

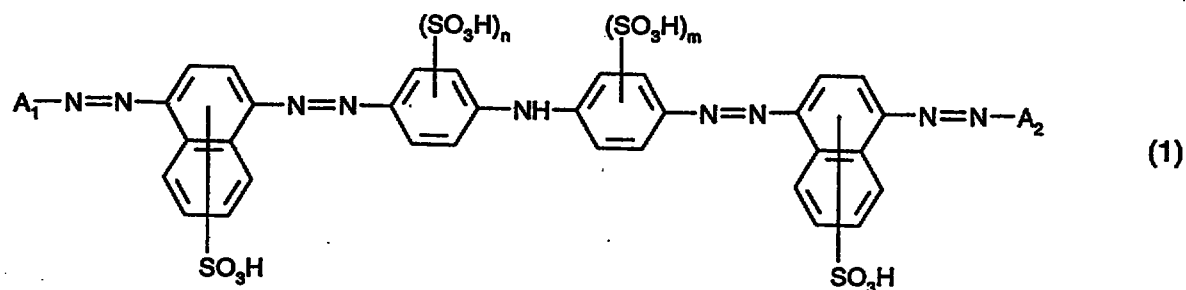
Azo dye mixtures, azo dyes, processes for their preparation, and their use

The present invention relates to novel mixtures of azo dyes, to novel azo dyes, to processes for their preparation and to their use for dyeing and printing fibre materials, especially textile fibre materials.

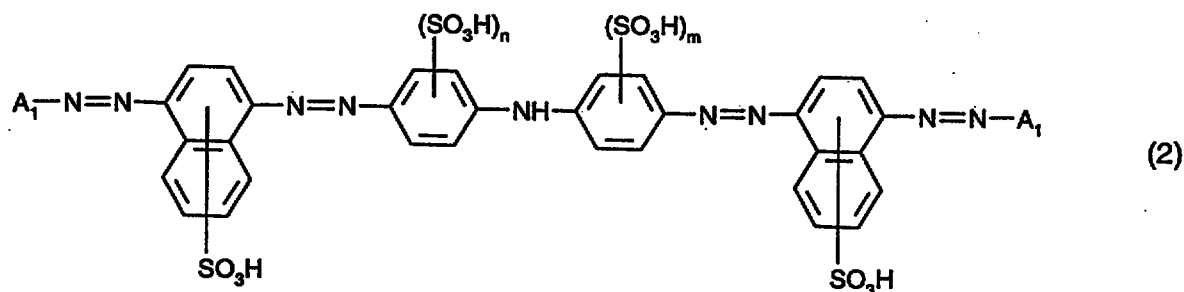
The object on which the present invention is based was to find dye mixtures and dyes that are suitable for dyeing nitrogen-containing and hydroxyl-containing fibre materials, especially cellulosic fibre materials, have good fastness properties and are stable at high temperatures.

It has now been found that the azo dye mixtures and azo dyes set out below go a very long way towards meeting these requirements.

The present invention accordingly provides dye mixtures comprising at least one dye of the formula (1)



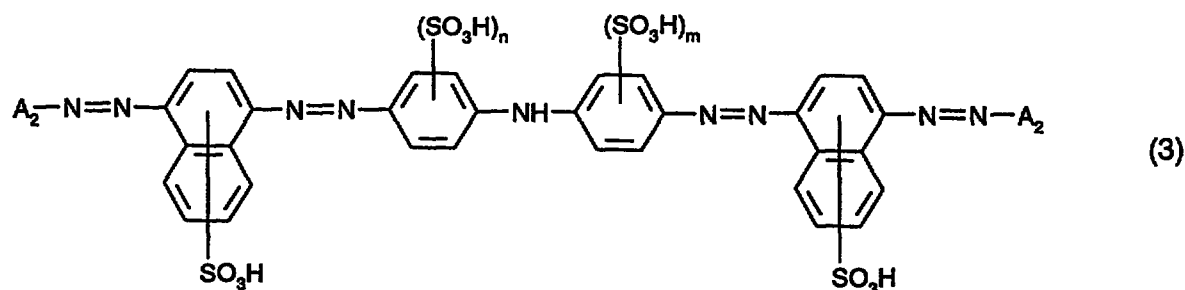
together with at least one dye of the formula (2) or (3)



or

This Sheet Has Been Replaced





in which

A_1 and A_2 independently of one another are each the radical of a coupling component of the benzene or naphthalene series or of the heterocyclic series and

n and m are 0 or 1.

The coupling components A_1 -H and A_2 -H on which the compounds of the formulae (1), (2) and (3) are based are known per se and are described in large number in, for example, Venkataraman "The Chemistry of Synthetic Dyes" Volume 6, pages 213-297, Academic Press, New York, London 1972.

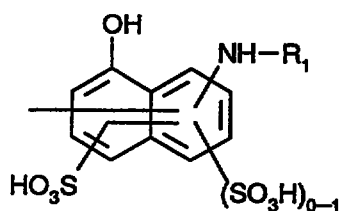
A_1 and A_2 independently of one another are each preferably the radical of a benzene, naphthalene, pyrazolone, aminopyrazole, pyridone, pyrimidine, indole, naphthylimidazole, diphenylamine, pyrazolo[2,3-a]pyrimidine or tetrahydroquinoline coupling component, it being possible for these radicals to be substituted further.

A_1 and A_2 independently of one another are each with particular preference a benzene, naphthalene, 6-hydroxy-2-pyridone, 1-phenyl-5-aminopyrazole, 1-phenyl-5-pyrazolone or indole radical. With very particular preference, A_1 and A_2 independently of one another are each a benzene, naphthalene, 1-phenyl-5-pyrazolone or indole radical, especially a benzene, naphthalene or indole radical and, preferably, a naphthalene or indole radical. Naphthalene radicals are of particular interest.

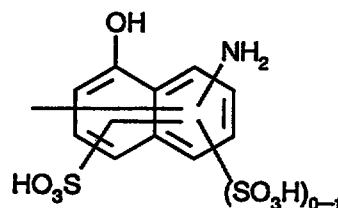
Examples that may be mentioned as substituents of the radical A_1 or A_2 are the following: C_1 - C_6 alkyl, meaning generally methyl, ethyl, *n*- or iso-propyl, *n*-, iso-, sec- or tert-butyl or straight-chain or branched pentyl or hexyl; C_1 - C_4 alkoxy, meaning generally methoxy, ethoxy, *n*- or iso-propoxy or *n*-, iso-, sec- or tert-butoxy, hydroxy- C_1 - C_4 alkoxy; phenoxy;

unsubstituted or e.g. hydroxy- or methoxy-substituted C₂-C₈alkanoylamino, such as acetylamino, hydroxyacetylamino, methoxyacetylamino or propionylamino; naphthoylamino or benzoylamino, unsubstituted or substituted in the aryl moiety by hydroxy or methoxy, for example; C₂-C₈alkoxycarbonylamino, unsubstituted or substituted in the alkyl moiety by hydroxy, methyl or methoxy, for example; phenoxycarbonylamino, unsubstituted or substituted in the phenyl moiety by hydroxy, methyl or methoxy, for example; amino; substituents N-C₁-C₄alkyl- or N,N-di-C₁-C₄alkylamino, unsubstituted or substituted in the alkyl moiety by hydroxy, C₁-C₄alkoxy, carboxyl, cyano, halogen, sulfo, sulfato, phenyl or sulfophenyl, for example, such as methylamino, ethylamino, N,N-dimethylamino, N,N-diethylamino, β-cyanoethylamino, β-hydroxyethylamino, N,N-di-β-hydroxyethylamino, β-sulfoethylamino, γ-sulfo-n-propylamino, β-sulfatoethylamino, N-ethyl-N-(3-sulfobenzyl)amino, N-(β-sulfoethyl)-N-benzylamino; cyclohexylamino; N-phenylamino or N-C₁-C₄alkyl-N-phenylamino, unsubstituted or substituted in the phenyl moiety by C₁-C₄alkyl, C₁-C₄alkoxy, carboxyl, halogen or sulfo, for example; C₂-C₄alkoxycarbonyl, for example methoxy- or ethoxycarbonyl; trifluoromethyl; nitro; cyano; halogen, meaning generally, for example, fluorine, bromine or, in particular, chlorine; ureido; hydroxyl; carboxyl; sulfo; sulfomethyl; carbamoyl; sulfamoyl; N-phenylsulfamoyl or N-C₁-C₄alkyl-N-phenylsulfamoyl, unsubstituted or substituted in the phenyl moiety by sulfo or carboxyl; or methyl- or ethylsulfonyl.

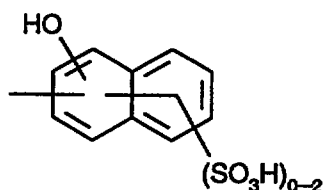
In a particular embodiment of the present invention, A₁ and A₂ independently of one another are each a radical of the formula (4), (5) or (6)



(4),



(5) or



(6), in which

R_1 is substituted or unsubstituted phenyl or naphthyl or is a radical of the formula $-\text{CO}-R$, where R is substituted or unsubstituted $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_5\text{-C}_7$ cycloalkyl, phenyl, phenoxy or naphthyl, and n and m are 0 or 1.

Examples of $\text{C}_1\text{-C}_6$ alkyl for R are methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, isobutyl, pentyl or hexyl, especially $\text{C}_1\text{-C}_4$ alkyl, preferably methyl or ethyl and, with very particular preference, methyl. These alkyl radicals can be unsubstituted or substituted further by, for example, hydroxyl, $\text{C}_1\text{-C}_4$ alkoxy, carboxyl, cyano, sulfo, sulfato or halogen.

The definition sulfo embraces generally the free acid form ($-\text{SO}_3\text{H}$) and the salt form, with alkali metal salts (Li, Na, K) or ammonium salts being particularly suitable.

Examples of $\text{C}_1\text{-C}_6$ alkoxy for R are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentyloxy or hexyloxy, especially $\text{C}_1\text{-C}_4$ alkoxy, preferably methoxy. These alkoxy radicals can be unsubstituted or substituted further by, for example, hydroxyl, $\text{C}_1\text{-C}_4$ -alkoxy, carboxyl, cyano, sulfo, sulfato or halogen.

Examples of $\text{C}_5\text{-C}_7$ cycloalkyl for R are cyclopentyl, cyclohexyl or cycloheptyl, and especially the cyclohexyl radical. These cycloalkyl radicals can be unsubstituted or can be substituted, for example, by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, carboxyl or halogen, especially methyl.

Suitable phenyl, phenoxy or naphthyl radicals for R , in addition to the corresponding unsubstituted radicals, are the radicals substituted, for example, by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, ureido, carboxyl, $\text{C}_2\text{-C}_4$ alkanoylamino, sulfo or halogen.

R is preferably unsubstituted or hydroxyl-, $\text{C}_1\text{-C}_4$ alkoxy-, sulfo-, sulfato- or halogen-substituted $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_1\text{-C}_6$ alkoxy; unsubstituted or $\text{C}_1\text{-C}_4$ alkyl- or halogen-substituted $\text{C}_5\text{-C}_7$ cycloalkyl, or unsubstituted or $\text{C}_1\text{-C}_4$ alkyl-, $\text{C}_1\text{-C}_4$ alkoxy-, sulfo- or halogen-substituted phenyl, phenoxy or naphthyl.

With particular preference, R is unsubstituted or hydroxyl-, $\text{C}_1\text{-C}_4$ alkoxy- or halogen-substituted $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_1\text{-C}_6$ alkoxy or unsubstituted or $\text{C}_1\text{-C}_4$ alkyl-, $\text{C}_1\text{-C}_4$ alkoxy-, sulfo- or halogen-substituted phenyl or phenoxy.

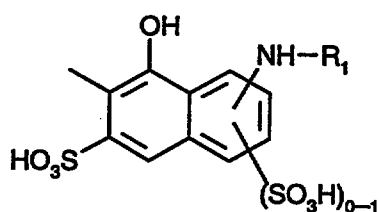
With very particular preference R is C₁-C₄alkyl, especially methyl or ethyl, C₁-C₄alkoxy, especially methoxy or ethoxy, or phenyl.

