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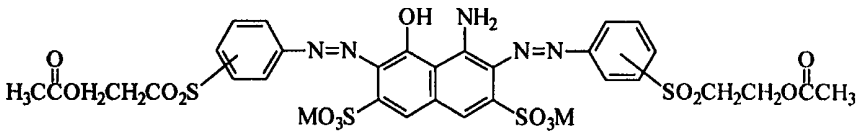
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(54) Title: REACTIVE BLACK DYES CONTAINING ACETOXYETHYL SULFONE MOIETY



(1)

(57) Abstract

This invention relates to a reactive black dye containing acetoxyethyl sulfone moiety and more particularly, to the reactive black dye containing acetoxyethyl sulfone moiety of formula (1), which is characterized by lessening the loss of dyes in filtering process owing to the low solubility by introducing the aminophenyl-β-acetoxyethyl sulfone moiety, saving the cost for waste water treatment by using a small amount of salt in salting-out process and furthermore obtaining bright color with high dyeing yield and good substantivity wherein M is an alkaline metal atom.

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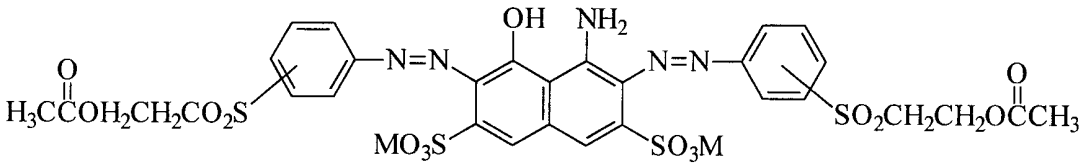
REACTIVE BLACK DYES CONTAINING ACETOXYETHYL SULFONE MOIETY

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a reactive black dye containing acetoxyethyl sulfone moiety and more particularly, to the reactive black dye containing acetoxyethyl sulfone moiety of the following formula 1, which is characterized by lessening the loss of dyes in filtering process owing to the low solubility by introducing the aminophenyl-β-acetoxyethyl sulfone moiety, saving the cost for waste water treatment by using a small amount of salt in salting-out process and furthermore obtaining bright color with high dyeing yield and good substantivity:

Formula 1



wherein M is an alkaline metal atom.

Description of the Related Art

Conventionally, salting-out method has been adapted in order to isolate dyes from reaction mixture after synthesizing the reactive dyes. However, if aminophenyl-β-sulphatoethylsulfone is used as an intermediate in the course of manufacturing vinylsulfone-based reactive dyes, spray-dry method is adapted or large amount of salts is used because high water-solubility of dyes hinder the salting out. The isolation of dyes by spray-drying or by using large amount of salts may cause environmental pollution with waste water containing a good deal of dyes and salts and eventually require

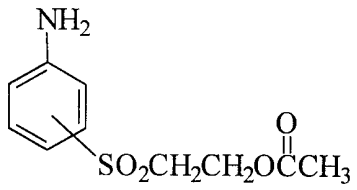
much expenses on sewage treatment.

Especially, reactive black aminophenyl-β-sulphatoethylsulfone group has problems such as putting a reddish hue and lowering its substantivity because of high water-solubility.

Recently, in some developed countries such as European countries and U. S. A., there is restriction on salt concentration in dye waterwaste, thus continuous studies have been conducted in order to obtain low-salt dye and succeeded in marketing. In addition, the liquid dyes are used more favorably because they can be exactly measured and from which the automatization of dyeing process and the promotion of worker's health can be achieved. Therefore, the highly concentrated dyes by removal of salts are required for the manufacture of the stable liquid dyes.

Therefore, in comparison with dyes synthesized with aminophenyl-β-sulphatoethylsulfone group, salting-out is generally easier in the dyes synthesized with aminophenyl-β-acetoxyethylsulfone group of following formula 2, which has relatively low water solubility:

