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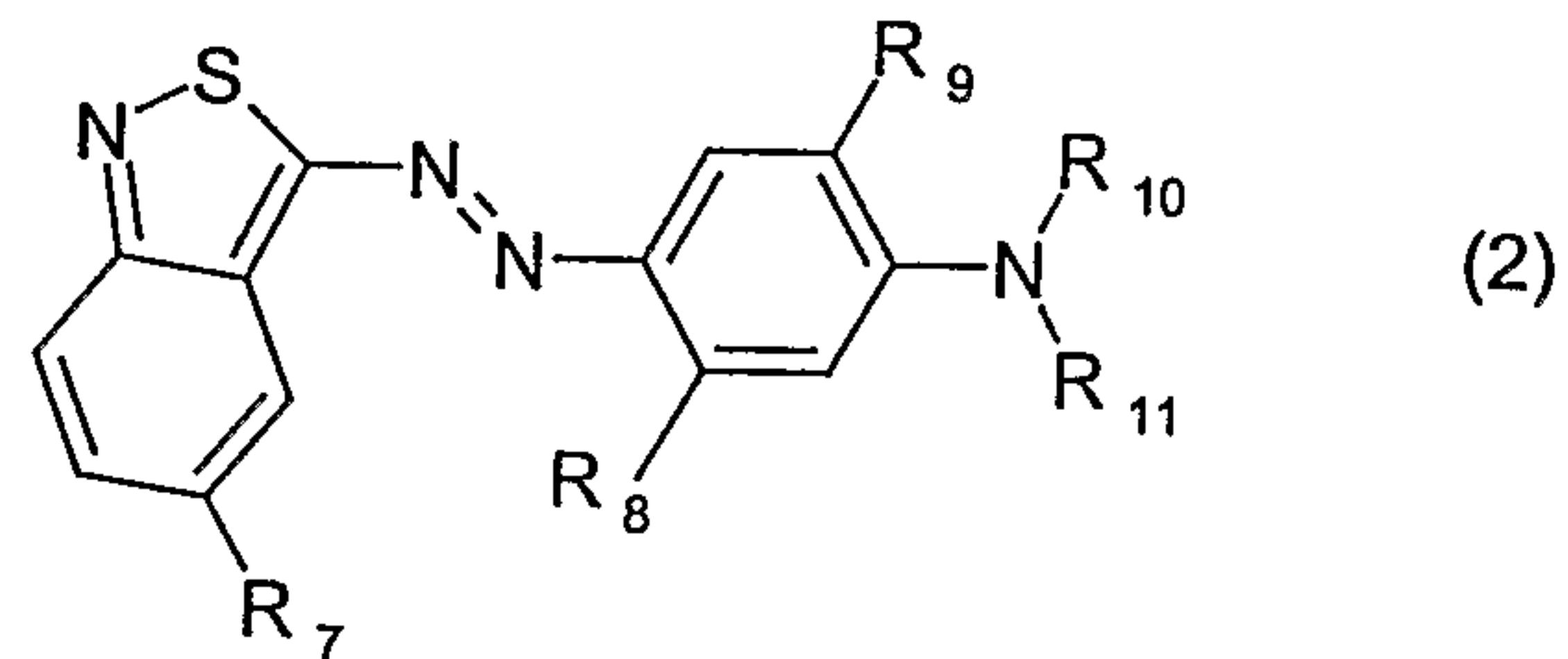
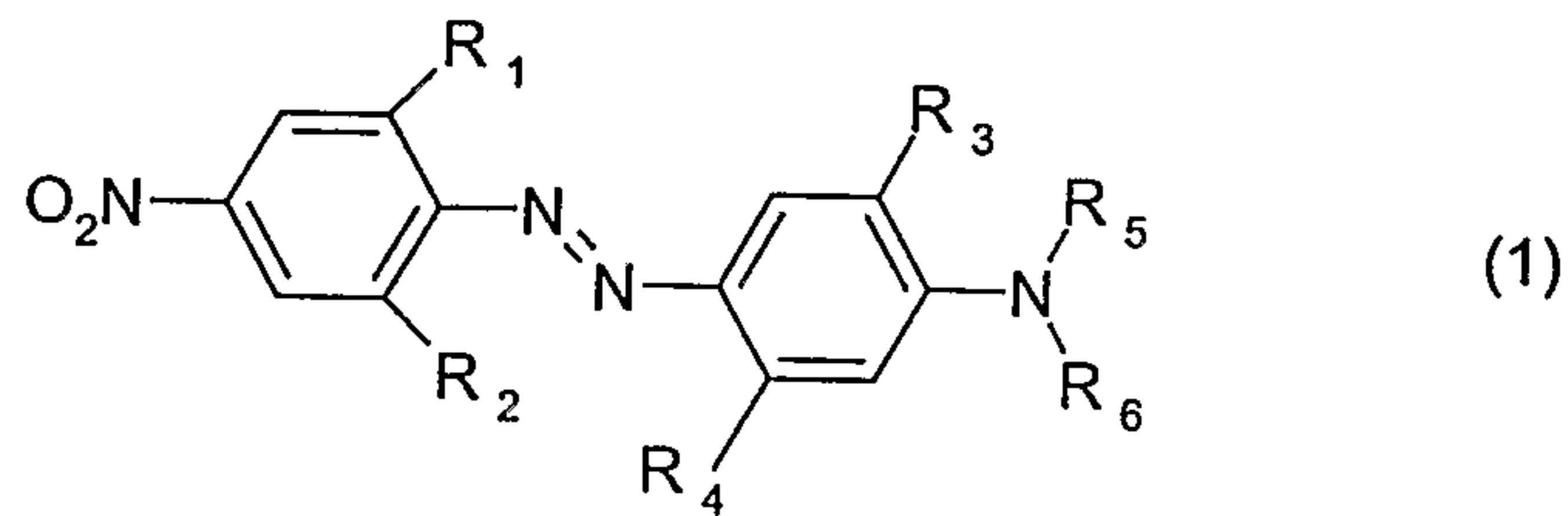
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(54) Titre : COMPOSITIONS COLORANTES DESTINEES A LA COLORATION OU A L'IMPRESSION DE PRODUITS
FIBREUX COMPRENANT DE L'ACETO-CELLULOSE
(54) Title: DYE COMPOSITIONS FOR DYEING OR PRINTING OF FIBRE PRODUCTS COMPRISING
CELLULOSEACETATE



(57) Abrégé/Abstract:

Dye mixture containing at least one dye of the formulae (1)(formula see enclosed paper copy)and at least one dye of the formulae (2)(formula see enclosed paper copy)where the substituents are each as defined in the claims. These mixtures are useful for dyeing or printing fibre materials comprising polyester and/or cellulose acetate.

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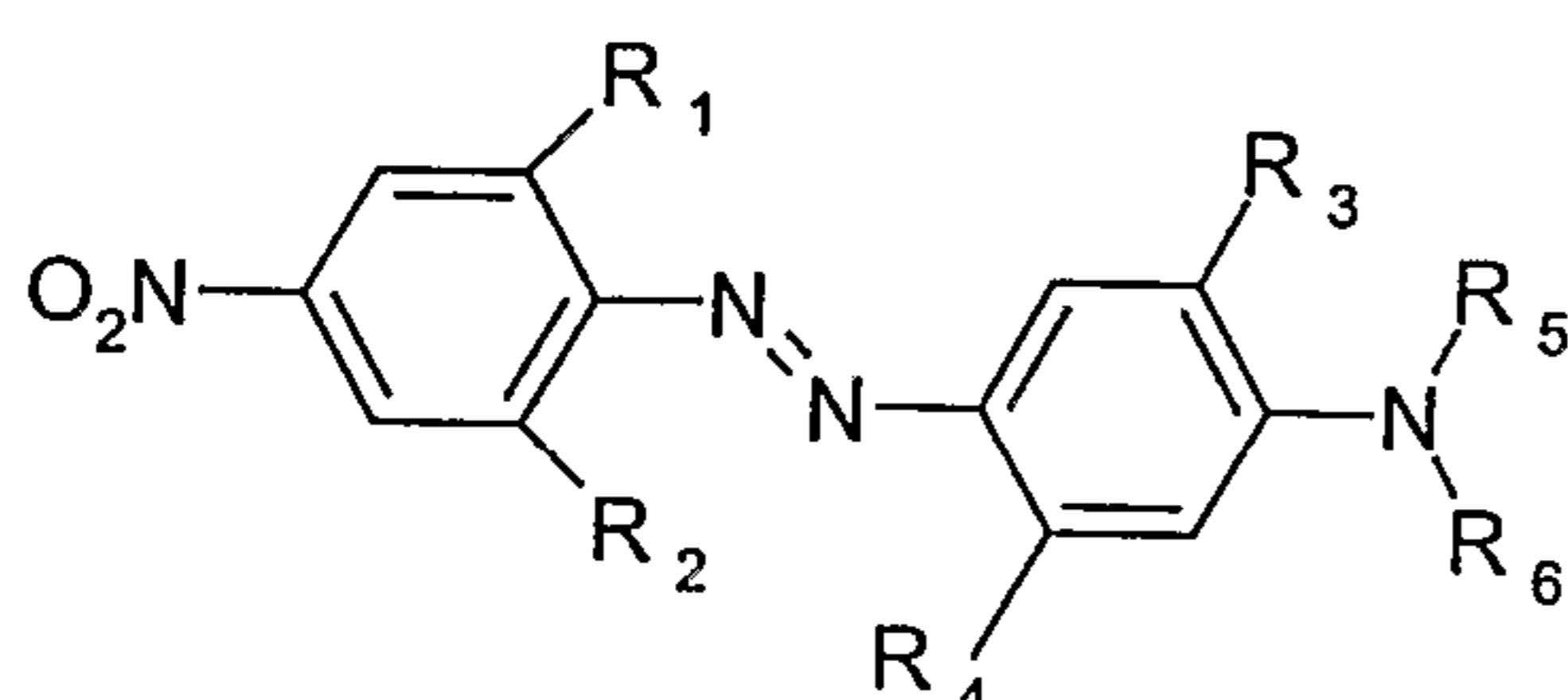
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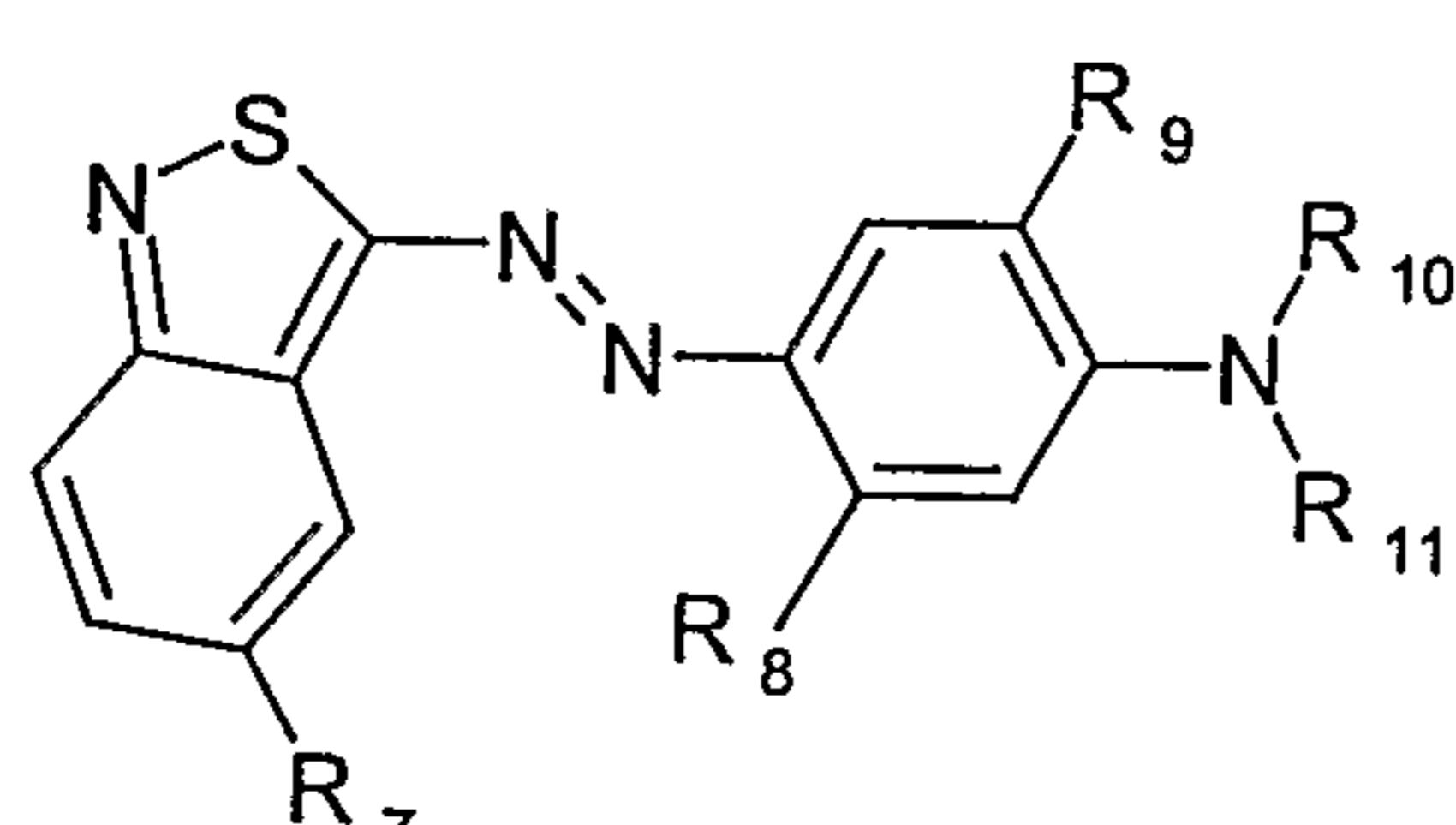
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DYE COMPOSITIONS FOR DYEING OR PRINTING OF FIBRE PRODUCTS COMPRISING CELLULOSEACETATE