Suitable phenyl or naphthyl radicals for R₁, in addition to the corresponding unsubstituted radicals, are the radicals substituted, for example, by C₁-C₄alkyl, C₁-C₄alkoxy, ureido, carboxyl, nitro, C₂-C₄alkanoylamino, sulfo or halogen.

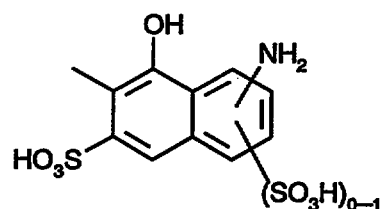
R₁ is preferably unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₂-C₄alkanoylamino-, nitro-, halogen-, carboxyl- or sulfo-substituted phenyl or naphthyl or is a radical of the formula -CO-R, where R is unsubstituted or hydroxyl-, C₁-C₄alkoxy- or halogen-substituted C₁-C₆alkyl or C₁-C₆alkoxy or is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, sulfo- or halogen-substituted phenyl or phenoxy.

With particular preference R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, halogen- or sulfo-substituted phenyl, especially phenyl, or is a radical of the formula -CO-R, where R is C₁-C₄alkyl, especially methyl or ethyl, C₁-C₄alkoxy, especially methoxy or ethoxy, or phenyl.

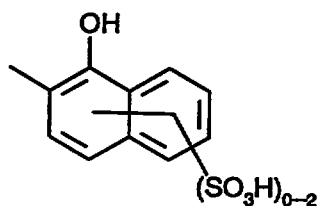
In a very particular embodiment of the present invention, A₁ and A₂ independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b)



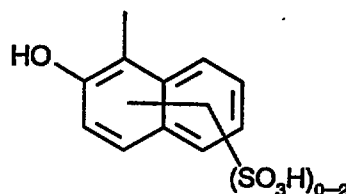
(4a),



(5a),



(6a) or

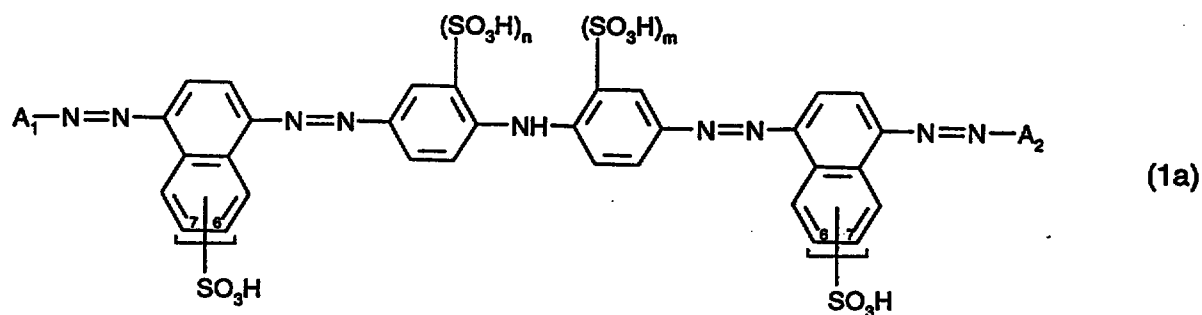


(6b),

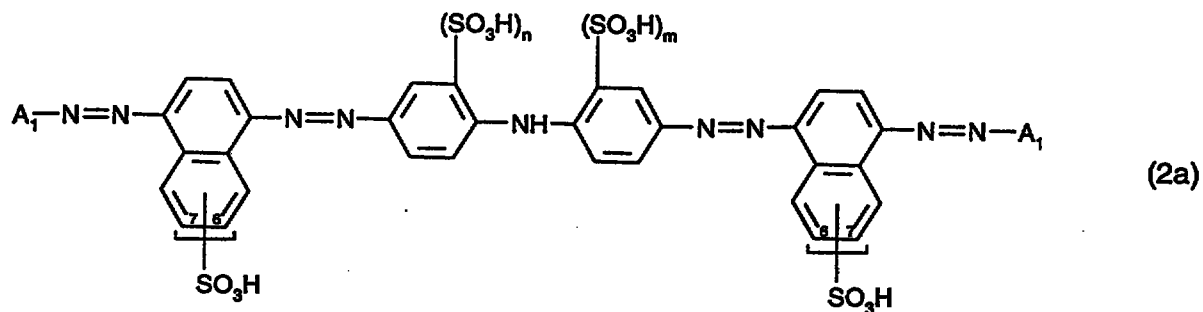
in which

R_1 is subject to the above definitions and preferences.

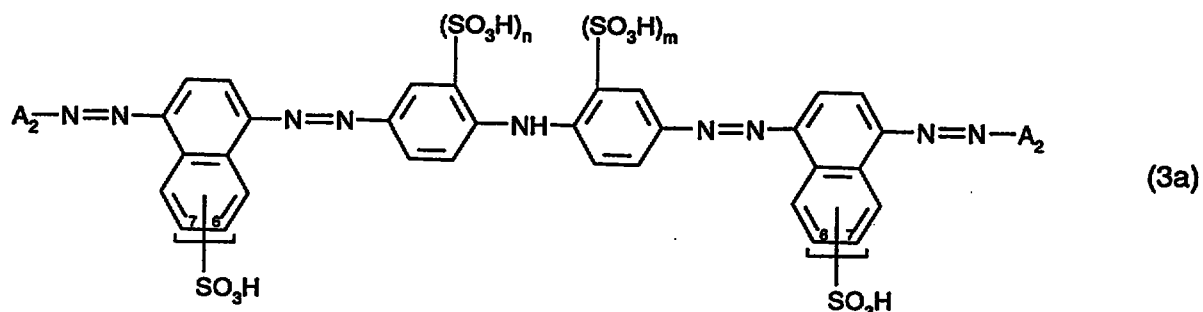
Preference is given to dye mixtures comprising at least one dye of the formula (1a)



together with at least one dye of the formula (2a) or (3a)



or



in which

the sulfo groups of the naphthalenesulfonic acid components independently of one another are each attached in position 6 or 7,

A_1 and A_2 independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b), preferably each a radical of the formula (4a), (5a) or (6b),

R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, halogen- or sulfo-substituted phenyl, preferably phenyl, or is a radical of the formula $-CO-R$, where

R is methyl, ethyl, methoxy, ethoxy or phenyl, preferably methyl, ethyl or phenyl, and the sum of n and m is 0 or 1.

Particular preference is given to dye mixtures comprising at least one dye of the formula (1a) together with at least one dye of the formula (2a) and at least one dye of the formula (3a).

In the dye mixtures of the invention the radicals A_1 and A_2 have different definitions.

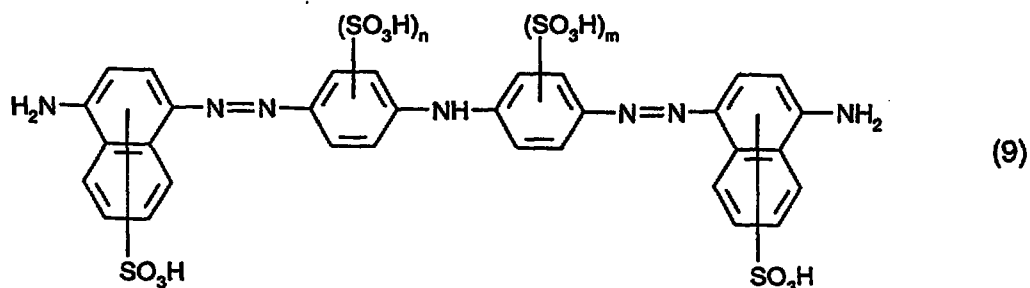
The present invention also provides a process for preparing the dye mixtures of the invention, which comprises diazotizing a compound of the formula (7)



coupling the product with a compound of the formula (8)



diazotizing the resulting compound of the formula (9)



and coupling the product with the compounds of the formulae (10) and (11)

A_1-H (10) and

A_2-H (11)

where A_1 and A_2 , n and m are each subject to the above conditions and preferences.

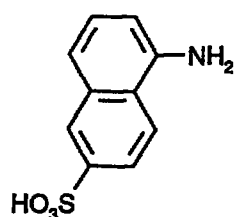
The compounds of the formulae (7) and (9) are diazotized in a manner known per se, for example with a nitrite, such as with an alkali metal nitrite such as sodium nitrite, in a mineral acid medium, for example in a hydrochloric acid medium, at temperatures of, for example, from -5 to 40°C and, preferably, from -5 to 10°C .

Coupling onto the coupling components of the formulae (8), (10) and (11) takes place in a manner known per se at an acidic or neutral to weakly alkaline pH, for example a pH of 5 to 10, and at temperatures of, for example, from -5 to 40°C , preferably from 0 to 30°C .

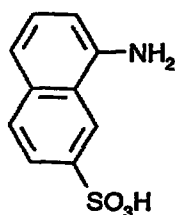
The compounds of the formulae (7), (8), (10) and (11) are known or can be prepared in analogy to known compounds.

Preferred coupling components of the formula (8) are 1-aminonaphthalene-6-sulfonic acid, 1-aminonaphthalene-7-sulfonic acid, the mixtures of these compounds or the isomer mixture obtained in the synthesis of these compounds, consisting of 1-aminonaphthalene-6-sulfonic acid and 1-aminonaphthalene-7-sulfonic acid.

One particular embodiment of the process for preparing the dye mixtures of the invention comprises diazotizing a compound of the formula (7) and coupling the product in succession, or in any desired order, with compounds of the formulae (8a) and (8b)

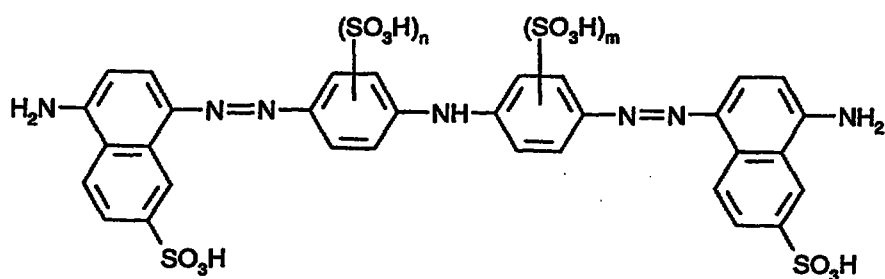


(8a) and



(8b)

to give the compound of the formula (9a)

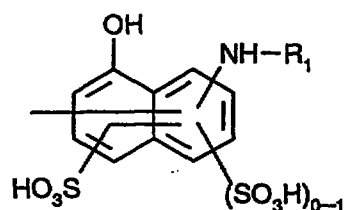


(9a)

which is asymmetric in terms of the position of the sulfo group of the aminonaphthalenesulfonic acid components.

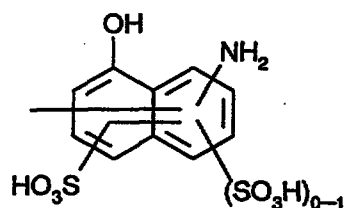
The compound of the formula (9a) is subsequently diazotized and the product is coupled with the compounds of the formulae (10) and (11).

Compounds of the formulae (10) or (11) in which A_1 and A_2 are a radical of the formula (4)



(4)

with R_1 defined as a radical of the formula $-CO-R$ can be obtained, for example, by reacting a compound of the formula (5)



(5)

with a compound which introduces the radical R_1 , for example the compound of the formula (13a)



(13a),

in which Hal is halogen, such as chlorine, bromine or iodine and, in particular, chlorine.

Examples of compounds of the formula (13a) are acetyl chloride, propionyl chloride, methoxyacetyl chloride, benzoyl chloride, ethyl chloroformate and phenyl chloroformate.

Further examples of compounds which introduce the radical R_1 , where R_1 is a radical of the formula $-CO-R$, are acetic anhydride and propionic anhydride.

The introduction of the radical R_1 can take place, for example, in dipolar aprotic solvents, such as dimethylformamide or dimethyl sulfoxide, or in pyridine or, preferably, in water, at a temperature of, for example, from 10 to 80°C, in particular from 10 to 50°C.