Formula 2

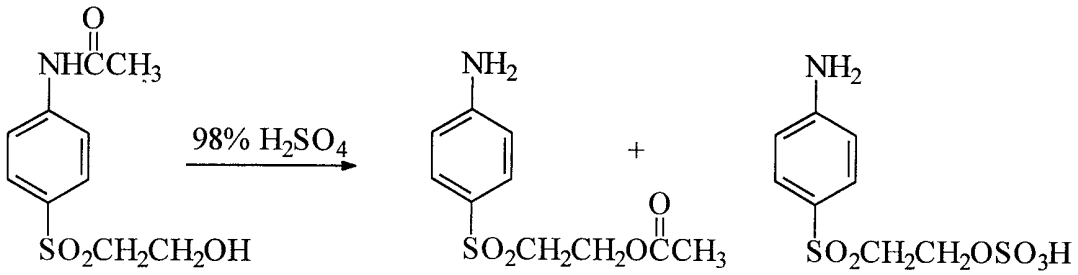


In synthesizing process of dyes with using aminophenyl-β-acetoxyethylsulfone group of the above formula 2, it is possible to lower the concentration of salt in water waste because only a small amount of salt is used in salting-out process than the conventional dyes. Also, it is cost-effective in sewage treatment because only a small amount of dyes is lost during the filtering owing to low solubility of dyes. Furthermore, thus prepared dyes has a high purity containing a small amount of salt and be able to lower the concentration of salt and make it easier desalting process in manufacturing

liquid dyes.

The composition of the above formula 2 is already known and its manufacturing method is also disclosed in various documents. Among the method, one preparation method of 4-aminophenyl-β-acetoxyethylsulfone is expressed in the following Scheme1(Japanese unexamined publication Sho 81-22354; German Patent No. 2 929 107):

Scheme1



(2) (3)

According to the above Scheme1, 4-acetaminophenyl-β-hydroxyethylsulfone and 98% of sulfuric acid is reacted to get a mixture of 70 % of above formula 2 and 30 % of above formula 3, and it is reported that the dyes synthesized with the mixture shows good dyeing properties. However, it has a problem that the substantivity is lowered because of high water-solubility due to the existence of 4-aminophenyl-β-sulphatoethylsulfone.

But no report has been made on synthesizing reactive black dyes introducing aminophenyl-β-acetoxyethylsulfone group of the above formula 2.

SUMMARY OF THE INVENTION

As a result of continuous studies in order to prepare reactive black dyes of high yield rate and high purity, the inventors completed this invention by synthesizing a reactive black dye introducing aminophenyl-β-ethoxyethylsulfone as a reactant.

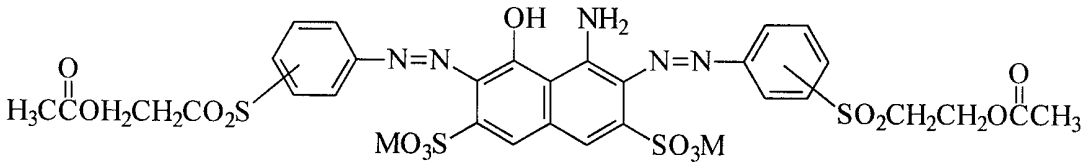
Therefore, the object of this invention is to provide a reactive black dye

of high brilliance, low degree of water- solubility and fixation, having acetoxyethylsulfone group, which decrease the amount of pollutant in process for manufacturing dye.

Detailed Description of the Invention

This invention is characterized by a reactive black dye which is combined with compounds having acetoxyethylsulfone group of the following formula 1:

Formula 1



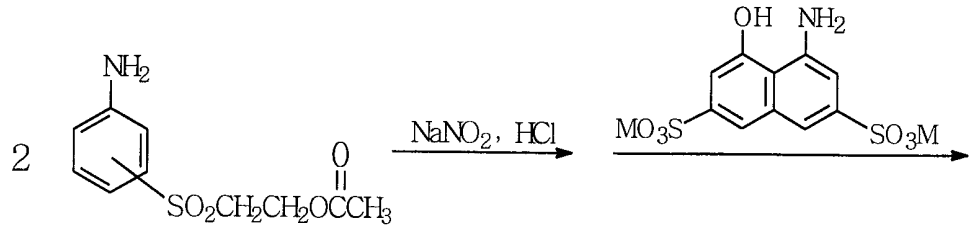
wherein M is an alkaline metal atom.