(1)

(57) Abstract: Dye mixture containing at least one dye of the formulae (1)(formula see enclosed paper copy) and at least one dye of the formulae (2)(formula see enclosed paper copy) where the substituents are each as defined in the claims. These mixtures are useful for dyeing or printing fibre materials comprising polyester and/or cellulose acetate.



(2)

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Dye compositions for dyeing or printing of fibre products comprising celluloseacetate

The present invention relates to mixtures of dyes, their preparation and their use for

5 dyeing or printing fibre materials which comprise polyester.

Dyes and dye mixtures for dyeing polyester are known. Similarly, dyes and dye mixtures for dyeing semisynthetic or synthetic hydrophobic fibre materials which comprise cellulose acetate such as for example cellulose secondary acetate and cellulose

10 triacetate are known. Cellulose secondary acetate means partially esterified cellulose having from 2 to 2,5 acetyl groups per anhydroglucose unit which is also known as 2¹/₂-acetate or 2¹/₂-celluloseacetate or cellulose-2¹/₂-acetate respectively.

Thus, it has been determined that these dyes or their mixtures do not always fully meet

15 the highest requirements, especially with regard to reproducibility, sensitivity to dyebath temperature or the suitability for specific dyeing processes, especially in relation to the use of a jigger or jet dyeing machine.

Moreover, dyes which dye polyester effectively often do not go readily onto cellulose

20 secondary acetate or cellulose triacetate fibres. On the other hand, dyes which dye cellulose secondary acetate or cellulose triacetate fibres effectively do not often go readily onto polyester.

EP347685 discloses mixtures of blue disperse dyes which leave accompanying fibres 25 fibers, like wool, cotton or regenerated cellulose other than made of polyester un-dyed or even un-soiled.

GB2346150 discloses disperse dye mixtures and their use of these mixtures for dyeing or printing semisynthetic hydrophobic cellulose acetate-containing fibre materials.

30 These mixtures do not stain wool or cotton if present in blends with cellulose acetate.

In addition, certain dyes which are suitable for acetate fibres exhibit a considerable temperature sensitivity, so that a poor appearance or depth of shade likewise results when the temperature distribution in the dyeing liquor is not uniform.

5 C.I. Disperse Blue 183 and its derivatives cannot be dyed onto cellulose acetate and barely give uniform dyeings when exhaust-dyed onto polyester.

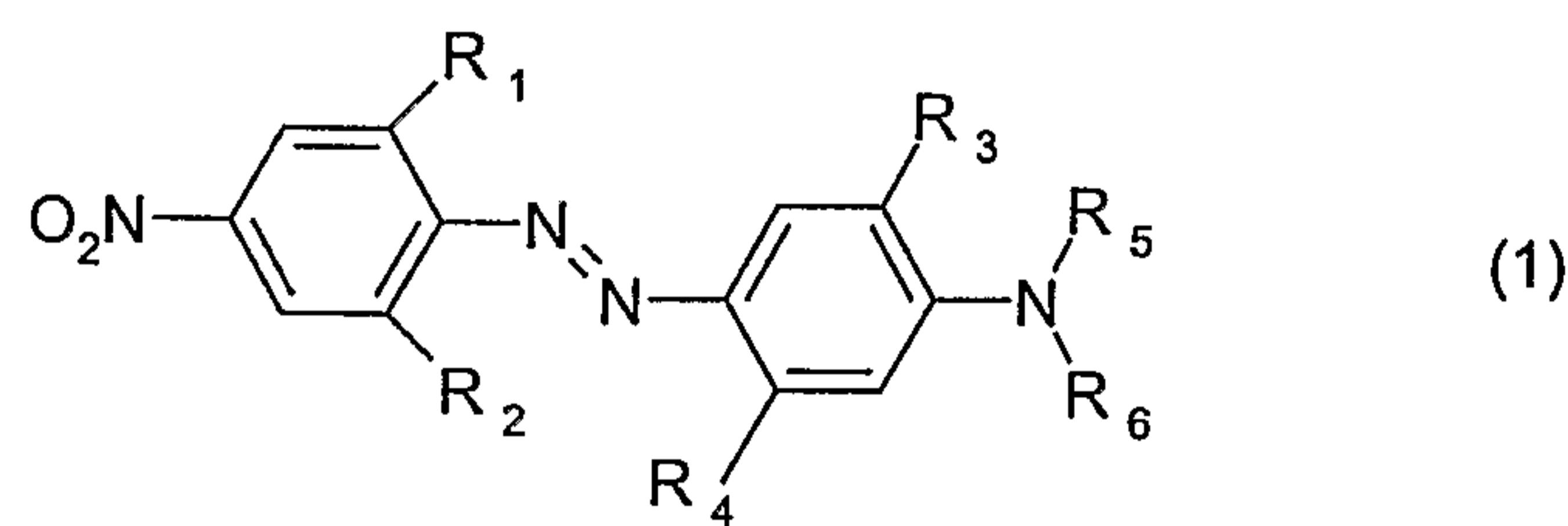
There is therefore a need for novel dyes or dye mixtures which do not have these disadvantages and yet lead to dyeings having a hue angle (hue as defined in DIN

10 5033-1: 1979-03) of 295 to 305° (preferably 298 to 302°) at a 1/1 standard depth of shade on polyester (as defined in DIN 5033 Part 3) and the same or substantially the same hue as C.I. Disperse Blue 183 coupled with the same or superior fastnesses.

It has now been found that, surprisingly, the mixtures according to the invention

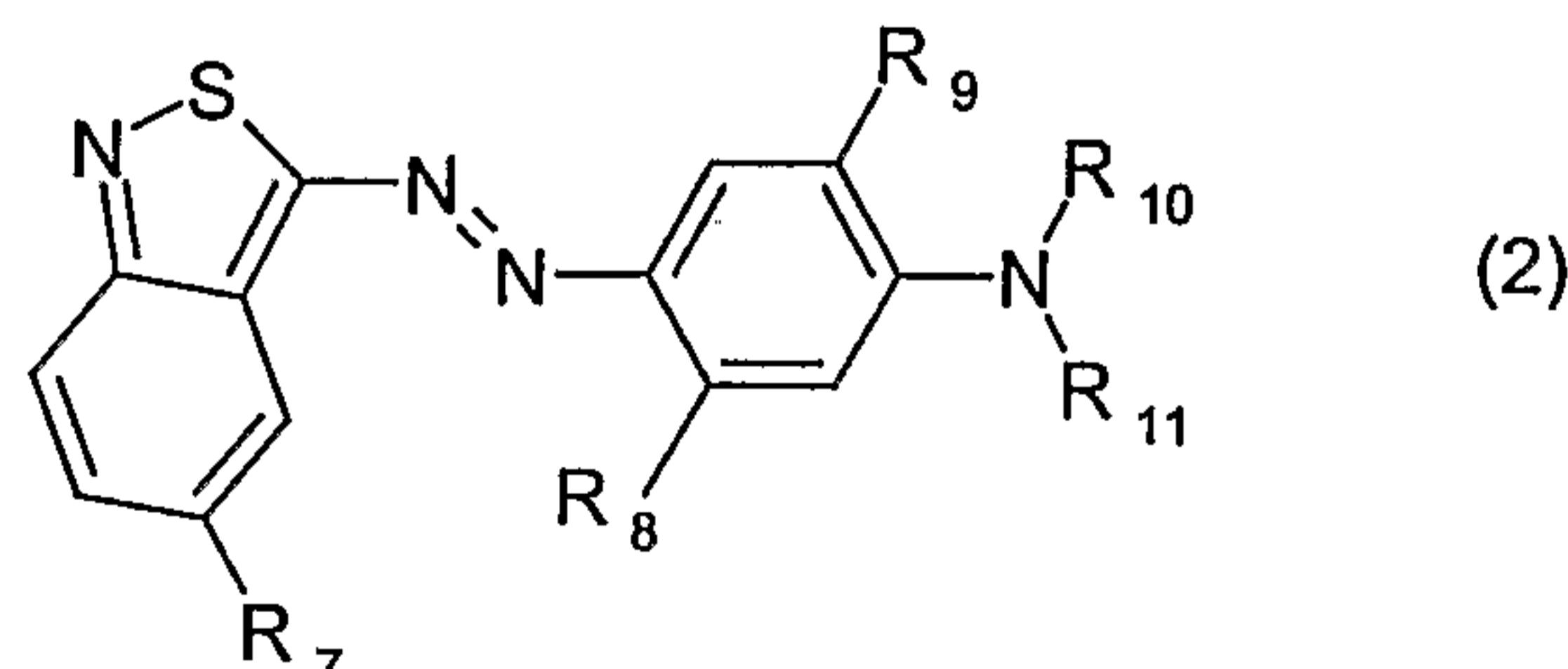
15 substantially fulfil the above-indicated criteria, whereas the properties of the individual dyes fulfil these criteria only insufficiently, if at all.

