

Description

This invention relates to a black water-soluble dye composition and a recording liquid containing the same for use in ink-jet recording or in writing instruments.

Several colorimetric systems have been examined in order to quantitatively deal with colors that are perceived by the human sense. The present specification employs the (L*a*b) colorimetric system which has recently been evaluated as most suitable. The symbols a* and b* mean chromaticness indices defined in the CIE 1976 (L*, a*, b*) space (see pages 137—143, "Handbook Science of Color, New Edition", edited by the Japanese Society of Science of Color).

A Color which looks black to the human eye is generally in the region defined by

$$0 \leq \sqrt{a^{*2} + b^{*2}} \leq 2.$$

It is said that as this value approaches zero, the color becomes an ideal black color.

For the preparation of black color recording liquids for ink-jet recording, there have previously been known a method comprising mixing yellow, magenta and cyan as described, for example, in the published specifications of Japanese Patent Applications Nos. 5771/1982, 76071/1982, 164170/1982 and 101171/1982, a method comprising mixing greenish black with red or violet as described, for example, in the specifications of Japanese Patent Applications Nos. 183765/1983, 183766/1983, 183767/1983, and 201863/1983, and a method comprising mixing bluish black with greenish black as described, for example, in the specifications of Japanese Patent Applications (OPI) Nos. 93766/1984 and 93767/1984.

JP—A—59—93 768 discloses a recording liquid containing C. I. Food Black and a specific black dye, for example C. I. Acid Black 24 as water-soluble dyes.

JP—A—58—183 764 discloses a black recording solution, containing a specific compound together with a violet acid dye.

JP—A—57—115 468 discloses an ink containing a trisazo dye and a tetrazo dye.

DE—A—34 38 421 discloses a recording liquid which contains C. I. Food Black 2 in combination with red, yellow or blue dyes.

However, recording liquids prepared by mixing yellow, magenta and cyan, or by mixing greenish black with red or violet have the disadvantage that when they are used in recording on paper or when recorded images get wet with water or alcohol, color separation occurs in the surrounding parts of recorded dots owing to slight differences of the individual colors in their affinity for paper and their solubility in solvents, and the quality of printed characters is markedly degraded.

The method comprising mixing bluish black with greenish black has the disadvantage that a region having a

$$\sqrt{a^{*2} + b^{*2}}$$

value of 0 to 2 is very difficult to obtain, and the color of the recording liquid varies greatly depending upon the type of paper.

Accordingly, the object of this invention is to provide a black water-soluble dye composition and a black recording liquid containing the same for use in ink-jet recording or in writing instruments which has high solubility in a liquid medium component, high solution stability for a long period of time, does not significantly clog ejection orifices, assumes a black color having an ideal color value, varies very little in color depending upon the type of paper, and has excellent light fastness.

This object is solved according to the invention by a recording liquid comprising at least two water-soluble dyes and a liquid medium consisting of water or a mixture of water with a water-soluble organic solvent, wherein the total content of the water soluble dyes is 0.5 to 15% by weight based on the total weight of the recording liquid, each of the dyes satisfying the condition defined by the following expression (I), and a mixture of these at least two dyes satisfying the condition defined by the following expression (II)

$$0 \leq \sqrt{a^{*i2} + b^{*i2}} \leq 10 \quad \text{[I]}$$

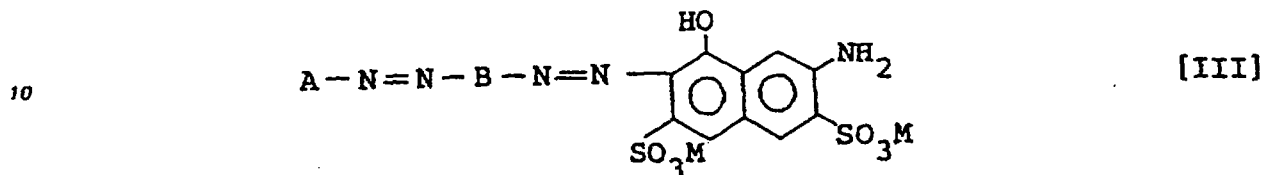
$$0 \leq \sqrt{\left(\sum_{i=1}^n a^{*i}\right)^2 + \left(\sum_{i=1}^n b^{*i}\right)^2} \leq 2 \quad \text{[II]}$$

wherein a* and b* are chromaticness indices defined in the CIE 1976 (L*, a*, b*) space, i indicates the i-th dye of the dyes used together, and n is an integer of 2 or more, wherein at least one of the water-soluble

dyes is selected from dyes of group X given below, and one of the others is selected from dyes of group Y given below:

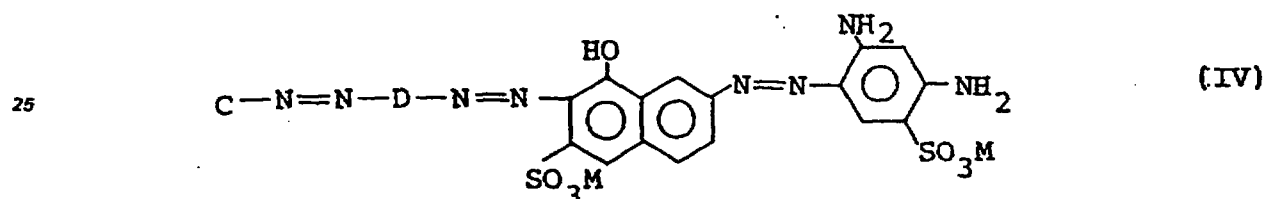
Dyes of group X

5 Dyes represented by the following formula (III)



15 wherein A represents a phenyl group substituted by a lower alkylcarbonylamino group, a lower alkoxy group, the group SO₃M or a phenylazo group which may optionally be substituted by the group SO₃M, or a naphthyl group substituted by the group SO₃M, B represents a naphthyl group substituted by the group SO₃M or a phenyl group substituted by a lower alkoxy group, and M represents an alkali metal, ammonium or an amine;

20 Dyes represented by the following general formula (IV)

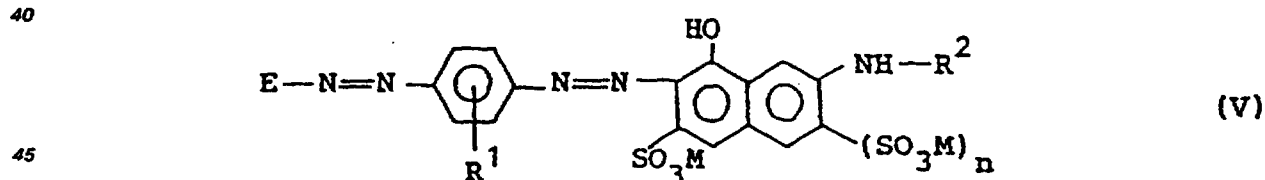


30 wherein C represents a phenyl or naphthyl group substituted by the group SO₃M, D represents a phenyl group substituted by a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, and M is as defined above; or dyes selected among

- 35 C. I. Direct Black-19, -22, -62, -108, -113, -154 and -159; and
C. I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 and -208:

Dyes of group Y

Dyes represented by the following formula (V)



45 wherein E represents a naphthyl group substituted by the group SO₃M or a phenyl group substituted by a lower alkyl group, a lower alkoxy group, a lower alkylcarbonylamino group, or a phenylazo group which may optionally be substituted by the group SO₃M, R¹ represents a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, R² represents a hydrogen atom or a phenyl group substituted by the group SO₃M, n represents 0 or 1, and M is as defined above; or dyes selected among

- 50 C. I. Acid Black-27, -137 and -158;
C. I. Direct Black-64, -93 and -94; and
55 C. I. Direct Brown-59 and -127.

Furthermore the object is solved according to the invention by a water-soluble dye composition comprising a mixture of at least two water-soluble dyes, each of the dyes satisfying the condition defined by the following expression (I), and the mixture of at least two water-soluble dyes satisfying the condition defined by the following expression (II):

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$$0 \leq \sqrt{a \cdot i^2 + b \cdot i^2} \leq 10 \quad \text{[I]}$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad [II]$$

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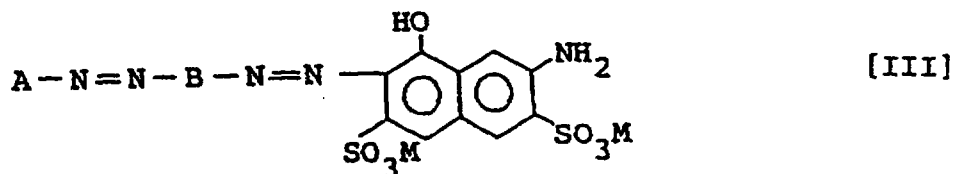
wherein a^* and b^* are chromaticness indices defined in the CIE 1976 (L^* , a^* , b^*) space, i indicates the i th dye of the dyes used together, and n is an integer of 2 or more, wherein at least one of the water-soluble dyes is selected from dyes of group X given below, and one of the others is selected from dyes of group Y given below:

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Dyes of group X

dyes represented by the following formula (III)

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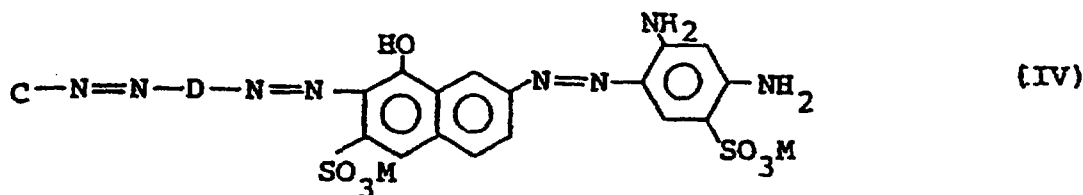
20

wherein A represents a phenyl group substituted by a lower alkylcarbonylamino group, a lower alkoxy group, the group SO_3M or a phenylazo group which may optionally be substituted by the group SO_3M , or a naphthyl group substituted by the group SO_3M , B represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkoxy group, and M represents an alkali metal, ammonium or an amine;

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dyes represented by the following general formula (IV)

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wherein C represents a phenyl or naphthyl group substituted by the group SO_3M , D represents a phenyl group substituted by a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, and M is as defined above; or dyes selected among

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C. I. Direct Black-19, -22, -62, -108, -113, -154 and -159; and

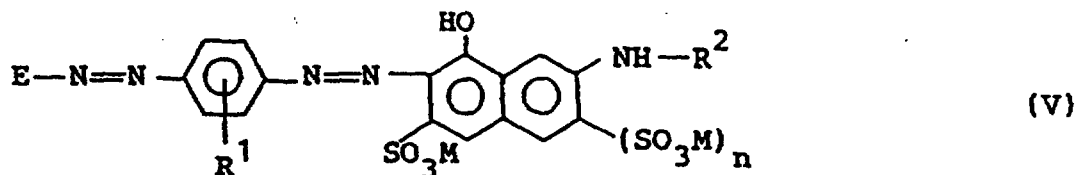
C. I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 and -208;

Dyes of group Y

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dyes represented by the following formula (V)

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wherein E represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkyl group, a lower alkoxy group, a lower alkylcarbonylamino group, or a phenylazo group which may optionally be substituted by the group SO_3M , R^1 represents a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, R^2 represents a hydrogen atom or a phenyl group substituted by the group SO_3M , n represents 0 or 1 and M is as defined above; or dyes selected among

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C. I. Acid Black-27, -137 and -158;

C. I. Direct Black-64, -93 and -94; and

C. I. Direct Brown-59 and -127.

Combinations of dyes represented by the formula (III) or (IV) with dyes represented by the formula (V) are preferred.

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In the present invention, the lower alkyl group and the lower alkoxy group denote alkyl groups and

alkoxy groups having 1 to 4 carbon atoms such as methyl, ethyl, propyl, methoxy, ethoxy and propoxy. Examples of the alkali metal represented by M are Na, K and Li, and examples of the amine are lower alkanolamines such as ethanolamine.

The amount of the mixed dye in the recording liquid is determined depending upon the type of the liquid medium component, the properties required of the recording liquid, etc. Generally, it is 0.5 to 15% by weight, preferably 1 to 8% by weight, based on the total amount of the recording liquid.

Water or mixtures of water with various water-soluble organic solvents may be used as the liquid medium component of the recording liquid of this invention. Examples of the water-soluble organic solvents include alkylalcohols having 1 to 4 carbon atoms such as methylalcohol, ethylalcohol, n-propylalcohol, isopropylalcohol, n-butylalcohol, sec-butylalcohol, tert-butylalcohol and isobutylalcohol; amides such as dimethylformamide and dimethylacetamide; ketones or ketonealcohols such as acetone and diacetonealcohol; ethers such as tetrahydrofuran and dioxane; nitrogen-containing heterocyclic ketones such as N-methyl-2-pyrrolidone and 1,3-dimethyl-2-imidazolidinone; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols containing 2 to 6 carbon atoms in the alkylene group such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol and diethylene glycol; glycerol; lower alkyl ethers of polyhydric alcohols such as ethylene glycol methyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether.

The content of the water-soluble organic solvent in the recording liquid is generally 5 to 95%, preferably 10 to 80%, more preferably 20 to 50%, by weight based on the total weight of the recording liquid.

The content of water at this time, is determined over a wide range depending upon the type of the solvent component, its composition, or the desired properties of the recording liquid. It is generally 10 to 90%, preferably 10 to 70%, more preferably 20 to 70%, based on the total weight of the recording liquid.

The recording liquid of this invention prepared from the aforesaid components has excellent recording characteristics (signal response, stability of liquid droplet formation, ejection stability, continuous recordability for a long period of time, ejection stability after stopping long-term recording), storage stability, fixability to a recording substrate, and the light resistance, weatherability and water resistance of recorded images in a well-balanced combination. In order to improve these properties further, various additives known heretofore may be further incorporated.

Examples of the additives include viscosity adjusting agents such as polyvinyl alcohol, celluloses and water-soluble resins; surface-active agents of the cationic, anionic or nonionic type; surface tension adjusting agents such as diethanolamine or triethanolamine; pH adjusting agents such as buffers; and antifungal agents.

