

TRISAZO COMPOUND AND RECORDING LIQUID CONTAINING THE SAMEFIELD OF THE INVENTION

The present invention relates to novel water-soluble trisazo compounds which can be used either as blue to black dyes or as blue to green dyes. The present invention also relates to recording liquids containing such water-soluble trisazo compounds. More specifically, the present invention relates to novel naphthalene trisazo dyes suitable for use in recording liquids, novel recording liquids containing said dyes, particularly ones which are suitable for use in a recording system wherein recording is performed by ejecting recording liquid droplets through fine spouts (discharging orifices) on the recording head, and a recording method employing such recording liquids.

BACKGROUND OF THE INVENTION

For recording on recording media such as papers, etc., by writing instruments (e.g., a fountain pen, a felt pen, etc.), there have hitherto been used inks, which are solutions of various dyes dissolved in water or organic solvents.

It is also known that in a so-called ink-jet recording system wherein recording is performed by ejecting a recording liquid in a recording head through

discharging orifices by vibration of piezo oscillators, the electrostatic attraction caused by the application of a high voltage, etc., recording liquids obtained by dissolving various dyes in water or organic solvents are
5 used. However, for the ink-jet recording liquid, more restrict performance characteristics are requested than for a general writing ink for writing instruments such as a fountain pen, a felt pen, etc.

In such a recording system recording is performed
10 by ejecting droplets of a recording liquid (a recording ink) onto a recording media, such a recording liquid is fundamentally composed of a recording agent (a dye or a pigment) and a liquid medium (water, an organic solvent or a mixture of them) for dissolving or dispersing the
15 recording agent and, if necessary, various additives are added to the recording liquid.

Preferred conditions required for this kind of recording liquid are as follows:

(1) The recording liquid possesses liquid properties (viscosity, surface tension, electric conductivity,
20 etc.) matching the discharging conditions (a driving voltage and a driving frequency of a piezo electric element, the form and material of orifices, the diameter of orifices, etc.).

25 (2) The recording liquid can be stored for a

long period of time and does not cause clogging of orifices at use.

(3) The recording liquid is quickly fixed onto recording media such as papers, films, etc., the out-
5 lines of the resulting ink dots are smooth, and blotting of the dotted ink is minimized.

(4) The recorded image of the recording liquid has a clear color tone and a high density.

(5) The recorded image of the recording liquid
10 is excellent in water resistance and light resistance.

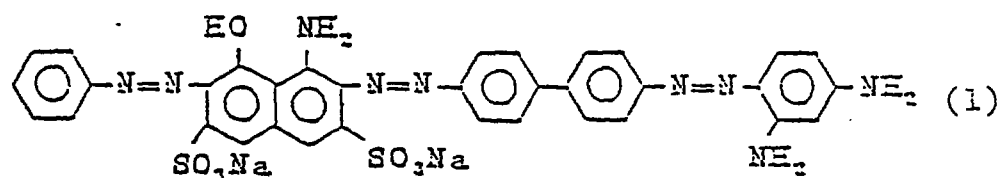
(6) The recording liquid does not attack or erode surrounding materials (the container for the recording liquid, connecting tubes for discharging orifices, sealants, etc.).

15 (7) The recording liquid has no unpleasant smell, toxicity, inflammability, etc.

As this kind of recording liquid, there are known solutions or dispersions of various dyes or pigments in aqueous or nonaqueous solvents as disclosed, for example,
20 in Japanese Patent Publication Nos. 8361/1975, 40484/1976, 13126/1977 and 13127/1977, and Unexamined Published Japanese Patent Application No. 95008/1975. However, none of these prior art recording liquids are completely satisfactory since they do not possess all of the features
25 (1) to (7) required for ideal recording liquids.

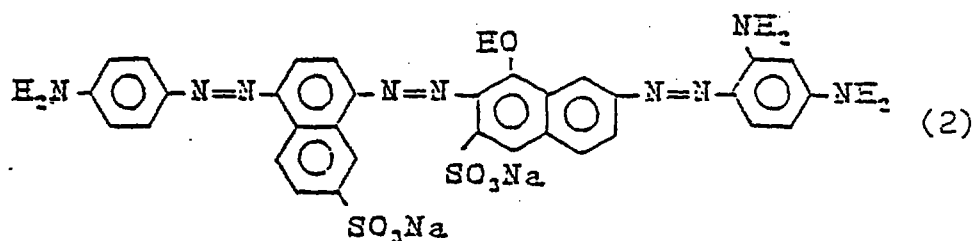
Recording liquids are basically composed of dyes and solvents therefor, and their performance depends largely upon the inherent properties of the dyes. Therefore, choosing dyes that provide recording liquids with the desired features (1) to (7) is a very important factor in the art concerned.

Trisazo compounds known as black dyes have the following formulae:



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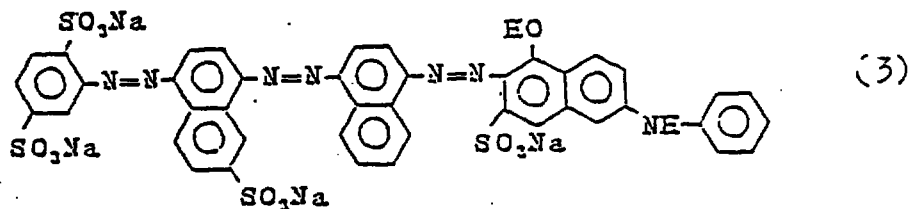
C.I. Direct Black-38



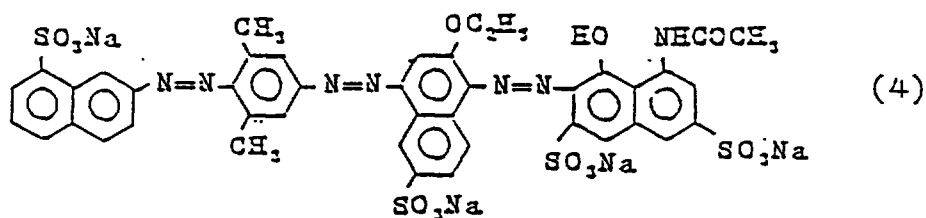
C.I. Direct Black-9

Compounds known as blue and green dyes have the following formulae, respectively:

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C.I. Direct Blue-78



C.I. Direct Green-33

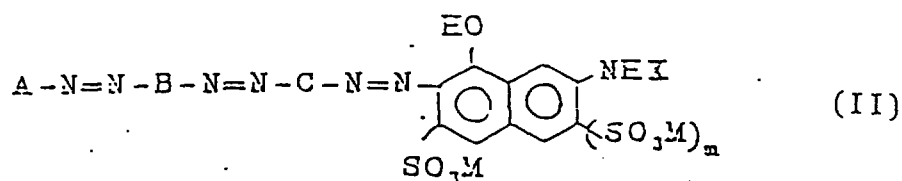
These dyes, however, are unsatisfactory for use in recording liquids and further improvements are desirable with respect to solubility, light resistance, stability in extended storage, and stability during dis-

SUMMARY OF THE INVENTION

One object, therefore, of the present invention is to provide novel trisazo compounds which can be used either as blue to black dyes or as blue to green dyes.

Another object of the present invention is to provide novel recording liquids which contain said compounds as dyes and which satisfy all of the requirements (1) to (7) listed above.

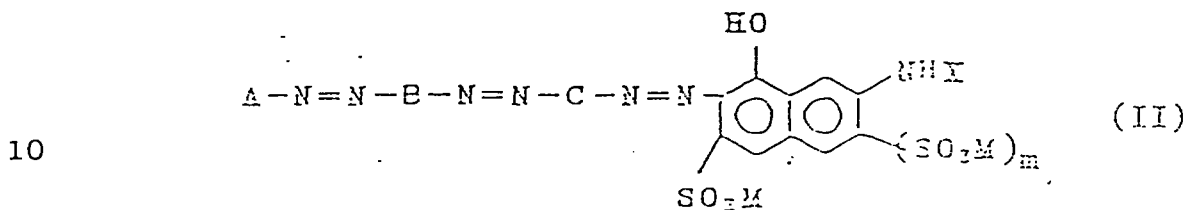
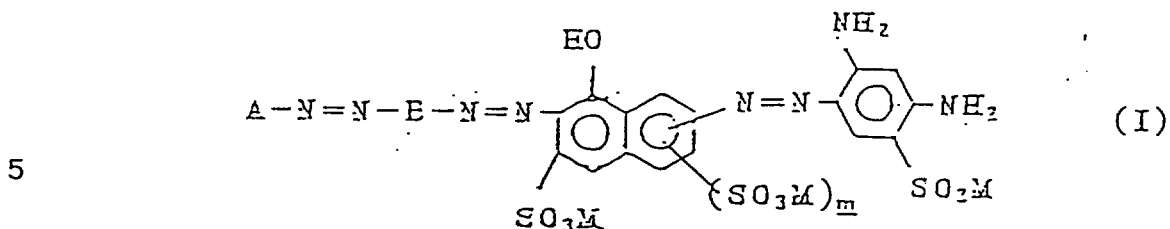
The novel dyes of the present invention are naphthalene trisazo compounds which are represented by the following formula (II):



wherein X represents a hydrogen atom, a lower alkyl group, a phenyl group or a phenyl group substituted by -SO₃M; m represents zero or 1; M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine); A represents an unsubstituted or substituted benzene or naphthalene ring; B and C each represents an unsubstituted or substituted 1,4-phenylene or 1,4-naphthylene group provided that B and C do not represent a naphthylene group at the same time; and provided that the substituents for each of A, B and C are selected from the group consisting of -SO₃M, lower alkyl, lower alkoxy, lower alkyl carbonylamino, -COOM, and halogen.