This invention is described in more detail as follows:

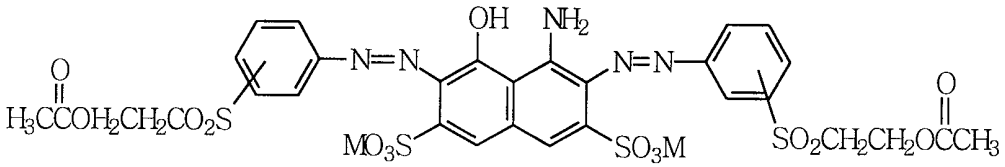
The reactive black dyes having acetoxyethylsulfone group of the above formula 1 according to this invention may be prepared in various synthesizing methods according to the kind of starting material used. For example, the following Scheme2 shows the preparing method of a reactive black dye with using aminophenyl-β-acetoxyethylsulfone as a starting material and the following Scheme3 shows another method with using aminophenyl-β-hydroxyethylsulfone as a staring material.

According to the following Scheme2, the reactive black dye is prepared by (a) diazotizing aminophenyl-β-acetoxyethylsulfone compound; (b) neutralizing 1-naphtol-8-amino-3,6-disulfonic acid compound with acid group; and (c) mixing two reaction solutions prepared in the manners as defined in (a) and (b) at temperature 0-5℃ and stirring the mixture with adjusting the pH below 7 through adding acid.

Scheme2



(2)



(1)

wherein M is an alkaline metal atom.

Hereunder, the preparation method according to the above Scheme2 is described more in detail.

Aminophenyl-β-acetoxyethylsulfone of formula 2 is diazotized. The diazotization method adapted in this invention is conventional one, which means that after dispersing aminophenyl-β-acetoxyethylsulfone in water at 0-5℃, the diazotization reaction is carried with adding conc. hydrochloric acid and $NaNO_2$.

And through neutralizing 1-naphthol-8-amino-3,6-disulfonic acid with using base in another reaction vessel, sulfonic acid group ($-SO_3H$) of 1-naphthol-8-amino-3,6-disulfonic acid is transformed into sulfonic acid metal salt ($-SO_3M$). The bases conventionally used in this reaction are alkaline metal hydroxide and alkaline metal carbonate salt and preferably NaOH, LiOH, Na_2CO_3 and Li_2CO_3 are used. The amount of base is determined by equivalent rate to the amount of 1-naphthol-8-amino-3,6-disulfonic acid.

After the reaction, the neutralized solution of 1-naphthol-8-amino-3,6-disulfonic acid is cooled down below 5℃ with ice, which is to carry out the

coupling reaction with diazo compound at 0-5℃.

After mixing the above diazo compound and the neutralized solution of 1-naphthol-8-amino-3,6-disulfonic acid and adding base, the reaction solution is stirred at below pH 7 at 0-5℃ and resulted in reactive black dye of above formula 1. The amount of diazo compound is preferable 2-3 equivalent weight rate to 1-naphthol-8-amino-3,6-disulfonic acid. If the amount get out of the scope, side reaction may be occurred. If the pH of reaction solution exceeds 7, there is a problem in that the reaction group is hydrolyzed. If the reaction temperature becomes below 0℃, the reaction is not occurred satisfactorily and in the case of exceeding 5℃, side reaction may be occurred.

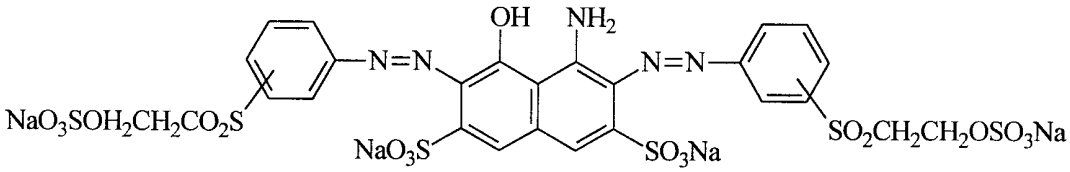
Aminophenyl-β-acetoxyethylsulfone of the above formula 2, which is used as a starting material in the above Scheme2 is prepared by reacting acetaminophenyl-β-hydroxyethylsulfone with acetic acid solution containing hydrochloric acid.

With the preparation method according to the above Scheme2, wherein aminophenyl-β-acetoxyethylsulfone compound of the above formula 2 is used as a starting material, bright colored and high purity dyes can be synthesized which cannot be acquired with aminophenyl-β-sulfatoethylsulfone.