A specific resistance adjusting agent, for example inorganic salt such as lithium chloride, ammonium chloride or sodium chloride is added in order to prepare a recording liquid which is used in an ink-jet recording method of the type involving charging the recording liquid.

Thermal properties (such as specific heat, the coefficient of thermal expansion, thermal conductivity, etc.) of the recording liquid may sometimes be adjusted when it is applied to an ink-jet recording method of the type in which the recording liquid is ejected by the action of thermal energy.

Recording by using the recording liquid of this invention may be carried out by known methods of recording, for example the method described in U.S. Patent 4,295,889.

The use of the recording liquid of this invention makes it possible to obtain black recorded images having an ideal color value.

The viscosity and surface tension of the recording liquid of this invention are within proper ranges. Hence, it does not clog fine orifices, and recorded images having a sufficiently high density can be obtained.

Furthermore, the recording liquid of this invention do not change in physical properties, nor cause precipitation of solids, during storage.

In addition, the recording liquid of this invention can permit recording on various recording substrate without any particular restriction. It has a high speed of fixation and can give images having excellent water resistance, light resistance, abrasion resistance, resolution and printed character quality.

In addition to its application to ink-jet recording, the recording liquid of this invention can also be used as ink for writing instruments.

The present invention is explained in more detail by reference to the following examples.

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Example 1

A black recording liquid for ink-jet recording having the following composition was prepared.

Composition of the recording liquid	Amount (wt%)
C. I. Direct Black-154 ($a^*-3.0$, $b^*-3.6$)	1.5
C. I. Direct Brown-59 ($a^* 2.1$, $b^* 5.3$)	1.5
Diethylene glycol	20
N-methyl-2-pyrrolidone	15
Deionized water (simply water hereinafter)	62

The a^* and b^* values of a single dye were determined on Zerox Paper 4024 (made by Zerox Corporation). This applies also to the subsequent Examples.

The above ingredients were fully mixed in a vessel and filtered under pressure through a filter made of Teflon (Trademark) having a pore size of 1 micron. The liquid was subjected to deaerating treatment using a vacuum pump to form a recording liquid.

The resulting recording liquid was evaluated in regard to the following properties (T_1) to (T_5) by means of a recording device having an on-demand type recording head (ejection orifice diameter 50 microns; piezo vibrator driving voltage 60 V, frequency 4 KHz) adapted to eject the recording liquid by a piezo vibrator. Good results were obtained in each of these test items.

(T_1) Storability of the recording liquid over a long period of time

The recording liquid was sealed up in a glass container, and stored for 6 months both at -30°C and at 60°C . After this storage, precipitation of insoluble matter was not observed, and there was no change in the properties or color of the liquid.

(T_2) Ejection stability

The recording liquid was continuously ejected for 24 hours in an atmosphere kept at room temperature, 5°C , and 40°C , respectively. Under any of these conditions, high quality stable recording could be always carried out.

(T_3) Ejection response

The recording liquid was ejected intermittently at intervals of 2 seconds. Furthermore, after standing for 2 months, the recording liquid was ejected. In either case, the recording liquid did not clog the tip portion of the orifice, and stable and uniform recording could be achieved.

(T_4) Quality of recorded images

Images recorded on the two recording substrates shown in Table 1 below had a high density and were clear. The colors (a^* and b^* values) of the images are shown in Table 1. After exposure of the images to indoor light for 3 months, the percent decrease of their density was less than 1%. When the images were dipped for 1 minute in water, the bleeding of the images was only slight.

(T_5) Fixability to various recording substrates

By using the recording liquid, characters were printed on each of the recording substrates indicated in the following table for 15 seconds, and then the printed portion was rubbed with a finger and examined for image deviation and blotting. In all cases, there was no image deviation nor blotting, and the recording liquid showed excellent fixability to the substrates.

Example 2

Composition of the recording liquid	Amount (wt%)
C. I. Direct Black-19 ($a^*0.1$, $b^*-4.1$)	1.0
C. I. Acid Black-109 ($a^*-1.5$, $b^*-1.9$)	1.0
C. I. Direct Black-64 ($a^*2.1$, $b^*2.3$)	1.0
Ethylene glycol	20
N-methyl-2-pyrrolidone	10
Water	67

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A recording liquid of the above composition was prepared in the same way as in Example 1, and then examined for (T₁) to (T₅) using a recording device having an on-demand type multihead (ejection orifice diameter 35 microns, the resistance of a heat-generating resistance body 150 ohms, driving voltage 30 V, frequency 2 KHz) adapted to perform recording by giving thermal energy to the recording liquid within the recording head and generating liquid droplets of the recording liquid. In all tests, the recording liquid produced excellent results. The colors of the resulting recorded images are shown in Table 1.

Example 3

Composition of the recording liquid	Amount (wt%)
Dye No. 4 in Table 2 (a*-4.4, b*-2.1)	2.5
Dye No. 1 in Table 4 (a*4.4, b*-0.9)	2.5
Ethylene glycol	15
1,3-Dimethyl-2-imidazolidinone	30
Water	50

A recording liquid of the above composition was prepared in the same way as in Example 1, and then examined for (T₁) to (T₅) using a recording device having an on-demand type multihead (ejection orifice diameter 35 microns, the resistance of a heat-generating resistance body 150 ohms, driving voltage 30 V, frequency 2 KHz) adapted to perform recording by giving thermal energy to the recording liquid within the recording head and generating liquid droplets of the recording liquid. In all tests, the recording liquid produced excellent results.

The colors of the resulting recorded images are shown in Table 1.

Example 4

Composition of the recording liquid	Amount (wt%)
Dye No. 1 in Table 2 (a*-5.4, b*-1.5)	2.0
Dye No. 2 in Table 4 (a*5.3, b*0.6)	2.0
Diethylene glycol	25
Ethylene glycol monomethyl ether	10
Water	61

A recording liquid of the above composition was prepared in the same way as in Example 1, and then examined for (T₁) to (T₅) using a recording device having an on-demand type multihead (ejection orifice diameter 35 microns, the resistance of a heat-generating resistance body 150 ohms, driving voltage 30 V, frequency 2 KHz) adapted to perform recording by giving thermal energy to the recording liquid within the recording head and generating liquid droplets of the recording liquid. In all tests, the recording liquid produced excellent results.

The colors of the resulting recorded images are shown in Table 1.

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Example 5

	Composition of the recording liquid	Amount (wt%)
5	C. I. Direct Black-19 (a*0.1, b*-4.1)	1.5
	C. I. Direct Black-93 (a*-0.6, b*3.2)	1.0
	Dye No. 3 in Table 2 (a*-1.5, b*-4.8)	1.5
10	Dye No. 3 in Table 4 (a*5.3, b*1.5)	1.0
	Ethylene glycol	15
15	N-methylpyrrolidone	10
	Water	70

20 A recording liquid of the above composition was prepared in the same way as in Example 1, and then examined for (T₁) to (T₅) using a recording device having an on-demand type multihead (ejection orifice diameter 35 microns, the resistance of a heat-generating resistance body 150 ohms, driving voltage 30 V, frequency 2 KHz) adapted to perform recording by giving thermal energy to the recording liquid within the recording head and generating liquid droplets of the recording liquid. In all tests, the recording liquid
25 produced excellent results.

The colors of the resulting recorded images are shown in Table 1.

Table 1

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Recording substrates (by tradename)

	Xerox paper 4024 (made by Zerox Corporation)		Mitsubishi Diaform (made by Mitsubishi Paper Mills, Ltd. (basis weight: 64 g/cm ²)	
	a*	b*	a*	b*
35				
40				
	Example 1	-0.5 0.4	-0.6	0.2
	Example 2	0.3 -0.4	0.2	-0.5
45	Example 3	0.2 -1.1	-0.1	-0.9
	Example 4	0.2 -0.5	0.6	-0.4
50	Example 5	0.4 -0.8	0.3	-0.6

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Table 2

Dye No.

Structural formula in formula (III)

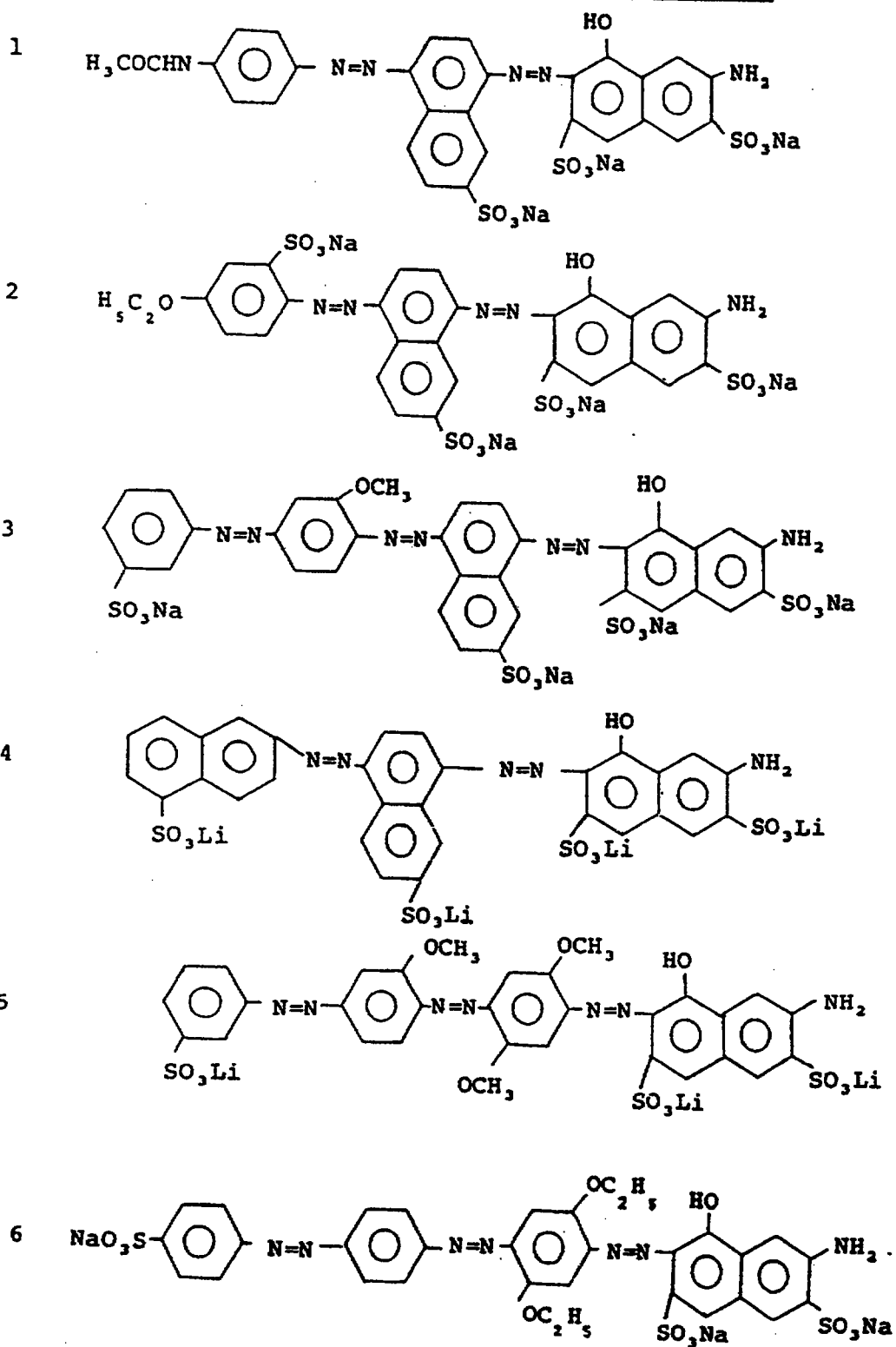


Table 3

Dye No. Structural formula in formula [IV]

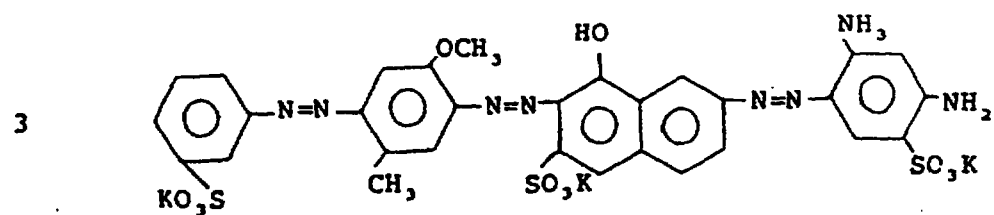
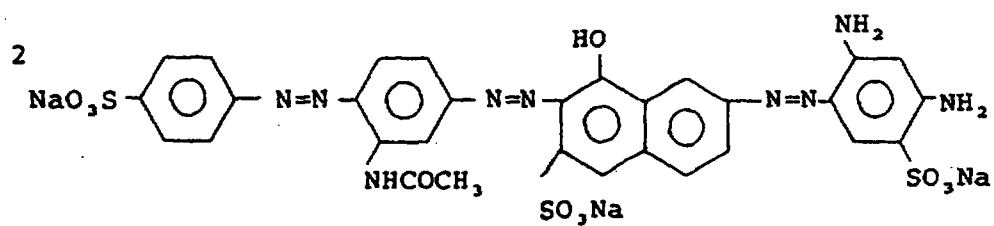
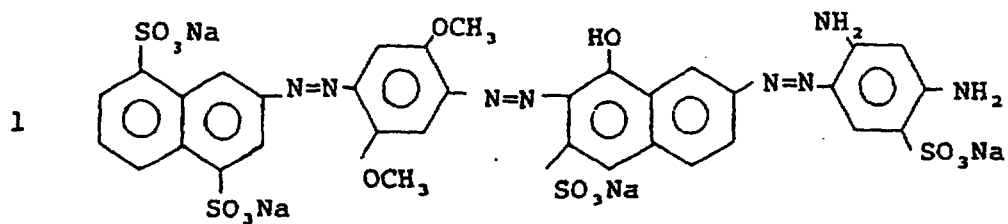
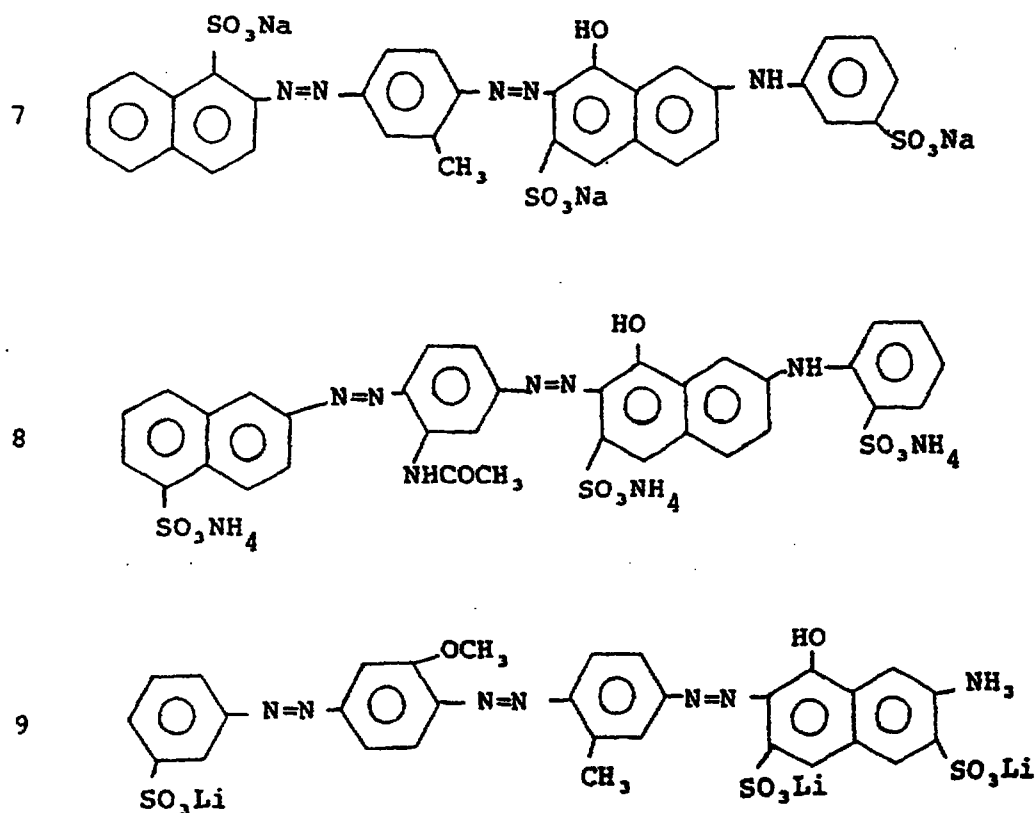