The reaction with acetic anhydride takes place in general in an aqueous medium in the presence of a base, such as an alkali metal carbonate or alkali metal hydroxide, examples

being sodium carbonate, potassium carbonate and sodium hydroxide, at a temperature of, for example, from 20 to 60°C, in particular from 30 to 50°C, and at a pH of, for example, from 4 to 7, in particular from 5 to 6.

Compounds of the formula (10) or (11) in which A_1 and A_2 are a radical of the formula (4) with R_1 defined as a substituted or unsubstituted phenyl or naphthyl radical can be obtained, for example, by reacting a compound of the formula (5) with a compound which introduces the radical R_1 , for example the compound of the formula (13b)



in a Bucherer reaction. The Bucherer reaction is known per se and is described in detail, for example, in Org. Reactions, 1, (1942) 105.

The proportion of the dyes of the formulae (1), (2) and (3) in the dye mixtures of the invention may vary within wide ranges and depends on the proportion of the coupling components of the formulae (10) and (11) that are reacted with the diazo component of the formula (9). In this case compounds of the formulae (10) and (11) are employed in a molar ratio to one another which is greater than 5:95 and less than 95:5. In this context, the compounds of the formulae (10) and (11) are preferably employed in a molar ratio of from 10:90 to 90:10, in particular in a molar ratio of from 20:80 to 80:20.

The dye mixtures of dyes of the formulae (1), (2) and (3) can also be prepared, for example, by mixing the individual dyes. This mixing process takes place, for example, in appropriate mills, for example ball mills and pinned-disc mills, and also in mixers or kneading apparatus.

The dye mixtures may additionally be prepared, for example, by spray-drying the aqueous dye mixtures.

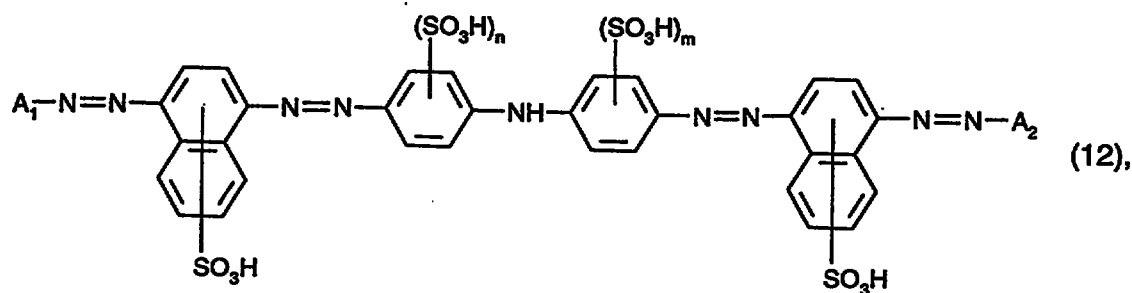
The dye mixtures contain preferably from 5 to 95% by weight, in particular from 10 to 90% by weight, and, preferably, from 20 to 80% by weight of a dye of the formula (1), based on the overall amount of the dyes of the formulae (1), (2) and (3). With particular preference, the dye mixtures contain from 25 to 75% by weight of a dye of the formula (1); based on the overall amount of the dyes of the formulae (1), (2) and (3).

The dyes of the formulae (1), (2) and (3) of the dye mixtures of the invention which comprise a radical A_1 of the formula (5) and a radical A_2 of the formula (4) can also be obtained by first of all diazotizing a compound of the formula (7), coupling the product with a compound of the formula (8), diazotizing the resulting compound of the formula (9) and coupling the product with a compound of the formula (10) in which the radical A_1 is a radical of the formula (5), and subsequently reacting some of the amino groups of the radical A_1 of the resulting dye of the formula (2) with a compound which introduces the radical R_1 .

The dyes of the dye mixtures of the invention are present either in the form of their free acid or, preferably, as the salts thereof.

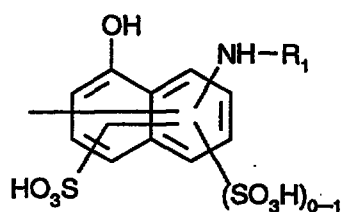
Examples of suitable salts are the alkali metal, alkaline earth metal or ammonium salts, or the salts of an organic amine. Examples are the sodium, lithium, potassium or ammonium salts or the salt of mono-, di- or triethanolamine.

The present invention additionally provides azo dyes of the formula (12)

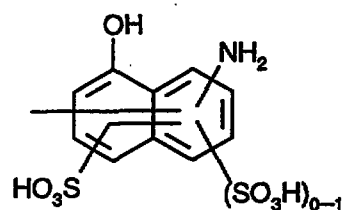


wherein

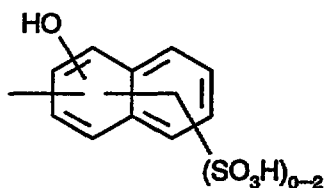
A_1 and A_2 independently of one another are each a radical of the formula (4), (5) or (6)



(4),



(5) or

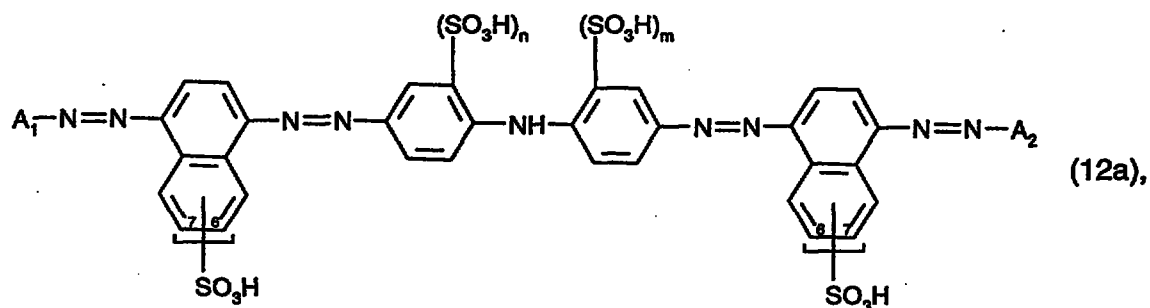


(6)

in which

R_1 , n and m are subject to the above definitions and preferences, with the proviso that, if A_1 and A_2 are identical radicals of the formula (5) and the sum of n and m is 1, the radicals A_1 and A_2 are not simultaneously 2- or 3- or 4-amino-8-hydroxy-6-sulfonaphth-7-yl or 1-amino-8-hydroxy-3,6-disulfonaphth-7-yl.

The azo dyes of the formula (12) are, with particular preference, dyes of the formula (12a)

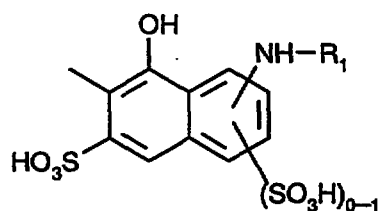


(12a),

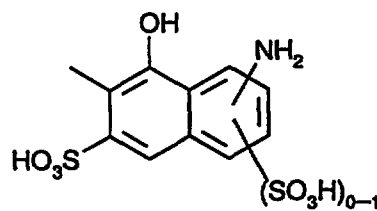
in which

the sulfo groups of the naphthalenesulfonic acid components independently of one another are each attached in position 6 or 7,

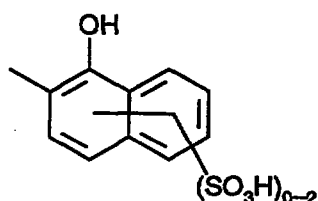
A_1 and A_2 independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b)



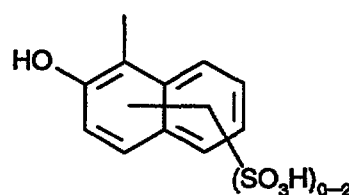
(4a)



(5a)



(6a) or



(6b)

in which

R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, halogen- or sulfo-substituted phenyl, especially phenyl, or is a radical of formula $-CO-R$, where

R is methyl, ethyl, methoxy, ethoxy or phenyl and

the sum of n and m is 0 or 1.

In the azo dyes of the invention the radicals A_1 and A_2 have different or identical meanings.

In one particular embodiment the radicals A_1 and A_2 in the azo dyes of the invention have different meanings.

The azo dyes of the formula (12) can be obtained in principle in the same way as the dyes of the formula (1), (2) or (3) of the dye mixtures of the invention, for example by diazotizing a compound of the formula (7), coupling the product with a compound of the formula (8), diazotizing the resulting compound of the formula (9) and coupling the product with the compounds of the formulae (10) and (11). Where A_1 and A_2 are not identical the molar ratio of the compounds of the formulae (10) and (11), for example, is chosen so that the yield of the compound of the formula (1) that is asymmetrical in terms of radicals A_1 and A_2 is as high as possible, for example a molar ratio of 1:1, and the compounds of the formulae (2) and/or (3) that are symmetrical in terms of the radicals A_1 and A_2 are separated by appropriate purification methods, for example by recrystallization or reprecipitation, from the asymmetric compound of the formula (1).

The present invention also provides for the use of the dye mixtures of the invention for dyeing or printing nitrogen-containing and especially hydroxyl-containing fibre materials.

The dye mixtures of the invention are therefore suitable for dyeing and printing nitrogen-containing or, in particular, cellulosic fibre materials, preferably textile fibre materials, comprising silk, wool or synthetic polyamides, and preferably comprising cellulosic fibres, such as rayon, cotton or hemp.

In terms of their dyeing properties they can be referred to as C.I. direct dyes.

It is likewise possible to dye textile fibre materials comprising mixed fibres, for example wool/cotton, nylon/cotton, polyacrylic/cotton or, in particular, polyester/cotton blends by single-bath dyeing processes and in the presence of dyes for each different type of fibre.

The textile fibre materials can be in a very wide variety of processing states, for instance as fibre, yarn, wovens or knits.

As well as the textile substrates it is also possible to dye leather and paper with the dye mixtures of the invention.

Level dyeings are obtained in shades having good all-round fastness properties and, in particular, good rub, wet, wet-rub, perspiration and light fastness. Where necessary, the wet fastness properties, especially the wash fastness, of the resulting direct dyeings and prints can be improved substantially by aftertreatment with fixing agents.

The dye mixtures of the invention can be combined readily with other dyes, especially disperse dyes. The dye mixtures of the invention are of sufficient high-temperature stability, and so dyeing can be carried out under the dyeing conditions for polyester fibres, i.e. at temperatures in the range from about 100 to 150°C, preferably from 110 to 130°C, from an aqueous liquor and at a pH of from 4 to 7.5, preferably from 5 to 7.

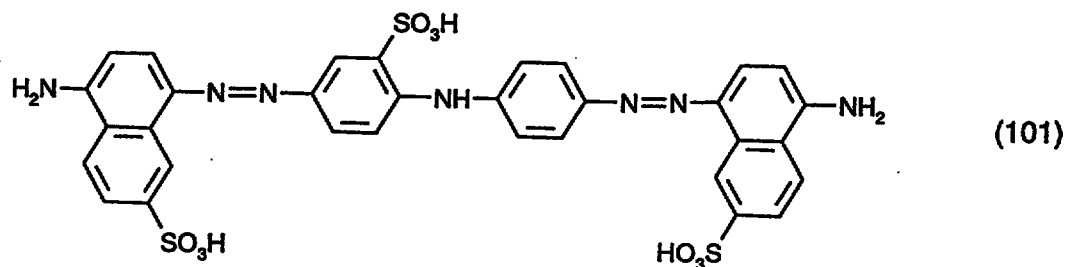
It is therefore possible to employ customary disperse dyes together with the dye mixtures of the invention in a single-stage, one-bath process for dyeing polyester/cotton mixed fibres

(blend fabric), the two types of fibre each being dyed by the respective dye in a uniform and colourfast way. Using a disperse dye in the same shade as the dye mixtures of the invention makes it possible, in addition, to obtain solid dyeings.