A recording liquid according to the invention when used in ink jet printing comprises a recording agent as a recording-image forming component and a mixture of water and a water-soluble organic solvent for dissolving or dispersing said recording agent, wherein said recording agent comprises at least one naphthalene trisazo compound selected from the group

consisting of compounds represented by the general formula (I) or (II):



wherein X represents a hydrogen atom, a lower alkyl group, a phenyl group or a phenyl group substituted by -SO₃M; m represents zero or 1; M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine); and wherein in formula (I), A is a -SO₃M substituted naphthyl group, and B is phenylene substituted by at least one substituent selected from the group consisting of lower alkyl and lower alkoxy, and in formula (II), A represents an unsubstituted or substituted benzene or naphthalene ring; B and C each represents an unsubstituted or substituted 1,4-phenylene or 1,4-naphthylene group provided that B and C do not represent a naphthylene group at the same

time; and provided that the substituents for each of A, B and C are selected from the group consisting of $-\text{SO}_3\text{M}$, lower alkyl, lower alkoxy, lower alkyl carbonylamino, $-\text{COOM}$, and halogen.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 2 are schematic views showing ink-jet recorders;

Fig. 3A is an enlarged sectional view of a head of an ink-jet recorder taken along the flowing passageway of ink;

Fig. 3B is a cross sectional view taken along line A-B of the head shown by Fig. 3A; and

Fig. 4 is a perspective view of a multi-head which is an array of such heads as shown in Figs. 3A and 3B.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The compounds represented by the formula (I) are blue or black dyes. The

term "lower" means the presence of 1 to 4 carbon atoms. M represents the same as defined hereinabove. Examples of Am include a substituted or unsubstituted alkylamine.

Preferable dyes of the formula (I) are those wherein A is a $-\text{SO}_3\text{M}$ substituted naphthyl group, B is a phenylene group substituted by a lower alkyl or lower alkoxy group, M is Li or Na, and m is zero or 1.

The compounds represented by the formula (II) are blue to green dyes. The term "lower"

means the presence of 1 to 4 carbon atoms. M represents the same as defined hereinabove. Examples of Am include a substituted or unsubstituted alkylamine.

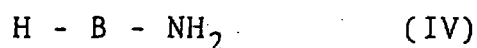
Preferable dyes of the formula (II) are those wherein A is a phenyl group which is substituted by $-SO_3M$ and which may be further substituted by a lower alkyl group or a lower alkoxy group, B is a 1,4-phenylene group substituted by a lower alkyl or lower alkoxy group, C is a $-SO_3M$ substituted 1,4-naphthylene group or a 1,4-phenylene group which is substituted by a lower alkyl or alkoxy group, X is H, m is 1, and M is Na or Li.

The compounds of the present invention may be prepared by the following procedures in accordance with known methods such as, for example, the one described in Yutaka Hosoda, Shin Senryo Kagaku (New Dyestuff Chemistry), page 397, line 27 to page 398, line 19, published by Gihodo Co., December 21, 1973:

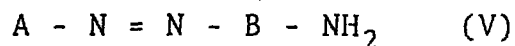
An amine of the formula (III):



(wherein A is the same as defined above) is diazotized with sodium nitrite or any other appropriate compound in a mineral acid such as hydrochloric acid or sulfuric acid, and the resulting diazotized amine is coupled
 5 with an amine of the formula (IV):

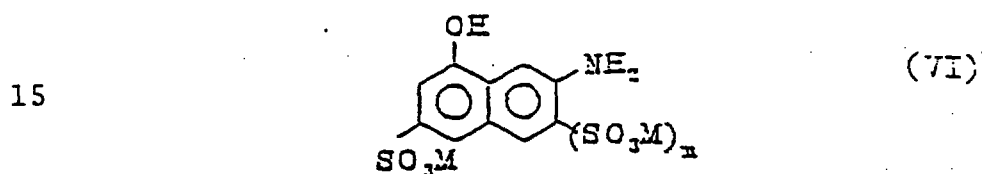


(wherein B is the same as defined above) to form a mono-azo compound of the formula (V):

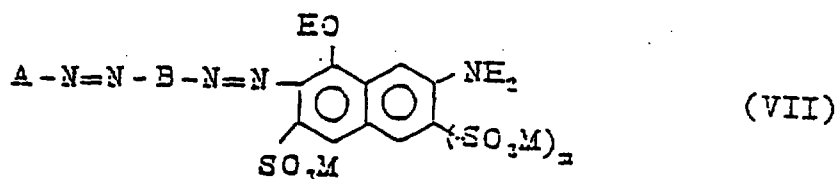


(wherein A and B are the same as defined above).

If a compound of the formula (I) is desired, the
 10 monozao compound formed above is diazotized with sodium nitrite or any other appropriate compound in a mineral acid such as hydrochloric acid or sulfuric acid, and the resulting diazotized compound is coupled with a naphthol compound represented by formula (VI):



(wherein m and M are the same as defined above) to form a disazo compound of the formula (VII):



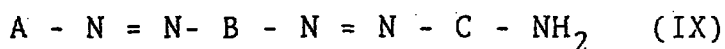
(wherein A, B, M and m are the same as defined above).

The so formed disazo compound is diazotized with sodium sulfite or any other appropriate compound in a mineral acid such as hydrochloric acid or sulfuric acid
5 or an organic acid such as acetic acid, and the resulting diazotized compound is coupled with metaphenylene-diamine sulfonic acid to form the intended trisazo compound.

If a compound of the formula (II) is desired, the
10 monoazo compound of formula (V) is diazotized with sodium nitrite or any other appropriate compound in a mineral acid such as hydrochloric acid or sulfuric acid, and the resulting diazotized compound is coupled with an amine of the formula (VIII):



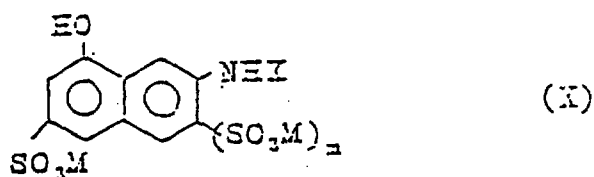
15 (wherein C is the same as defined above) to form a disazo compound of the formula (IX):



(wherein A, B and C are the same as defined above).

The so formed disazo compound is diazotized with sodium nitrite or any other appropriate compound in a
20 mineral acid such as hydrochloric acid or sulfuric acid or an organic acid such as acetic acid, and the resulting diazotized compound is coupled with a naphthol compound

represented by formula (X):

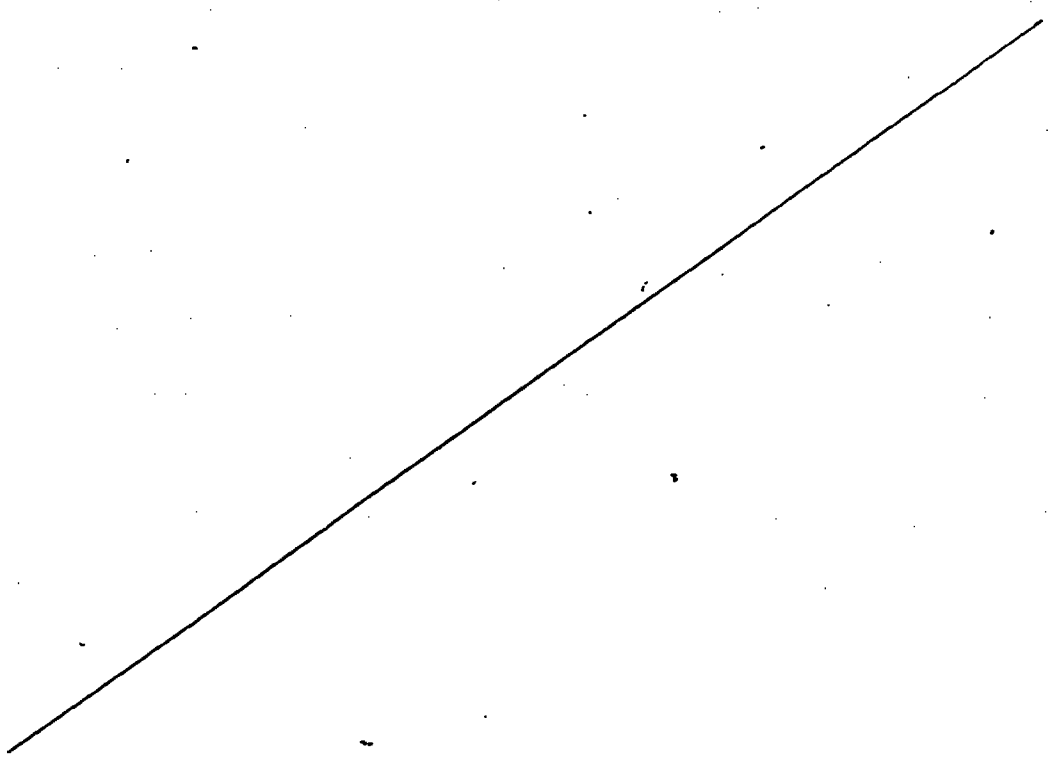


(wherein X, M and m are the same as defined above) to form the intended trisazo compound (II) of the present invention.