The present invention accordingly provides a dye mixture containing at least one dye of the formulae (1)



20

and at least one dye of the formula (2)



where

R₁ is hydrogen, halogen, nitro or cyano

25 R₂ is hydrogen, halogen, nitro or cyano

R₃ is hydrogen, halogen, C₁-C₄-alkoxy or C₁-C₄-alkyl

R₄ is hydrogen, C₁-C₄-alkyl

R₅ is hydrogen, unsubstituted or hydroxyl-, cyano-, C₁-C₄-alkylcarbonyloxy-, substituted C₁-C₄-alkyl or C₁-C₄-alkenyl

R₆ is unsubstituted or hydroxyl-, cyano-, C₁-C₄-alkylcarbonyloxy-, C₁-C₄-

5 alkoxy carbonyl-substituted C₁-C₄-alkyl or C₁-C₄-alkenyl,

R₇ is nitro, C₁-C₄-alkoxy or the radical -SO₂CH₃

R₈ is hydrogen or C₁-C₄-alkyl,

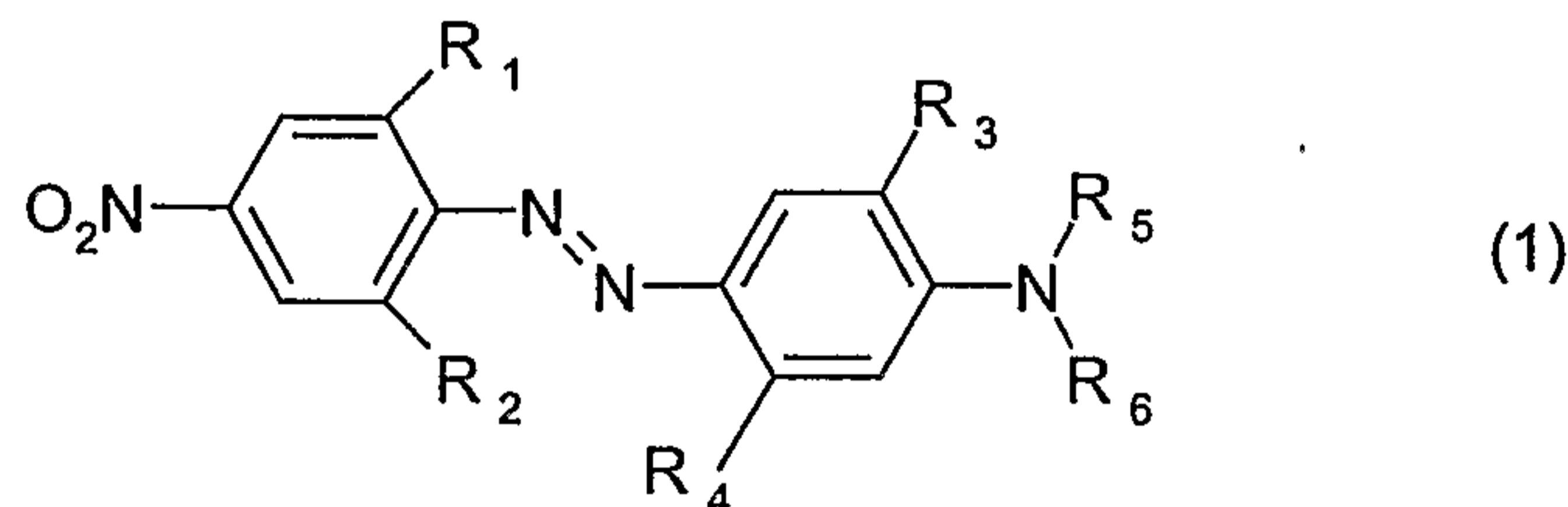
R₉ is hydrogen or C₁-C₄-alkyl,

R₁₀ is unsubstituted or hydroxyl- or cyano-substituted C₁-C₄-alkyl,

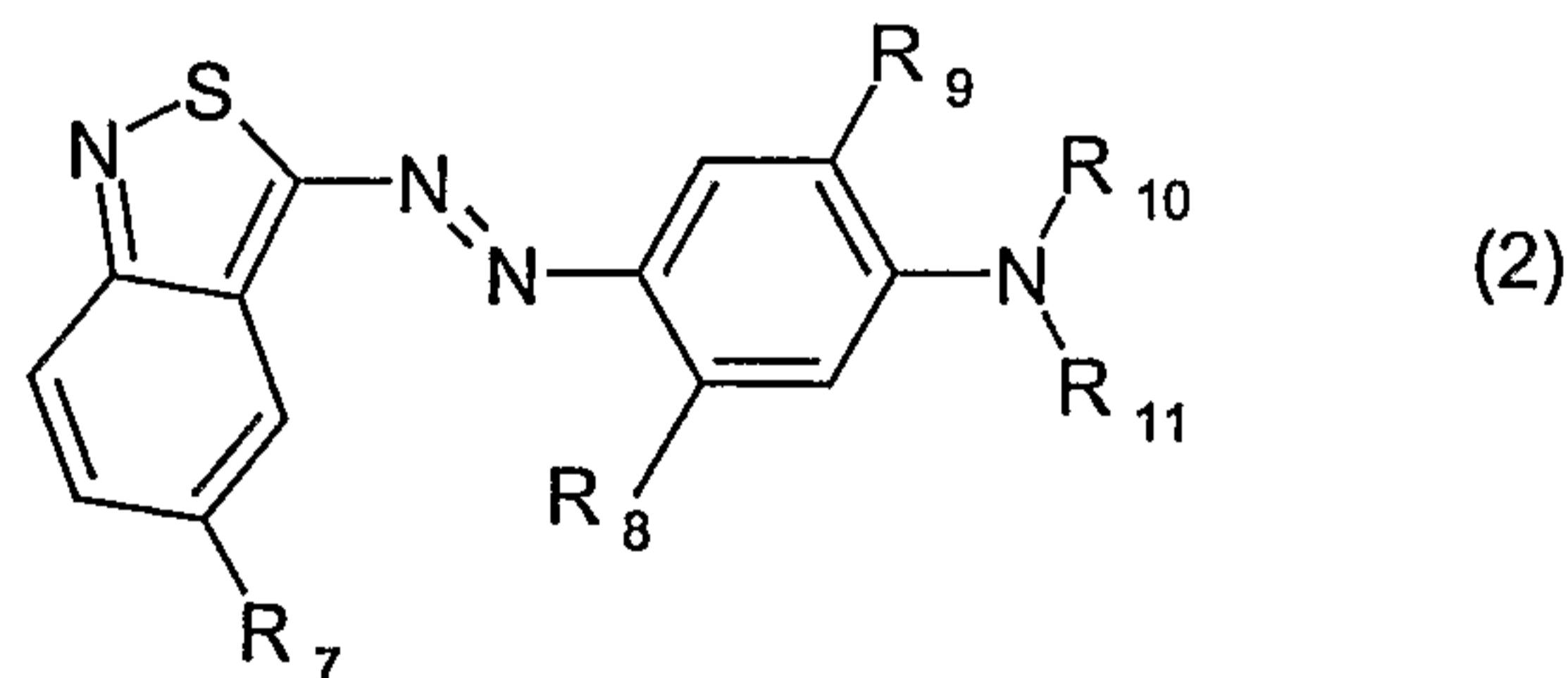
10 R₁₁ is unsubstituted C₁-C₄-alkyl or is C₁-C₄-alkyl which is substituted by the radical -O-COR₁₂, where R₁₂ is C₁-C₄-alkyl.

The present invention thus provides a dye mixture which leads to dyeings having a hue angle (DIN 5033-1: 1979-03) of 295 to 305° (and preferably 298 to 302°) at a 1/1

15 standard depth of shade on polyester (as defined in DIN 5033 Part 3) and the same or substantially the same hue as C.I. Disperse Blue 183 at similar or superior fastnesses, characterized in that they contain at least one dyes of the formulae (1)



and at least one dye of the formula (2)



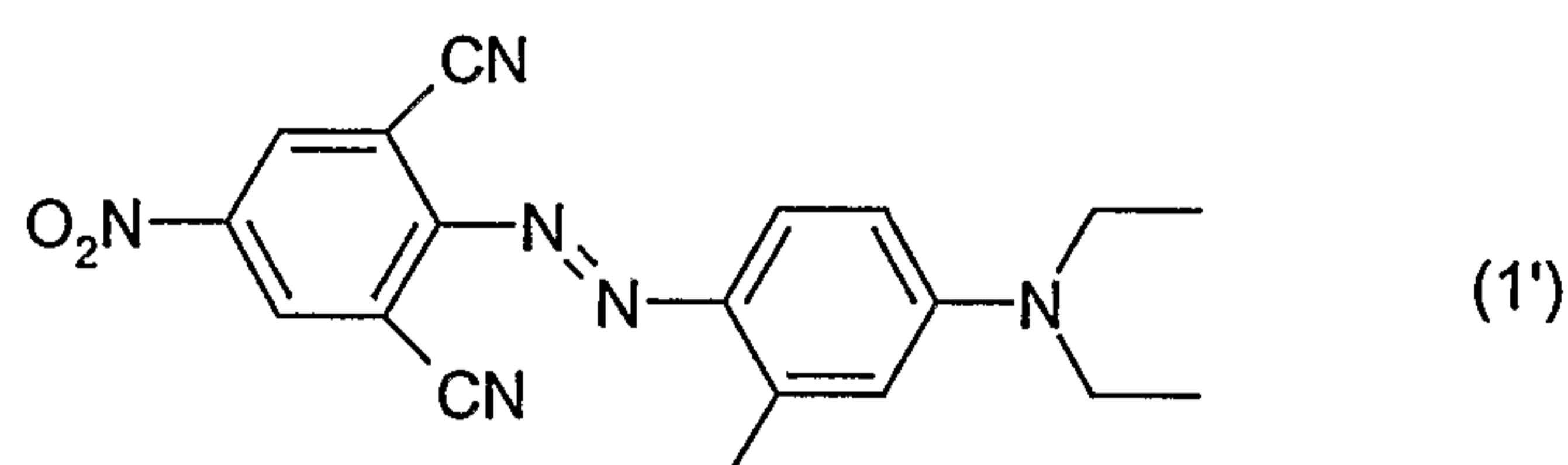
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where the substituents are each as defined above.

Preferred dye mixture containing at least one dyes of the formulae (1) and at least one dyes of the formulae (2) where R₄ is C₁-C₄-alkyl and R₇ is nitro.