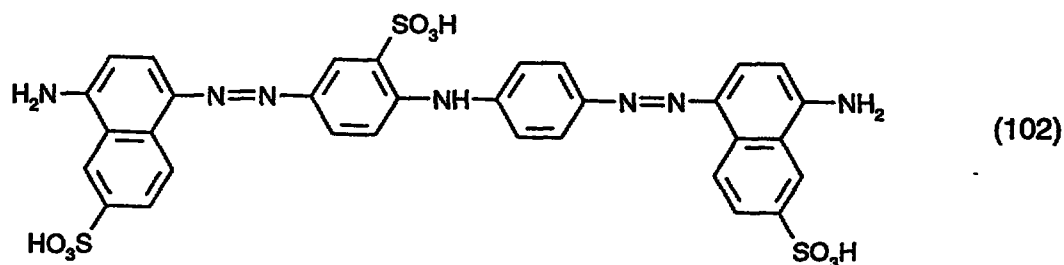
The provision of the dye mixtures of the invention allows substantial simplification of the dyeing of textile mixed fibres (blend fabrics), for example those comprising polyester fibres and cellulose fibres. The otherwise common dyeing of each type of fibre of a fibre blend in a separate operation employing different dyeing conditions is thus no longer necessary.

The examples which follow serve to illustrate the invention. Parts and percentages are by weight unless stated otherwise. The relationship between parts by weight and parts by volume is the same as that between the kilogram and the litre. The temperatures are indicated in degrees Celsius.

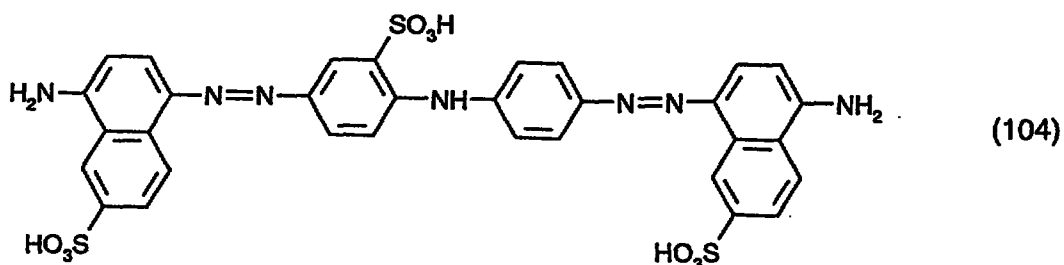
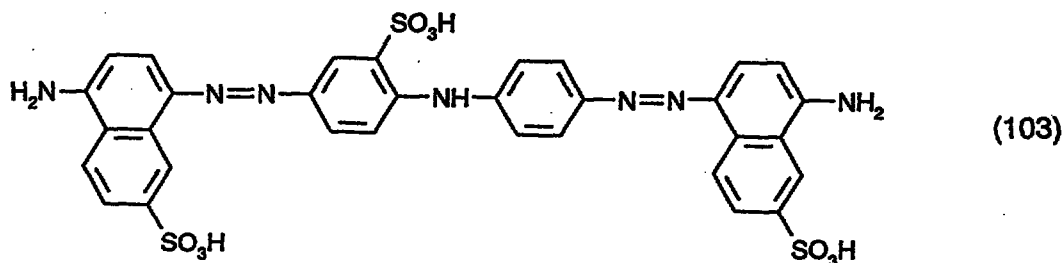
Example 1: 27.9 parts of 4,4'-diaminodiphenylamine-2-sulfonic acid are stirred with 400 parts of water, and 47.5 parts of concentrated hydrochloric acid are added. After cooling to 0-5°C, 58.5 parts of 4-normal sodium nitrite solution are added dropwise. After the end of diazotization, the undissolved residue is separated off by clarifying filtration. The resulting solution is added dropwise to a solution consisting of 44.6 parts of 1-aminonaphthalene-6-sulfonic acid in 600 parts of water at a pH of 8. In the course of the coupling the pH is maintained at from 8 to 8.5 by adding sodium hydroxide solution. After the end of coupling the reaction mixture is acidified and the precipitated product is filtered off. Drying gives a compound which in the form of the free acid is of the formula (101)



Example 2: In the same way as described in Example 1 it is possible to use, instead of 44.6 parts of 1-aminonaphthalene-6-sulfonic acid, 44.6 parts of 1-aminonaphthalene-7-sulfonic acid as the coupling component. The compound thus prepared is, in the form of the free acid, of the formula (102)



Example 3: Using 44.6 parts of a mixture of 1-aminonaphthalene-6-sulfonic acid and 1-aminonaphthalene-7-sulfonic acid as coupling components, instead of 44.6 parts of 1-aminonaphthalene-6-sulfonic acid as described in Example 1, gives a mixture of the compounds which in the form of free acid is of the formula (101), (102), (103) and (104).

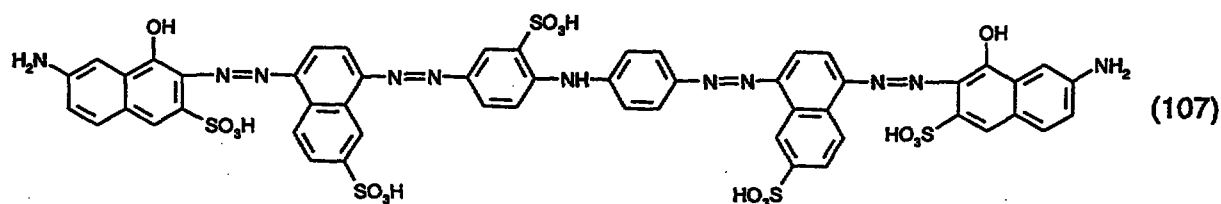
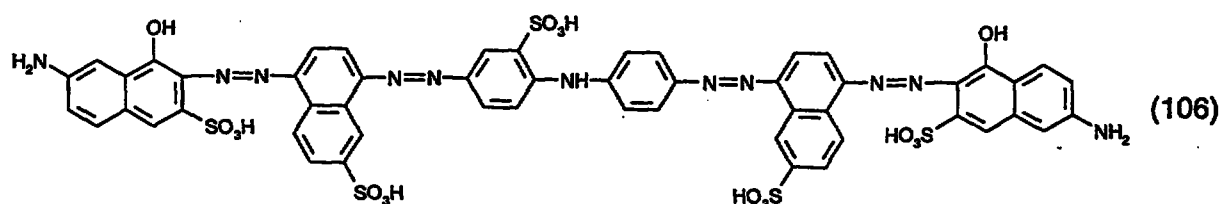
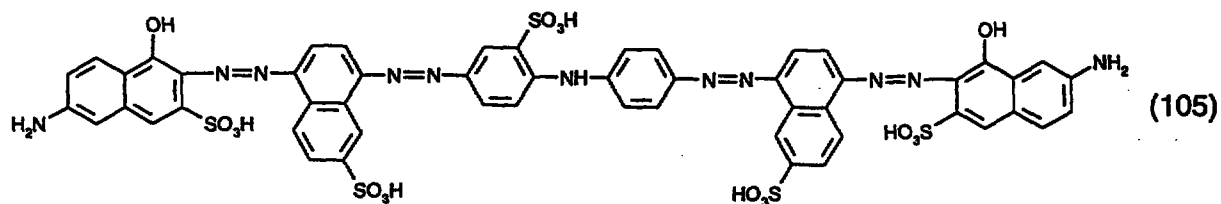


Example 4: 27.9 parts of 4,4'-diaminodiphenylamin-2-sulfonic acid are stirred with 400 parts of water, and 47.5 parts of concentrated hydrochloric acid are added. After cooling to 0-5°C,

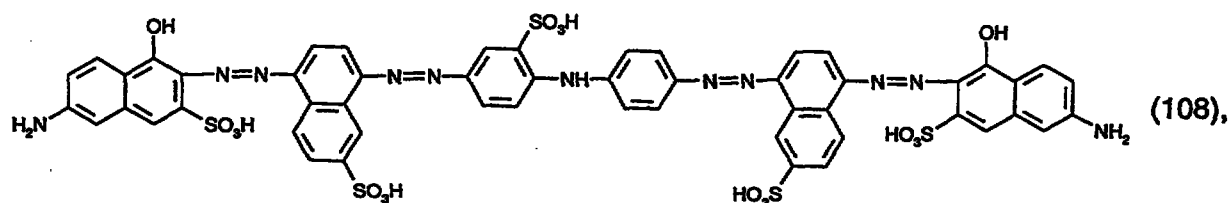
58.5 parts of 4-normal sodium nitrite solution are added dropwise. After the end of diazotization, the undissolved residue is separated off by clarifying filtration. To this solution is added, dropwise, a solution consisting of 22.7 parts of 1-aminonaphthalene-6-sulfonic acid in 400 parts of water. The pH in the course of coupling is held at 3. Reaction is allowed to continue for 2-3 hours. Subsequently, at a pH of 6, a solution consisting of 22.7 parts of 1-aminonaphthalene-7-sulfonic acid in 400 parts of water is added dropwise and the pH is adjusted to 6 using 4-normal sodium hydroxide solution. Reaction is allowed to continue overnight. The product is precipitated by adding sodium chloride and then filtered off. Drying gives a compound which in the form of the free acid is of the formula (103).

Example 5: Following the procedure described in Example 4 but carrying out the dropwise addition not of 22.7 parts of 1-aminonaphthalene-7-sulfonic acid in 400 parts of water but of a mixture consisting of 11.35 parts of 1-aminonaphthalene-7-sulfonic acid and 11.35 parts of 1-aminonaphthalene-6-sulfonic acid in 400 parts of water gives a mixture of compounds which in the form of the free acid are of the formulae (101) and (103).

Example 6: 22.4 parts of a compound of the formula (101) from Example 1 are dissolved in 400 parts of water at a temperature of 75°C, and 17.6 parts of 4-normal sodium nitrite solution are added. The solution is added dropwise over the course of 20 minutes and at a temperature of from 0 to 5°C to 400 parts of ice and 14.3 parts of concentrated hydrochloric acid. The resulting brown suspension is stirred for one hour, and then its pH is adjusted to 4 using sodium carbonate solution (10%). The diazo suspension is then added dropwise over the course of 60 minutes and at a temperature of from 0 to 5°C to a coupling solution which contains 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid in 400 parts of water and 63.5 parts of 1-normal sodium hydroxide solution. During coupling, the pH is held at 5. Reaction is allowed to continue for 2 hours at a temperature of from 0 to 5°C and then overnight at room temperature. The bluish black suspension is filtered and the filter product is washed with water. The moist residue is then stirred with 1000 parts of water, and the pH is adjusted to 8 with about 67 parts of 1-normal sodium hydroxide solution. At a temperature of 60°C, 70 parts of sodium chloride are added and the fine suspension is filtered at a temperature of 50°C. Drying gives a mixture of compounds which in the form of the free acid are of the formulae (105), (106), (107) and (108)

