between the dyes to be jointly used in the ink, a new
criterion of chromatographic characteristics of these
dyes has been employed. This has sufficiently removed
25 the drawbacks of the prior art.

The present invention will be described more
specifically below by way of Examples, Comparative

1 Examples and Application Example. Parts or % in the following is on weight basis unless otherwise specified.

5 Examples 1 to 5 and Comparative Examples 1 to 2 :

The components of the following composition were stirred to dissolve the water-soluble dyes. The resulting solution was filtered to remove the insolubles, whereby five inks of the present invention and two inks of Comparative Examples were prepared.

The values in parentheses given to each dye refer to the tone and flow rate of the dye.

Example 1

15	C.I. Acid Black 107	2.5 parts
	(a*=0.6, b*=3.4, Rf=0.85)	
	C.I. Acid Black 24	2.5 parts
	(a*=2.0, b*=2.0, Rf=0.93)	
	Diethylene glycol	30 parts
20	Deionized water	65 parts

Example 2

	C.I. Acid Yellow 29	2.5 parts
	(a*=2.0, b*=42.4, Rf=0.82)	
25	C.I. Acid Yellow 38	2.5 parts
	(a*=3.7, b*=43.4, Rf=0.85)	
	Diethylene glycol	30 parts

1 Deionized water 65 parts

Example 3

C.I. Acid Red 106 2.5 parts
 5 (a*=43.9, b*=5.2, Rf=0.99)
 C.I. Acid Red 161 2.5 parts
 (a*=42.7, b*=3.7, Rf=0.86)
 Diethylene glycol 30 parts
 Deionized water 65 parts

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Example 4

C.I. Acid Red 145 2.5 parts
 (a*=39.2, b*=21.0, Rf=0.92)
 C.I. Acid Red 131 2.5 parts
 15 (a*=37.8, b*=19.8, Rf=0.96)
 Diethylene glycol 30 parts
 Deionized water 65 parts

Example 5

20 C.I. Acid Black 26 2.0 parts
 (a*=2.3, b*=4.8, Rf=0.90)
 C.I. Acid Black 52:1 1.5 parts
 (a*=4.2, b*=4.7, Rf=0.97)
 C.I. Acid Black 139 1.5 parts
 25 (a*=4.1, b*=5.3, Rf=0.90)
 Diethylene glycol 30 parts
 Deionized water 65 parts

1 Comparative Example 1

	C.I. Acid Black 24	2.5 parts
	(a*=2.0, b*=2.0, Rf=0.93)	
	C.I. Acid Black 110	2.5 parts
5	(a*=4.4, b*=11.9, Rf=0.86)	
	Diethylene glycol	30 parts
	Deionized water	65 parts

Comparative Example 2

10	C.I. Acid Black 24	2.5 parts
	(a*=2.0, b*=2.0, Rf=0.93)	
	C.I. Acid Black 26	2.5 parts
	(a*=0.7, b*=1.1, Rf=0.72)	
	Diethylene glycol	30 parts
15	Deionized water	65 parts

Using the above prepared inks of Examples and Comparative Examples, recording was conducted on the following various recording materials by means of a recording apparatus of on-demand type recording head (PJ-1210, manufactured by CANON K.K.) wherein inks were to be discharged by a piezo vibrator. With the inks of the present invention, there was no separation of water-soluble dyes from each other on the recording materials; ink tones could be reproduced; and clear images of excellent color could be obtained. Meanwhile, with the inks of Comparative Examples, ink tones could

1 not be reproduced and unclear images were obtained.

Recording materials

- 3 (1) Ginwa (trade name) (high quality paper,
manufactured by Sanyo-kokusaku Pulp Co., Ltd.)
- (2) Seven Star (trade name) (high quality paper,
manufactured by Hokuetsu Paper Mills, Ltd.)
- (3) Hakubotan (trade name) (medium quality paper,
manufactured by Honshu Paper Co., Ltd.)
- 10 (4) Toyo Roshi No. 4 (trade name) (non-sized paper,
manufactured by Toyo Roshi K.K.)

Each of the inks of Examples and Comparative
Examples was charged into a felt pen and recording was
conducted on papers with these pens. In the case of
15 the inks of the present invention, no color separation
on paper occurred and clear images of the same tones
as those of the inks were obtained. In the case of
the inks of Comparative Examples, separation of dyes
from each other occurred on the papers; the ink tones
20 could not be reproduced; and the images were unclear.

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1 CLAIMS

1. A recording liquid containing a plurality of water-soluble dyes, said water-soluble dyes giving
5 a tone satisfying the following formula (I) and having a chromatographic characteristic satisfying the following formula (II):

$$0 \leq \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2} \leq 10 \quad (I)$$

$$0 \leq \Delta Rf \leq 0.2 \quad (II)$$

10 wherein (I), Δa^* and Δb^* represent respectively a difference in a^* and b^* between any two dyes selected from said plurality of dyes in CIE-L*a*b*, and ΔRf represents a difference of Rf value in paper chromatography
15 between the two dyes when the recording liquid contains only two dyes or between the dyes having the highest and the lowest flow rates when the recording liquid contains three or more dyes.

2. A recording liquid according to Claim 1,
wherein the content of the dyes is in the range of
from 0.5 to 30 % by weight based on the total weight
20 of the recording liquid.

3. A recording liquid according to Claim 1,
wherein said recording liquid further contains water
and a water-soluble organic solvent as liquid media
25 for dissolving or dispersing the dyes.

4. A recording method wherein recording is



- 1 conducted by depositing droplets of a recording liquid
 onto a recording medium, said recording liquid
 containing a plurality of water-soluble dyes; the
 water-soluble dyes giving a tone satisfying the
 5 following formula (I) and having a chromatographic
 characteristic satisfying the following formula (II);
 and the recording medium containing a cellulose fiber
 exposed at the surface of the recording material:

$$0 \leq \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2} \leq 10 \quad (I)$$

10 $0 \leq \Delta R_f \leq 0.2 \quad (II)$

- wherein (I), Δa^* and Δb^* represent respectively a
 difference of a^* or b^* between any two dyes selected
 from said plurality of dyes in CIE- $L^*a^*b^*$, and ΔR_f
 represents a difference of R_f value in paper
 15 chromatography between any two dyes selected from said
 plurality of dyes.

5. A recording method according to Claim 4,
 wherein the content of the dyes in the recording liquid
 20 is in the range of from 0.5 to 30 % by weight based
 on the total weight of the recording liquid.

6. A recording method according to Claim 4,
 wherein the recording liquid contains water and a
 25 water-soluble organic solvent as liquid media for
 dissolving or dispersing the dyes.



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7. An ink, substantially as described with reference to any of Examples 1 to 5.



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