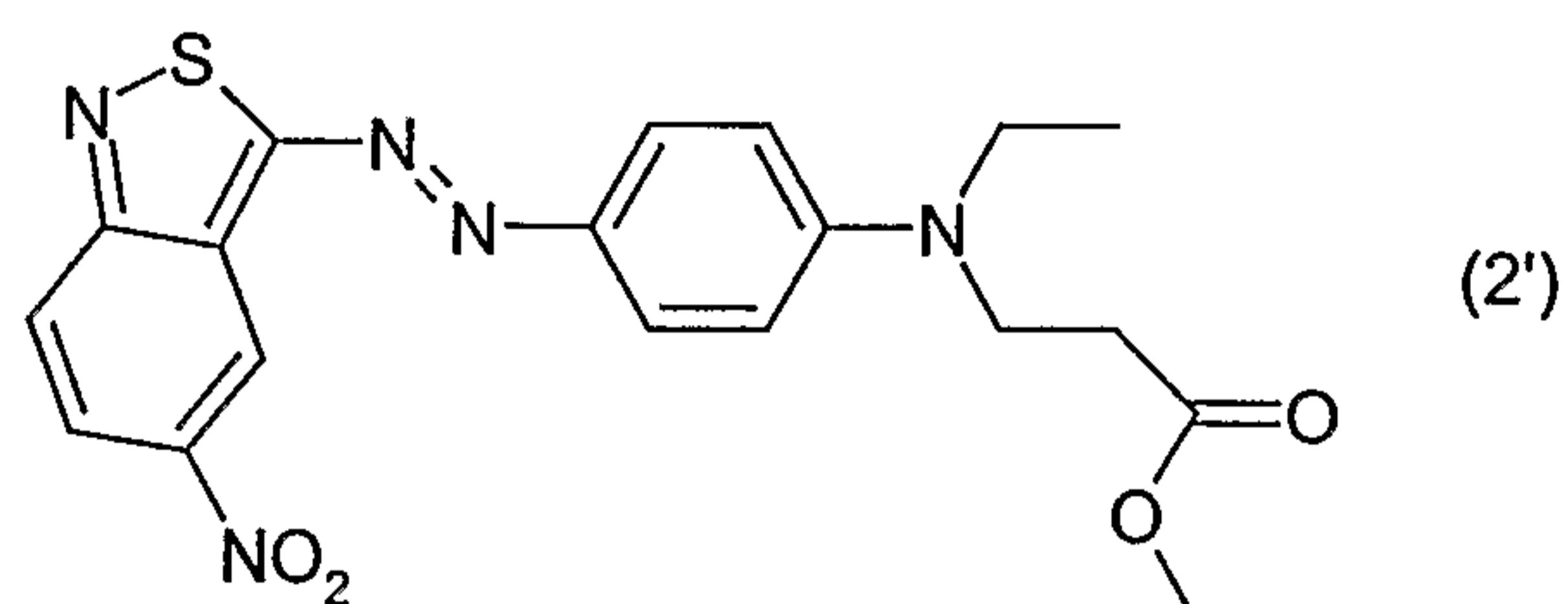
The preferred dye mixtures contain up to 60% of a dye as per the formula (1) based on the sum total of dyes (1) and (2). Particularly preferred dye mixture contain up to 50% of a dye as per the formula (1) based on the sum total of dyes (1) and (2). In very particularly preferred dye mixtures the ratio between (1) and (2) is 0.9 to 1.1:1.8:2.2, ie. 5 around 1:2. The proportion of (2) can be up to 99% based on the sum total of dyes (1) and (2), in preferred cases up to 95% based the sum total of dyes (1) and (2).

Particular preference is given to mixtures containing at least one dye of the formulae (1')



10

and at least one dye of the formula (2')



Particular preference is further given to mixtures which lead to dyeings having a hue 15 angle (DIN 5033-1: 1979-03) of 295 to 305° (and preferably 298 to 302°) at a 1/1 standard depth of shade on polyester (as defined in DIN 5033 Part 3) and the same or substantially the same hue as C.I. Disperse Blue 183 at similar or superior fastnesses, characterized in that they contain at least one dyes of the formulae (1') and at least one dye of the formula (2').

20

The dye mixtures of the invention may contain further disperse dyes which serve to shade the dye mixture, in an amount of up to 5% by weight. These "shading dyes" can be added by customary mixing.

25 The dye mixtures according to the invention may contain further disperse dyes, even in an amount of more than 5% by weight. These dye mixtures too are preparable by

customary mixing, so that deep blue, brown and black dyeings are preparable on, inter alia, polyester and/or cellulose acetate fibre materials for example.

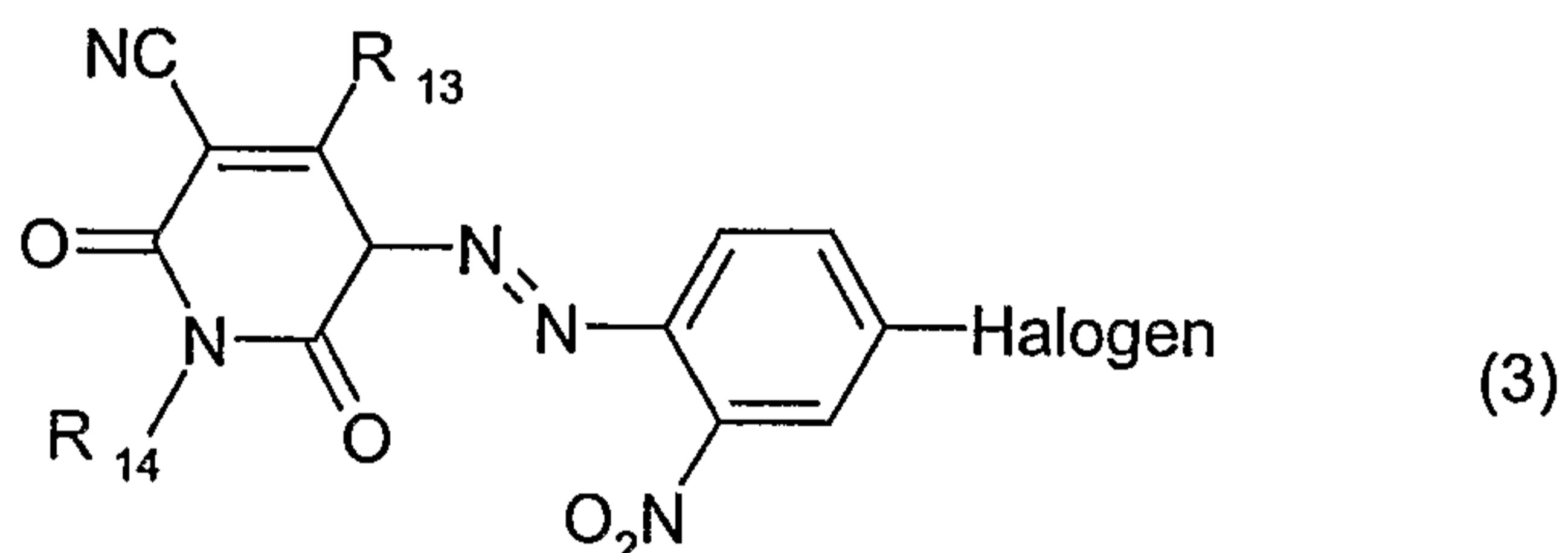
Deep blue, brown and black dyeings (for example on polyester and/or on cellulose acetate materials and/or fibre materials which may consist of blends of polyester and/or on cellulose acetate fibre materials) are readily obtainable with the abovementioned dye mixtures comprising at least two dyes of the formulae (1) and formula (2) or at least two dyes of the formulae (1') and formula (2') together with at least one disperse dye selected from a yellow, red and/or orange disperse dye.

10

As orange, yellow or red component it is possible to use any orange, yellow or red disperse dye as long as it is compatible with the mixture according to the invention. These orange, yellow or red components may also be mixtures of different yellow, red and/or orange disperse dyes as long these mixtures are compatible with the mixture according to the invention.

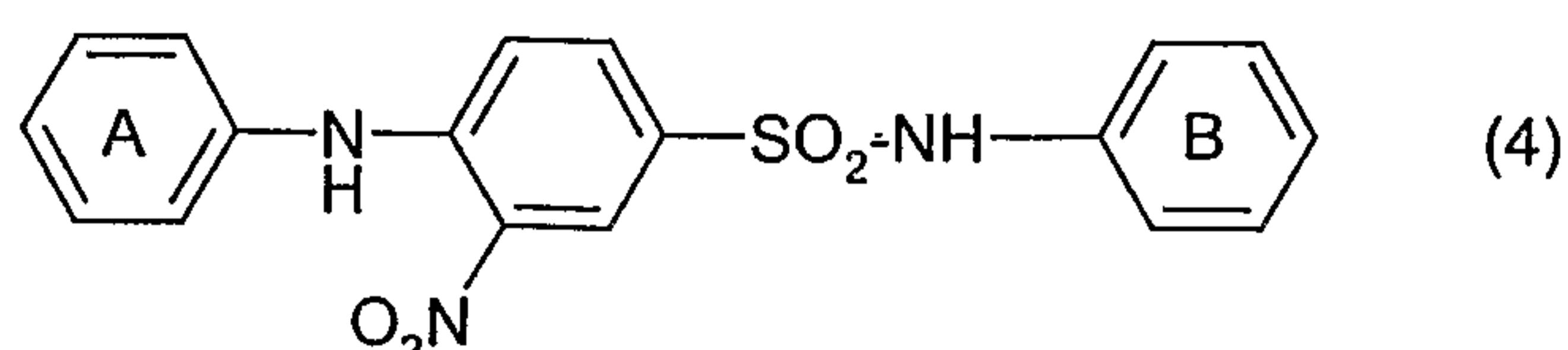
The invention further provides a mixture which contains at least one dye of the formula (1), at least one dye (2) and at least one of the following dyes of the formula (3) or (4) or (5) or (6) or (7) or (8) or (9) or (10) or (11) or (12):

20



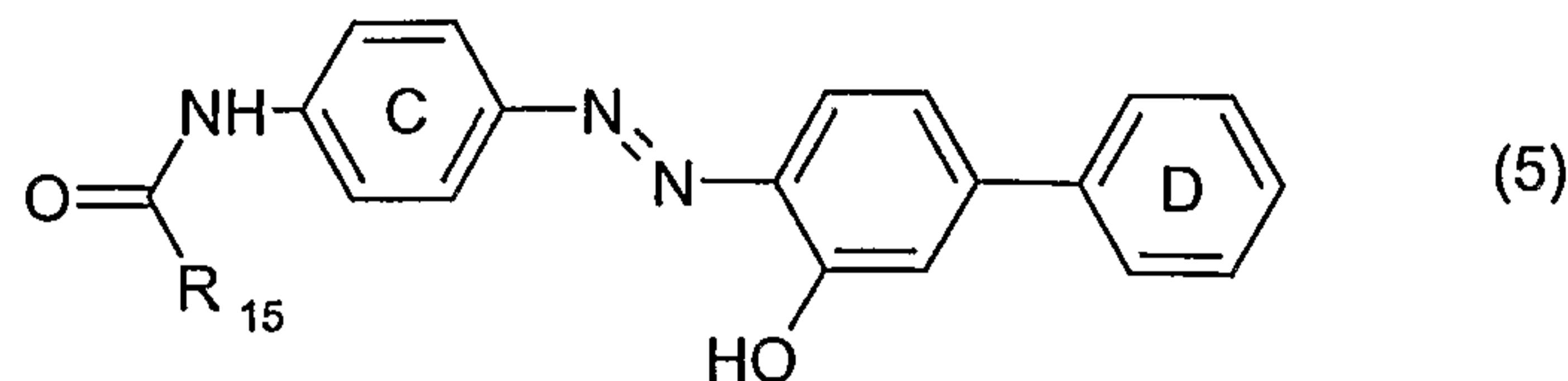
where

R₁₃ is C₁-C₄-alkyl, R₁₄ is C₁-C₄-alkyl and Halogen denotes the halogen atoms,



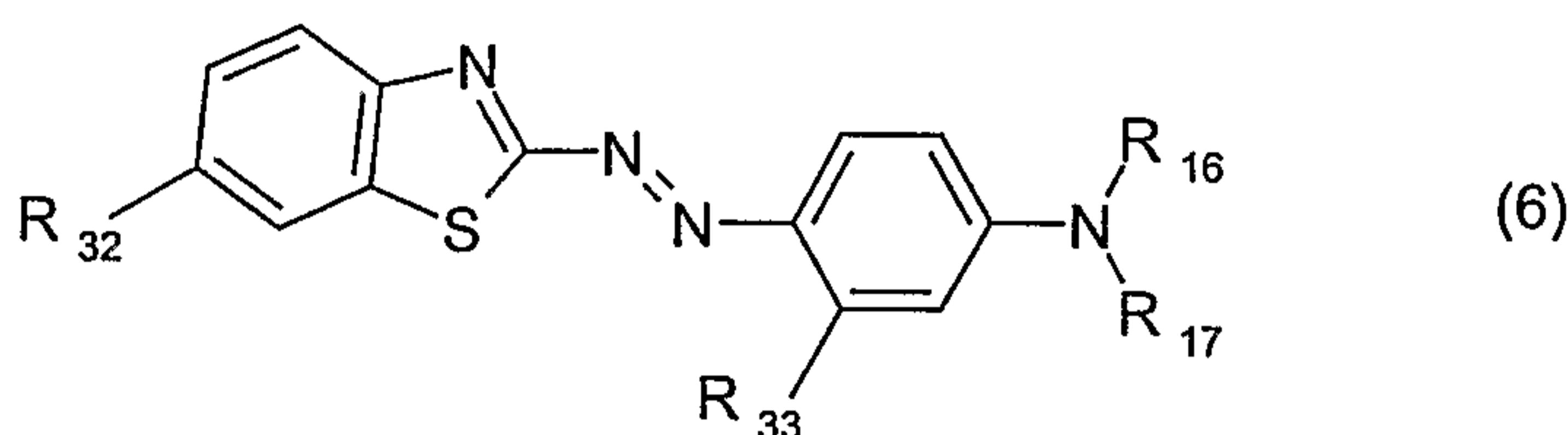
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where the rings A and B may be further substituted,