5 The recording liquid of the present invention is prepared using the trisazo compound of formula (I) or (II) as a recording agent. The resulting recording liquid satisfies all of the requirements (1) to (7) listed hereinabove and is particularly superior to recording liquids using the known dyes (1) to (4) in terms of stability in extended storage and prevention of the clogging of discharging orifices. The notable advantage of using the dye of formula (I) is that it provides a recording liquid having good response in discharging, 10 while the dye of formula (II) ensures the production of a highly light-resistant recording liquid. Therefore, the recording liquid of the present invention offers definite advantages over the ones which employ known dyes. 15

Prevention of clogging of orifices is a very important subject matter in the ink-jet recording system from a viewpoint of reliability thereof. Hitherto it has been prevented mainly by using mechanical method such as
5 an auto-capping method (surrounding a nozzle with a saturated vapor while the nozzle is not used) or a method using a hand-operated pump. However, such methods do not provide satisfactory effects at present.

In the ink-jet recording liquid a liquid medium
10 mainly comprising of water is used from a viewpoint of safety. Generally, a low volatile water soluble organic solvent such as a glycol is used as a wetting agent. Solubility of dyes to these liquid media changes delicately according on the chemical structure of the dyes, and



solubility of dyes to water and that to a glycol have a tendency to be contrary to each other. At the top of the nozzle there is a tendency that water which is a highly volatile component volatilizes to make the concentration of a glycol high. Therefore, if the recording liquid contains a dye having a low solubility to a glycol, there is a large possibility for clogging the nozzle by precipitation of the dye.

The above-described conventional dyes (1) to (4) have a good solubility to water, however, they are inferior in solubility to a glycol. On the other hand, the dyes of the present invention which are represented by formula (I) and (II) have an improved solubility to a glycol maintaining the solubility thereof to water to be in the range sufficient for practical use. Therefore, the recording liquid containing the dyes of the present invention hardly cause clogging of a nozzle.

The content of the dye in the recording liquid of this invention is determined according to the nature of the liquid medium component, the characteristics required for the recording liquid, etc., but is generally in the range of 0.1 to 20% by weight, preferably 0.5 to 15% by weight, more preferably 1 to 10% by weight to the total weight of

the recording liquid.

The dyes in this invention can be used solely or as a combination of two or more kinds of them, or further may be used as the indispensable component together with other dye
5 or dyes such as a direct dye, an acid dye, etc. the amount of such conventional dyes which can be used together with the dye of this invention is usually 0 to 30% by weight of the dye for use in this invention.

As a liquid medium component for the recording liquid
10 of this invention, a mixture of water and a water-soluble organic solvent or solvents is used. Examples of the water-soluble organic solvents which can be used for the recording liquids of this invention are alkyl alcohols having 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, n-
15 propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, etc.; amides such as dimethylformamide, dimethylacetamide, etc.; ketones or ketone alcohols such as acetone, diacetone alcohol, etc.; ethers such as tetra-hydrofuran, dioxane, etc.; nitrogen-
20 containing heterocyclic ketones such as N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, etc.; polyalkylene glycols such as polyethylene glycol, polypropylene glycol, etc.; alkylene glycols the alkylene moiety of which has 2 to 6 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol,
25 thiodiglycol, hexylene glycol, diethylene glycol, etc.;

glycerol; lower alkyl ethers (the alkyl moiety having usually 1 to 4 carbon atoms) of polyhydric alcohols such as ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, triethylene glycol monomethyl (or ethyl) ether, etc.

The content of the foregoing water-soluble organic solvent in the recording liquid is usually in the range of 5 to 89.9% by weight, preferably 10 to 80% by weight, more preferably 20 to 50% by weight to the total weight of the recording liquid.

In this case, the content of water is determined in a wide range according to the nature of the foregoing solvent component, the composition of the solvents, and the desired characteristics of the recording liquid but is usually in the range of 10 to 90% by weight, preferably 10 to 70% by weight, more preferably 20 to 70% by weight.

The recording liquid of this invention can be easily prepared by mixing the necessary components by an ordinary manner without need of any troublesome procedures.

The recording liquids of this invention have balanced excellency by themselves in recording characteristics (e.g., a recording response, a stability of droplet formation, a discharging stability, a long continuous recording property, a discharging stability after resting the recording

for a long period of time, etc.), a storage stability, a fixing property onto recording media, and the light resistance, weather resistance, water resistance, etc., of recorded images but for further improving these
5 properties, the recording liquids may contain various additives conventionally known in the field of the art.

Examples of these additives are viscosity controlling agents (for usually imparting a viscosity of 1 to 20 c.p. to the recording liquids), such as polyvinyl alcohol,
10 celluloses, water-soluble resins, etc.; surface tension controlling agents (for preferably adjusting the surface tension of the recording liquids to 40 to 65 dynes/cm), such as various cationic, anionic or nonionic surface active agents, diethanolamine, triethanolamine, etc.;
15 pH-controlling agents (for preferably adjusting the pH of the recording liquids to 4 to 10), such as buffers; and fungicides such as sodium dehydroacetoacetate, 1,2-benzisothiazolin-3-one, 6-acetoxy-2,4-dimethylmetadioxane, etc.).

20 Also, for preparing the recording liquid of this invention which is used for an ink-jet recording system of a type that a recording liquid is charged with electricity, a specific resistance controlling agent such as an inorganic salt (e.g., lithium chloride, ammonium chloride,
25 sodium chloride, etc.), etc., is added to the recording

liquid.

Furthermore, when the recording liquid of this invention is applied to an ink-jet recording system of a type that a recording liquid is ejected by the action
5 of heat energy, the thermal properties (e.g., the specific heat, the coefficient of thermal expansion, the heat conductivity, etc.) of the recording liquid is controlled by suitably selecting the kind of the solvent of the recording liquid, the component ratio of the
10 recording liquid, etc.

The recording liquid of this invention possess the following merits. That is, the physical properties such as viscosity, surface tension, etc., thereof are in the proper ranges, the recording liquid does not clog fine
15 discharging orifices of an ink-jet recorder, the recording liquid provides recorded images having high density, the recording liquid does not cause change in physical properties or deposition of solid components during the storage of the liquid, the recording liquid can record on
20 various recording media without restriction of the kind of the recording media, and also the recording liquid is fixed quickly and gives recorded images excellent in water resistance, light resistance, abrasion resistance and resolution.

25 Then, an ink-jet recording system is explained

hereinbelow.

There are various ink-jet recording systems according to the difference in the method of generating recording droplets and of controlling the flying direction of the droplets.

An example of the recording systems is shown in Fig. 1. That is, Fig. 1 is a schematic view showing an ink-jet recording system which performs recording by applying recording signals to the recording head having a piezo electric oscillator to generate droplets of recording liquid in response to the recording signals. As shown in Fig. 1, a recording head 1 is provided with a piezo electric oscillator 2a, a vibration plate 2b, an inlet 3 for a recording liquid, a liquid-holding chamber 4, and a discharging orifice 5. A recording liquid 7 stored in a storage tank 6 is introduced into the liquid chamber 4 through a feed pipe 8. In addition, as the case may be, an intermediate treating means 9, such as a pump, filter, etc., is equipped to the feed pipe 8. Pulsed signals converted from recording signals S by a signal-processing means 10 (e.g., a pulse convertor), are applied to the piezo electric oscillator 2a to vary the pressure of the recording liquid in the liquid chamber 4 in response to the pulsed signals, whereby the recording liquid 7 is ejected in the form of droplets 11 from the discharging orifice 5 to make

a record on the surface of a recording medium 12.

Besides the aforesaid ink-jet recording system, there are known various types of ink-jet recording systems. For example, Fig. 2 shows a modification in recording head 1 of the recording device shown in Fig. 1, in which a cylindrical piezo electric oscillator 2a is disposed around a nozzle-formed liquid-holding chamber 4. The mechanism of generating recording liquid droplets is fundamentally same as in the recording system shown in Fig. 1.