Table 4

Dye No.	Structural formula in formula [V]
1	
2	
3	
4	
5	
6	

Table 4 continued

Dye No. Structural formula in formula (V)



Examples 6 to 15

Recording liquids having the compositions shown in Table 5 were prepared by the same method as in Example 1, and examined for (T₁) to (T₅) as in Example 1. In all tests, good black images could be obtained, and the results were excellent.

Examples 16 to 25

Each of recording liquids of Examples 6 to 15 having the compositions shown in Table 5 below was filled in hollow felt pens. Using each felt pen, writing was made on a median quality paper ("HAKUBOTAN", tradename, a product of Honshu Papermills Co.). As a result, each felt pen was written with good black and without blurring.

The cap of each felt pen was removed, and each felt pen without cap was allowed to stand for 24 hours. The writing property of the pen was tested. As a result, good writing was made for each pen.

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TABLE 5

Example No.	Composition of the recording liquid	Amount (Wt%)
6	C. I. Direct Black-22	1.0
	C. I. Direct Black-113	1.0
	C. I. Acid Black-7	1.0
	C. I. Acid Black-27	1.0
	C. I. Acid Black-158	1.0
	Diethylene glycol	15
	Dimethylacetamide	15
	Water	65
7	C. I. Direct Black-62	1.5
	C. I. Acid Black-52:1	1.0
	C. I. Acid Black-208	1.0
	C. I. Direct Brown-127	1.5
	Propylene glycol	10
	Dioxane	10
	Water	75
8	C. I. Direct Black-108	1.5
	C. I. Acid Black-9	0.5
	C. I. Acid Black-100	1.0
	C. I. Acid Black-158	2.0
	Ethylene glycol	15
	Glycerol	10
	Triethylene glycol monomethyl ether	10
	Water	60
9	C. I. Direct Black-159	1.0
	C. I. Acid Black-137	1.0
	Dye No. 2 in Table 2	2.0
	Dye No. 4 in Table 4	1.0
	Diethylene glycol	10
	N-methylpyrrolidone	10
	Water	75

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Example No.	Composition of the recording liquid	Amount (Wt%)
10	Dye No. 1 in Table 3	1.0
	Dye No. 2 in Table 3	1.0
	Dye No. 6 in Table 4	2.0
	Polyethylene glycol	10
	N-methylpyrrolidone	16
	Water	70
11	Dye No. 3 in Table 3	1.5
	Dye No. 5 in Table 2	1.5
	Dye No. 5 in Table 4	2.0
	Ethylene glycol	15
	1,3-Diethylimidazolidinone	15
	Water	65
12	C. I. Direct Black-154	1.5
	Dye No. 6 in Table 2	1.5
	Dye No. 7 in Table 4	1.0
	Dye No. 8 in Table 4	1.0
	Diethylene glycol	15
	N-methylpyrrolidone	10
	Water	70
13	C. I. Acid Black-9	1.0
	C. I. Acid Black-94:1	1.0
	C. I. Direct Black-94	1.0
	Ethylene glycol	17
	Dimethylacetamide	10
	Water	70
14	C. I. Acid Black-29	0.5
	C. I. Acid Black-48	0.5
	C. I. Acid Black-187	1.0
	C. I. Direct Brown-59	2.0
	Ethylene glycol	16
	1,3-Dimethylimidazolidinone	10
	Water	70

Example No.	Composition of the recording liquid	Amount (Wt%)
5	Dye No. 3 in Table 2	3.0
	Dye No. 9 in Table 4	1.0
	Diethylene glycol	21
10	N-methylpyrrolidone	20
	Water	55

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Referential Example 1

Synthesis of Dye No. 3 in Table 2:

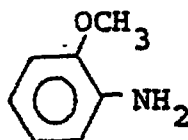
(1) Production of a first diazo solution

Metanilic acid (17.3 g) was added to 346 ml of 3% hydrochloric acid. The mixture was stirred for 3 hours to form a uniform slurry. Ice (200 g) was added to cool the slurry to 3°C. An aqueous solution composed of 73 ml of water and 7.3 g of sodium nitrite was added to the slurry. The mixture was stirred at 3°C for 1 hour to perform diazotization. Sulfamic acid (3 g) was added to remove the remaining sodium nitrite and to obtain a first diazo solution.

(2) First coupling

12.3 g of ortho-anisidine of the following formula

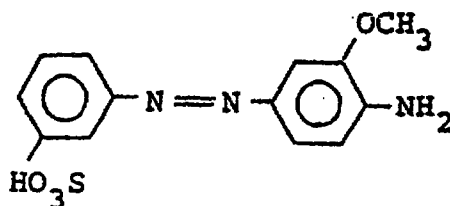
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was added to 450 ml of 50% methanol-water and dissolved. To the solution were added the first diazo solution obtained in (1) above and 10 ml of 25% sodium hydroxide, and the mixture was stirred at a temperature of 0 to 3°C and a pH of 2 to 3 for 15 hours to perform coupling. Sodium chloride (200 g) was added to perform salting out. The precipitated monoazo compound was filtered, washed with 500 ml of a 10% aqueous solution of sodium chloride, and dried to give 28.2 g of a monoazo compound of the following formula.

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(3) Production of a second diazo solution

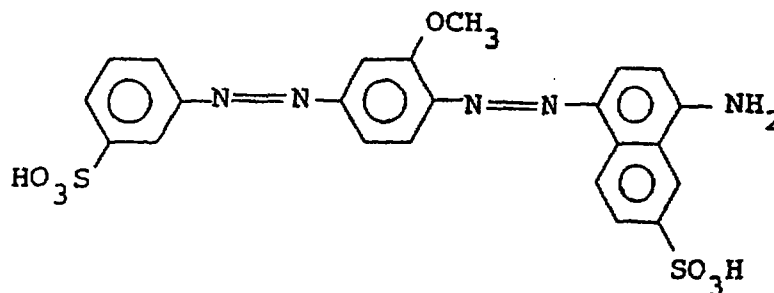
To 300 ml of 5% hydrochloric acid was added 15.4 g of the monoazo compound obtained in (2) above, and the mixture was stirred for 5 hours to form a uniform slurry. Ice (250 g) was added to cool the slurry to 3°C. An aqueous solution composed of 38 ml of water and 3.8 g of sodium nitrite was added to the slurry, and the mixture was stirred at 3°C for 10 hours to perform diazotization. One gram of sulfamic acid was added to remove the remaining sodium nitrite and to form a second diazo solution.

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(4) Second coupling

To 230 ml of water was added 11.2 g of 1-amino-naphthalene-7-sulfonic acid, and 400 g of ice, the second diazo solution obtained in (3) above and 10 ml of 25% sodium hydroxide were added. The mixture was subjected to coupling treatment at a temperature of 2 to 5°C and a pH of 2 to 3. After the mixture was stirred for 5 hours at the above temperature and pH, 100 g of sodium chloride was added to perform salting out. The precipitated compound was filtered, washed with 300 ml of 10% aqueous sodium chloride solution, and dried to give 23.8 g of a disazo compound of the following formula.

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(5) Production of a third diazo solution

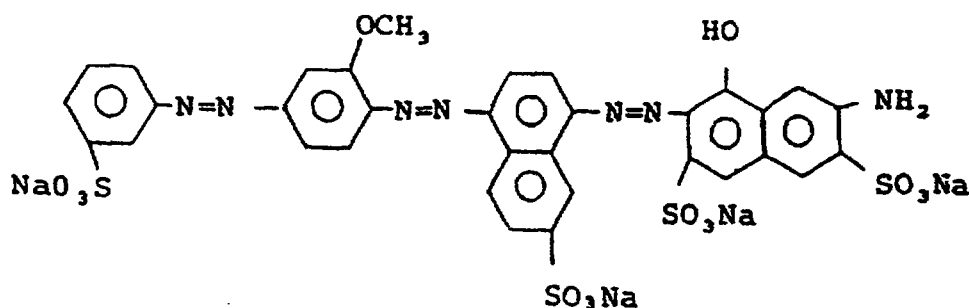
13.5 g of the disazo compound obtained in (4) above was added to 300 ml of 3% hydrochloric acid and 100 ml of acetic acid. The mixture was stirred for 3 hours to form a uniform slurry. Ice (300 g) was added to cool the slurry to 3°C. A solution of 1.8 g of sodium nitrite in 20 ml of water was added to the slurry, and the mixture was stirred at 3°C for 24 hours to perform diazotization. Then, 0.5 g of sulfamic acid was added to remove the remaining sodium nitrite and to form a third diazo solution.

(6) Third coupling

8.0 g of 1-hydroxy-7-amino-naphthalene-3,6-disulfonic acid was added to 320 ml of water, and 600 g of ice, the third diazo solution obtained in (5), and 45 ml of 25% sodium hydroxide were added. The mixture was subjected to coupling treatment at a pH of 8 to 10 and a temperature of 2 to 5°C. After the mixture was stirred at this temperature and pH, 250 g of sodium chloride was added to perform salting out.

The precipitated compound was filtered and then washed with 400 ml of 20% aqueous sodium chloride solution to form 85 g of a wet cake.

The wet cake was subjected to de-salting treatment, and then dried to give 18.3 g of the desired compound of the following formula.



The yield was 76.3%.

This dye had a maximum absorption wavelength, in water, of 615 nm.

Referential Example 2

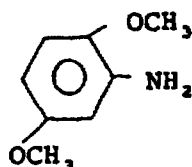
Synthesis of compound No. 1 in Table 3:

(1) Production of a first diazo solution

30.2 g of 2-amino-naphthalene-4,8-disulfonic acid was added to 600 ml of 3% hydrochloric acid, and the mixture was stirred for 3 hours to form a uniform slurry. Ice (400 g) was added to cool the slurry to 3°C. A solution of 7.3 g of sodium nitrite in 73 ml of water was added to the slurry, and the mixture was then stirred at 3°C for 1 hour to perform diazotization. Then, 3 g of sulfamic acid was added to remove the remaining sodium nitrite and to obtain a first diazo solution.

(2) First coupling

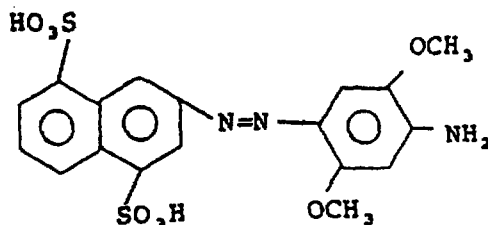
15.3 g of 2,5-dimethoxyaniline having the following formula



was added to 450 ml of water, and the mixture was stirred for 2 hours to form a uniform slurry. Ice (300 g),

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the first diazo solution obtained in (1) above, and 20 ml of 25% sodium hydroxide were added. The mixture was subjected to coupling treatment by stirring it at a temperature of 0 to 3°C and a pH of 2 to 3 for 15 hours. Then, 200 g of sodium chloride was added to perform salting out. The precipitated monoazo compound was filtered, washed with 500 ml of a 10% aqueous solution of sodium chloride, and dried to obtain 41.0 g of a monoazo compound having the following formula.

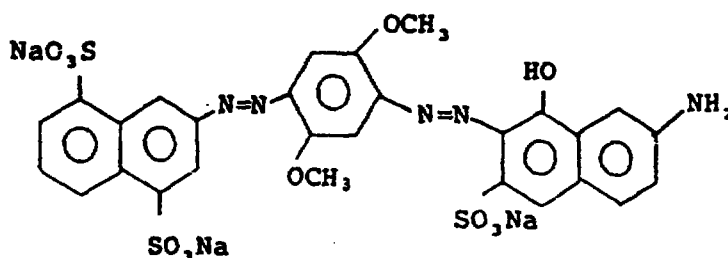


(3) Production of a second diazo solution

23.3 g of the monoazo compound obtained in (2) above was added to 410 ml of 5% hydrochloric acid, and the mixture was stirred for 5 hours to form a uniform slurry. Ice (300 g) was added to cool the slurry to 3°C. A solution of 3.8 g of sodium nitrite in 38 ml of water was added to the slurry, and the mixture was then stirred at 3°C for 10 hours to perform diazotization. One gram of sulfamic acid was added to remove the resulting sodium nitrite and to obtain a second diazo solution.