where

R_{15} is C_1 - C_4 -alkyl and the rings C and D may be further substituted,

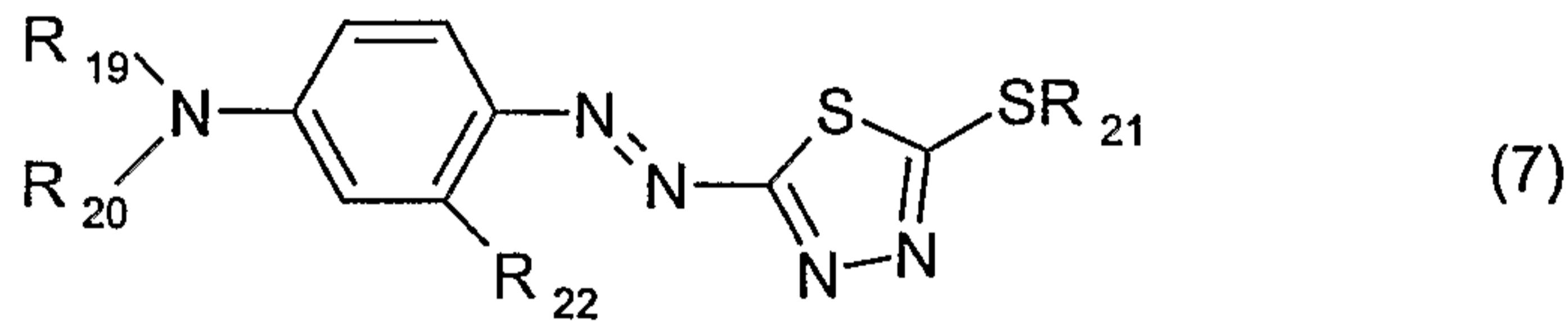


5

where

R_{16} is unsubstituted or hydroxyl- or cyano-substituted C_1 - C_4 -alkyl, R_{17} is unsubstituted C_1 - C_4 -alkyl or C_1 - C_4 -alkyl which is substituted by the radical $-O-COR_{18}$, where R_{18} is C_1 - C_4 -alkyl, R_{32} is nitro, C_1 - C_4 -alkoxy or the radical $-SO_2CH_3$ and R_{33} is hydrogen or

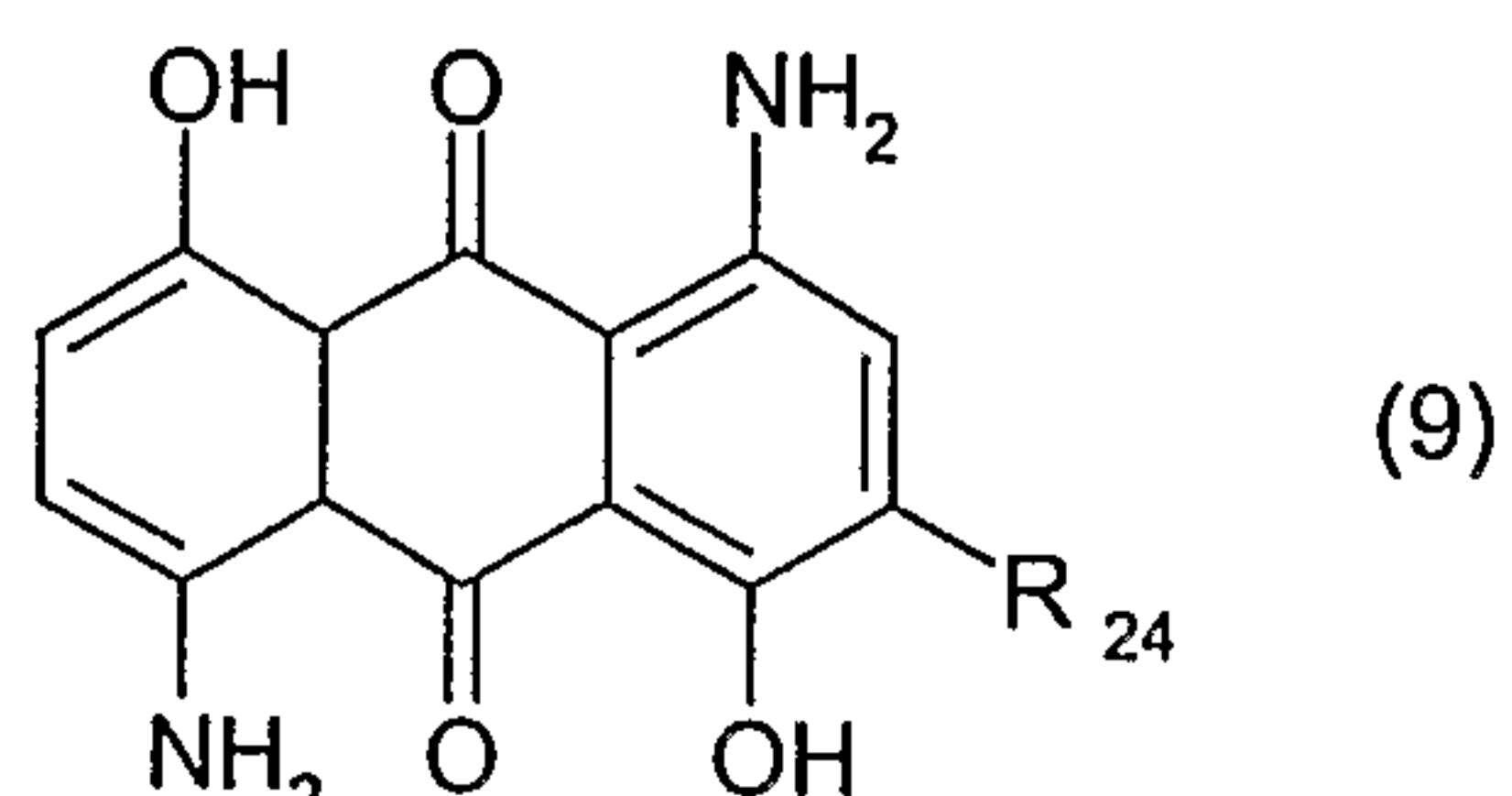
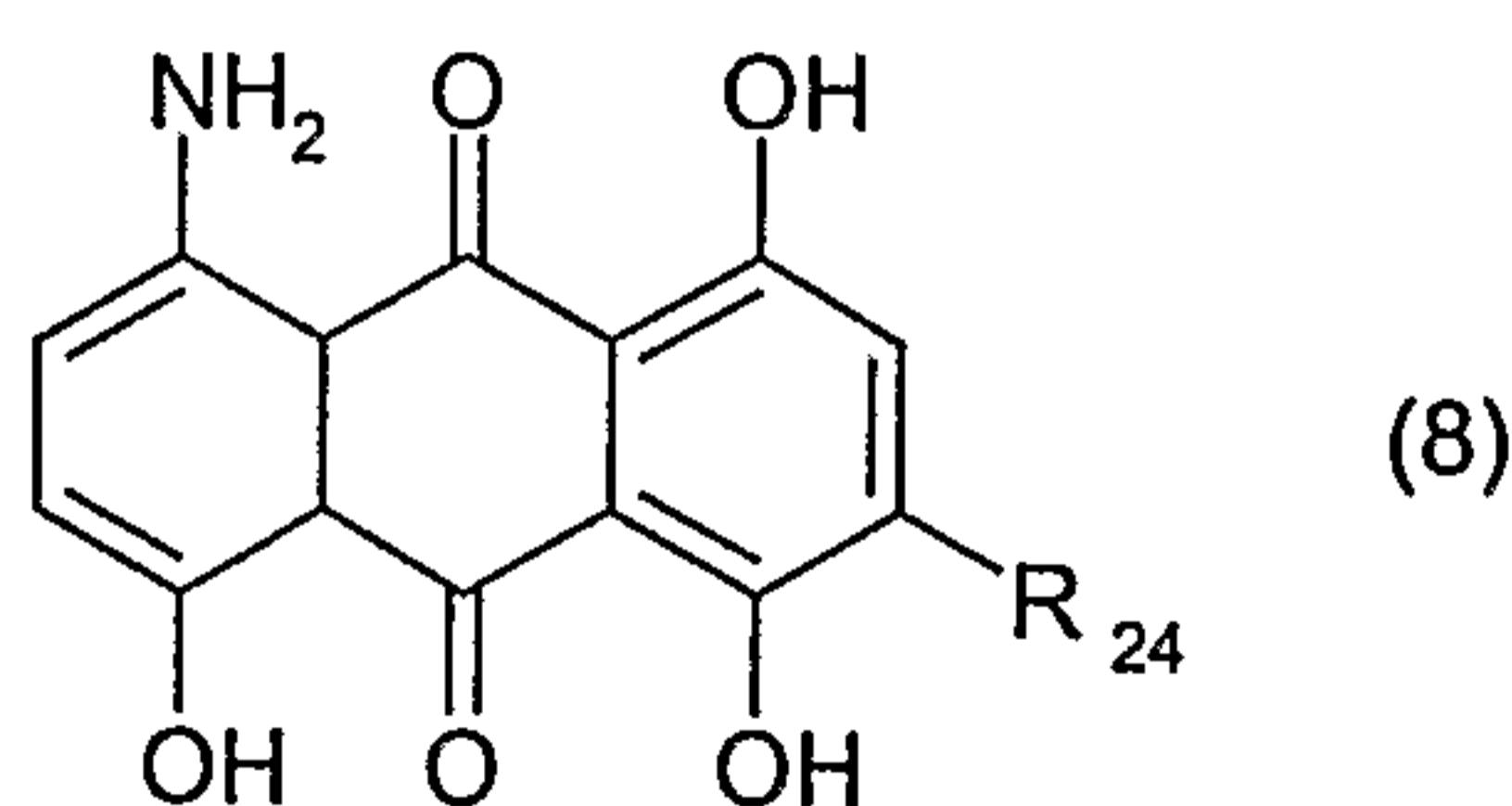
10 C_1 - C_4 -alkyl,