Moreover, there are known a ink-jet recording system in which electrically charged droplets are continuously generated and parts of the droplets are used for recording, and an ink-jet recording system in which thermal energy is applied to the recording liquid in the liquid chamber in a recording head in response to recording signals to generate droplets of the recording liquid by the thermal energy.

An example of these recording systems is shown in Fig. 3A, Fig. 3B and Fig. 4.

A recording head 13 is composed of a glass, ceramic or plastic plate having an ink-passing channel 14 and a heating head 15, which is used for heat-sensitive recording, bonded to the plate. In addition, a thin film-type head is illustrated in Fig. 3A as the heating head 15.

but the heating head for use in this invention is not restricted to the type. The heating head 15 is composed of a protective film 16 made of silicon oxide, etc., aluminum electrodes 17 - 1 and 17 - 2, a heating resistor layer 18 made of nichrome, etc., a heat accumulating layer 19, and a substrate 20 having a good heat radiating property, such as alumina, etc.

An ink 21 is filled in the channel 14 up to a discharging orifice 22 and forms a meniscus 23.

10 Now, on applying electric signals onto the electrodes 17 - 1 and 17 - 2, the heating head 15 rapidly generates heat at the region shown by n to form bubbles in the ink 21 which is in contact with the region, the meniscus 23 of the ink is projected by the action of the pressure, 15 and the ink 21 is ejected to a recording medium 25 from the discharging orifice 22 as recording droplets 24.

Fig. 4 shows an external appearance of a multiple head composed of an array of a number of the recording heads shown in Fig. 3A. The multi-head is made by bonding a 20 glass plate 27 having a number of channel 26 with a heating head similar to the one illustrated in Fig. 3A.

Fig. 3A is a cross sectional view of the recording head 15 taken along the passageway of ink and Fig. 3B is a cross sectional view taken along line A-B in Fig. 3A.

The following synthesis examples and working examples are provided for the purpose of further illustrating the present invention but are in no sense to be taken as limiting.

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SYNTHESIS EXAMPLE 1

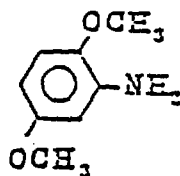
(Synthesis of Dye No. 1-1 in Table 1)

(1) Preparation of the first diazo liquid:

To 600 ml of 3% hydrochloric acid, 30.2 g of 2-amino-naphthalene-4,8-disulfonic acid was added and the
10 resulting mixture was stirred for 3 hours to form a uniform slurry. Ice (400 g) was added to the slurry to cool it to 3°C. An aqueous solution of sodium nitrite (7.3 g) in water (73 ml) was added to the cooled slurry. The
mixture was stirred for 1 hour to 3°C to effect diazotiza-
15 tion and the residual sodium nitrite was removed by addition of sulfamic acid (3 g) so as to obtain the first diazo liquid.

(2) First coupling:

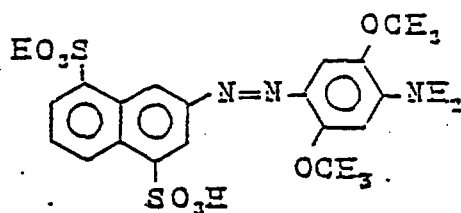
To 450 ml of water, 15.3 g of 2,5-dimethoxyaniline
20 of the formula:



was added, and the resulting mixture was stirred for 2 hours to form a uniform slurry. To the slurry, 300 g

of ice, the first diazo liquid prepared in step (1), and 20 ml of 25% sodium hydroxide aqueous solution were added and the mixture was stirred at 0 - 3°C and at a pH of 2 - 3 for 15 hours to effect coupling reaction.

5 Thereafter, the mixture was subjected to salting-out with 200 g of sodium chloride. The precipitating monoazo compound was recovered by filtration, washed with 500 ml of 10% sodium chloride aqueous solution, and dried to obtain 41.0 g of a monoazo compound having the following
10 formula:

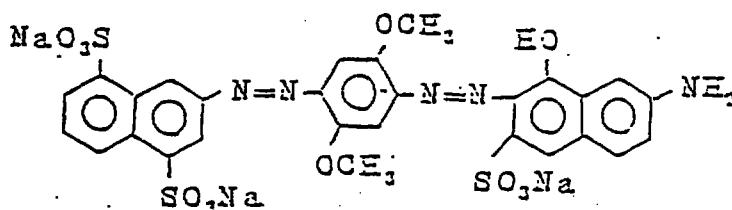


(3) Preparation of the second diazo liquid:

The monoazo compound (23.3 g) obtained in step (2) was added to 410 ml of 5% hydrochloric acid and the
15 mixture was stirred for 5 hours to form a uniform slurry. The slurry was cooled to 3°C by addition of 300 g of ice. An aqueous solution of sodium nitrite (3.8 g) in water (38 ml) was added to the cooled slurry. The mixture was stirred for 10 hours at 3°C to effect diazotization
20 and the residual sodium nitrite was removed by addition of sulfamic acid (1 g) so as to obtain the second diazo liquid.

(4) Second coupling:

To 460 ml of water, 12.0 g of 1-hydroxy-7-amino-naphthalene-3-sulfonic acid was added. To the resulting mixture, 800 g of ice, the second diazo liquid prepared
5 in step (3) and 55 ml of 25% sodium hydroxide aqueous solution were added, and the mixture was subjected to coupling reaction at 2 - 5°C and at a pH of 8 - 10. After stirring for 5 hours at the same temperature and pH, 250 g of sodium chloride was added to perform salting-
10 out. The precipitating compound was recovered by filtration, washed with 300 ml of 10% sodium chloride aqueous solution, and dried to obtain 31.3 g of a disazo compound having the following formula:



15 (5) Preparation of the third diazo liquid:

The disazo compound (19.6 g) obtained in step (4) was added to 400 ml of 3% hydrochloric acid and 100 ml of acetic acid. The mixture was stirred for 3 hours to make a uniform slurry, which was cooled to 3°C by addition
20 of ice (300 g). An aqueous solution of sodium nitrite (1.8 g) in water (20 ml) was added to the cooled slurry. The mixture was stirred for 24 hours at 3°C to effect

diazodization, and the residual sodium nitrite was removed by addition of sulfamic acid (0.5 g) so as to obtain the third diazo liquid.

(6) Third coupling:

- 5 To 100 ml of water, 4.7 g of 1,3-diamino-benzene-4-sulfonic acid was added, and the mixture was cooled to 3°C by addition of ice (50 g). After addition of the third diazo liquid prepared in step (5), the mixture was stirred at 2 - 5°C for 10 hours to effect coupling reaction.
- 10 Thereafter, the mixture was subjected to salting-out with 250 g of sodium chloride. The precipitating compound was recovered by filtration and washed with 400 ml of 20% sodium chloride aqueous solution to obtain a wet cake (65 g). The cake was desalted and dried to obtain 18.6 g
- 15 of the end compound (No. 1-1 in Table 1) in a yield of 74.1%. Elemental analysis of the compound gave the following result:

	<u>C</u>	<u>H</u>	<u>N</u>
<u>Calculated (%)</u>	40.6	2.4	11.2
<u>Found (%)</u>	40.4	2.1	11.5

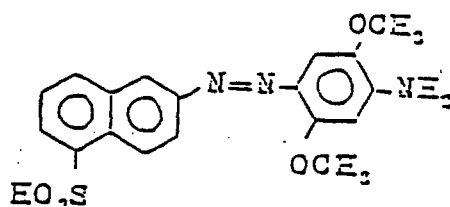
SYNTHESIS EXAMPLE 2

(Synthesis of Dye No. 1-3 in Table 1)

- 20 (1) Preparation of the first diazo liquid and first coupling:
The procedures of steps (1) and (2) in Synthesis

Example 1 were repeated except that 22.3 g of 2-amino-naphthalene-5-sulfonic acid was used instead of 2-amino-naphthalene-4,8-disulfonic acid. As a result, 34.8 g of a monoazo compound having the following formula:

5



was obtained.

(2) Preparation of the second diazo liquid:

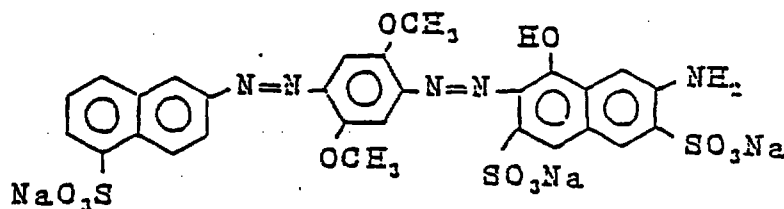
The second diazo liquid was prepared by repeating step (3) in Synthesis Example 1 except that 19.4 g of the monoazo compound obtained in step (1) was used as the starting material.