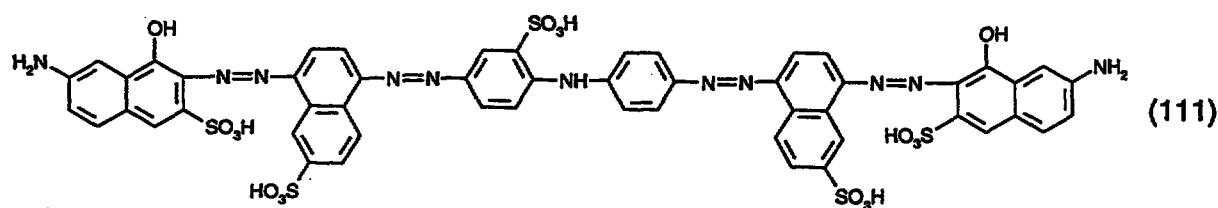
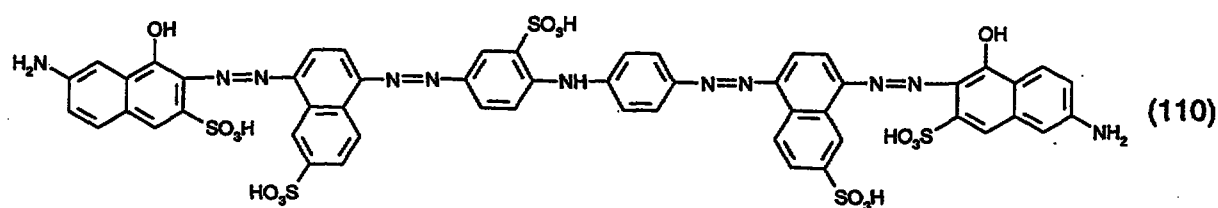
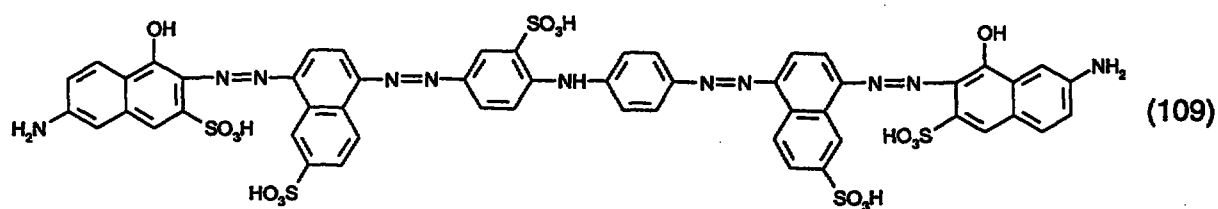


and

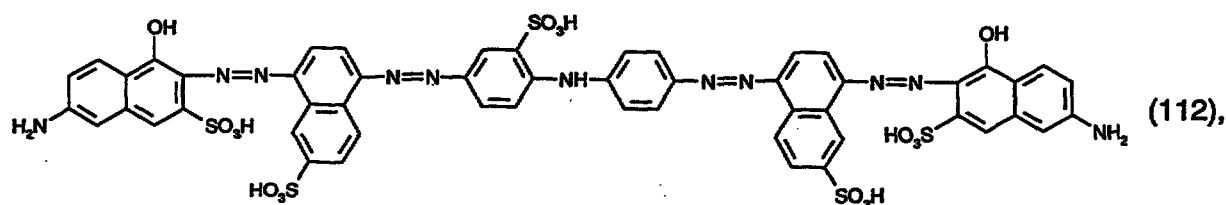


consist to the extent of about 50% by weight of the compounds of the formulae (105) and (106) and dye cotton in navy blue shades. The λ_{max} of the dye mixture is 578 nm.

Example 7: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the compound of the formula (102) from Example 2 gives a mixture of compounds which in the form of the free acid are of the formulae (109), (110), (111) and (112)

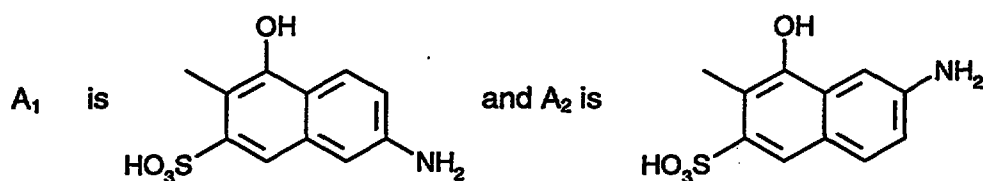
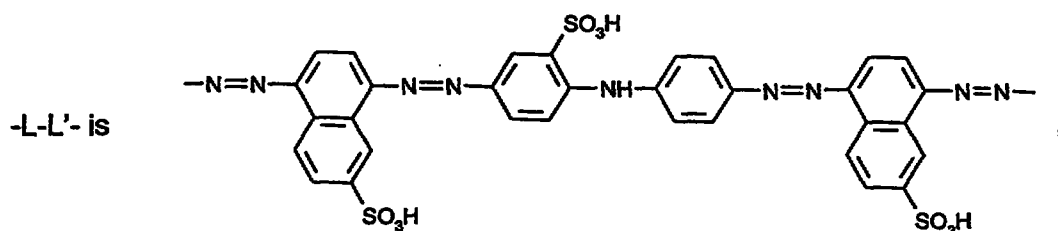


and



consist to the extent of about 50% by weight of the compounds of the formulae (109) and (110) and dye cotton in navy blue shades. The λ_{max} of the dye mixture is 590 nm.

Example 8: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the compound of the formula (103) from Example 4 gives a mixture of compounds which are in the form of the free acid are of the formulae (113), (114), (115) and (116)

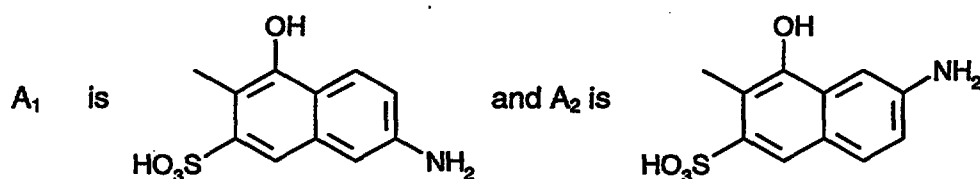
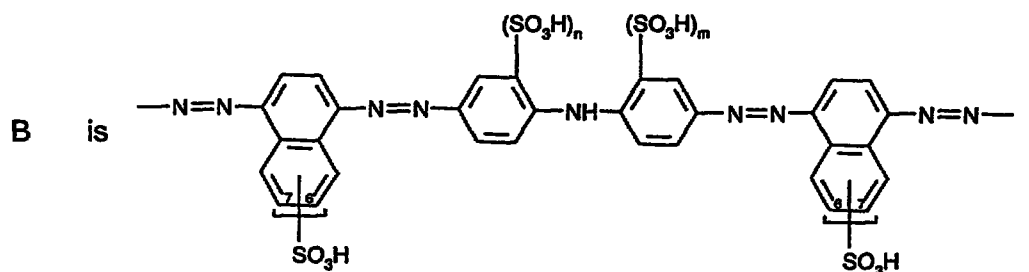
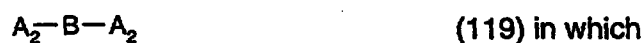


which consist to the extent of about 50% by weight of the compounds of the formulae (113) and (114) and dye cotton in navy blue shades.

Example 9: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the mixture of the compounds of Example 5 gives a mixture of compounds which in the form of the free acid are of the formulae (105), (106), (107), (108), (113), (114), (115) and (116), consist to the extent of about 50% by weight of the compounds of the formulae (105), (106), (113) and (114) and dye cotton in navy blue shades. The $\lambda_{\max}$ of the dye mixture is 583 nm.

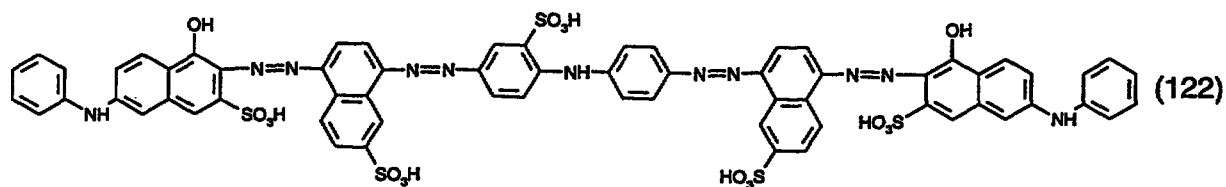
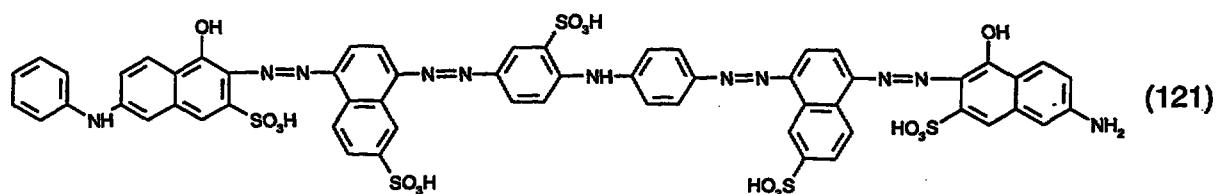
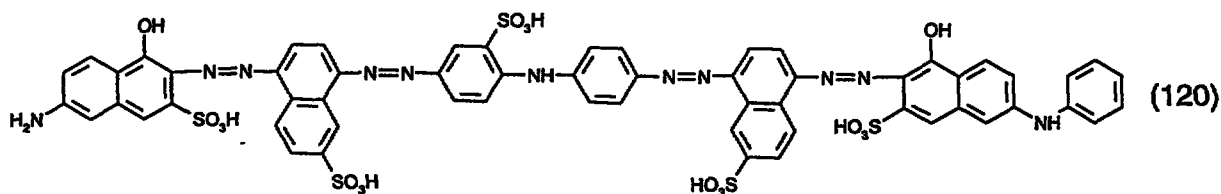
Example 10: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the mixture of the compounds of Example 3

gives a mixture of compounds which in the form of the free acid are of the formulae (117), (118) and (119)

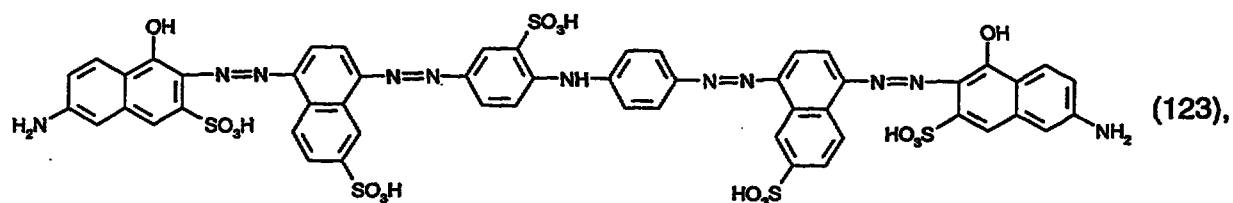


the sulfo groups of the aminonaphthalenesulfonic acid components of component B independently of one another are each in position 6 or 7, and the sum of n and m is 1. The mixtures of the compounds of the formulae (117), (118) and (119) consist to the extent of about 50% by weight of the compound of the formula (117) and dye cotton in navy blue shades. The $\lambda_{\max}$ of the dye mixture is 589 nm.

Example 11: Following the procedure of Example 6 but using, instead of 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid, a mixture of 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid and 9.9 parts of 2-phenylamino-5-naphthol-7-sulfonic acid gives a mixture of compounds which in the form of the free acid are of the formulae (120), (121), (122) and (123)



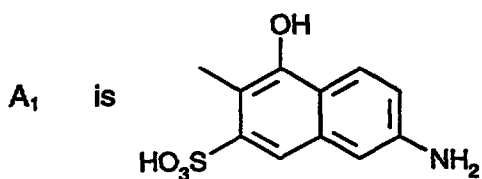
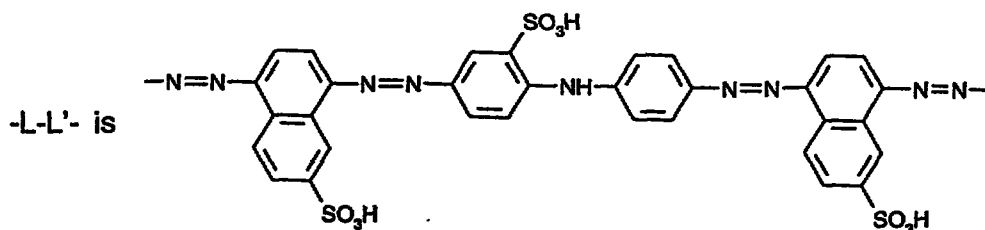
and



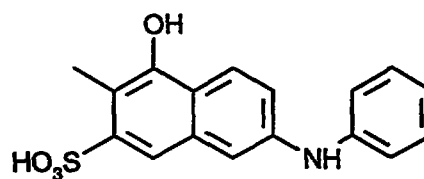
consist to the extent of about 50% by weight of the compounds of the formulae (120) and (121) and dye cotton in navy blue shades. The λ_{max} of the dye mixture is 584 nm.