(4) Second coupling

12.0 g of 1-hydroxy-7-amino-naphthalene-3-sulfonic acid was added to 460 ml of water, and 800 g of ice, the second diazo solution obtained in (3) above, and 55 ml of 25% sodium hydroxide were added to perform coupling at a temperature of 2 to 5°C and a pH of 8 to 10. After the mixture was stirred at the above temperature and pH, 250 g of sodium chloride was added to perform salting out. The precipitated compound was filtered, washed with 300 ml of a 10% aqueous solution of sodium chloride, and dried to give 31.3 g of a disazo compound having the following formula.



(5) Production of a third diazo solution

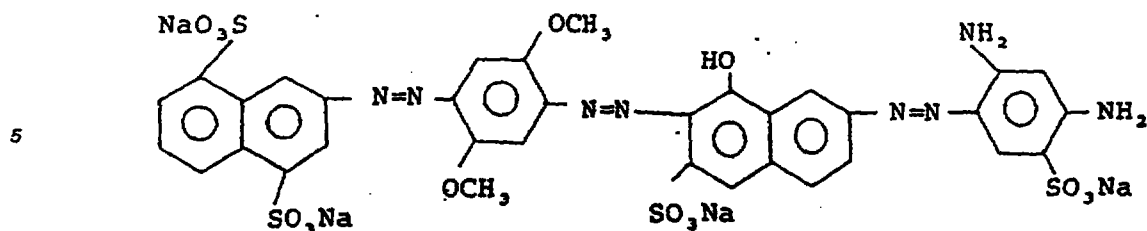
19.6 g of the disazo compound obtained in (4) above was added to 400 ml of 3% hydrochloric acid and 100 ml of acetic acid, and the mixture was stirred for 3 hours to form a uniform slurry. Ice (300 g) was added to cool the slurry to 3°C. A solution of 1.8 g of sodium nitrite in 20 ml of water was added to the slurry, and the mixture was stirred at 3°C for 24 hours to perform diazotization. Then, 0.5 g of sulfamic acid was added to remove the remaining sodium nitrite and to obtain a third diazo solution.

(6) Third coupling

4.7 g of 1,3-diamino-benzene-4-sulfonic acid was added to 100 ml of water, and 50 g of ice was added to the mixture to cool it to 3°C. Then, the third diazo solution obtained in (5) above was added, and the mixture was stirred at 2 to 5°C for 10 hours to perform coupling. Then, 250 g of sodium chloride was added to perform salting out.

The precipitated compound was filtered, and then washed with 400 ml of a 20% aqueous solution of sodium chloride to give 65 g of a wet cake.

The wet cake was subjected to de-salting treatment, and then dried to give 18.6 g of the desired compound of the following formula



10

The yield was 74.1%.

This dye had a maximum absorption wavelength, in water, of 596 nm.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

15

Claims

1. A recording liquid comprising at least two water-soluble dyes and a liquid medium consisting of water or a mixture of water with a water-soluble organic solvent, wherein the total content of the water soluble dyes is 0.5 to 15% by weight based on the total weight of the recording liquid, each of the dyes satisfying the condition defined by the following expression (I), and a mixture of these at least two dyes satisfying the condition defined by the following expression (II)

25

$$0 \leq \sqrt{a^*i^2 + b^*i^2} \leq 10 \quad [I]$$

30

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad [II]$$

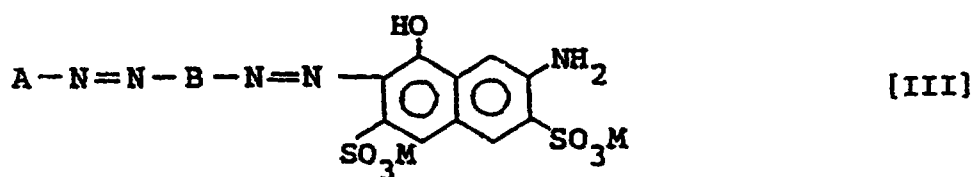
wherein a^* and b^* are chromaticness indices defined in the CIE 1976 (L^* , a^* , b^*) space, i indicates the i th dye of the dyes used together, and n is an integer of 2 or more, wherein at least one of the water-soluble dyes is selected from dyes of group X given below, and one of the others is selected from dyes of group Y given below:

35

Dyes of group X

40 Dyes represented by the following formula (III)

45

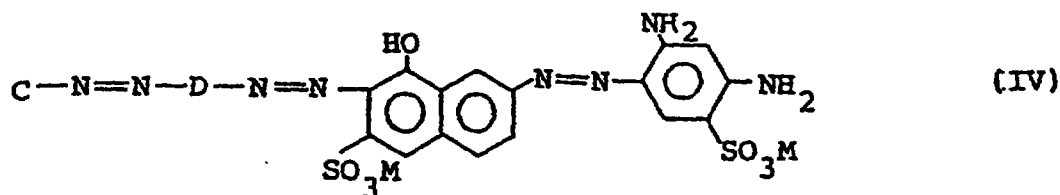


wherein A represents a phenyl group substituted by a lower alkylcarbonylamino group, a lower alkoxy group, the group SO_3M or a phenylazo group which may optionally be substituted by the group SO_3M , or a naphthyl group substituted by the group SO_3M , B represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkoxy group, and M represents an alkali metal, ammonium or an amine;

50

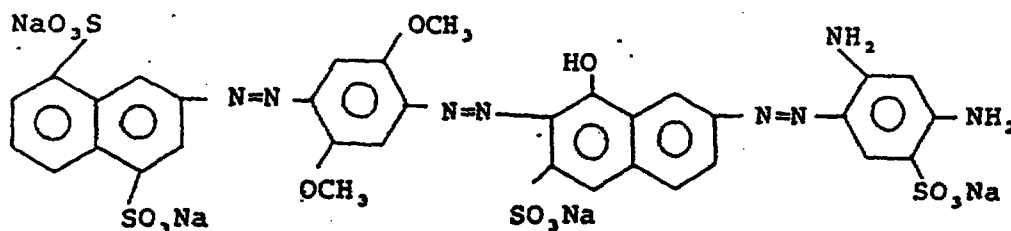
Dyes represented by the following general formula (IV)

55



60

65 wherein C represents a phenyl or naphthyl group substituted by the group SO_3M , D represents a phenyl



The yield was 74.1%.

This dye had a maximum absorption wavelength, in water, of 596 nm.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A recording liquid comprising at least two water-soluble dyes and a liquid medium consisting of water or a mixture of water with a water-soluble organic solvent, wherein the total content of the water soluble dyes is 0.5 to 15% by weight based on the total weight of the recording liquid, each of the dyes satisfying the condition defined by the following expression (I), and a mixture of these at least two dyes satisfying the condition defined by the following expression (II)

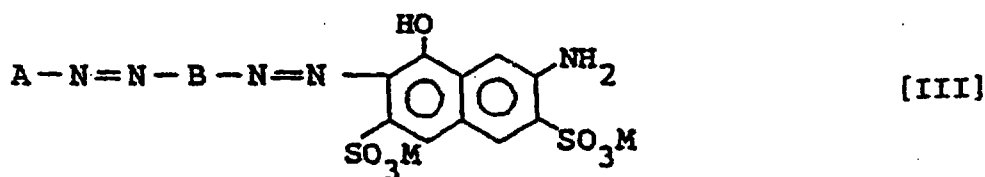
$$0 \leq \sqrt{a^*i^2 + b^*i^2} \leq 10 \quad \text{[I]}$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad \text{[II]}$$

wherein a^* and b^* are chromaticness indices defined in the CIE 1976 (L^* , a^* , b^*) space, i indicates the i th dye of the dyes used together, and n is an integer of 2 or more, wherein at least one of the water-soluble dyes is selected from dyes of group X given below, and one of the others is selected from dyes of group Y given below:

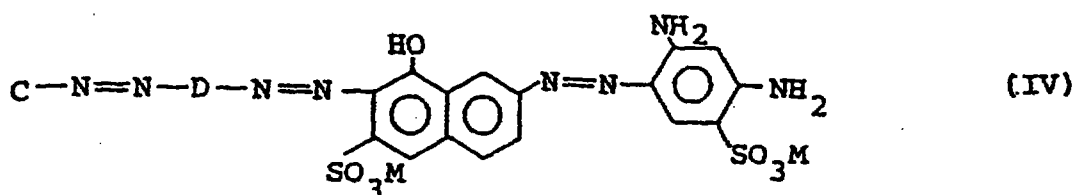
Dyes of group X

Dyes represented by the following formula (III)



wherein A represents a phenyl group substituted by a lower alkylcarbonylamino group, a lower alkoxy group, the group SO_3M or a phenylazo group which may optionally be substituted by the group SO_3M , or a naphthyl group substituted by the group SO_3M , B represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkoxy group, and M represents an alkali metal, ammonium or an amine;

Dyes represented by the following general formula (IV)



wherein C represents a phenyl or naphthyl group substituted by the group SO_3M , D represents a phenyl

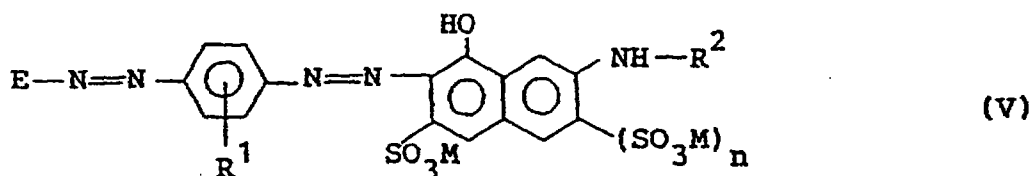


group substituted by a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, and M is as defined above; or dyes selected among

- C. I. Direct Black-19, -22, -62, -108, -113, -154 and -159; and
C. I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 and -208;

Dyes of group Y

Dyes represented by the following formula (V)



wherein E represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkyl group, a lower alkoxy group, a lower alkylcarbonylamino group, or a phenylazo group which may optionally be substituted by the group SO_3M , R^1 represents a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, R^2 represents a hydrogen atom or a phenyl group substituted by the group SO_3M , n represents 0 or 1, and M is as defined above; or dyes selected among

- C. I. Acid Black-27, -137 and -158;
C. I. Direct Black-64, -93 and -94; and
C. I. Direct Brown-59 and -127.

2. The recording liquid according to claim 1, wherein in general formula (III), A is a phenyl group having at least one substituent selected from a lower alkylcarbonylamino group, a lower alkoxy group, the group SO_3M and a SO_3M -substituted phenylazo group.

3. The recording liquid according to claim 1, wherein in the formula (III), A is a naphthyl group substituted by the group SO_3M .

4. The recording liquid according to claim 1, wherein in the formula (III), B is a naphthyl group substituted by the group SO_3M , or a di-lower alkoxy-substituted phenyl group.

5. The recording liquid according to claim 1, wherein in the formula (III), M is Na or Li.

6. The recording liquid according to claim 1, wherein in the formula (IV), C is a phenyl group substituted by the group SO_3M .

7. The recording liquid according to claim 1, wherein in the formula (IV), C is a naphthyl group substituted by the group SO_3M .

8. The recording liquid according to claim 1, wherein in the formula (IV), D is a lower alkoxy-substituted phenyl group or a lower alkylcarbonylamino-substituted phenyl group.

9. The recording liquid according to claim 1, wherein in the formula (V), E is a phenylazo group substituted by the group SO_3M .

10. The recording liquid according to claim 1, wherein in the formula (V), E is a naphthyl group substituted by the group SO_3M .

11. The recording liquid according to claim 1, wherein in the formula (V), R^1 represents a methyl, methoxy, ethoxy or acetyl amino group.

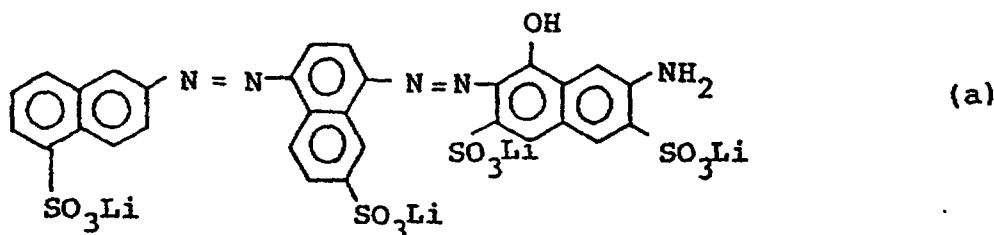
12. The recording liquid according to claim 1, wherein in the formula (V), R^2 is a phenyl group substituted by the group SO_3M .

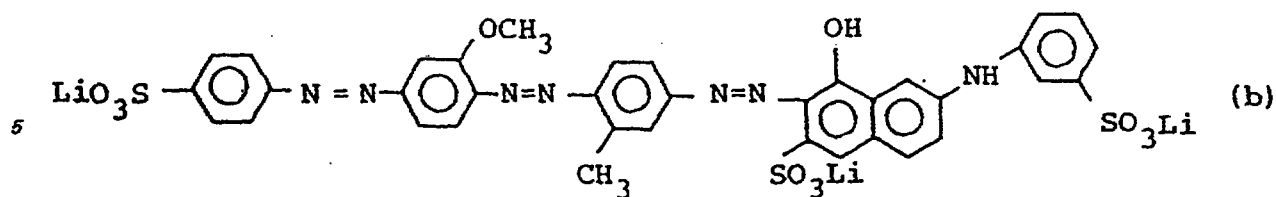
13. The recording liquid according to claim 1, wherein in the formula (V), M is Na, Li or a lower alkanol-ammonium.

14. The recording liquid according to claim 1, wherein the water-soluble dyes are a mixture of C. I. Direct Black-154 as a dye of group X and C. I. Direct Brown-59 as a dye of group Y.