10

(3) Second coupling:

Step (4) in Synthesis Example 1 was repeated except that 16.0 g of 1-hydroxy-7-amino-naphthalene-3,6-disulfonic acid was used instead of 1-hydroxy-7-amino-naphthalene-3-sulfonic acid. As a result, 32.9 g of a disazo compound having the following formula:

15



was obtained.

(4) Preparation of the third diazo liquid:

The third diazo liquid was prepared by repeating step (5) in Synthesis Example 1 except that 19.6 g of the disazo compound obtained in step (3) was used as the starting material.

(5) Third coupling:

Step (6) in Synthesis Example 1 was repeated except that the third diazo liquid obtained in step (4) was coupled with 1,3-diamine-benzene-4-sulfonic acid. The end compound (No. 1-3 in Table 1) was obtained in an amount of 20.0 g (yield, 79.5%). Elemental analysis of the compound gave the following result:

	<u>C</u>	<u>H</u>	<u>N</u>
<u>Calculated (%)</u>	40.6	2.4	11.2
<u>Found (%)</u>	40.8	2.3	11.0

SYNTHESIS EXAMPLE 3

Dye compounds were prepared as in Synthesis Examples 1 and 2 and their structural formulae and maximum absorption wavelengths are listed in Table 1.

SYNTHESIS EXAMPLE 4

(Synthesis of Dye No. 2-1 in Table 1)

(1) Preparation of the first diazo liquid:

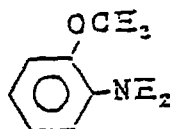
Metanilic acid (17.3 g) was added to 346 ml of 3% hydrochloric acid and the mixture was stirred for 3 hours to form a uniform slurry, which was cooled to

3°C by addition of ice (200 g). An aqueous solution of sodium nitrite (7.3 g) in water (73 ml) was added to the cooled slurry. The mixture was stirred for 1 hour at 3°C to effect diazotization, and the residual sodium
5 nitrite was removed by addition of sulfamic acid (3 g) so as to obtain the first diazo liquid.

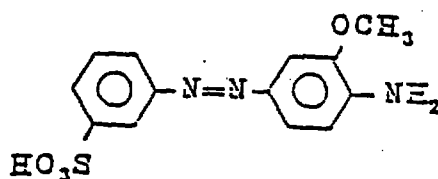
(2) First coupling:

Orthoanisidine (12.3 g) having the following formula:

10



was added to 450 ml of 50% aqueous methanol. To the resulting solution, ice (300 g), the first diazo liquid prepared in step (1), and 10 ml of 25% sodium hydroxide aqueous solution were added and the mixture was stirred
15 for 15 hours at 0 - 3°C and at a pH of 2- 3 to effect coupling reaction. The mixture was then subjected to salting-out with 200 g of sodium chloride. The precipitating monozao compound was recovered by filtration, washed with 500 ml of 10% sodium chloride aqueous
20 solution and dried to obtain 28.2 g of a monoazo compound having the following formula:

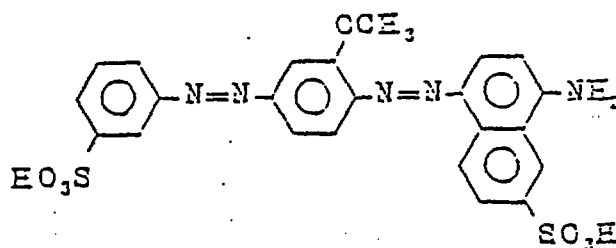


(3) Preparation of the second diazo liquid:

The monoazo compound (15.4 g) obtained in step (2) was added to 300 ml of 5% hydrochloric acid and the mixture was stirred for 5 hours to form a uniform slurry, which
5 was cooled to 3°C by addition of ice (250 g). An aqueous solution of sodium nitrite (3.8 g) in water (38 ml) was added to the cooled slurry. The mixture was stirred for 10 hours at 3°C to effect diazotization, and the residual sodium nitrite was removed by addition of sulfamic acid
10 (1 g) so as to obtain the second diazo liquid.

(4) Second coupling:

To 230 ml of water, 11.2 g of 1-amino-naphthalene-7-sulfonic acid was added. Ice (400 g), the second diazo liquid obtained in step (2) and 10 ml of 25% sodium
15 hydroxide aqueous solution were added to the solution, and the mixture was subjected to coupling reaction at a pH of 2 - 3 and at a temperature of 2 - 5°C. The mixture was stirred for 5 hours at the same temperature and pH. Thereafter, the mixture was subjected to salting-out by
20 addition of sodium chloride (100 g). The precipitating compound was recovered by filtration, washed with 300 ml of 10% sodium chloride aqueous solution and dried to obtain 23.8 g of a disazo compound having the following formula:



(5) Preparation of the third diazo liquid:

The disazo compound (13.5 g) obtained in step (4) was added to 300 ml of 3% hydrochloric acid and 100 ml of acetic acid. The mixture was stirred for 3 hours to form a uniform slurry, which was cooled to 3°C by addition of ice (300 g). An aqueous solution of sodium nitrite (1.8 g) in water (20 ml) was added to the cooled slurry. The mixture was then stirred for 24 hours at 3°C to effect diazotization, and the residual sodium nitrate was removed by addition of sulfamic acid (0.5 g) so as to obtain the third diazo liquid.

(6) Third coupling:

Eight grams of 1-hydroxy-7-amino-naphthalene-3,6-disulfonic acid was added to 320 ml of water. To the solution, 600 g of ice, the third diazo liquid obtained in step (5) and 45 ml of 25% sodium hydroxide aqueous solution were added and the mixture was subjected to coupling reaction at a pH of 8 - 10 and at a temperature of 2 - 5°C. The mixture was stirred for 5 hours at the same temperature and pH, followed by salting-out with

sodium chloride (250 g). The precipitating compound was recovered by filtration and washed with 400 ml of 20% sodium chloride aqueous solution to obtain 85 g of a wet cake. The cake was desalted and dried to obtain 5 18.3 g of the end compound (No. 2-1 in Table 2) in a yield of 76.3%. Elemental analysis of this compound gave the following result:

	<u>C</u>	<u>H</u>	<u>N</u>
<u>Calculated (%)</u>	41.3	2.2	10.2
<u>Found (%)</u>	41.4	2.1	10.0

SYNTHESIS EXAMPLE 5

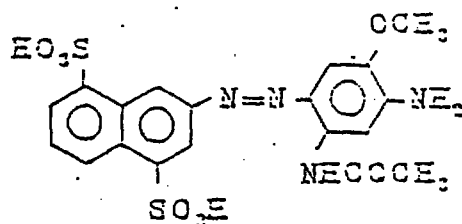
(Synthesis of Dye No. 2-7 in Table 2)

(1) Preparation of the first diazo liquid:

10 The first diazo liquid was prepared as in Step (1) in Synthesis Example 4 except that 30.2 g of 2-amino-naphthalene-4,8-disulfonic acid was used instead of metanilic acid.

(2) First coupling:

15 Step (2) in Synthesis Example 4 was repeated except that 18.0 g of 2-methoxy-5-acetylamino-aniline was used instead of orthoanisidine. As a result, 42.4 g of a monoazo compound having the following formula:



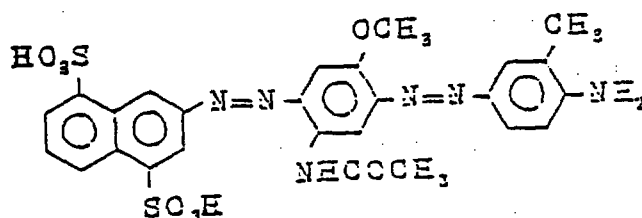
was obtained.

(3) Preparation of the second diazo liquid:

The second diazo liquid was prepared as in Synthesis Example 4 except that 24.7 g of the monoazo compound obtained in Step (2) was used as the starting material.

(4) Second coupling:

Step (4) in Synthesis Example 4 was repeated except that 5.4 g of orthotoluidine was used instead of 1-amino-naphthalene-7-sulfonic acid. As a result, 23.2 g of a diazo compound having the following formula:



was obtained.

(5) Preparation of the third diazo liquid:

The third diazo liquid was prepared as in step (4) in Synthesis Example 4 except that 15.3 g of the disazo compound obtained in Step (4) was used.

(6) Third coupling:

The procedures of step (6) in Synthesis Example 4

were repeated except that 9.9 g of 1-hydroxy-7-(3'-sulfophenyl)aminonaphthalene-3-sulfonic acid was used instead of 1-hydroxy-7-amino-naphthalene-3,6-sulfonic acid. As a result, 19.6 g of the end compound (Dye No. 2-7 in Table 2) was obtained in a yield of 71.1%. Elemental analysis of this compound gave the following result:

	<u>C</u>	<u>H</u>	<u>N</u>
<u>Calculated (%)</u>	44.7	2.7	10.2
<u>Found (%)</u>	44.5	2.7	10.3

SYNTHESIS EXAMPLE 6

Dye compounds were prepared as in Synthesis Examples 4 and 5 and their structural formulas and maximum absorption wavelengths are listed in Table 2.