Example 12: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the mixture of the compounds of Example 5 and, instead of 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid, a mixture of 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid and 9.9 parts of 2-phenylamino-5-naphthol-7-sulfonic acid gives a mixture of compounds which in the

form of the free acid are of the formulae (120), (121), (122), (123) and (124), (125), (126) and (127)



and A_2 is



which consist to the extent of about 50% by weight of the compounds of the formulae (120), (121), (124) and (125) and which dye cotton in navy blue shades. The $\lambda_{\max}$ of the dye mixture is 590 nm.

Example 13: Following the procedure of Example 6 but using, instead of 22.4 parts of the compound of the formula (101), 22.4 parts of the mixture of the compounds of Example 5 and, instead of 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid, a mixture of 11.5 parts of 2-amino-5-naphthol-7-sulfonic acid and 3.9 parts of 2-phenylamino-5-naphthol-7-sulfonic acid gives a mixture of compounds which in

the form of the free acid are of the formulae (120), (121), (122), (123), (124), (125), (126) and (127), consist to the extent of about 33% by weight of the compounds of the formulae (120), (121), (124) and (125) and dye cotton in navy blue shades. The λ_{max} of the dye mixture is 590 nm.

Examples 14 to 22: Following the procedure of Example 6 but using, instead of 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid, the respective equimolar amount of a mixture of the coupling components indicated in Table 1 gives mixtures of compounds which in the form of the free acid are of the formulae

A_1-B-A_2 , A_1-B-A_1 and A_2-B-A_2 in which B is

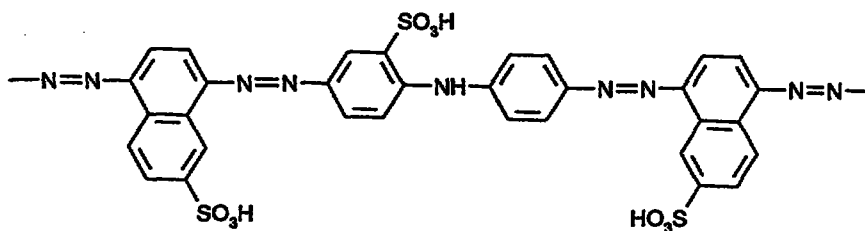
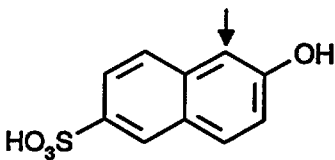
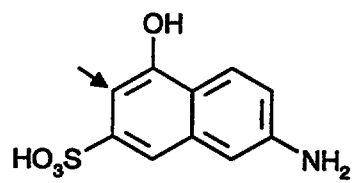
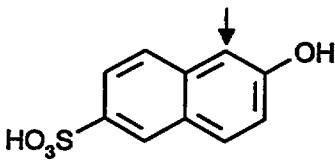
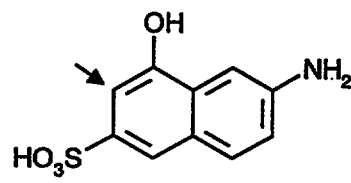
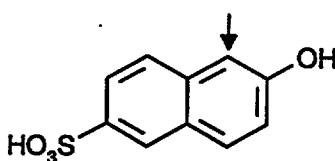
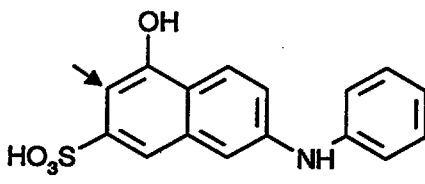
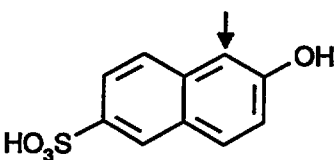
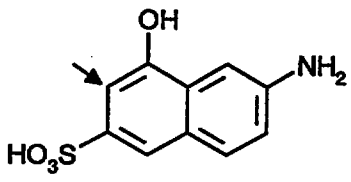
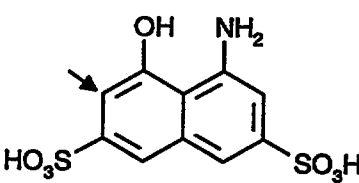
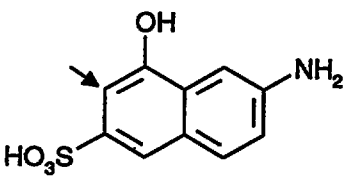
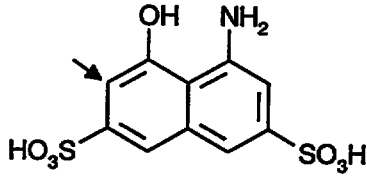
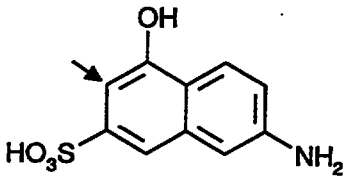
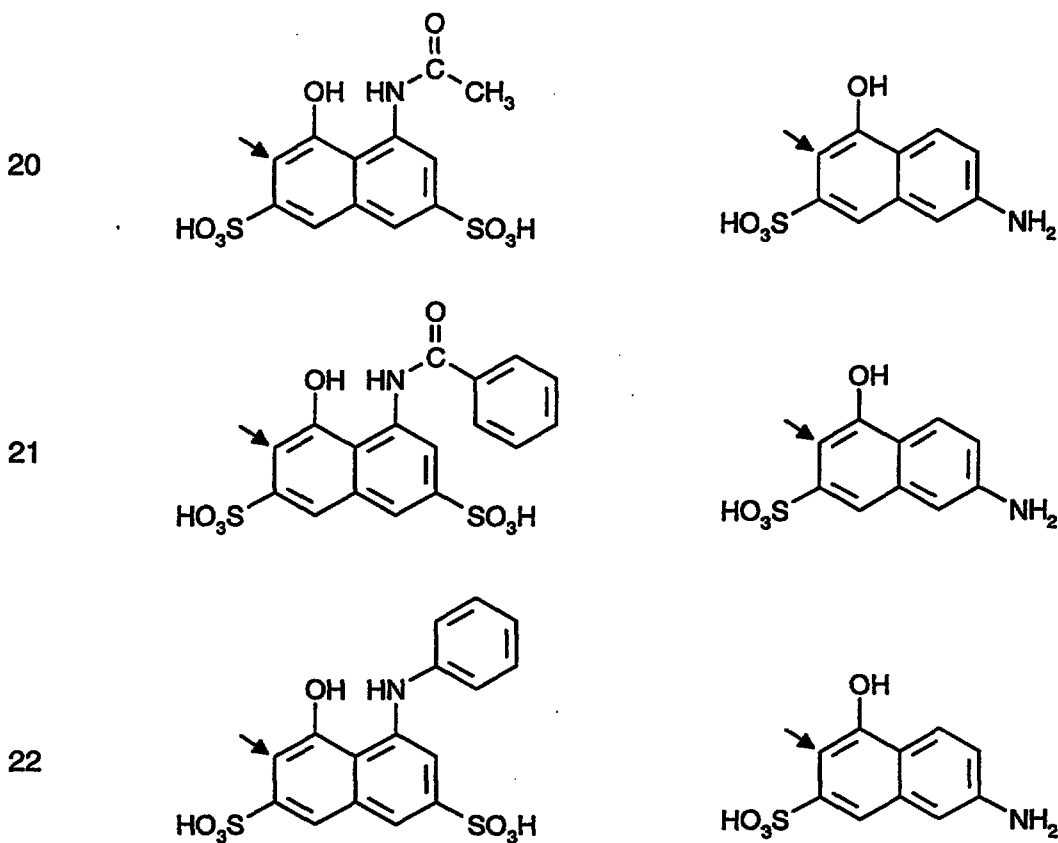


Table 1

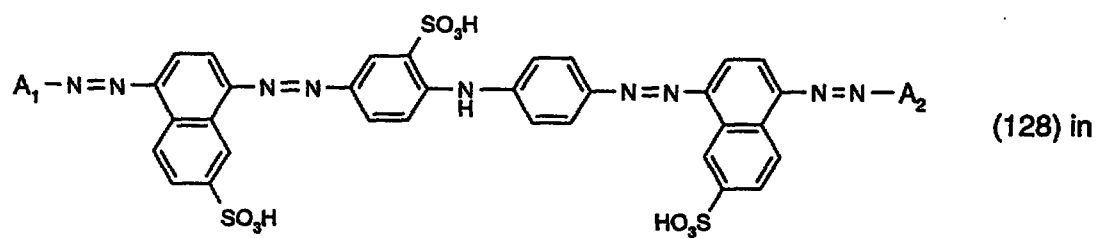
Example	A ₁ -H	A ₂ -H
14		
15		
16		
17		
18		
19		



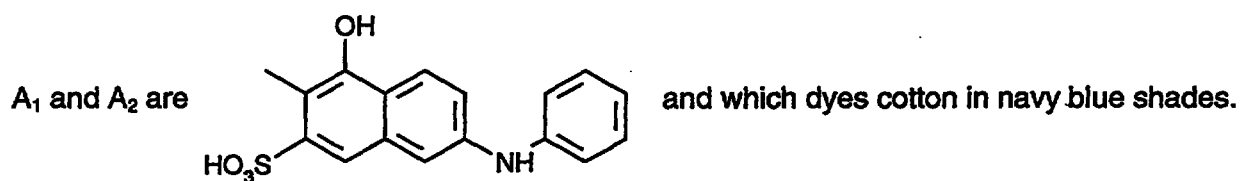
The arrow in Table 1 denotes in each case the position of coupling. The mixtures of Examples 14 to 22 dye cotton in navy blue shades.

Proceeding in analogy to the indications in Examples 14 to 22 it is possible, instead of 22.4 parts of the compound of the formula (101), to use either 22.4 parts of the compound of the formula (102) of Example 2, 22.4 parts of the compound of the formula (103) from Example 4, a mixture of the compounds of the formulae (101), (102), (103) and (104) of Example 3 or a mixture of the compounds of the formulae (101) and (103) of Example 5, giving dye mixtures which dye cotton in navy blue shades.

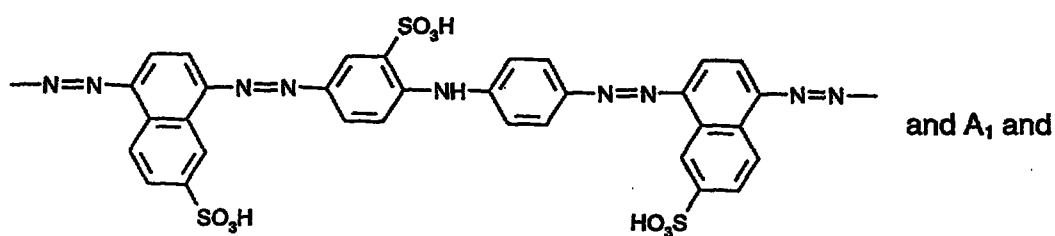
Example 23: Following the procedure of Example 6 but using, instead of the mixture of 7.2 parts of 2-amino-8-naphthol-6-sulfonic acid and 7.2 parts of 2-amino-5-naphthol-7-sulfonic acid, 19.7 parts of 2-phenylamino-5-naphthol-7-sulfonic acid gives a compound which in the form of the free acid is of the formula (128)



which



Examples 24 to 27: Following the procedure of Example 23 but using, instead of 19.7 parts of 2-phenylamino-5-naphthol-7-sulfonic acid, an equimolar amount of the coupling components indicated in Table 2 gives compounds which in the form of the free acid, are of the formula A_1-B-A_2 in which B is



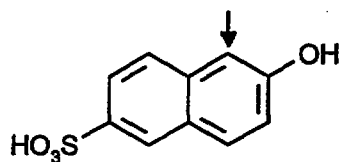
A_2 are identical.