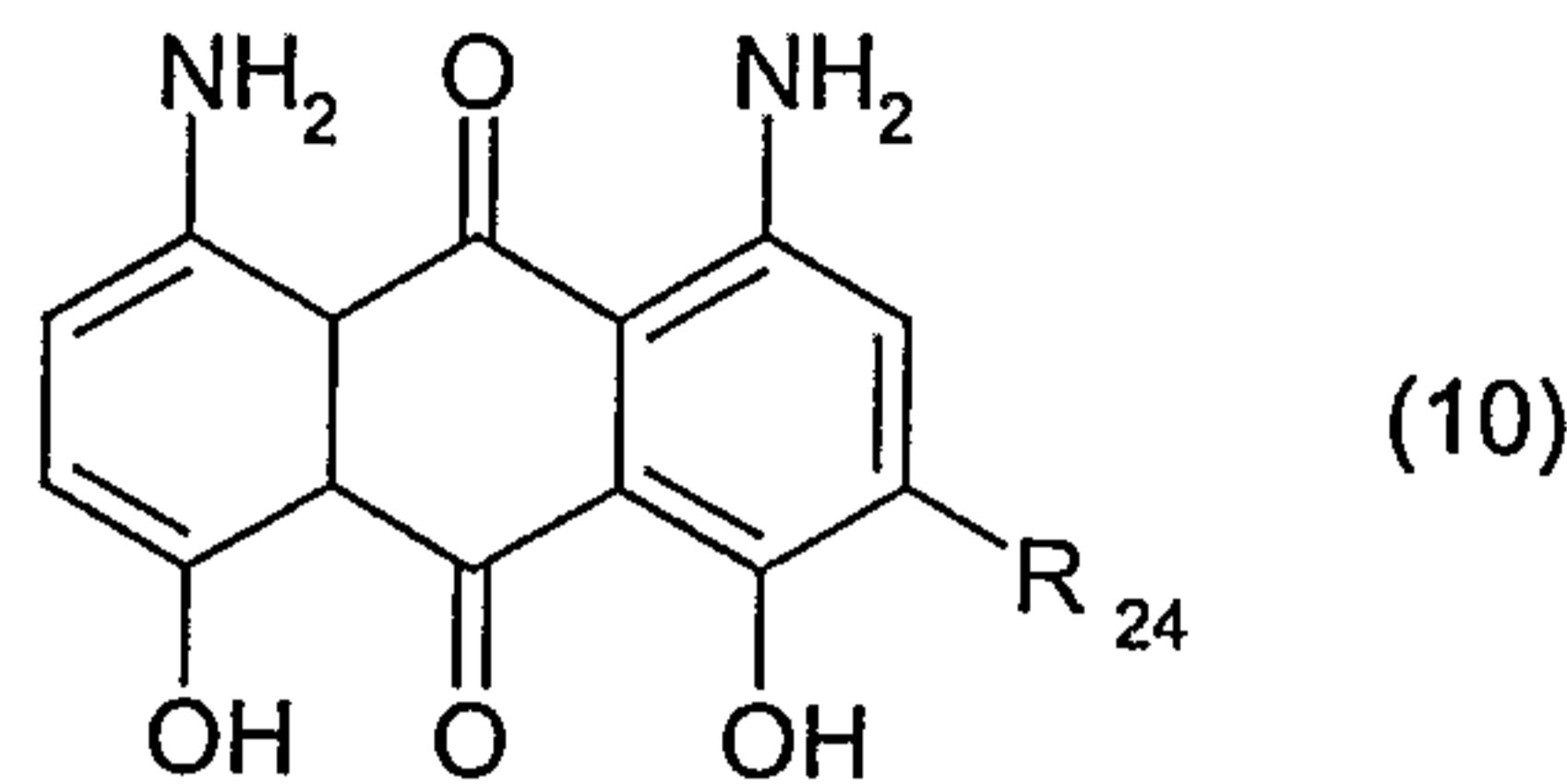


where

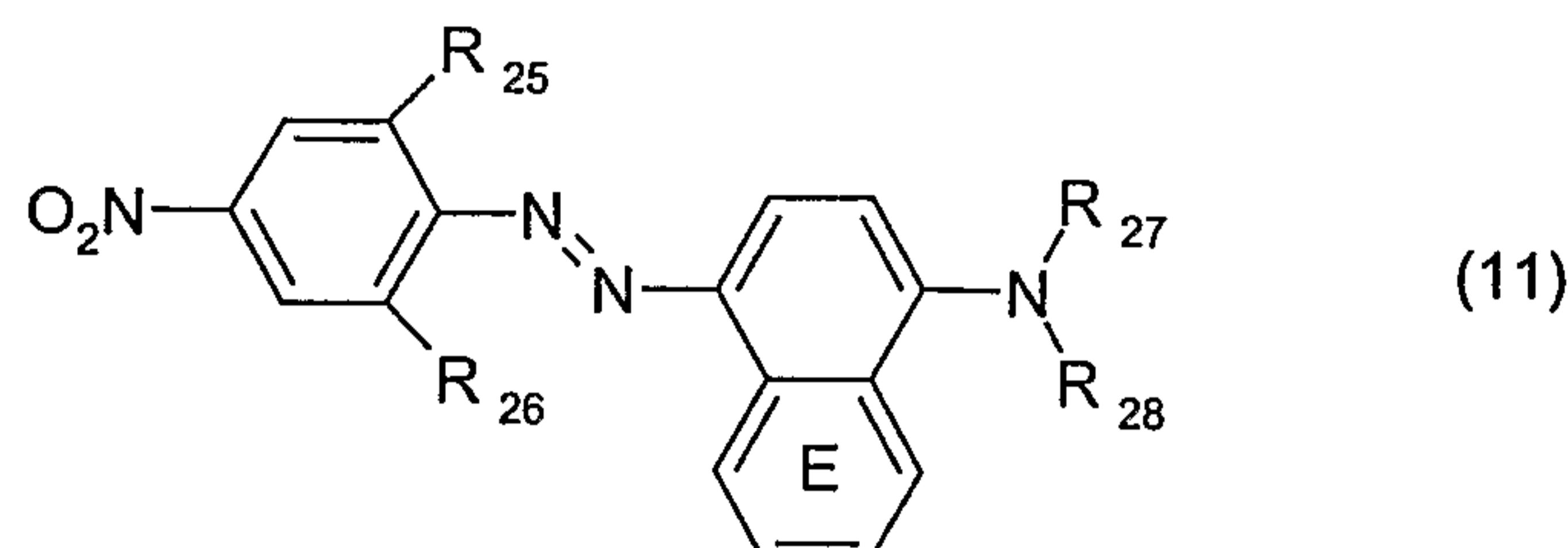
R_{19} is C_1 - C_4 -alkyl, R_{20} is C_1 - C_4 -alkyl, R_{15} is C_1 - C_4 -alkyl and R_{22} is C_1 - C_4 -alkyl or the

15 radical $-NHCOR_{23}$, where R_{23} is C_1 - C_4 -alkyl,





where R₂₄ is halogen,

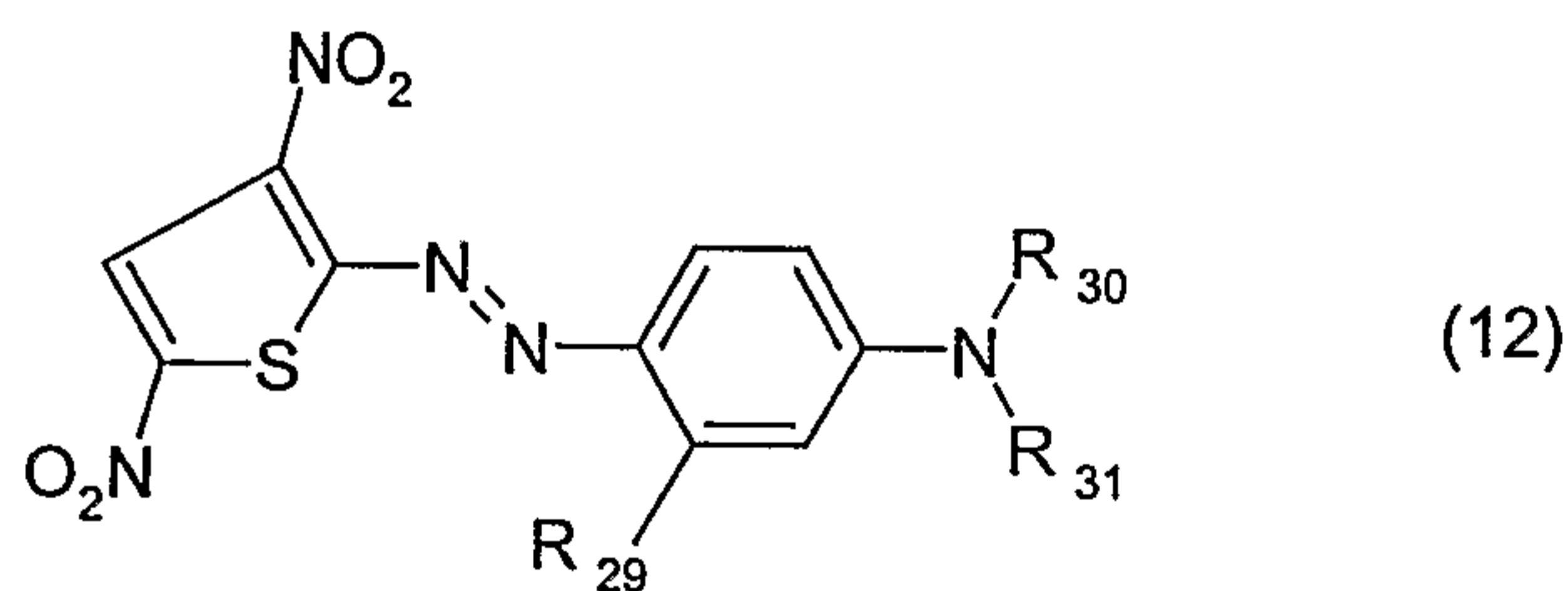


5

where

R₂₅ is cyano, nitro or halogen, R₂₆ is halogen, R₂₇ is unsubstituted or hydroxyl-substituted C₁-C₄-alkyl and R₂₈ is unsubstituted or hydroxyl-substituted C₁-C₄-alkyl and the naphthyl ring E may be further substituted,

10 and/or



where

R₂₆ is C₁-C₄-alkyl or the radical NHCOR₁₇, where R₁₇ is C₁-C₄-alkyl, R₂₇ is C₁-C₄-alkyl

15 or C₁-C₄-alkylcarbonyloxy-C₁-C₄-alkyl and R₂₈ is C₁-C₄-alkyl or C₁-C₄-alkylcarbonyloxy-C₁-C₄-alkyl.

C₁-C₄-Alkyl as such and as a radical in C₁-C₄-alkylcarbonylamino or C₁-C₄-alkylcarbonyloxy is methyl, ethyl, propyl, isopropyl, n = butyl, isobutyl, sec-butyl or 20 tert-butyl.

C₁-C₄-Alkoxy as such or as a radical in C₁-C₄-alkoxycarbonyl is for example methoxy, ethoxy, propoxy or butoxy.

R₁, R₃, R₂₅ and R₂₆ as halogen are for example bromine or preferably chlorine.

R₂ and R₂₄ as halogen are for example chlorine or preferably bromine.

Halogen in the formula (3) is for example bromine or preferably chlorine.

5 R₅, R₆ and R₁₆ as C₁-C₄-alkyl are propyl or isopropyl and in particular ethyl.

R₁₃, R₁₅, R₁₈, R₂₂, R₂₃, R₈, R₃₁ and R₃₃ as C₁-C₄-alkyl are preferably ethyl and especially methyl.

R₁₄, R₁₉, R₂₁, R₁₁, R₃₀ and R₂₅ as C₁-C₄-alkyl are preferably methyl and especially ethyl.

R₁₉, R₂₀, R₂₇, and R₂₈ as C₁-C₄-alkyl are preferably ethyl and especially propyl.