Particularly, aminophenyl-β-acetoxyethylsulfone of formula 2 has no sulfonic acid group (-SO_3H), which existed in aminophenyl-β-sulfatoethylsulfone of formula 3, so that the amount of alkali used in netrulization for coupling reaction can be reduced. Furthermore, in comparision with the conventional method of following formula 4, in which aminophenyl-β-sulfatoethylsulfone of formula 3 is used, the preparation method according to Scheme2 with aminophenyl-β-acetoxyethylsulfone of formula 2 as a starting material has little amount of by product and it is advantageous in obtaining bright colored dye just with spray-drying the reaction solution.

In isolation process of dye, salting-out is impossible due to the high degree of water solubility of dye of formula 4 but this invention make it possible to obtain pure dye of high degree of concentration, which contain small amount of salt and by product with salting-out isolation process of reactive black dye of formula 1 according to this invention.

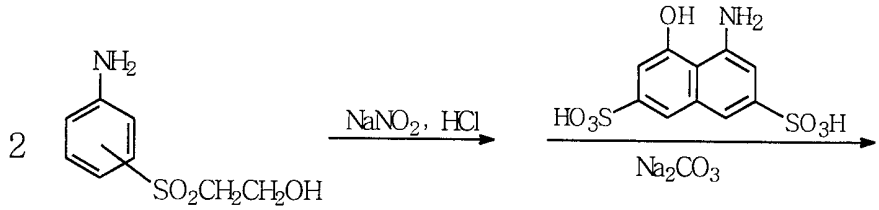
Formula 4



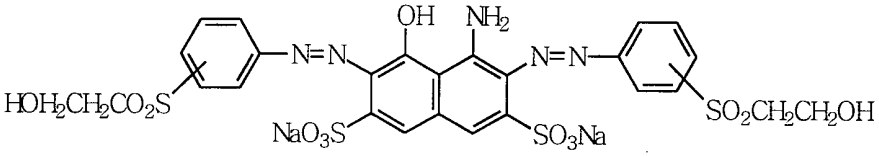
Another method for preparing a reactive black dye of formula 1 according to the invention is defined in the following Scheme3.

According to the following Scheme3, the reactive black dye of formula 1 is prepared by (a) diazotizing aminophenyl-β-hydroxyethylsulfone compound; (b) neutralizing 1-naphtol-8-amino-3,6-disulfonic acid compound with acid group; (c) mixing two reaction solutions prepared in the manners as defined in (a) and (b) at 0-5℃ and stirring the mixture with adjusting the pH below 7 through adding acid; and (d) dissolving the intermediate of formula 6 prepared in the manners of (a), (b) and (c) with anhydrous acetic acid and stirring the solution at 80-90℃.

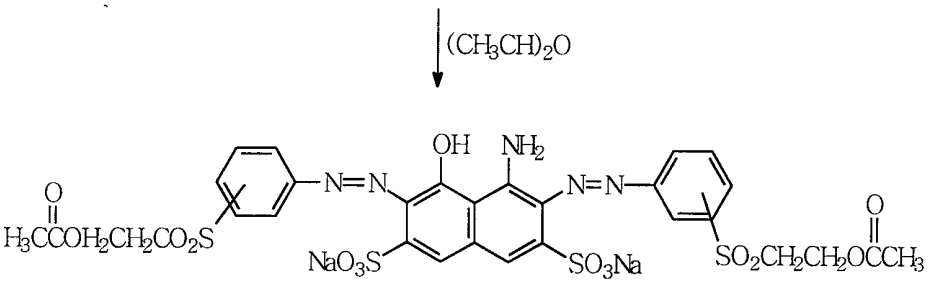
Scheme 3



(5)



(6)



(1)

But the preparation method of Scheme3 has a problem that small amount of red by-product are made during the reaction and the intermediate of formula 6 should be reacted with anhydrous acetic acid after completely dried.

The reactive dye according to the invention is distinguished by high degree of fastness in case of dyeing to fabrics such as cotton, wool and silk. Further, the reactive black dye of formula 1 shows better color yield, fixation and fastness than the dye of formula 4.

The following specific examples are intended to be illustrative of the invention and should not be construed as limiting the scope of the invention as defined by appended claims.