Table 2

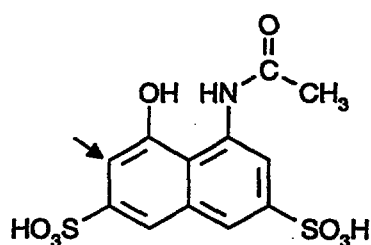
Example

$A_1-H = A_2-H$

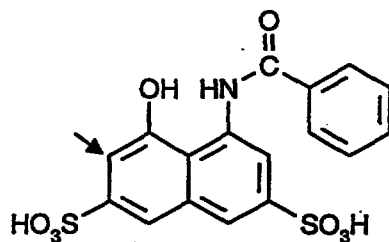
24



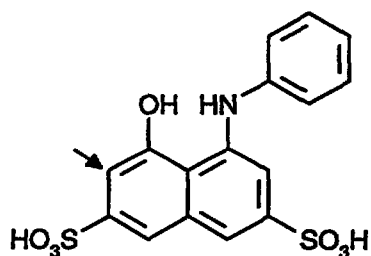
25



26



27



The arrow in Table 2 denotes in each case the position of coupling. The dyes of Examples 24 to 27 dye cotton in navy blue shades.

Proceeding in analogy to the indications in Examples 23 to 27 it is possible, instead of 22.4 parts of the compound of the formula (101), to use either 22.4 parts of the compound of the formula (102) of Example 2, 22.4 parts of the compound of the formula (103) from Example 4, a mixture of the compounds of the formulae (101), (102), (103) and (104) of Example 3 or

a mixture of the compounds of the formulae (101) and (103) of Example 5, giving dyes or dye mixtures which dye cotton in navy blue shades.

Dyeing instructions 1

10 parts of cotton fabric (bleached and mercerized) are introduced at about 30°C into a dye bath containing 200 parts of water and 0.2 part of the dye mixture of Example 5. The liquor is heated to 95°C over the course of 30 minutes and is left at this temperature for 15 minutes. Then 4 parts of sodium sulfate are added and dyeing is continued at 95°C for 45 minutes. The dye bath is then cooled to 80°C over the course of 15 minutes and is left at this temperature for 15 minutes more. The dyeing is then rinsed thoroughly with cold water and dried.

Dyeing instructions 2

10 parts of a 50:50 fibre blend of polyester and cotton are introduced at about 50°C into a dye bath containing 200 parts of water, a dye mixture consisting of 0.1 part of C.I. Disperse Blue 79 and 0.1 part of the dye mixture of Example 5, 0.4 part of ammonium sulfate and 0.2 part of an anionic dispersant (e.g. formaldehyde condensation product of naphthalenesulfonic acid). The dye bath is adjusted with formic acid to a pH of 5.5, 2 parts of sodium sulfate are added, and then the bath is heated to about 130°C over the course of 45 minutes. Dyeing is continued at 130°C for 45 minutes, then the dye bath is cooled to about 80°C over the course of 30 minutes and is left at this temperature for a further 45 minutes. The dyeing is then rinsed thoroughly with cold water and dried.

Dyeing instructions 3

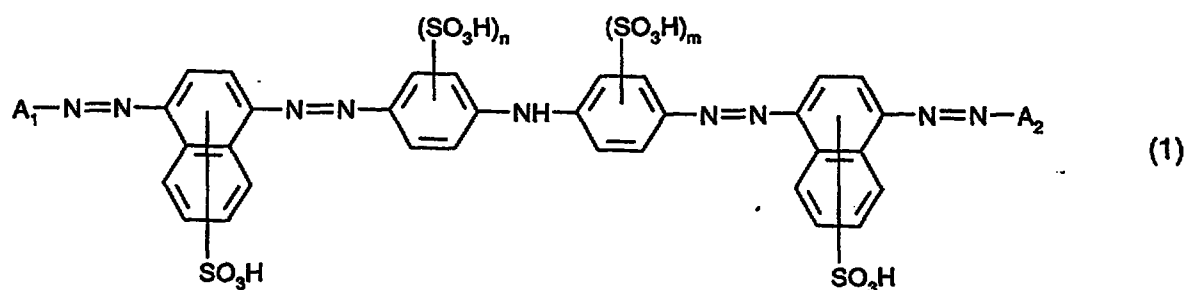
The procedure of dyeing instructions 1 or 2 is followed except that, after the end of the dyeing process, the cold-rinsed dyeing is placed in a fresh bath which is at a temperature of about 30°C and contains 200 parts of water and 0.2-0.6 part of a cationic aftertreatment agent (amine-formaldehyde-dicyandiamide condensation product or preparation based on dicyandiamide and diethylenetriamine). The dyeing is aftertreated at 30°C for 30 minutes and then dried without a further rinsing process; a dyeing having improved wet fastness properties is obtained.

Dyeing instructions 4

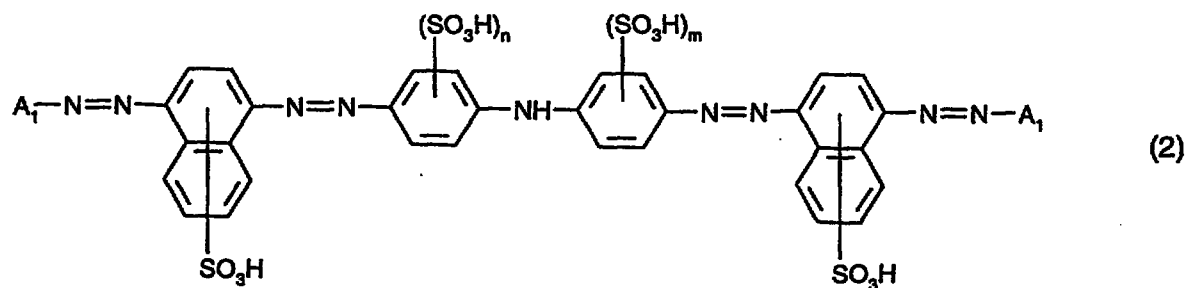
The procedure of dyeing instructions 1 or 2 is followed except that, after the end of the dyeing process, the cold-rinsed dyeing is placed in a fresh bath which is at a temperature of about 25°C and contains 200 parts of water, 1 part of sodium sulfate and 0.6 part of a fibre-reactive cationic aftertreatment agent based on N-methyldialkylamine and epichlorohydrin. The temperature is raised to 40°C over the course of 15 minutes, 0.8 part of 30% sodium hydroxide solution is added, and the dyeing is treated at 40°C for a further 45 minutes. The dyeing is finally hot-rinsed and dried; it features improved wet fastness properties.

WHAT IS CLAIMED IS:

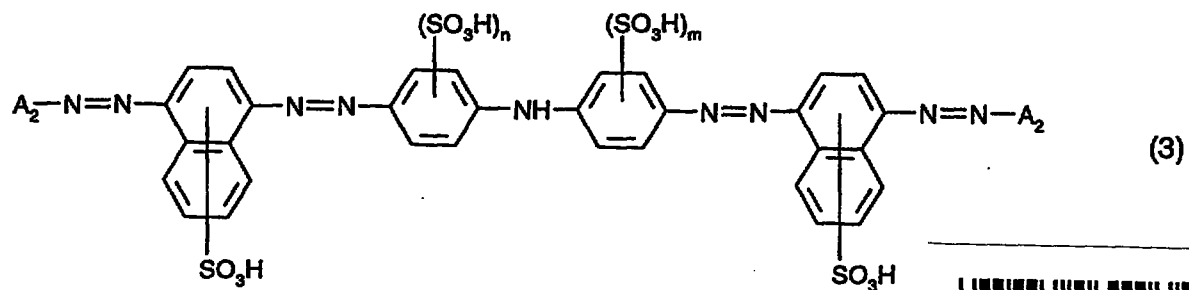
1. A dye mixture comprising at least one dye of the formula (1)



together with at least one dye of the formula (2) or (3)



or



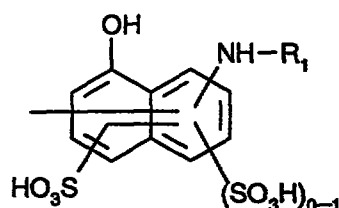
in which

A₁ and A₂ independently of one another are each the radical of a coupling component of the benzene or naphthalene series or of the heterocyclic series and

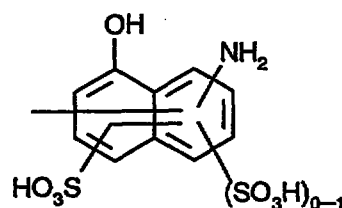
n and m are 0 or 1.

2. A dye mixture according to claim 1, wherein

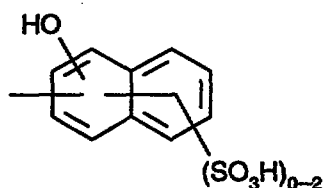
A₁ and A₂ independently of one another are each a radical of the formula (4), (5) or (6)



(4),



(5) or



(6)

in which

R₁ is unsubstituted or substituted phenyl or naphthyl or is a radical of formula -CO-R, where R is unsubstituted or substituted C₁-C₆alkyl, C₁-C₆alkoxy, C₅-C₇cycloalkyl, phenyl, phenoxy or naphthyl.

3. A dye mixture according to claim 2, wherein

R is unsubstituted or hydroxyl-, C₁-C₄alkoxy-, sulfo-, sulfato- or halogen-substituted

C₁-C₆alkyl or C₁-C₆alkoxy; unsubstituted or C₁-C₄alkyl- or halogen-substituted

C₅-C₇cycloalkyl, or unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, sulfo- or halogen-substituted phenyl, phenoxy or naphthyl.

4. A dye mixture according to one of claims 2 and 3, wherein

R is unsubstituted or hydroxyl-, C₁-C₄alkoxy- or halogen-substituted C₁-C₆alkyl or

C₁-C₆alkoxy or is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, sulfo- or halogen-substituted phenyl or phenoxy.

5. A dye mixture according to one of claims 2 to 4, wherein

R is C₁-C₄alkyl, especially methyl or ethyl, C₁-C₄alkoxy, especially methoxy or ethoxy, or phenyl.



6. A dye mixture according to claim 2, wherein

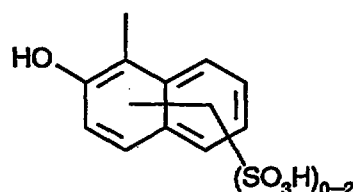
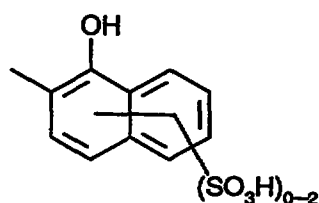
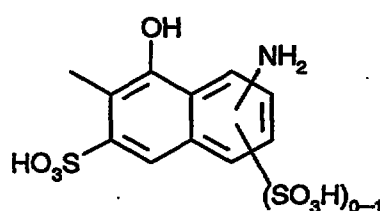
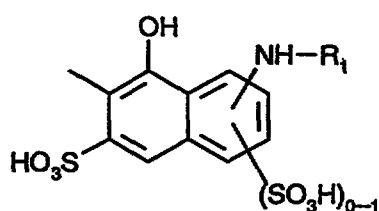
R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_2 - C_4 alkanoylamino-, nitro-, halogen-, carboxy- or sulfo-substituted phenyl or naphthyl or is a radical of the formula $-CO-R$, where R is unsubstituted or hydroxyl-, C_1 - C_4 alkoxy- or halogen-substituted C_1 - C_6 alkyl or C_1 - C_6 alkoxy or is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, sulfo- or halogen-substituted phenyl or phenoxy.

7. A dye mixture according to one of claims 2 and 6, wherein

R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, halogen- or sulfo-substituted phenyl, especially phenyl, or is a radical of the formula $-CO-R$, where R is C_1 - C_4 alkyl, especially methyl or ethyl, C_1 - C_4 alkoxy, especially methoxy or ethoxy, or phenyl.