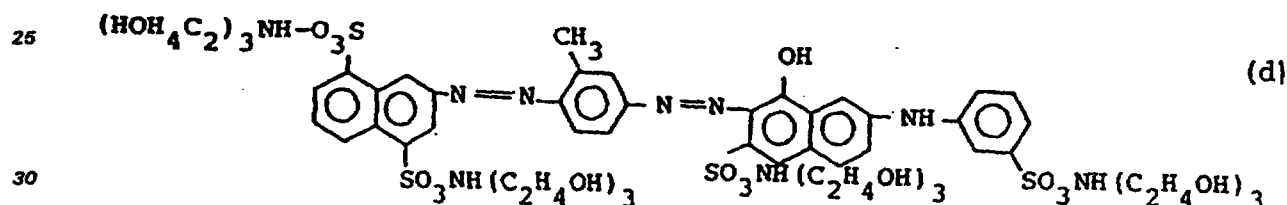
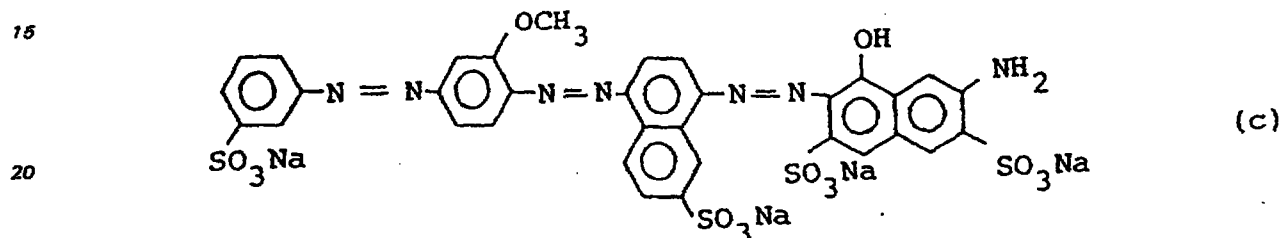
15. The recording liquid according to claim 1, wherein the water-soluble dyes are a mixture of C. I. Direct Black-19 and Acid Black-109 as dyes of group X and C. I. Direct Black-64 as a dye of group Y.

16. The recording liquid according to claim 1, wherein the water-soluble dyes are a mixture of a dye of the following formula (a) in group X, and a dye of the following formula (b) in group Y:





10 17. The recording liquid according to claim 1, wherein the water-soluble dyes are a mixture of C. I. Direct Black-19 and a dye of the following formula (c) in group X and C. I. Direct Black-93 and a dye of the following formula (d) in group Y:



18. The recording liquid according to claim 1, wherein the total content of the water-soluble dyes is 1 to 8% by weight based on the total weight of the recording liquid.

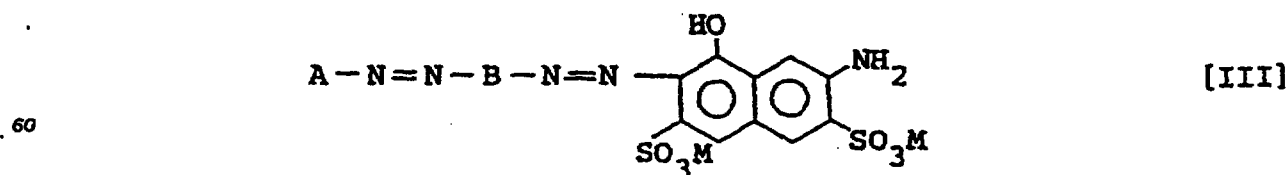
19. A water-soluble dye composition comprising a mixture of at least two water-soluble dyes, each of the dyes satisfying the condition defined by the following expression (I), and the mixture of at least two water-soluble dyes satisfying the condition defined by the following expression (II):

$$0 \leq \sqrt{a \cdot i^2 + b \cdot i^2} \leq 10 \quad [I]$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad \text{[II]}$$

wherein a^* and b^* are chromaticness indices defined in the CIE 1976 (L^* , a^* , b^*) space, i indicates the i th dye of the dyes used together, and n is an integer of 2 or more, wherein at least one of the water-soluble dyes is selected from dyes of group X given below, and one of the others is selected from dyes of group Y given below:

Dyes of group X
dyes represented by the following formula (III)

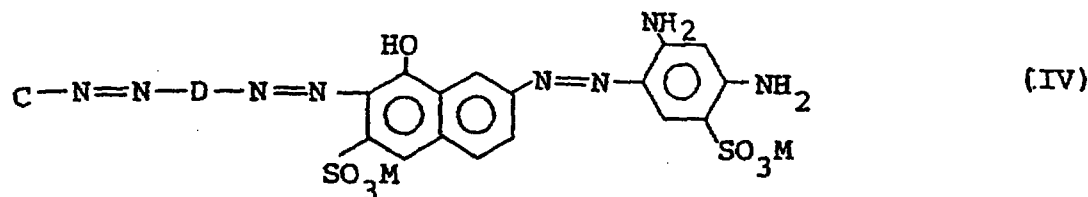


65 wherein A represents a phenyl group substituted by a lower alkylcarbonylamino group, a lower alkoxy group, the group SO₂M or a phenylazo group which may optionally be substituted by the group SO₂M, or a



naphthyl group substituted by the group SO_3M , B represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkoxy group, and M represents an alkali metal, ammonium or an amine;

dyes represented by the following general formula (IV)



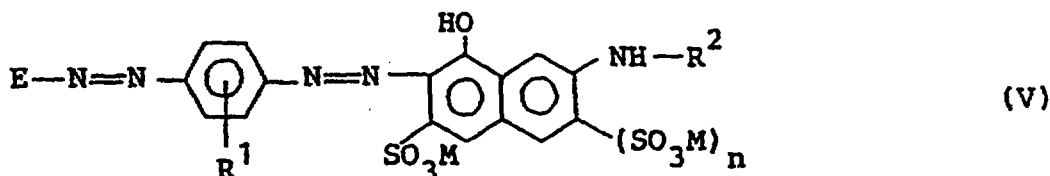
15 wherein C represents a phenyl or naphthyl group substituted by the group SO_3M , D represents a phenyl group substituted by a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, and M is as defined above; or dyes selected among

C. I. Direct Black-19, -22, -62, -108, -113, -154 and -159; and

C. I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 and -208;

20 *Dyes of group Y*

dyes represented by the following formula (V)



35 wherein E represents a naphthyl group substituted by the group SO_3M or a phenyl group substituted by a lower alkyl group, a lower alkoxy group, a lower alkylcarbonylamino group, or a phenylazo group which may optionally be substituted by the group SO_3M , R^1 represents a lower alkyl group, a lower alkoxy group or a lower alkylcarbonylamino group, R^2 represents a hydrogen atom or a phenyl group substituted by the group SO_3M , n represents 0 or 1, and M is as defined above; or dyes selected among

C. I. Acid Black-27, -137 and -158;

C. I. Direct Black-64, -93 and -94; and

C. I. Direct Brown-59 and -127.

40 20. The water-soluble dye composition according to claim 19, wherein in the formula (III), A is a phenyl group having at least one substituent selected from a lower alkylcarbonylamino group, a lower alkoxy group, the group SO_3M and a SO_3M -substituted phenylazo group.

21. The water-soluble dye composition according to claim 19, wherein in the formula (III), A is a naphthyl group substituted by the group SO_3M .

45 22. The water-soluble dye composition according to claim 19, wherein in the formula (III), B is a naphthyl group substituted by the group SO_3M or a di-lower alkoxy-substituted phenyl group.

23. The water-soluble dye composition according to claim 19, wherein in the formula (III), M is Na or Li.

24. The water-soluble dye composition according to claim 19, wherein in the formula (IV), C is a phenyl group substituted by the group SO_3M .

50 25. The water-soluble dye composition according to claim 19, wherein in the formula (IV), C is a naphthyl group substituted by the group SO_3M .

26. The water-soluble dye composition according to claim 19, wherein in the formula (IV), D is a lower alkoxy-substituted phenyl group or a lower alkylcarbonylamino-substituted phenyl group.

27. The water-soluble dye composition according to claim 19, wherein in the formula (V), E is a phenylazo group substituted by the group SO_3M .

55 28. The water-soluble dye composition according to claim 19, wherein in the formula (V), E is a naphthyl group substituted by the group SO_3M .

29. The water-soluble dye composition according to claim 19, wherein in the formula (V), R^1 represents a methyl, methoxy, ethoxy or acetylamino group.

60 30. The water-soluble dye composition according to claim 19, wherein in the formula (V), R^2 is a phenyl group substituted by the group SO_3M .

31. The water-soluble dye composition according to claim 19, wherein the formula (V), M is Na, Li or a lower alkanolammonium.

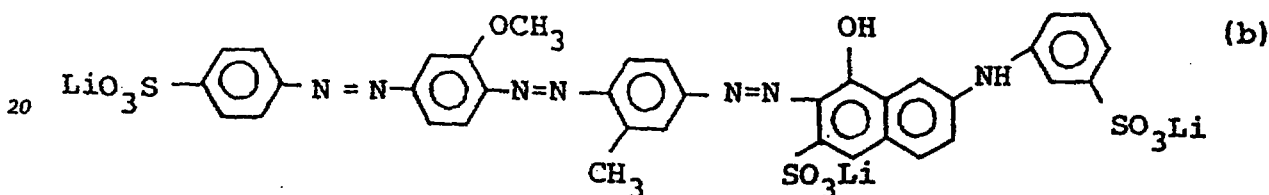
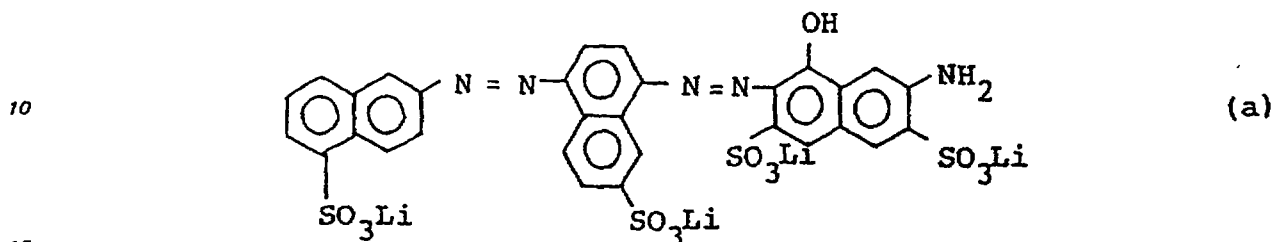
65 32. The water-soluble dye composition according to claim 19, wherein the water-soluble dyes are a mixture of C. I. Direct Black-154 as a dye of group X and C. I. Direct Brown-59 as a dye of group Y.



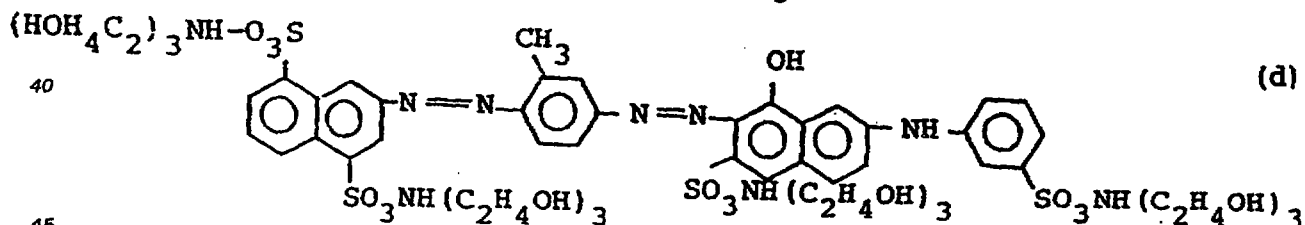
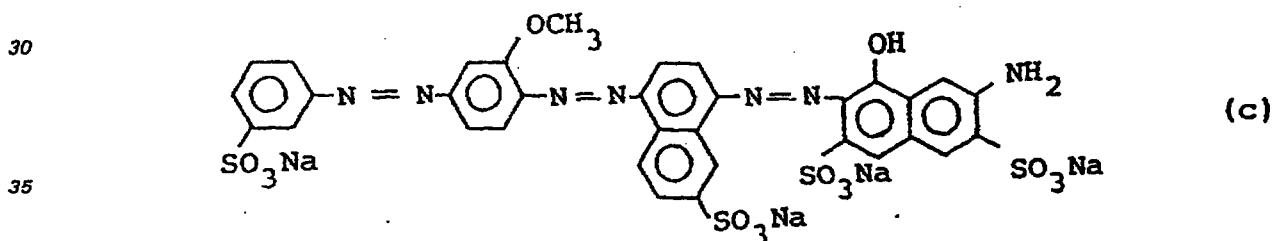
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33. The water-soluble dye composition according to claim 19, wherein the water-soluble dyes are a mixture of C. I. Direct Black-19 and Acid Black-109 as dyes of group X and C. I. Direct Black-64 as a dye of group Y.