Manufacturing example: Preparation of 4-aminophenyl-β-acetoxyethylsulfone

After attaching condenser with rubber balloon to reaction vessel of 100 ml, 60g (1mol) of acetic acid and 1.8g (0.1mol) of water are put into it. With maintaining the reaction solution at 15 ℃, 5.5g (0.15mol) of hydrogen chloride gas is added slowly for 1.5 to 2 hours. After adding 24.3g (0.1mol) of 4-acetaminophenyl-β-hydroxyethylsulfone, the solution, whose temperature is slowly raised to 70~75 ℃ is stirred for 9 hours.

Then the solution is cooled down to room temperature with slow stirring, filtered and rinsed twice with acetic acid (5ml). After drying the filtered solid at 60℃ in vacuum and dispersing it at 10g of ice and 25ml of water, this solution is neutralized with 10% of sodium carbonate solution and filtered the crystals. With rinsing with water (5ml) three times and drying, white pure 20.6g of 4-aminophenyl-β-acetoxyethylsulfone (yield 84.8%, purity 97.5%) in solid type is obtained.

melting point : 92-93℃

Example 1

3N $NaNO_2$ (40ml, 0.12mol) is added to the dispersed solution of 26.76g (0.11mol) 4-aminophenyl-β-acetoxyethylesulfone and 200ml of water with maintaining the temperature at 0-5℃ and 90g of ice is added; this is followed by the addition of 24ml (0.276mol) of 35% HCl and and diazotization. The diazotization is completed and excess nitrous acid is then destroyed by means of sulfamic acid.

15.97g (0.05mol) of 1-naphthol-8-amino-3,6-disulfonic acid is dissolved in 200 ml of water, neutralized with 2.0g (0.05mol) of NaOH and is cooled down to 0-5℃. The diazotized solution is added at once to 1-naphthol-8-amino-3,6-disulfonic acid neutralization solution and then it is reacted with

maintaining pH below 7 by means of slow addition of NaOH solution. In the middle of reaction, 30g of ice is added three times in order to prevent the raise of temperature. The reaction is ended after 4 hours of stirring and then reactive dyes is obtained by spray-drying.

^{1}H-NMR(300MHz, DMSO-d_6): δ 1.75(3H, s), 1.77(3H, s), 3.73(2H, t), 3.79(2H, t), 4.28(4H, q), 7.42(1H, s), 7.48(1H, s), 7.92(2H, d), 8.00(2H, d), 8.03(2H, d), 8.26(2H, d), 10.41(1H, s), 10.61(1H, s), 15.36(1H, s)

Example 2

An intermediate is prepared by coupling reaction in the same manner of Example 1 except using 4.06g of 4-aminophenyl-β-hydroxyethylsulfone instead of 4-aminophenyl-β-acetoxyethylsulfone. After adding 20ml anhydrous acetic acid to 1g of dried intermediate, it is reacted for 8 hours at 80-90℃ and resulted in reactive black dyes.

Example 3

3-aminophenyl-β-acetoxyethylesulfone is dispersed with 120ml of water and 19.0ml (0.22mol) of 35% HCl is added. The temperature is maintained at 0~5 ℃ and then 60g of ice is added. The solution is diazotized by means of addition of 3N NaNO2 (40ml, 0.12mol). The diazotization is completed and excess nitrous acid is then destroyed by means of sulfamic acid.

15.97g (0.05mol) of 1-naphthol-8-amino-3,6-disulfonic acid is dissolved in 120ml of water, neutralized with 2.0g (0.05mol) of NaOH and cooled down to 0-5℃. The diazotized solution is added at once to 1-naphthol-8-amino-3,6-disulfonic acid neutralization solution and then it is reacted with maintaining pH below 7 by means of slow addition of NaOH solution. In the middle of

reaction, 25g of ice is added three times in order to prevent the raise of temperature. The reaction is ended after 4 hours of stirring and then reactive black dye is obtained by salting-out and filtering.

^{1}H-NMR(300MHz, DMSO-d_6): δ 1.75(3H, s), 1.76(3H, s), 3.78(2H, t), 3.82(2H, t), 4.30(2H, t), 4.32(2H, t), 7.41(1H, s), 7.48(1H, s), 7.66-7.81(3H, m), 7.92(1H, d), 8.27(1H, d), 8.29(1H, s), 8.37(1H, d), 8.61(1H, s), 10.37(1H, s), 10.49(1H, s), 15.47(1H, s)

Experimental example

The reactive black dye prepared by the above Example 1 is used for exhaust-dyeing the fabrics such as cotton, wool and silk. After dyeing the fabrics in line with Remazol Black B (formerly Reactive Black 5) and absorbency, it is compared with those dyed with Remazol Black B.