10 R₃₀ and R₃₁ are preferably C₁-C₄-alkyl.

R₂₆ is preferably nitro or the radical -SO₂CH₃.

The C₁-C₄-alkyl radicals are generally 1- or 2-tuply substituted with the aforementioned substituents.

15

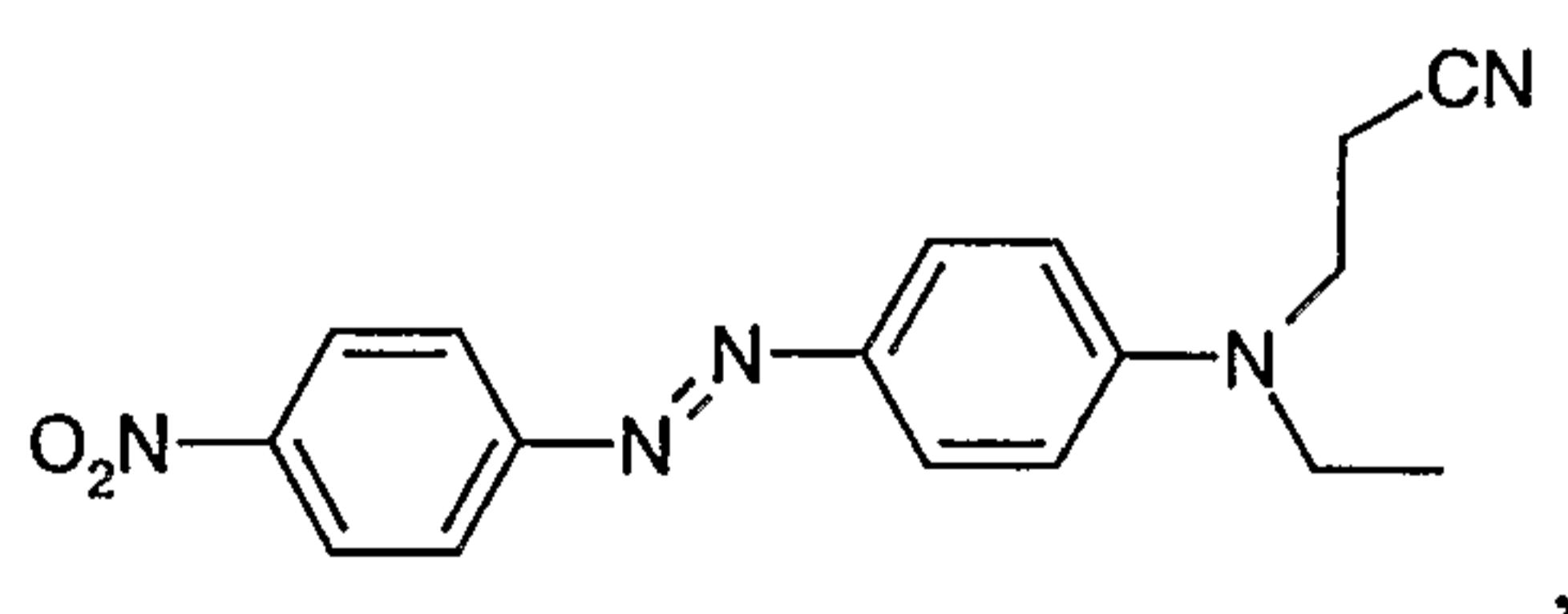
The rings A to E may each be independently substituted for example by C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen, nitro, cyano or acylamino.

The invention further provides a mixture which contains at least one dye of the formula

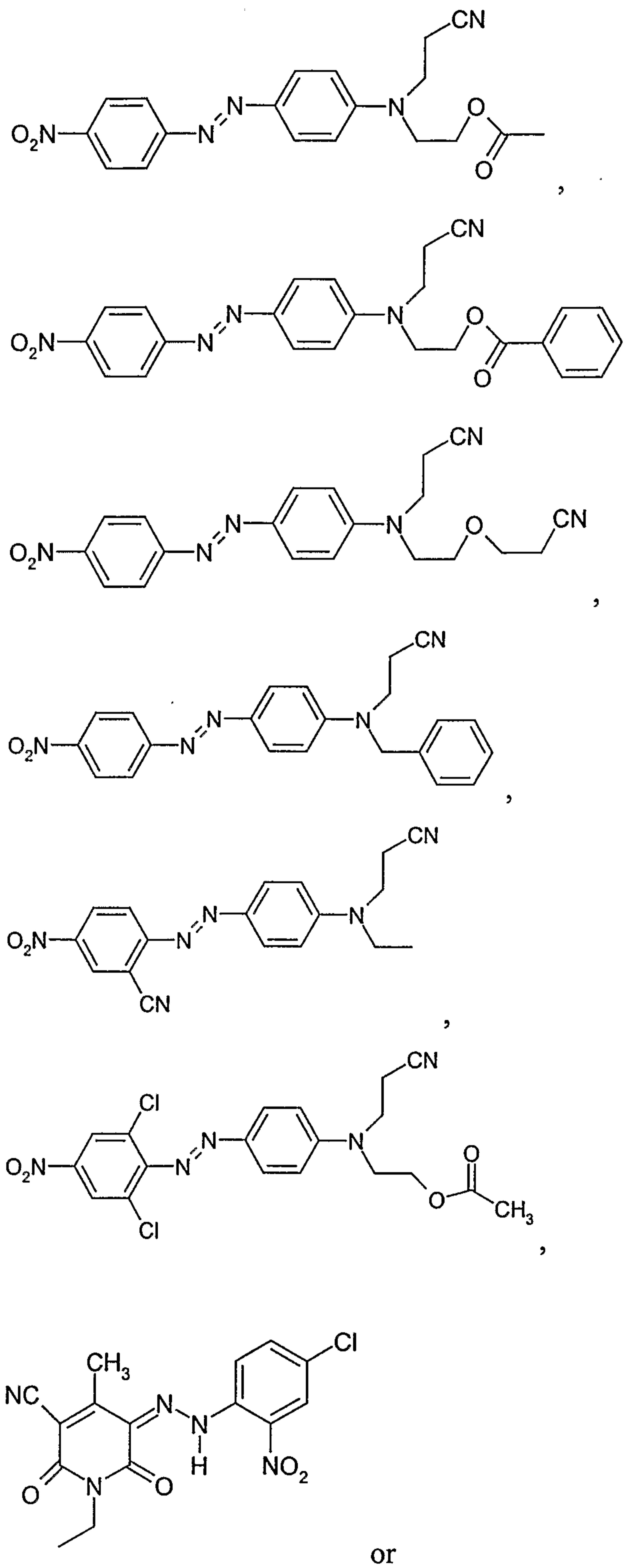
20 (1'), at least one dye (2') and at least one of the dyes having the formulae (3) and/or (4) and/or (5) and/or (6) and/or (7) and/or (8) and/or (9) and/or (10) and/or (11) and/or (12).

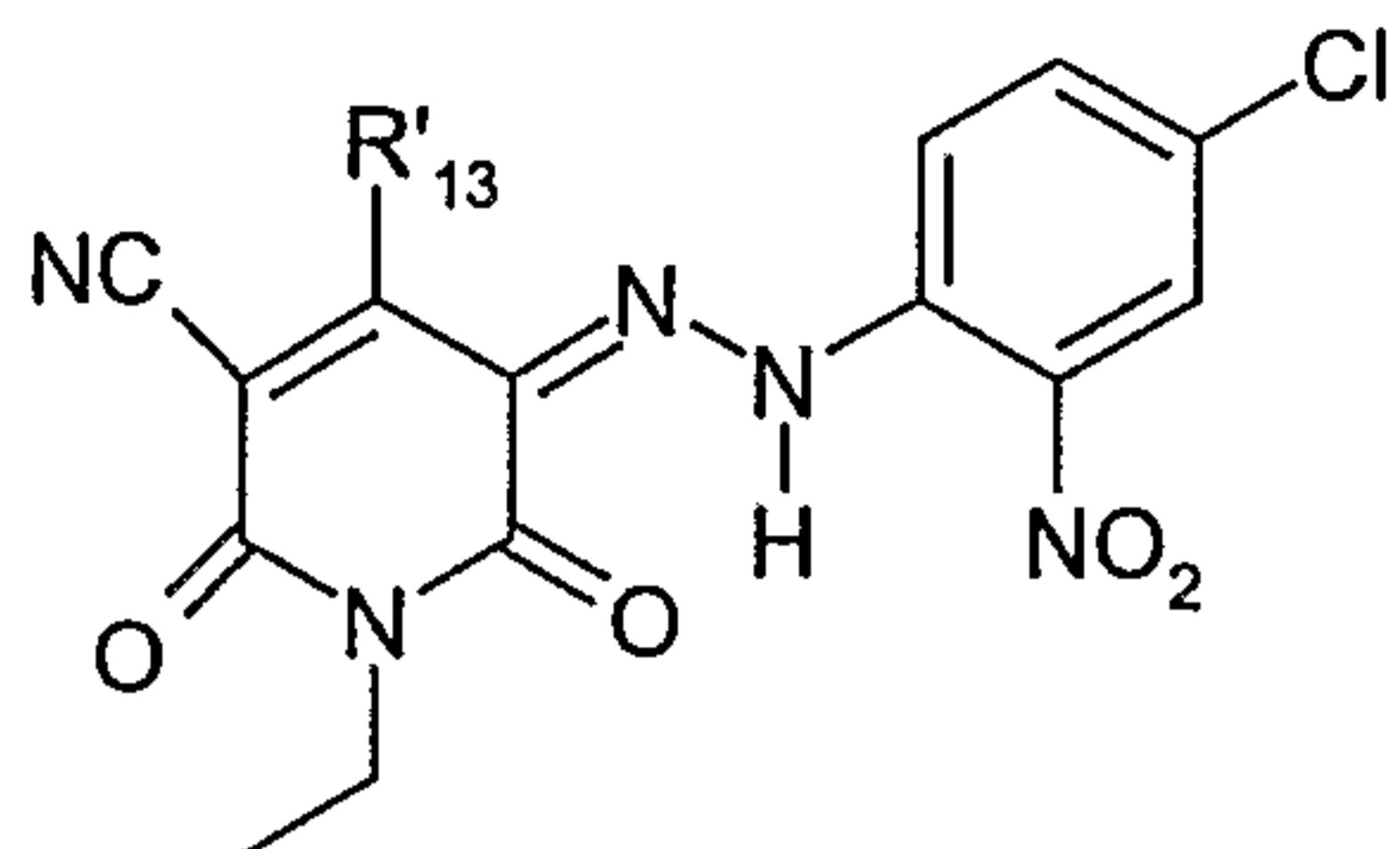
Preferred mixtures are mixture which contains at least one dye of the formula (1), at least one dye (2) and at least one one of the following dyes:

25



9





where R'₁₃ is C₂ to C₄ alkyl.

The preparation of the abovementioned dyes is known.

5 The dye mixtures of the invention can be used as dyes for dyeing and printing polyester fibre materials, especially textile materials. These fibre materials may additionally contain semisynthetic hydrophobic and/or cellulose acetate fibres such as for example viscose or polyamide. Textile materials composed of blend fabrics which contain semisynthetic or hydrophobic cellulose acetate textile materials and for example viscose

10 or polyamide are likewise dyeable or printable with the aid of the dye mixtures according to the invention.

As semisynthetic hydrophobic textile materials comprising polyester it is possible to use in particular cellulose secondary acetate and cellulose triacetate and cellulose acetate.

15 The application to textile materials of the compounds according to the invention is effected according to known dyeing processes. For example, cellulose secondary acetate is preferably dyed between about 65 to 95°C and cellulose triacetate at temperatures between 65 and 130°C and especially between 90 and 125°C. Pure polyester fibre materials are dyeable at temperatures up to 130°.