34. The water-soluble dye composition according to claim 19, wherein the water-soluble dyes are a mixture of a dye of the following formula (a) in group X, and a dye of the following formula (b) in group Y:



25 35. The water-soluble dye composition according to claim 19, wherein the water-soluble dyes are a mixture of C. I. Direct Black-19 and a dye of the following formula (c) in group X and C. I. Direct Black-93 and a dye of the following formula (d) in group Y:



Patentansprüche

1. Aufzeichnungsflüssigkeit, die wenigstens zwei wasserlösliche Farbstoffe und ein flüssiges Medium, das aus Wasser oder einer Mischung von Wasser mit einem wasserlöslichen organischen Lösungsmittel besteht, enthält, wobei der auf die gesamte Masse der Aufzeichnungsflüssigkeit bezogene Gesamtgehalt der wasserlöslichen Farbstoffe 0,5 bis 15 Masse% beträgt, jeder der Farbstoffe die Bedingung erfüllt, die durch den folgenden Ausdruck (I) definiert ist, und eine Mischung dieser wenigstens zwei Farbstoffe die Bedingung erfüllt, die durch den folgenden Ausdruck (II) definiert ist:

$$0 \leq \sqrt{a^*i^2 + b^*i^2} \leq 10 \quad [I]$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad [II]$$

65 worin a^* und b^* Farbmaßzahlen sind, die in dem Raum (L^*, a^*, b^*) des CIE-1976-Systems definiert sind, /

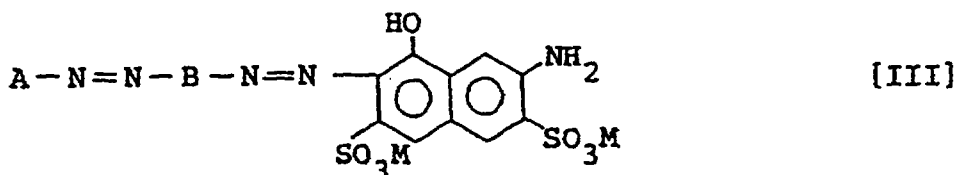


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den *i*-ten Farbstoff der zusammen verwendeten Farbstoffe anzeigt und *n* eine ganze Zahl ist, die wenigstens 2 beträgt, wobei wenigstens einer der wasserlöslichen Farbstoffe aus Farbstoffen der nachstehend angegebenen Gruppe X ausgewählt ist und einer der anderen aus Farbstoffen der nachstehend angegebenen Gruppe Y ausgewählt ist:

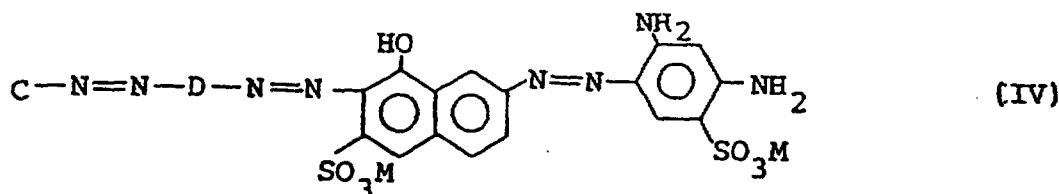
Farbstoffe der Gruppe X

Farbstoffe, die durch die folgende Formel (III) wiedergegeben werden:



worin A eine Phenylgruppe, die durch eine Niederalkylcarbonylaminogruppe, eine Niederalkoxygruppe, die Gruppe SO_3M oder eine Phenylazogruppe, die wahlweise durch die Gruppe SO_3M substituiert sein kann, substituiert ist, oder eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, B eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine Phenylgruppe, die durch eine Niederalkoxygruppe substituiert ist, bedeutet und M ein Alkalimetall, Ammonium oder ein Amin bedeutet;

Farbstoffe, die durch die folgende allgemeine Formel (IV) wiedergegeben



worin C eine Phenyl- oder Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, D eine Phenylgruppe, die durch eine Niederalkylgruppe, eine Niederalkoxygruppe oder eine Niederalkylcarbonylaminogruppe substituiert ist, bedeutet, und M wie vorstehend definiert ist; oder Farbstoff, die aus

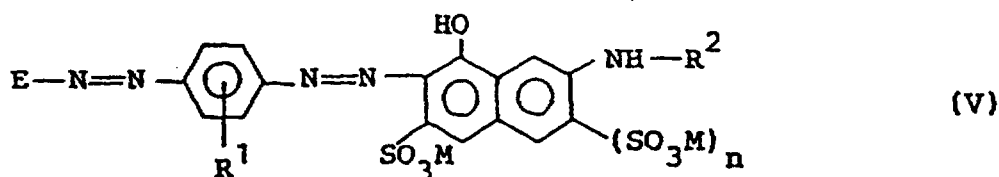
C.I. Direct Black-19, -22, -62, -108, -113, -154 und -159 und

C.I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 und -208

ausgewählt sind;

Farbstoffe der Gruppe Y

Farbstoffe, die durch die folgende Formel (V) wiedergegeben werden:



worin E eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine Phenylgruppe, die durch eine Niederalkylgruppe, eine Niederalkoxygruppe, eine Niederalkylcarbonylaminogruppe oder eine Phenylazogruppe, die wahlweise durch die Gruppe SO_3M substituiert sein kann, substituiert ist, bedeutet, R^1 eine Niederalkylgruppe, eine Niederalkoxygruppe oder eine Niederalkylcarbonylaminogruppe bedeutet, R^2 ein Wasserstoffatom oder eine Phenylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, *n* 0 oder 1 bedeutet und M wie vorstehend definiert ist; oder Farbstoffe, die aus

C.I. Acid Black-27, -137 und -158;

C.I. Direct Black-64, -93 und -94 und

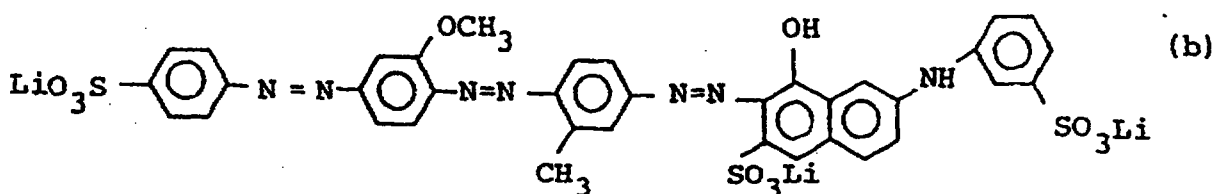
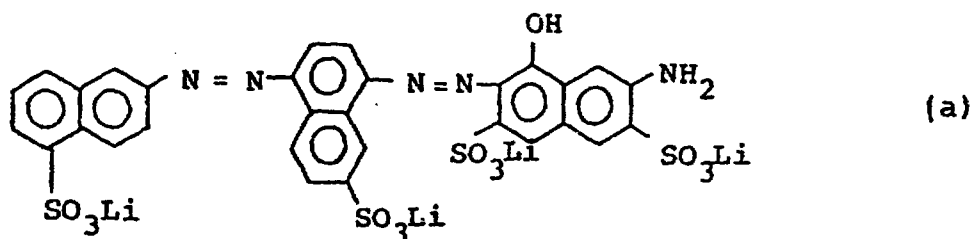
C.I. Direct Brown-59 und -127

ausgewählt sind.

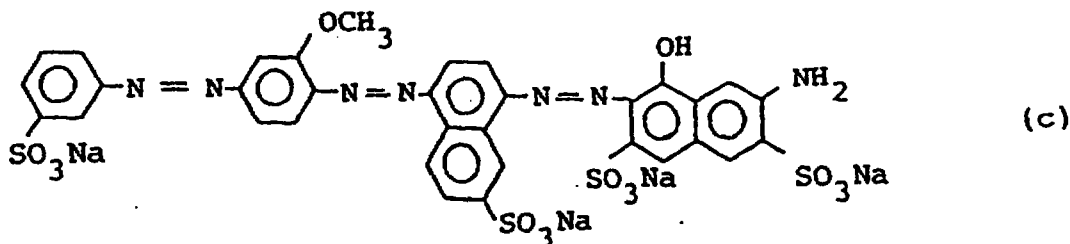
2. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der allgemeinen Formel (III) A eine Phenylgruppe ist, die wenigstens einen aus einer Niederalkylcarbonylaminogruppe, einer Niederalkoxygruppe, der Gruppe SO_3M und einer SO_3M -substituierten Phenylazogruppe ausgewählten Substituenten hat.

3. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (III) A eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

4. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (III) B eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine diniederalkoxysubstituierte Phenylgruppe ist.
5. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (III) M Na oder Li ist.
6. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (IV) C eine Phenylgruppe ist, die durch die Gruppe SO_3M substituiert ist.
7. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (IV) C eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.
8. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (IV) D eine niederalkoxy-substituierte Phenylgruppe oder eine niederalkylcarbonylaminosubstituierte Phenylgruppe ist.
9. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (V) E eine Phenylazogruppe ist, die durch die Gruppe SO_3M substituiert ist.
10. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (V) E eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.
11. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (V) R^1 eine Methyl-, Methoxy-, Ethoxy- oder Acetylaminogruppe bedeutet.
12. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (V) R^2 eine Phenylgruppe ist, die durch die Gruppe SO_3M substituiert ist.
13. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der in der Formel (V) M Na, Li oder ein Nieder-alkanolammonium ist.
14. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-154 als Farbstoff der Gruppe X und C.I. Direct Brown-59 als Farbstoff der Gruppe Y sind.
15. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-19 und C.I. Acid Black-109 als Farbstoffen der Gruppe X und C.I. Direct Black-64 als Farbstoff der Gruppe Y sind.
16. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der die wasserlöslichen Farbstoffe eine Mischung aus einem Farbstoff der folgenden Formel (a) in der Gruppe X und einem Farbstoff der folgenden Formel (b) in der Gruppe Y sind:

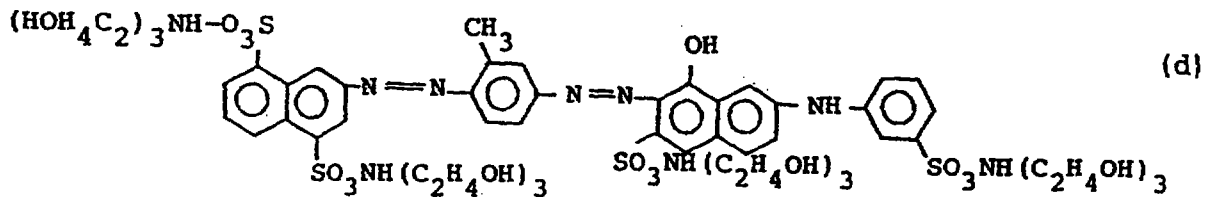


17. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-19 und einem Farbstoff der folgenden Formel (c) in der Gruppe X und C.I. Direct Black-93 und einem Farbstoff der folgenden Formel (d) in der Gruppe Y sind:





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18. Aufzeichnungsflüssigkeit nach Anspruch 1, bei der der auf die gesamte Masse der Aufzeichnungsflüssigkeit bezogene Gesamtgehalt der wasserlöslichen Farbstoffe 1 bis 8 Masse% beträgt.

19. Wasserlösliche Farbstoffzusammensetzung, die aus einer Mischung von wenigstens zwei wasserlöslichen Farbstoffen besteht, wobei jeder der Farbstoffe die Bedingung erfüllt, die durch den folgenden Ausdruck (I) definiert ist, und die Mischung von wenigstens zwei Farbstoffen die Bedingung erfüllt, die durch den folgenden Ausdruck (II) definiert ist:

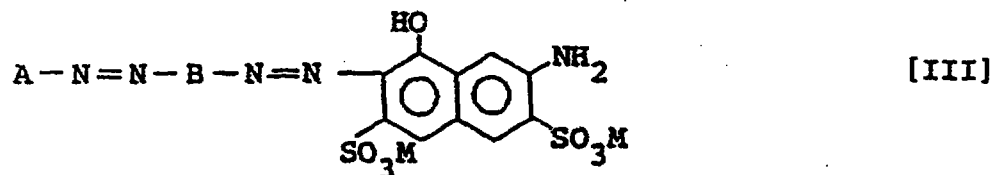
$$0 \leq \sqrt{a^*i^2 + b^*i^2} \leq 10 \quad [I]$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad [II]$$

worin a^* und b^* Farbmaßzahlen sind, die in dem Raum (L^*, a^*, b^*) des CIE-1976-Systems definiert sind, i den i -ten Farbstoff der zusammen verwendeten Farbstoffe anzeigt und n eine ganze Zahl ist, die wenigstens 2 beträgt, wobei wenigstens einer der wasserlöslichen Farbstoffe aus Farbstoffen der nachstehend angegebenen Gruppe X ausgewählt ist und einer der anderen aus Farbstoffen der nachstehend angegebenen Gruppe Y ausgewählt ist:

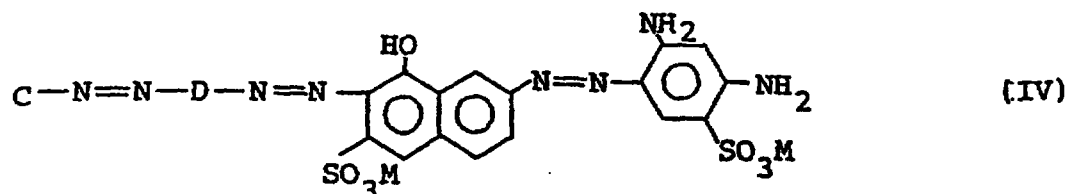
Farbstoffe der Gruppe X

Farbstoffe, die durch die folgende Formel (III) wiedergegeben werden:



worin A eine Phenylgruppe, die durch eine Niederalkylcarbonylaminogruppe, eine Niederalkoxygruppe, die Gruppe SO_3M oder eine Phenylazogruppe, die wahlweise durch die Gruppe SO_3M substituiert sein kann, substituiert ist, oder eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, B eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine Phenylgruppe, die durch eine Niederalkoxygruppe substituiert ist, bedeutet und M eine Alkalimetall, Ammonium oder ein Amin bedeutet;

Farbstoffe, die durch die folgende allgemeine Formel (IV) wiedergegeben werden:



worin C eine Phenyl- oder Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, D eine Phenylgruppe, die durch eine Niederalkylgruppe, eine Niederalkoxygruppe oder eine Niederalkylcarbonylaminogruppe substituiert ist, bedeutet, und M wie vorstehend definiert ist oder Farbstoffe, die aus

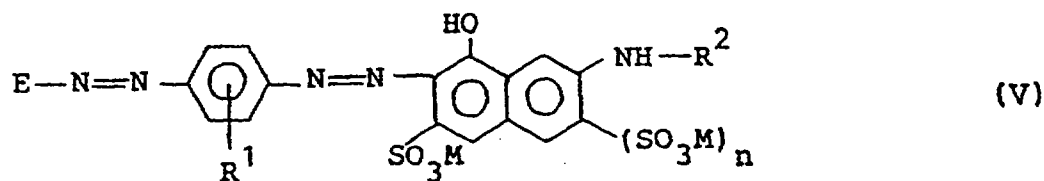
C.I. Direct Black-19, -22, -62, -108, -113, -154 und -159 und

C.I. Acid Black-7, -9, -29, -48, -52:1, -94:1, -109, -110, -187 und -208

ausgewählt sind;

Farbstoffe der Gruppe Y

Farbstoffe, die durch die folgende Formel (V) wiedergegeben werden:



worin E eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine Phenylgruppe, die durch eine Niederal kylgruppe, eine Niederal koxygruppe, eine Niederal kylcarbonylaminogruppe oder eine Phenylazogruppe, die wahlweise durch die Gruppe SO_3M substituiert sein kann, substituiert ist, bedeutet, R^1 eine Niederal kylgruppe, eine Niederal koxygruppe oder eine Niederal kylcarbonylaminogruppe bedeutet, R^2 ein Wasserstoffatom oder eine Phenylgruppe, die durch die Gruppe SO_3M substituiert ist, bedeutet, n 0 oder 1 bedeutet und M wie vorstehend definiert ist; oder Farbstoffe, die aus

C.I. Acid Black-27, -137 und -158;

C.I. Direct Black-64, -93 und -94 und

C.I. Direct Brown-59 und -127

ausgewählt sind.

20. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (III) A eine Phenylgruppe ist, die wenigstens einen aus einer Niederal kylcarbonylaminogruppe, einer Niederal koxygruppe, der Gruppe SO_3M und einer SO_3M -substituierten Phenylazogruppe ausgewählten Substituenten hat.

21. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (III) A eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

22. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (III) B eine Naphthylgruppe, die durch die Gruppe SO_3M substituiert ist, oder eine diniederal koxysubstituierte Phenylgruppe ist.

23. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (III) M Na oder Li ist.

24. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (IV) C eine Phenylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

25. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (IV) C eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

26. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (IV) D eine niederal koxysubstituierte Phenylgruppe oder eine niederal kylcarbonylaminosubstituierte Phenylgruppe ist.

27. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (V) E eine Phenylazogruppe ist, die durch die Gruppe SO_3M substituiert ist.

28. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (V) E eine Naphthylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

29. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (V) R^1 eine Methyl-, Methoxy-, Ethoxy- oder Acetylaminogruppe bedeutet.

30. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (V) R^2 eine Phenylgruppe ist, die durch die Gruppe SO_3M substituiert ist.

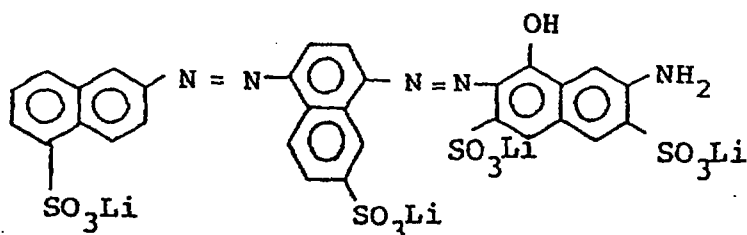
31. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der in der Formel (V) M Na, Li oder ein Niederal kanolammonium ist.

32. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-154 als Farbstoff der Gruppe X und C.I. Direct Brown-59 als Farbstoff der Gruppe Y sind.

33. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-19 und C.I. Acid Black-109 als Farbstoffen der Gruppe X und C.I. Direct Black-64 als Farbstoff der Gruppe Y sind.

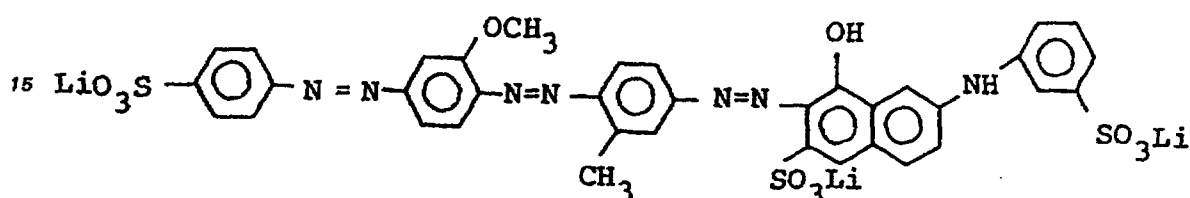
34. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der die wasserlöslichen Farbstoffe eine Mischung aus einem Farbstoff der folgenden Formel (a) in der Gruppe X und einem Farbstoff der folgenden Formel (b) in der Gruppe Y sind:





(a)

10

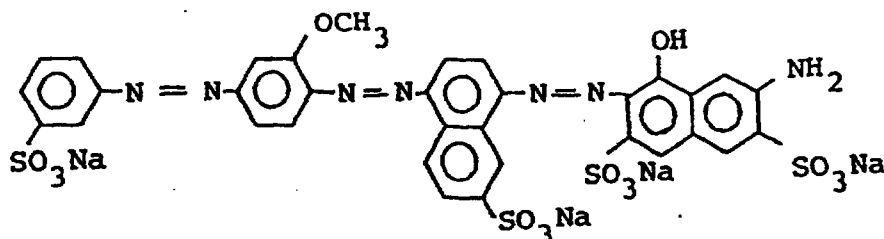


(b)

20

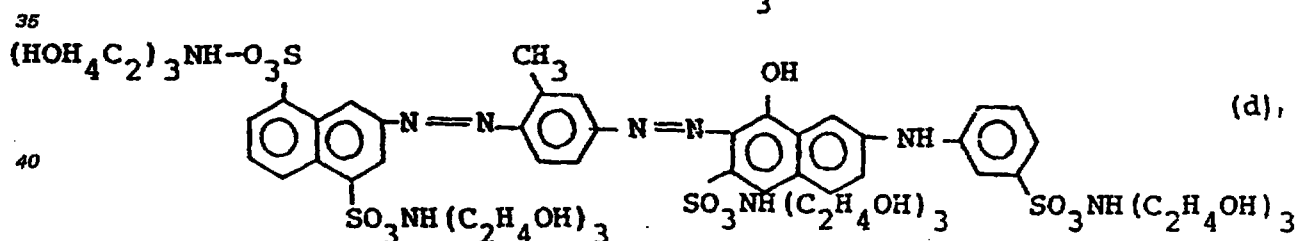
35. Wasserlösliche Farbstoffzusammensetzung nach Anspruch 19, bei der die wasserlöslichen Farbstoffe eine Mischung aus C.I. Direct Black-19 und einem Farbstoff der folgenden Formel (c) in der Gruppe X und C.I. Direct Black-93 und einem Farbstoff der folgenden Formel (d) in der Gruppe Y sind:

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(c)

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(d),

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45 Revendications

1. Liquide d'enregistrement comprenant au moins deux colorants hydrosolubles et un milieu liquide constitué d'eau ou d'un mélange d'eau et d'un solvant organique hydrosoluble, dans lequel la teneur totale en colorants hydrosolubles est de 0,5 à 15% en poids sur la base du poids total du liquide d'enregistrement, chacun des colorants satisfaisant à la condition définie par l'expression (I) ci-après, et un mélange de ces colorants au moins au nombre de deux satisfaisant à la condition définie par l'expression (II) ci-après

50

$$0 \leq \sqrt{a^*i^2 + b^*i^2} \leq 10 \quad [I]$$

55

$$0 \leq \sqrt{\left(\sum_{i=1}^n a^*i\right)^2 + \left(\sum_{i=1}^n b^*i\right)^2} \leq 2 \quad [II]$$

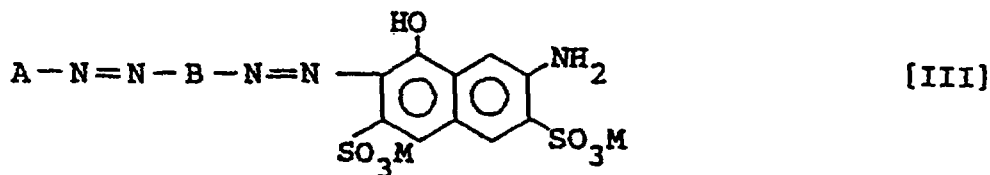
60

où a^* et b^* sont les indices de chromaticité définis dans l'espace (L^*, a^*, b^*) CIE 1976, i indique le colorant d'ordre i des colorants utilisés ensemble et n est un nombre entier égal ou supérieur à 2, l'un au moins des colorants hydrosolubles étant choisi parmi des colorants du groupe X indiqués ci-dessous et l'un des autres colorants étant choisi parmi des colorants du groupe Y indiqués ci-dessous:

65

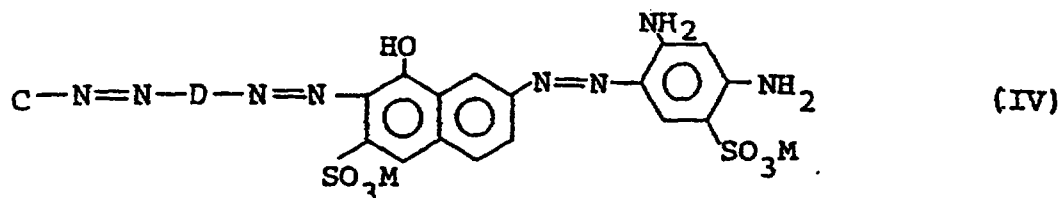
**Colorants du groupe X**

Colorants représentés par la formule (III) suivante:



dans laquelle A représente un groupe phényle substitué par un groupe (alkyle inférieur)-carbonylamino, un groupe alkoxy inférieur, le groupe SO₃M ou un groupe phénylazo qui peut facultativement être substitué par le groupe SO₃M, ou un groupe naphthyle substitué par le groupe SO₃M, B représente un groupe naphthyle substitué par le groupe SO₃M ou un groupe phényle substitué par un groupe alkoxy inférieur, et M représente un métal alcalin, l'ion ammonium ou une amine;

des colorants représentés par la formule générale (IV) suivante



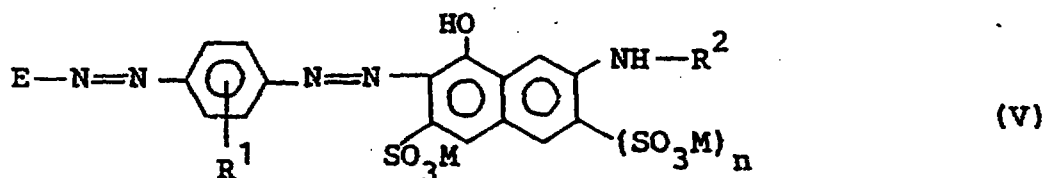
dans laquelle C représente un groupe phényle ou naphthyle substitué par le groupe SO₃M, D représente un groupe phényle substitué par un groupe alkyle inférieur, un groupe alkoxy inférieur ou un groupe (alkyle inférieur)-carbonylamino et M a la définition donnée ci-dessus; ou des colorants choisis parmi les colorants

Noir Direct C.I. 19, 22, 62, 108, 113, 154 et 159; et

Noir Acide C.I. 7, 9, 29, 48, 52:1, 94:1, 109, 110, 187 et 208.

Colorants du groupe Y

Colorants représentés par la formule (V)



dans laquelle E représente un groupe naphthyle substitué par le groupe SO₃M ou un groupe phényle substitué par un groupe alkyle inférieur, un groupe alkoxy inférieur, un groupe (alkyle inférieur)-carbonylamino ou un groupe phénylazo qui peut facultativement être substitué par le groupe SO₃M, R¹ représente un groupe alkyle inférieur, un groupe alkoxy inférieur ou un groupe (alkyle inférieur)-carbonylamino, R² représente un atome d'hydrogène ou un groupe phényle substitué par le groupe SO₃M, n a la valeur 0 ou 1 et M a la définition donnée ci-dessus; ou des colorants choisis parmi les colorants:

Noir Acide C.I. 27, 137 et 158;

Noir Direct C.I. 64, 93 et 94; et

Brun Direct C.I. 59 et 127.

2. Liquide d'enregistrement suivant la revendication 1, dans lequel A, dans la formule générale (III), représente un groupe phényle portant au moins un substituant choisi entre un groupe (alkyle inférieur)-carbonylamino, un groupe alkoxy inférieur, le groupe SO₃M et un groupe phénylazo à substituant SO₃M.

3. Liquide d'enregistrement suivant la revendication 1, dans lequel A dans la formule (III) est un groupe naphthyle substitué par le groupe SO₃M.

4. Liquide d'enregistrement suivant la revendication 1, dans lequel B dans la formule (III) est un groupe naphthyle substitué par le groupe SO₃M ou un groupe phényle portant deux substituants alkoxy inférieur.

5. Liquide d'enregistrement suivant la revendication 1, dans lequel M dans la formule (III) représente Na ou Li.

6. Liquide d'enregistrement suivant la revendication 1, dans lequel C dans la formule (IV) est un groupe



phényle substitué par le groupe SO_3M .

7. Liquide d'enregistrement suivant la revendication 1, dans lequel C dans la formule (IV) est un groupe naphthyle substitué par le groupe SO_3M .

8. Liquide d'enregistrement suivant la revendication 1, dans lequel D dans la formule (IV) est un groupe phényle à substituant alkoxy inférieur ou un groupe phényle à substituant (alkyle inférieur)-carbonylamino.

9. Liquide d'enregistrement suivant la revendication 1, dans lequel E dans la formule (V) est un groupe phénylazo substitué par le groupe SO_3M .

10. Liquide d'enregistrement suivant la revendication 1, dans lequel E dans la formule (V) est un groupe naphthyle substitué par le groupe SO_3M .

11. Liquide d'enregistrement suivant la revendication 1, dans lequel R^1 dans la formule (V) représente un groupe méthyle, méthoxy, éthoxy ou acétylamino.

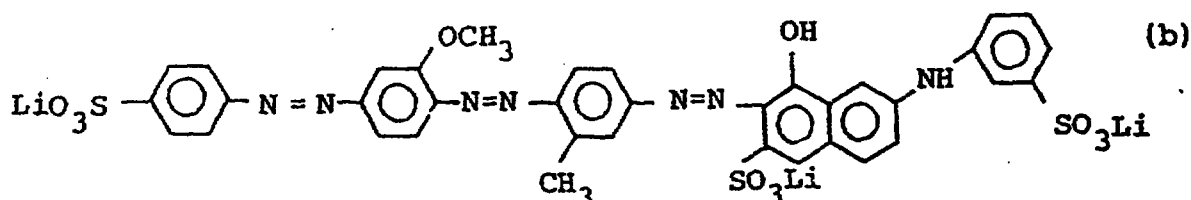
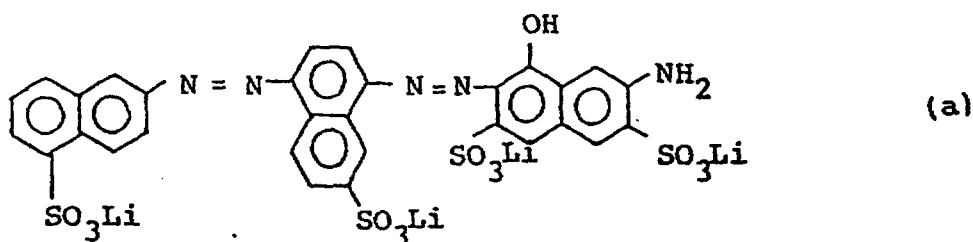
12. Liquide d'enregistrement suivant la revendication 1, dans lequel R^2 dans la formule (V) représente un groupe phényle substitué par le groupe SO_3M .