Table 1

Dye No.	Structural formula	Maximum absorption wavelength (in H ₂ O) (nm)
1-1		596
1-3		592
1-4		576

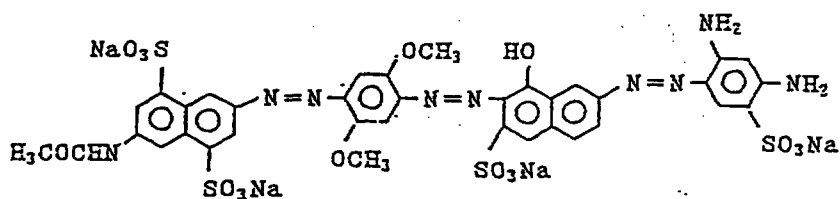
Dye No.	Structural formula	Maximum absorption wavelength (in H ₂ O) (nm)
1-15		562
1-17		570

Dye No.

Structural formula

Maximum
absorption
wavelength
(in H₂O)
(nm)

1-19



602

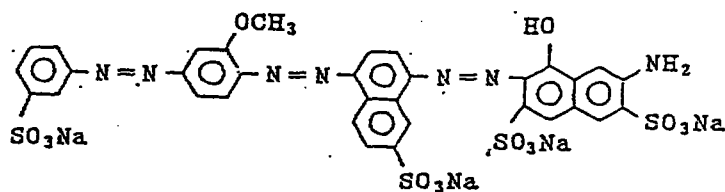
Table 2

Dye No.

Structural formula

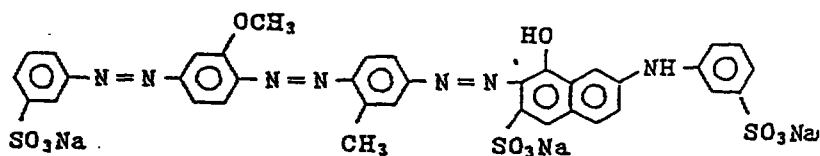
Maximum
absorption
wavelength
(in H₂O)
(nm)

2-1



615

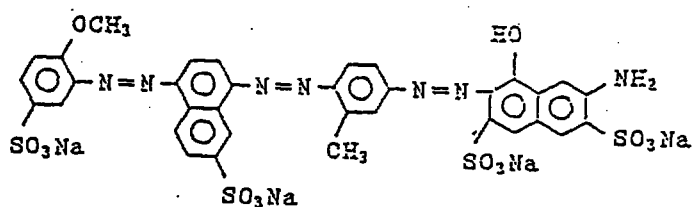
2-2



486

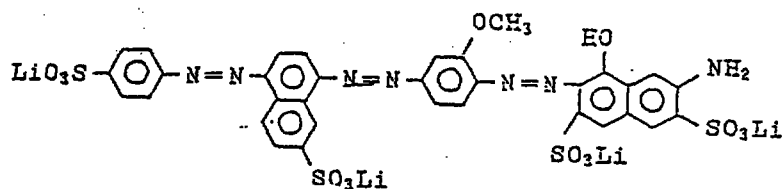
Dye No.	Structural formula	Maximum absorption wavelength (in H ₂ O) (nm)
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2-3



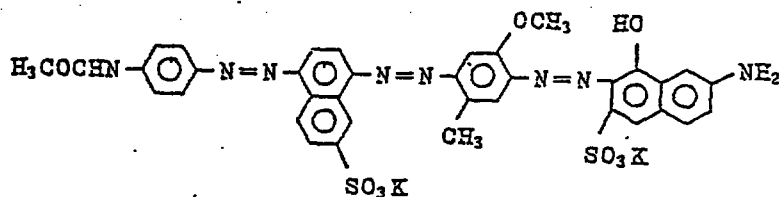
580

2-4



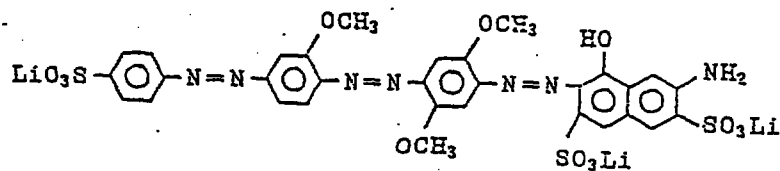
594

2-5



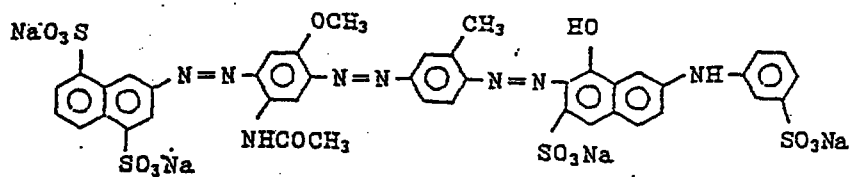
600

2-6



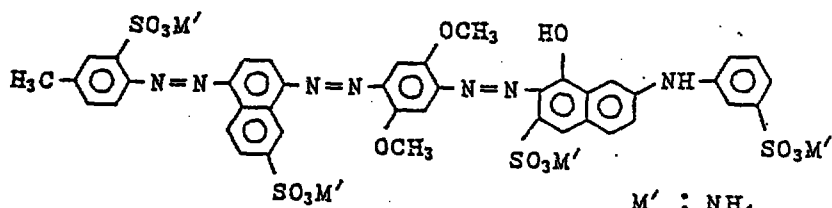
624

2-7



585

2-8



620

M' : NH₄

Dye No.

Structural formula

2-9		602
2-10	$M' : \text{NH}(\text{C}_2\text{H}_4\text{OH})_2$	580
2-11		617
2-12	$M' : \text{NH}(\text{CH}_3)_2$	590
2-13		620
2-14		620

Dye No.	Structural formula	Maximum absorption wavelength (in H ₂ O) (nm)
2-15		625
2-16		585
2-17		605
2-18		587
2-19		584
2-20		605

Example 1

Ion-exchanged water (hereinafter, is referred simply to as water)	71 wt. parts
Diethylene glycol	25 "
Dye No. 1 - 1	4 "
Total	100 wt. parts

The foregoing components were sufficiently mixed in a vessel to dissolve the solid components and after filtering the mixture with a Teflon (Trade Mark) filter having micro pores of 1 micron of pore size under pressure, the

filtrate was subjected to a degassing treatment using a vacuum pump to provide a recording liquid. The recording liquid thus obtained was subjected to following tests T_1 to T_5 using a recording device having on-demand type ink-

jet recording heads for discharging droplets of a recording liquid by a piezo electric oscillator (the discharging orifice diameter of 50 microns, the piezo electric oscillator driving voltage of 60 volts, and the frequency of 4 KHz). The results were all satisfactory. In addition,

when the same procedure as mentioned above was followed using Dye No. 2-1 in place of Dye No. 1-1 good results were obtained in all the tests;

Test T_1 : Long storage stability of recording liquid:

When the recording liquid was stored for 6

months at -30°C and 60°C in a closed glass container, the deposition of insoluble matters was not observed and the properties and color tone of the liquid were unchanged.

Test T_2 : Discharging stability:

5 When recording was performed by continuously ejecting the recording liquid for 24 hours in an atmosphere of room temperature, 5°C and 40°C , high-quality recording could be stably performed throughout the test period under each condition.

10 Test T_3 : Discharging response:

When the intermittent discharging of the recording liquid at two-second interval and the discharging after allowing to stand the recording liquid for 2 months were tested, no orifice top clogging occurred and stable and
15 uniform recording was performed in each case.

Test T_4 : Quality of recorded images:

The recorded images had high density and were clear. The density reduction percentage of the recorded images after exposing the images to a room lamp for 3
20 months was less than 1%. Also, when the recorded images were immersed in water for one minute, blotting of the images was very little.

Test T_5 : Fixability for various kinds of recording media:

25 Recorded images formed on each of the recording

papers shown in the following table were rubbed with a finger after 15 seconds since recording and the shift and blotting of the rubbed parts of the images were inspected. In each case, neither shift nor blotting of the images was observed, which showed the excellent fixability of the recording liquid.

	<u>Tradename of</u> <u>paper</u>	<u>Paper grade</u>	<u>Maker</u>
10	Ginwa	High quality paper	Sanyo Kokusaku Pulp Co., Ltd.
	Seven Star	"	Hokuetsu Seishi K.K.
	Haku Botan	Medium quality	Honshu Seishi K.K.
15	Toyo Filter Paper No. 4	Non-sized paper	Toyo Roshi K.K.