8. A dye mixture according to one of claims 1 to 7, wherein

A_1 and A_2 independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b)

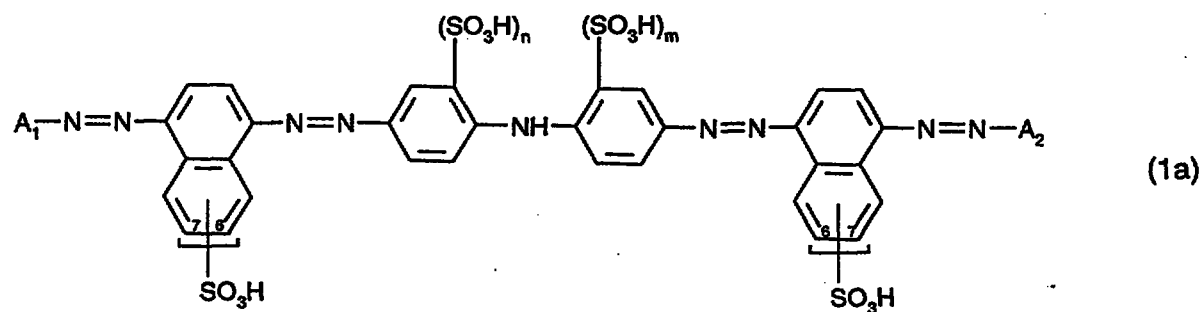


in which

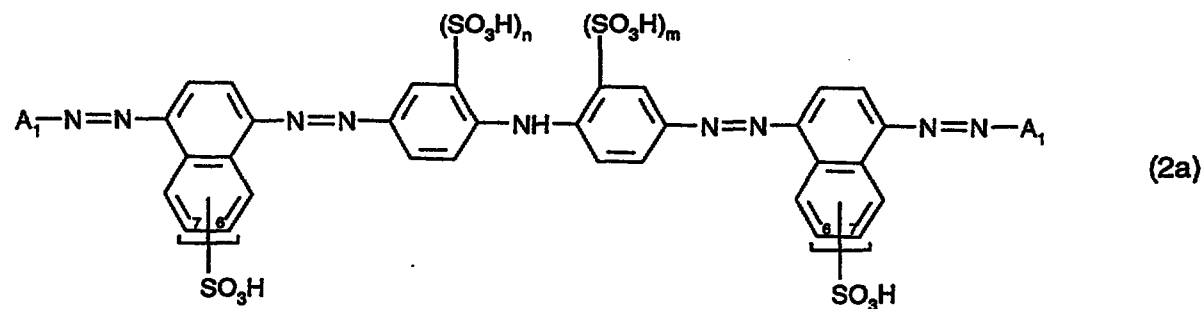
R_1 is unsubstituted or substituted phenyl or naphthyl or is a radical of the formula $-CO-R$, where R is unsubstituted or substituted C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_5 - C_7 cycloalkyl, phenyl, phenoxy or naphthyl.



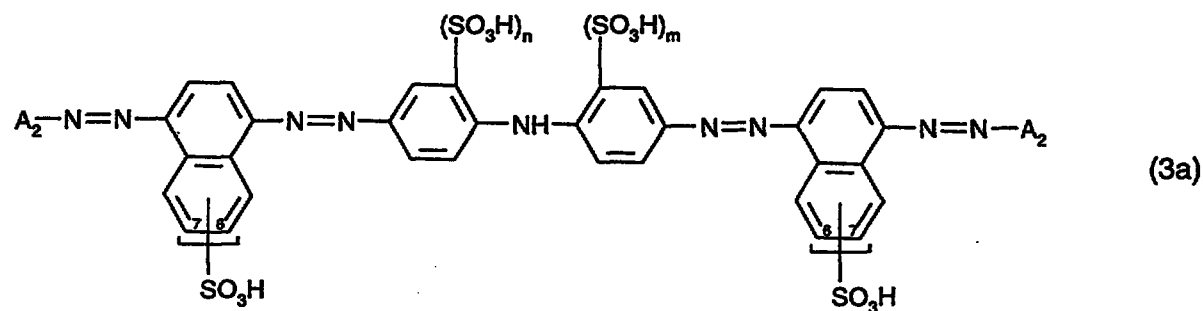
9. A dye mixture according to one of claims 1 to 8, comprising,
at least one dye of the formula (1a)



together with at least one dye of the formula (2a) or (3a)



or



in which

the sulfo groups of the naphthalenesulfonic acid components independently of one another
are each attached in position 6 or 7,



A₁ and A₂ independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b),

R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, halogen- or sulfo-substituted phenyl, or is a radical of the formula -CO-R, where

R is methyl, ethyl, methoxy, ethoxy or phenyl, and

the sum of n and m is 0 or 1.

10. A dye mixture according to claim 9, wherein

A₁ and A₂ independently of one another are each a radical of the formula (4a), (5a) or (6b),

R₁ is phenyl or a radical of the formula -CO-R, where

R is methyl, ethyl or phenyl.

11. A dye mixture according to one of claims 9 and 10, comprising

at least one dye of the formula (1a) together with at least one dye of the formula (2a) and at least one dye of the formula (3a).

12. A process for preparing a dye mixture according to claim 1, which comprises diazotizing a compound of the formula (7)

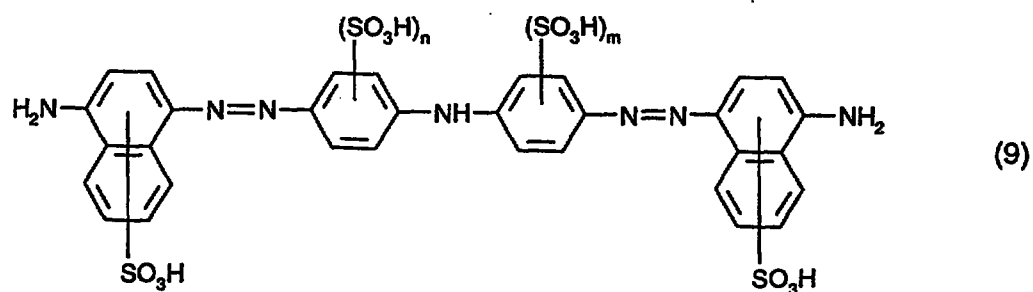


coupling the product with a compound of the formula (8)



diazotizing the resulting compound of the formula (9)





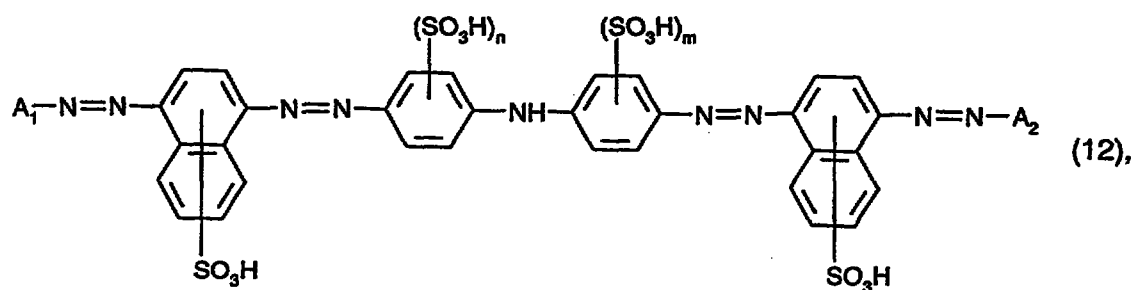
and coupling the product with the compounds of the formulae (10) and (11)

A_1-H (10) and

A_2-H (11)

where A_1 , A_2 , n and m are each as defined in claim 1.

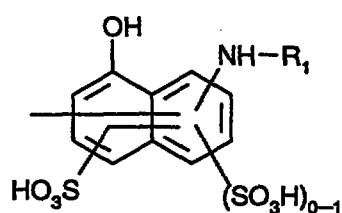
13. An azo dye of the formula (12)



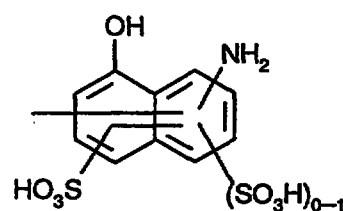
wherein

A_1 and A_2 independently of one another are each a radical of the formula (4), (5) or (6)

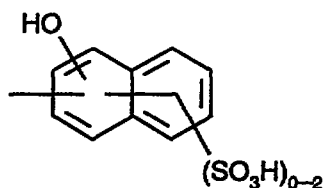




(4),



(5) or



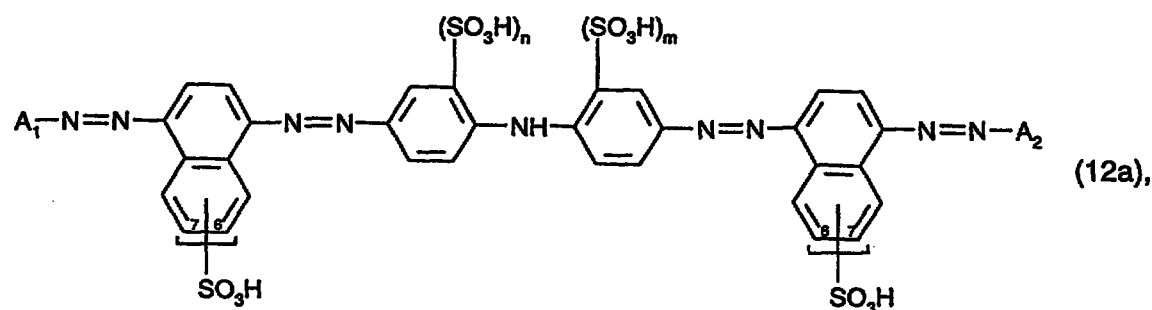
(6)

in which

n and m are 0 or 1 and

R_1 is as defined in claim 2, with the proviso that, if A_1 and A_2 are identical radicals of the formula (5) and the sum of n and m is 1, the radicals A_1 and A_2 are not simultaneously 2- or 3- or 4-amino-8-hydroxy-6-sulfonaphth-7-yl or 1-amino-8-hydroxy-3,6-disulfonaphth-7-yl.

14. An azo dye according to claim 13, of the formula (12a)



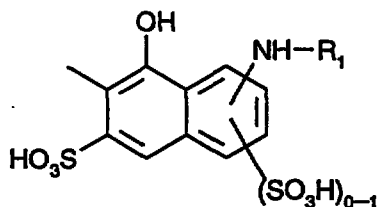
(12a),

in which

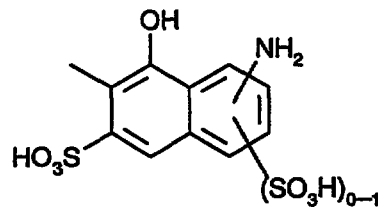
the sulfo groups of the naphthalenesulfonic acid components independently of one another are each attached in position 6 or 7,

A_1 and A_2 independently of one another are each a radical of the formula (4a), (5a), (6a) or (6b)

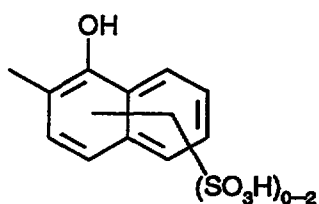




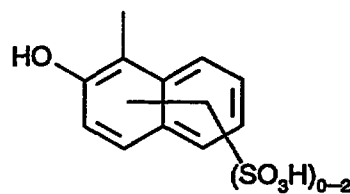
(4a)



(5a)



(6a) or



(6b)

in which

R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, halogen- or sulfo-substituted phenyl, especially phenyl, or is a radical of formula $-CO-R$, where

R is methyl, ethyl, methoxy, ethoxy or phenyl and

the sum of n and m is 0 or 1.

15. The use of the dye mixture according to one of claims 1 to 11 or of the dye mixture obtained according to claim 12 for dyeing or printing nitrogen-containing or hydroxyl-containing fibre materials.

16. The use according to claim 15, wherein fibre mixtures of synthetic fibres and cellulosic fibre materials, especially polyester/cotton blends, are dyed in the presence of a disperse dye for the polyester fibres under the dyeing conditions for polyester fibres.

17. A method of dyeing polyester/cotton blends with disperse and direct dyes, which comprises using dye mixtures according to claim 1 in addition to the disperse dyes in a single-stage, one-bath process and dyeing from an aqueous liquor at temperatures in the range from 100 to 150°C, preferably from 120 to 130°C, and at a pH of between 4 and 7.5.