13. Liquide d'enregistrement suivant la revendication 1, dans lequel M dans la formule (V) représente Na, Li ou un groupe alcanolammonium inférieur.

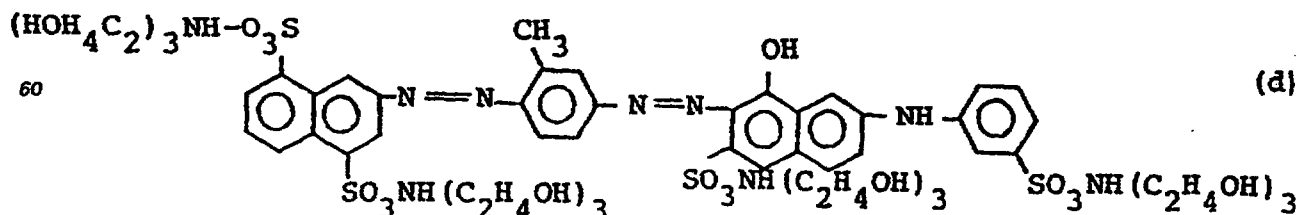
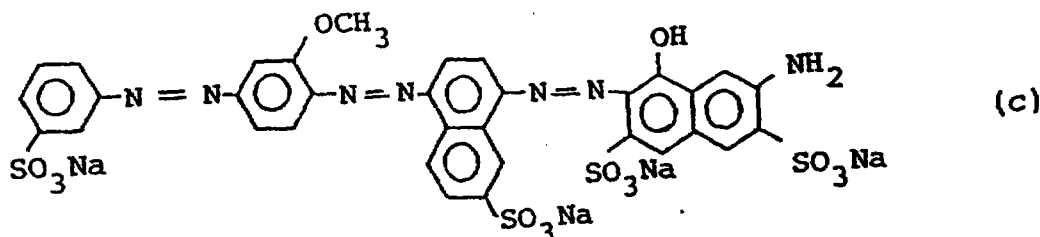
14. Liquide d'enregistrement suivant la revendication 1, dans lequel les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 154 en tant que colorant du groupe X et de Brun Direct C.I. 59 en tant que colorant du groupe Y.

15. Liquide d'enregistrement suivant la revendication 1, dans lequel les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 19 et de Noir Acide C.I. 109 en tant que colorants du groupe X et de Noir Direct C.I. 64 en tant que colorant du groupe Y.

16. Liquide d'enregistrement suivant la revendication 1, dans lequel les colorants hydrosolubles consistent en un mélange d'un colorant de formule (a) suivante dans le groupe X et d'un colorant de formule (b) suivante dans le groupe Y:



17. Liquide d'enregistrement suivant la revendication 1, dans lequel les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 19 et d'un colorant de formule (c) suivante dans le groupe X, et de Noir Direct C.I. 93 et d'un colorant de formule (d) suivante dans le groupe Y





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18. Liquide d'enregistrement suivant la revendication 1, dans lequel la teneur totale en colorants hydrosolubles va de 1 à 8% en poids sur la base du poids total du liquide d'enregistrement.

19. Composition à base de colorants hydrosolubles, comprenant un mélange d'au moins deux colorants solubles dans l'eau, chacun de ces colorants satisfaisant à la condition définie par l'expression (I) suivante et le mélange d'au moins deux colorants hydrosolubles satisfaisant à la condition définie par l'expression (II) suivante:

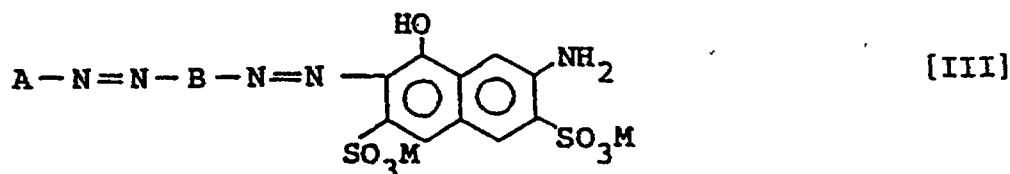
$$0 \leq \sqrt{a \cdot i^2 + b \cdot i^2} \leq 10 \quad [I]$$

$$0 \leq \sqrt{\left(\sum_{i=1}^n a \cdot i\right)^2 + \left(\sum_{i=1}^n b \cdot i\right)^2} \leq 2 \quad [II]$$

où a^* et b^* sont les indices de chromaticité définis dans l'espace (L^* , a^* , b^*) CIE 1976, i désigne le colorant d'ordre i parmi les colorants utilisés conjointement, et n est un nombre entier égal ou supérieur à 2, l'un au moins des colorants hydrosolubles étant choisi parmi les colorants du groupe X indiqué ci-dessous et l'un des autres colorants étant choisi parmi les colorants du groupe Y indiqués ci-dessous:

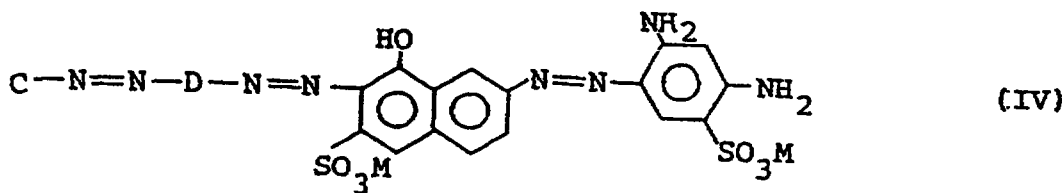
Colorants du groupe X

Colorants représentés par la formule (III) suivante



dans laquelle A représente un groupe phényle substitué par un groupe (alkyle inférieur)-carbonylamino, un groupe alkoxy inférieur, le groupe SO_3M ou un groupe phénylazo qui peut, facultativement, être substitué par le groupe SO_3M , ou un groupe naphyle substitué par le groupe SO_3M , B représente un groupe naphyle substitué par le groupe SO_3M ou un groupe phényle substitué par un groupe alkoxy inférieur et M représente un métal alcalin, un ion ammonium ou une amine;

les colorants représentés par la formule générale (IV) suivante



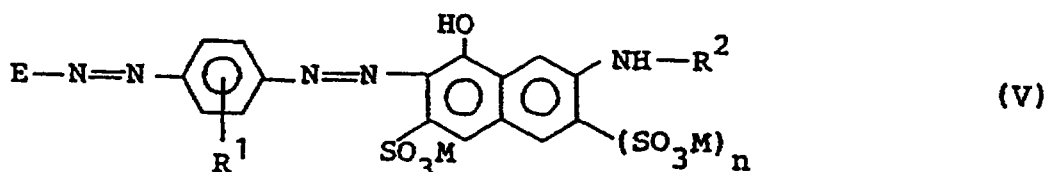
dans laquelle C représente un groupe phényle ou naphyle substitué par le groupe SO_3M , D représente un groupe phényle substitué par un groupe alkyle inférieur, un groupe alkoxy inférieur ou un groupe (alkyle inférieur)-carbonylamino et M a la définition donnée ci-dessus; ou des colorants choisis parmi les colorants:

Noir Direct C.I. 19, 22, 62, 108, 113, 154 et 159; et

Noir Acide C.I. 7, 9, 29, 48, 52:1, 94:1, 109, 110, 187 et 208.

Colorants du groupe Y

Colorants représentés par la formule (V) suivante





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dans laquelle E représente un groupe naphthyle substitué par le groupe SO_3M ou un groupe phényle substitué par un groupe alkyle inférieur, un groupe alkoxy inférieur, un groupe (alkyle inférieur)-carbonylamino ou un groupe phénylazo qui peut facultativement être substitué par le groupe SO_3M , R^1 représente un groupe alkyle inférieur, un groupe alkoxy inférieur ou un groupe (alkyle inférieur)-carbonylamino, R^2 représente un atome d'hydrogène ou un groupe phényle substitué par le groupe SO_3M , n a la valeur 0 ou 1 et M est tel que défini ci-dessus; ou des colorants choisis parmi les colorants

Noir Acide C.I. 27, 137 et 158;

Noir Direct C.I. 64, 93 et 94; et

Brun direct C.I. 59 et 127.

20. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle A dans la formule (III) est un groupe phényle portant au moins un substituant choisi entre un groupe (alkyle inférieur)-carbonylamino, un groupe alkoxy inférieur, le groupe SO_3M et un groupe phénylazo à substituant SO_3M .

21. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle A dans la formule (III) est un groupe naphthyle substitué par le groupe SO_3M .

22. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle B dans la formule (III) est un groupe naphthyle substitué par le groupe SO_3M ou un groupe phényle portant deux substituants alkoxy inférieur.

23. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle M dans la formule (III) représente le sodium ou le lithium.

24. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle C dans la formule (IV) est un groupe phényle substitué par le groupe SO_3M .

25. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle C dans la formule (IV) est un groupe naphthyle substitué par le groupe SO_3M .

26. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle D dans la formule (IV) est un groupe phényle à substituant alkoxy inférieur ou un groupe phényle à substituant (alkyle inférieur)-carbonylamino.

27. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle E dans la formule (V) est un groupe phénylazo substitué par le groupe SO_3M .

28. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle E dans la formule (V) est un groupe naphthyle substitué par le groupe SO_3M .

29. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle R^1 dans la formule (V) représente un groupe méthyle, méthoxy, éthoxy ou acétylamino.

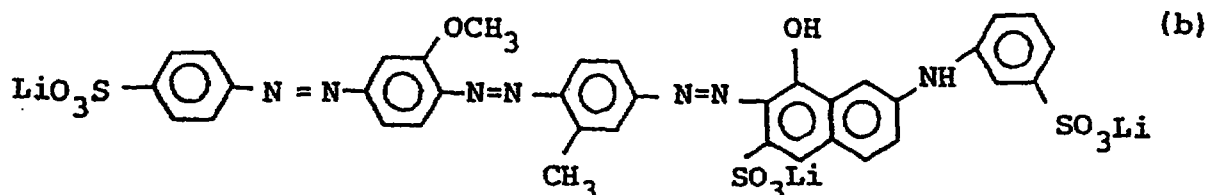
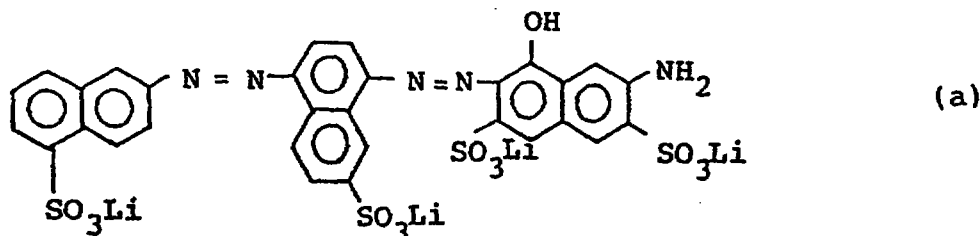
30. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle R^2 dans la formule (V) est un groupe phényle substitué par le groupe SO_3M .

31. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle M dans la formule (V) représente Na, Li ou un ion (alcanol inférieur)-ammonium.

32. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 154 en tant que colorant du groupe X et de Brun Direct C.I. 59 en tant que colorant du groupe Y.

33. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 19 et de Noir Acide C.I. 109 en tant que colorants du groupe X et de Noir Direct C.I. 64 en tant que colorant du groupe Y.

34. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle les colorants hydrosolubles consistent en un mélange d'un colorant de formule (a) suivante dans le groupe X et d'un colorant de formule (b) suivante dans le groupe Y:

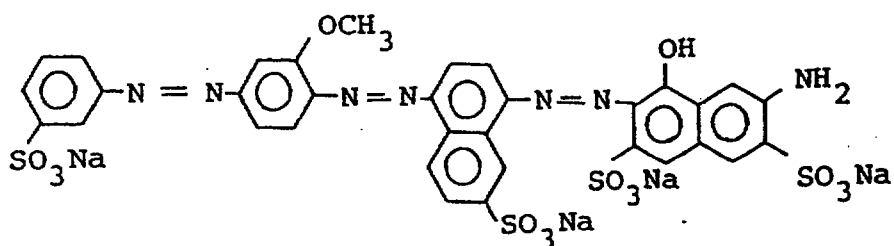




35. Composition à base de colorants hydrosolubles suivant la revendication 19, dans laquelle les colorants hydrosolubles consistent en un mélange de Noir Direct C.I. 19 et d'un colorant de formule (c) suivante dans le groupe X et de Noir Direct C.I. 93 et d'un colorant de formule (d) suivante dans le groupe Y:

5

10

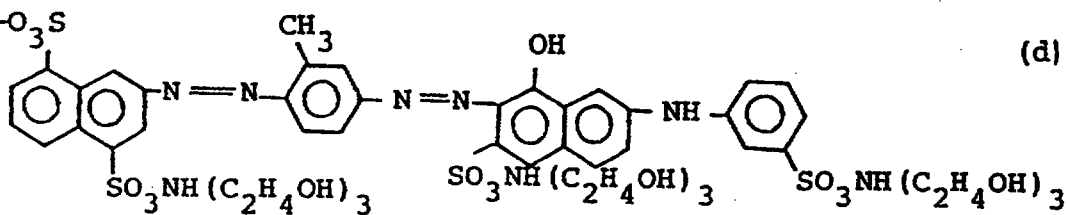


(c)

15

(HOH₄C₂)₃NH-O₃S

20



(d)

25

30

35

40

45

50

55

60

65