Example 2

20	Water	62 wt. parts
	N-methyl-2-pyrrolidone	15 "
	Diethylene glycol	19 "
	Dye No. 1-3	4 "

Total 100 wt. parts

A recording liquid having the above components was prepared by the same manner as in Example 1 and subjected to Test T_1 to T_5 as in Example 1 using a recording

device having an on-demand type multiple head (the discharging orifice diameter of 35 microns, the heating resistor resistance of 150Ω , the driving voltage of 30 volts, and frequency of 2 KHz) for recording by applying thermal energy to a recording liquid in the recording head to generate droplets of the recording liquid. The results are excellent in all the tests. The same procedure of this example was followed using Dye No. 2-5 in place of by No. 1-3 and excellent results were obtained in all the tests.

Example 3

	Water	45 wt. parts
	Ethylene glycol	20 "
	1,3-Dimethyl-2-imidazolidinone	30 "
15	Dye No. 2-7	5 "
	Total	100 wt. part

A recording liquid having the above composition was prepared by the same manner as in Example 1 and subjected to Tests T_1 to T_5 as in Example 2. were excellent in all the tests.

Example 4

Water	60 wt. parts
Diethylene glycol	36 "
Dye No. 2-10	4 "
Total	100 wt. parts

A recording liquid having the above components was prepared by the same manner as in Example 1 and subjected to Test T_1 to T_5 as in Example 2. The results were good in all the tests.

Example 5

Water	66 wt. parts
Diethylene glycol mono-	
methyl ether	30 "
Dyne No. 2-11	4 "
Total	100 wt. parts

A recording liquid having the above components was prepared by the same manner as in Example 1 and subjected to Tests T_1 to T_5 as in Example 2. The results were good in all the tests.

Example 6 to 13

Recording liquids having the components shown in Table 3 below as Examples 6 to 13 were prepared by the same manner as in Example 1. Each of the recording liquids was filled in a felt pen and after writing on a medium quality paper (Haku Botan, trade name, made by Honshu Seishi K. K.) using each recording liquid, the water resistance of the written images was tested. Furthermore, the writing property of each recording liquid after allowing to stand the felt pen for 24 hours without the cap was tested.

The recording liquids in the examples were excellent in water resistance and writing property after allowing to stand.

Table 3

<u>Example No.</u>	<u>Recording liquid component</u>	<u>Wt.part</u>
6	Water	71
	Diethylene glycol	25
	<u>Dye No. 2-3</u>	<u>4</u>
	Total	100
7	Water	45
	Ethylene glycol	20
	N-methyl-2-pyrrolidone	30
	<u>Dye No. 2-13</u>	<u>5</u>
	Total	100
8	Water	60
	Ethylene glycol monomethyl ether	35
	<u>Dye No.1-15 or 2-15</u>	<u>5</u>
	Total	100
9	Water	76
	Diethylene glycol	20
	<u>Dye No. 2-18</u>	<u>4</u>
	Total	100
10	Water	60
	N-methyl-2-pyrrolidone	15
	Ethylene glycol dimethyl ether	20
	<u>Dye No.1-4 or 2-20</u>	<u>5</u>
	Total	100

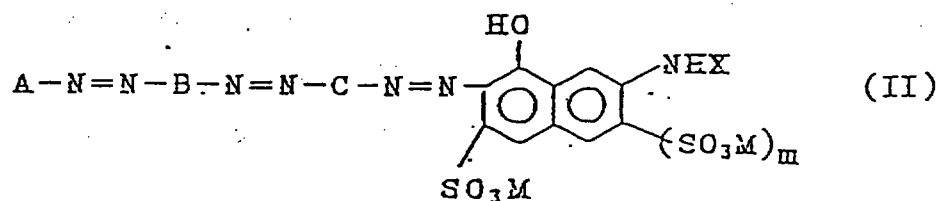
11	Water	71
	Diethylene glycol	25
	<u>Dye No. 2-2</u>	<u>4</u>
	Total	100
12	Water	60
	Ethylene glycol monomethyl ether	35
	<u>Dye No.1-17 or 2-4</u>	<u>5</u>
	Total	100
13	Water	60
	N-methyl-2-pyrrolidone	15
	Ethylene glycol dimethyl ether	20
	<u>Dye No.1-19 or 2-16</u>	<u>5</u>
	Total	100

The procedures of Example 6 were repeated except that dye compound No. 2-3 was replaced by No. 2-6, 2-8, 2-9 or 2-17. In addition, the procedures of Example 2 were repeated except that dye compound No. 2-5 was replaced
10 by No. 2-10, 2-12, 2-14 or 2-19. The recording liquids



CLAIMS:

1. A naphthalene trisazo compound represented by the general formula (II):



10 wherein X represents a hydrogen atom, a lower alkyl group, a phenyl group or a phenyl group substituted by -SO₃M; m represents zero or 1; M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine); A represents an unsubstituted or substituted benzene or naphthalene ring; B and C

15 each represents an unsubstituted or substituted 1,4-phenylene or 1,4-naphthylene group provided that B and C do not represent a naphthylene group at the same time; and provided that the substituents for each of A, B and C are selected from the group consisting of -SO₃M,

20 lower alkyl, lower alkoxy, lower alkyl carbonylamino, -COOM, and halogen.



2. A naphthalene trisazo compound as claimed in claim
1, wherein A in the general formula (II) represents a
-SO₃M substituted phenyl group or a -SO₃M
substituted phenyl group which is further substituted
5 by a lower alkyl group or a lower alkoxy group; B is
a 1,4-phenylene group substituted by a lower alkyl
group or a lower alkoxy group; C represents a -SO₃M
substituted 1,4-naphthylene group or a 1,4-phenylene group
substituted by a lower alkyl group or a lower alkoxy
10 group; and X represents a hydrogen atom or a -SO₃M
substituted phenyl group.

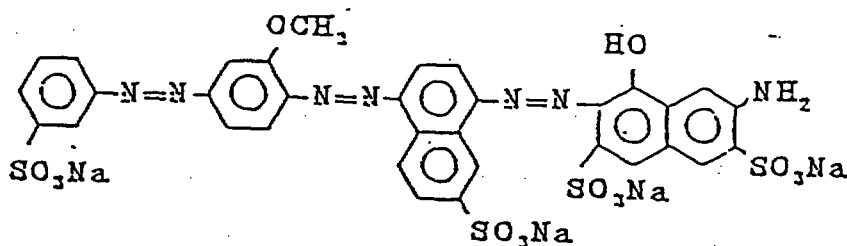
3. A naphthalene trisazo compound as claimed in
claim 1 or 2, wherein M represents Na or Li.

15

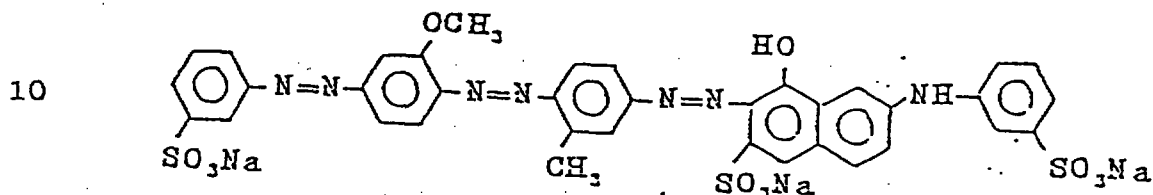
4. A naphthalene trisazo compound as claimed in claim
3, wherein A in the general formula (II) is an -SO₃M
substituted phenyl group; B is a 1,4-phenylene group
substituted by a lower alkoxy group; C is an -SO₃M
20 substituted 1,4-naphthylene group; X represents a hydrogen
atom or an -SO₃M substituted phenyl group; and M is
Na.



5. A naphthalene trisazo compound represented by the following structural formula:



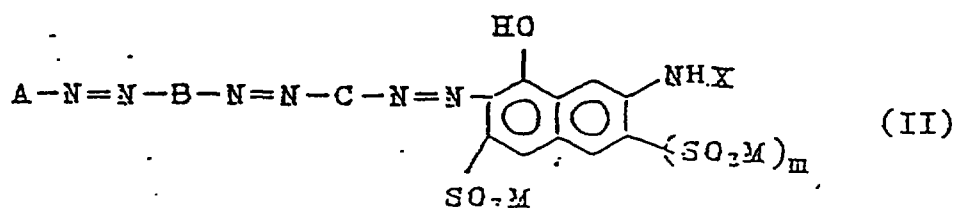
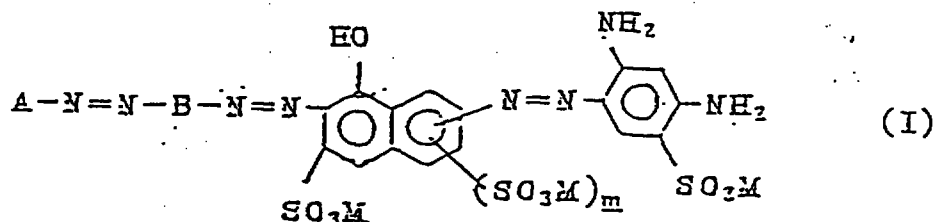
6. A naphthalene trisazo compound represented by the following structural formula:



7. A recording liquid when used in ink jet printing comprising a recording agent as a recording-image forming component and a mixture of water and a water-soluble organic solvent for dissolving or dispersing said recording agent, wherein said recording agent comprises at least one naphthalene trisazo compound selected from the group consisting of compounds represented by the general formula (I) or (II):

15

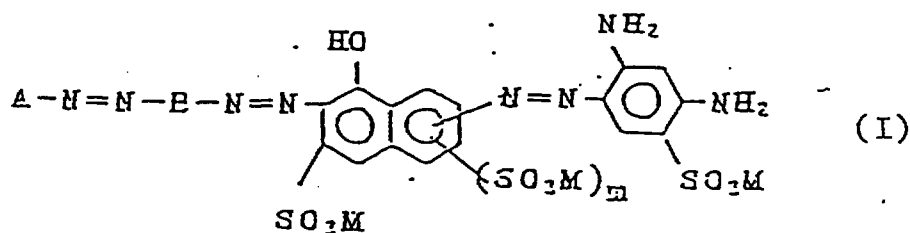
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wherein X represents a hydrogen atom, a lower alkyl group, a phenyl group or a phenyl group substituted by $-\text{SO}_3\text{M}$; m represents zero or 1; M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine); and wherein in formula (I), A is a $-\text{SO}_3\text{M}$ substituted naphthyl group, and B is phenylene substituted by at least one substituent selected from the group consisting of lower alkyl and lower alkoxy, and in formula (II), A represents an unsubstituted or substituted benzene or naphthalene ring; B and C each represents an unsubstituted or substituted 1,4-phenylene or 1,4-naphthylene group provided that B and C do not represent a naphthylene group at the same time; and provided that the substituents for each of A, B and C are selected from the group consisting of $-\text{SO}_3\text{M}$, lower alkyl, lower alkoxy, lower alkyl carbonylamino, $-\text{COOM}$, and halogen.

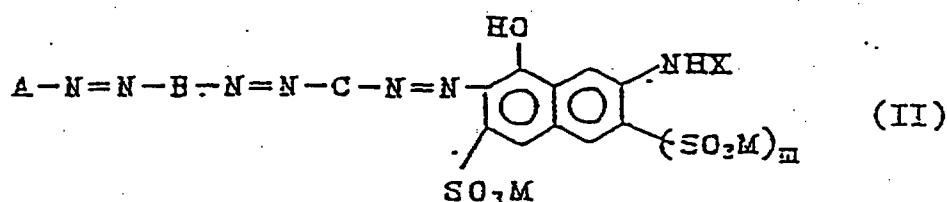
8. A recording liquid as claimed in claim 7, wherein said recording agent is a naphthalene trisazo compound represented by the general formula (I):





wherein A is a $-\text{SO}_3\text{M}$ substituted naphthyl group and B is 1,4-phenylene substituted by at least one lower alkyl or lower alkoxy group; m represents zero or 1; and M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine).

9. A recording liquid as claimed in claim 7, wherein said recording agent is a naphthalene trisazo compound represented by the general formula (II):



wherein X represents a hydrogen atom, a lower alkyl group, a phenyl group or a phenyl group substituted by $-\text{SO}_3\text{M}$; m represents zero or 1; M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine); A represents an unsubstituted or substituted benzene or naphthalene ring; B and C each represents an unsubstituted or substituted 1,4-phenylene or 1,4-naphthylene group provided that B and C do not represent a naphthylene group at the same time; and provided that the substituents for each of A, B and C are



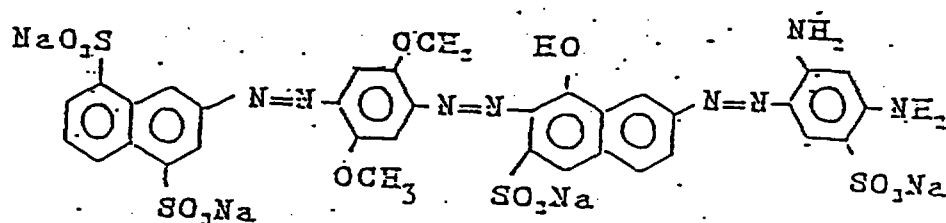
selected from the group consisting of $-\text{SO}_3\text{M}$, lower alkyl, lower alkoxy, lower alkyl carbonylamino, $-\text{COOM}$, and halogen.

- 5 10. A recording liquid as claimed in claim 7,
wherein A in the general formula (II) represents a
- SO_3M substituted phenyl group or a - SO_3M substituted
phenyl group which is further substituted by a
substituent selected from the group consisting of a
10 lower alkyl group and a lower alkoxy group; B is a
1,4-phenylene group substituted by a substituent
selected from the group consisting of a lower alkyl
group and a lower alkoxy group; C represents a - SO_3M
substituted 1,4-naphthylene group or a 1,4-phenylene group
15 substituted by a substituent selected from the group
consisting of a lower alkyl group and a lower alkoxy
group; and X represents a hydrogen atom or a - SO_3M
substituted phenyl group.
- 20 11. A recording liquid as claimed in any of claims 7
to 10, wherein M in the general formulae (I) and (II)
represents Na or Li.

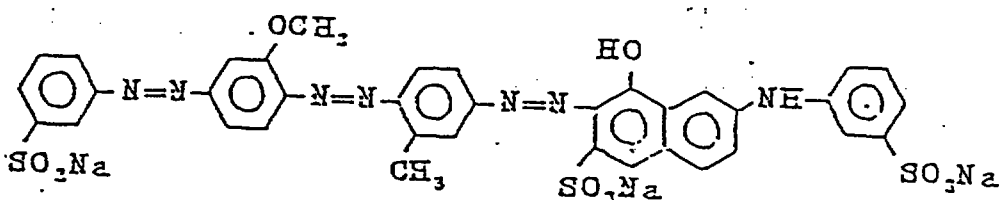


12. A recording liquid as claimed in claim 7, wherein said recording agent is selected from the group consisting of the compounds having the following structural formulae:

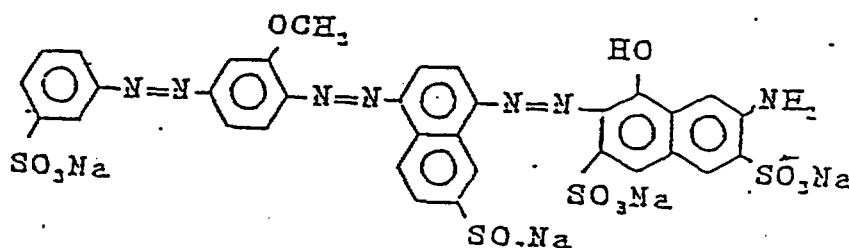
5



10



15



20

13. A recording liquid as claimed in any of claims 7 to 12, wherein the content of said compound is 0.1 to



20% by weight to the total weight of the recording liquid.

5 14. A recording liquid as claimed in any of claims 7 to 13, wherein the content of the water-soluble organic solvent is 5 to 89.9% by weight of the total weight of the recording liquid.

10 15. A recording liquid as claimed in any of claims 7 to 14, wherein the content of water is 10 to 90% by weight of the total weight of the recording liquid.

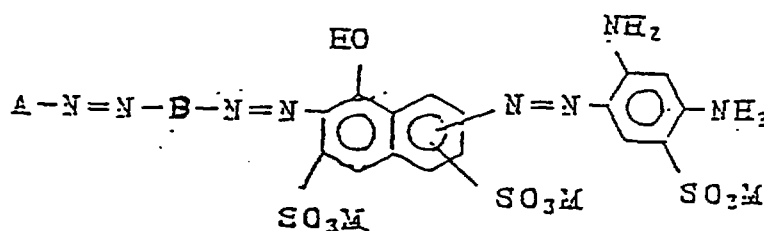
15 16. A recording liquid as claimed in any of claims 7 to 15, wherein the recording liquid further contains at least one of a viscosity controlling agent, a surface active agent, a surface tension controlling agent, a pH controlling agent, an fungicide agent, and
20 a specific resistance controlling agent.

17. Any one of dyes 1-1, 1-3, 1-4, 1-15, 1-17, 1-19 and 2-1 to 2-20 as described herein.



18. A recording liquid according to claim 7, as described herein with reference to any one of the Examples.

19. A recording liquid comprising a recording agent as a recording-image forming component and a mixture of water and a water-soluble organic solvent for dissolving or dispersing said recording agent, wherein said recording agent comprises at least one naphthalene trisazo compound represented by the general formula:



wherein:

M represents an alkali metal atom, ammonium or H.Am (wherein Am represents an amine);

A is a $-SO_3M$ substituted naphthyl group; and

B is phenylene substituted by at least one substituent selected from the group consisting of lower alkyl and lower alkoxy.