Dyeing method of cotton fabric

0.02g (1.0% o.w.f. dyeing) and 0.04g(2.0% o.w.f. dyeing) of each reactive black dye obtained from the above Example 1-2 and 0.06g(3.0% o. w. f. dyeing) of Remazol Black B are dissolved in 25ml of water; to this solution 2g of cotton fabric is introduced at 30℃and 0.75g of sodium sulfate is added. The temperature is raised then to 50℃and 0.5g of sodium carbonate is added. Dyeing is carried for 60 minutes and rinsed with cold water. The fabric is soaped off at 98℃ for 20 minutes, is rinsed once more and is dried.

Dyeing method of wool fabric

To 0.01g (1.0% o.w.f. dyeing) of reactive black dye obtained from the above Example 1 and Remazol Black B, 3ml of buffer solution of pH 5 and water is added to make 30ml of salt solution. 1g of wool fabric is introduced to

this solution and dyed for 60 minutes at 95℃. The fabric is then rinsed with cold water, is soaped off at 98 ℃ for 20 minutes, is rinsed once more and is dried.

Dyeing method of silk fabric

To 0.01g(1.0% o.w.f. dyeing) of reactive black dye obtained from the above Example 1 and Remazol Black B, 3ml of buffer solution of pH 7, 0.6g of sodium sulfate and water are added to make 20ml of salt solution. 1g of silk fabric is introduced to this solution and dyed for 60 minutes at 85℃. The fabric is then rinsed with cold water, is soaped off at 90℃ for 20 minutes, is rinsed once more and is dried.

When applied to cotton fabric, the reactive black dye of formula 1 according to the invention shows excellent dyeing levelness and reproducibility. And in comparison with Remazol Black B of formula 4, it shows almost same degree of color yield, fixation and superior light fastness (Dye of this invention: 4.5, Remazol Black B: 4). In other fastness, it shows similar properties. Dye of formula 1 synthesized according to Example 2 dyes fabric in red shade due to the red by-product produced during its synthesizing and its fixation value is 3% low than that of the dye prepared by the above Example 1 and its light fastness of 3.5 is also low.

When applied to wool fabric, the reactive black dyes according to the invention shows excellent dyeing levelness and reproducibility. And in comparison with Remazol Black B of formula 4, it shows superior color yield (Dye of this invention: 16.43, Remazol Black B : 13.51), fixation and light fastness (Dye of this invention: 4, Remazol Black B : 3). In other fastness, it shows similar properties.

When applied to silk fabric, reactive black dyes according to the invention shows excellent dyeing levelness and reproducibility. And in

comparison with Remazol Black B of formula 4, it shows almost same degree of color yield and fixation and superior light fastness (Dye of this invention: 4, Remazol Black B : 3). In other fastness, it shows similar properties.

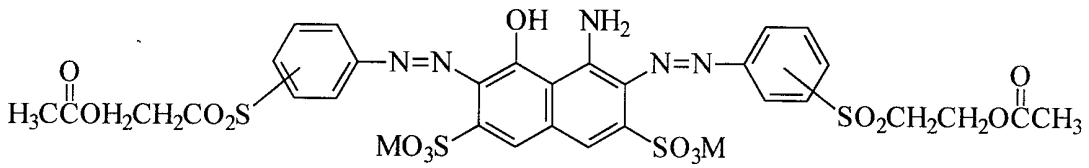
As described in the above, the reactive black dyes of this invention use aminophenyl-β-acetoxyethyl sulfone as reaction group instead of conventionally used aminophenyl-β-sulfatoethylsulfone, which can lessen the wastes in manufacturing. In particular, it shows bright color and superior light fastness to Remazol Black B.

CLAIMS

What is claimed is:

1. A reactive black dye of following formula 1:

Formula 1



wherein M is an alkaline metal atom.

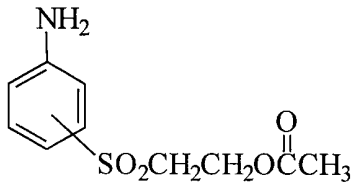
2. A method for preparing a reactive black dye of following formula 1, which comprises the steps of:

(a) diazotizing aminophenyl-β-acetoxyethylsulfone compound of formula 2;

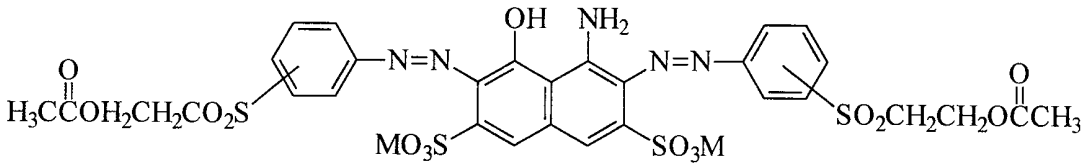
(b) neutralizing 1-naphtol-8-amino-3,6-disulfonic acid compound with acid; and

(c) mixing two reaction solution prepared in the manners as defined in (a) and (b) at temperature 0-5℃ and stirring the mixture with adjusting the pH below 7 through adding acid;

Formula 2



Formula 1



wherein M is an alkaline metal atom.

3. A preparing method of the reactive black dye of following formula 1, which comprises the steps of:

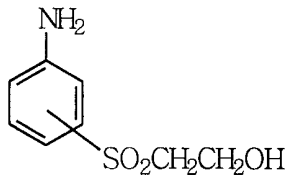
(a) diazotizing aminophenyl-β-hydroxyethylsulfone compound of formula 5;

(b) neutralizing 1-naphtol-8-amino-3,6-disulfonic acid compound with acid;

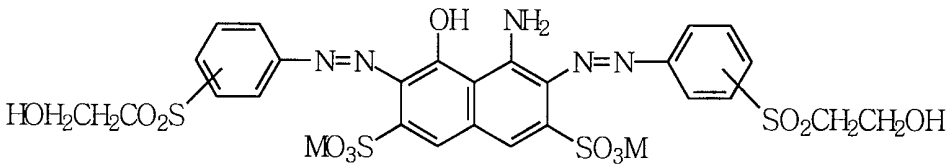
(c) mixing two reaction solution prepared in the manners as defined in (a) and (b) at temperature 0-5℃, stirring the mixture with adjusting the pH below 7 through adding acid and preparing intermediate of formula 6; and

(d) dissolving the above intermediate with anhydrous acetic acid and stirring the solution at temperature 80-90℃;

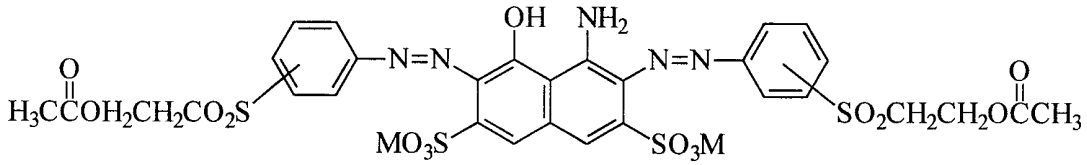
Formula 5



Formula 6



Formula 1



wherein M is an alkaline metal atom.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00144

A. CLASSIFICATION OF SUBJECT MATTER

IPC[6]: C 09 B 62/513

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[6]: C 09 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 122 600 A1 (AMERICAN HOECHST CORPORATION) 24 October 1984 (24.10.84), page 1, line 12 - page 3, line 13; page 7, example 6.	1-3
A	EP 0 149 170 A1 (CIBA-GEIGY AG) 24 July 1985 (24.07.85), claims 1,7; page 5, line 14 - page 6, line 4.	1-3
A	DE 30 25 572 A1 (HOECHST AG) 11 February 1982 (11.02.82), claims 1,9; page 18, example 12.	1-3

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
„L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed

„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 April 1999 (30.04.99)	29 June 1999 (29.06.99)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Hauswirth Telephone No. 1/53424/136

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00144

In Recherchenbericht angeführtes Patentdokument / Patent document cited in search report / Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung / Publication date / Date de publication	Mitglied(er) der Patentfamilie / Patent family member(s) / Membre(s) de la famille de brevets		Datum der Veröffentlichung / Publication date / Date de publication
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