20 The dye mixtures according to the invention dye adjacent wool and cotton only minimally, if at all, ie. exhibit a very good wool and cotton reserve, so that they may also be used to good effect for dyeing cellulose acetate-wool and cellulose acetate-cellulose blend fabrics or polyester alone.

25 The dye mixtures according to the invention are useful for dyeing by the thermosol process, in the exhaust process, pad-steam, pad-roll and pad-jig processes and for printing processes. Here printing processes, as well as the classic processes such as

roller printing and/or screen and transfer printing, also comprehends the ink jet printing processes such as the Ink Jet, Bubble Jet, Compound Jet, Dry Ink Jet or Hotmelt Ink Jet process.

5 The textile material mentioned may be present in the various processing forms, for example as a fibre, thread or web, as a woven fabric or as a loop-formingly knitted fabric.

It is advantageous to convert the dye mixtures according to the invention into a dye

10 formulation before use. To this end, the dye mixture is ground so that its particle size is between 0.1 and 10 microns. The grinding may preferably be effected in the presence of dispersants. For example, the dried dye mixture is ground with one or more dispersants or kneaded in paste form with one or more dispersants and then vacuum or spray dried. The formulations thus obtained can be used to prepare print pastes and dyebaths on
15 addition of water. Useful dispersants include the dispersants generally customary for dyeing with disperse dyes. These are for example those which are mentioned in EP-A-0 280 654 page 5 lines 40 to 56 as dispersing agents. This can be for example the sodium salt of a lignin sulphonate or the sodium salt of a further lignin sulphonate which is obtainable from the reaction of lignin with disodium sulphite and formaldehyde.

20

The dyes, however, can also be formulated alone as described above and then be converted into the corresponding dye formulations in a simple mixing operation.

25 The amount of the dispersant or dispersants in the dye formulation can be between 0% and 75% by weight, based on the weight of the dye formulation.

30 The amount of the dye mixtures in the dyeing liquor depends on the shade desired; amounts which will generally prove useful range from 0.01 to 15, especially from 0.02 to 10 and in particular from 0.1 to 5 per cent by weight, based on the weight of the fibre material to be dyed.

The dyeing liquors may also contain further additives, for example dyeing assistants, wetting agents and defoamers.

The dyeing liquors may further contain mineral acids, such as for example sulphuric acid or phosphoric acid, especially organic acids, such as for example formic acid or acetic acid and/or salts, such as ammonium acetate or sodium sulphate. The acids serve
5 in particular to set the pH of the dyeing liquors, which is preferably between 4 and 7.

Printing utilizes the customary thickeners, for example modified or non-modified natural products, for example alginates, British gum, gum arabic, crystal gum, carob bean flour, tragacanth, carboxymethylcellulose, hydroxyethylcellulose, starch or
10 synthetic products, for example polyacrylamides, polyacrylic acid or copolymers thereof or polyvinyl alcohols.

The dye mixtures according to the invention endow the materials mentioned, especially cellulose secondary acetate and cellulose triacetate, with level hues having very good
15 service fastnesses, such as in particular good light fastness, fastness to heat setting and pleating, chlorine and wet fastness such as fastness to water, perspiration and washing; the dyeings are further characterized by very good rub fastness. The dye mixtures according to the invention are further notable for the good colour yield and good build-up.

20

The dye mixtures according to the invention are also very useful for producing combination shades together with other dyes.

The dye mixtures according to the invention are also very useful for dyeing
25 hydrophobic textile material from supercritical CO₂.

The aforementioned use of the dye mixtures according to the invention constitutes as much a part of the subject-matter of the present invention as a process for dyeing or printing polyester and/or semisynthetic hydrophobic cellulose acetate fibre material,
30 especially textile material composed of cellulose secondary acetate, cellulose triacetate and polyester, which consists in the dye mixture according to the invention being applied to the material mentioned or incorporated therein. Further substrates which are treatable by the process according to the invention and also preferred process conditions

are to be found above in connection with the more particular description of the use of the dye mixtures according to the invention. The dye mixtures used according to the invention are subject to the definitions and preferences indicated above for the dyes and dye mixtures.

5

The present invention further provides the polyester, semisynthetic, cellulose acetate hydrophobic fibre material dyed or printed by the process mentioned, preferably textile material composed of cellulose secondary acetate, cellulose triacetate and polyester.

10 The examples which follow serve to illustrate the invention.

Example 1

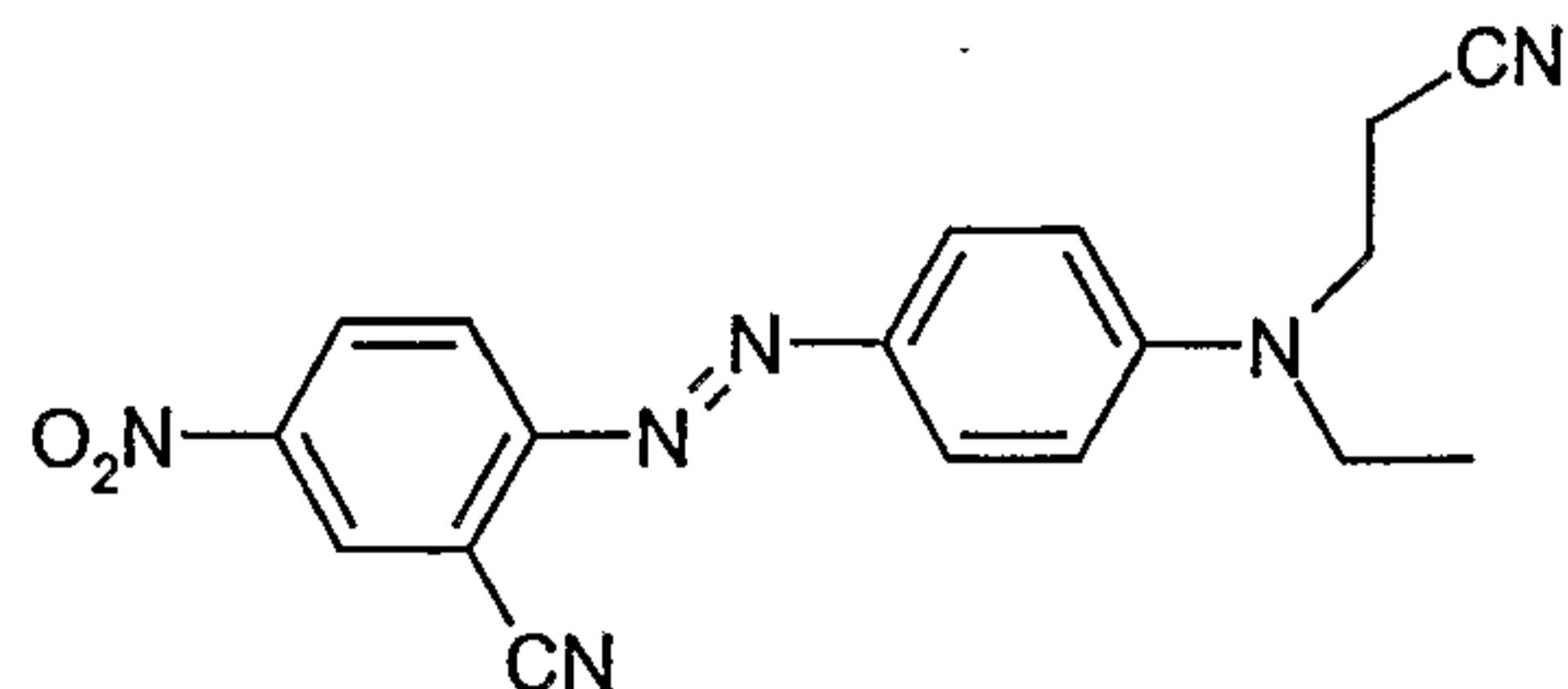
A mixture of the dyes (1') and (2') consisting of 12.5 parts of the dye (1') and 26.25 parts 15 of the dye (2') (the remainder (ad 100 parts) consists of a commercially available dispersant based on lignin sulphonate) was used for dyeing cellulose secondary acetate in a dyebath which had a temperature distribution from 90 to 110°C. After the cellulose secondary acetate textile piece had been reduction cleared by the usual method (see Example 4), a brilliantly blue cellulose secondary acetate fabric which had good 20 perspiration fastness and good light fastnesses and had been dyed at level was obtained.

Example 2

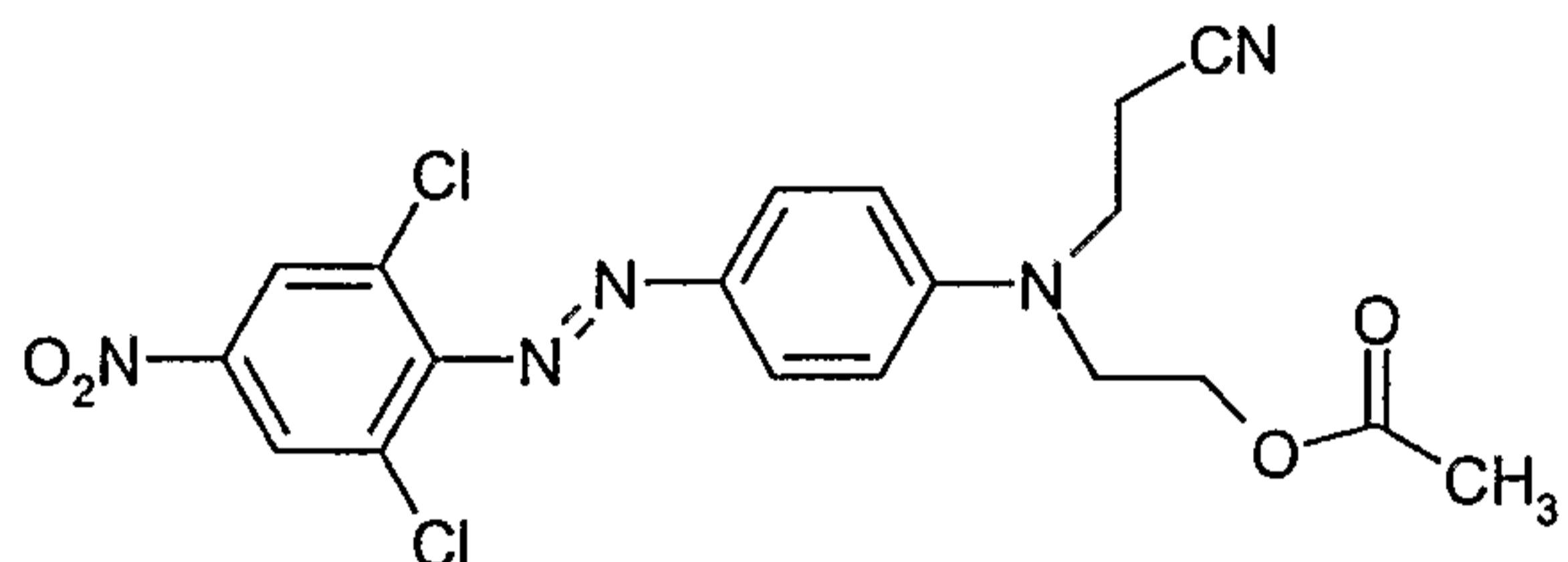
Example 1 was repeated, except that the temperature was maintained at 100°C in the 25 entire dyebath. The result was similar to that of Example 1.

Example 3

Cellulose secondary acetate fabric was dyed in a dyebath with the following dye 30 mixture under the usual conditions: 4.5 parts of dye (1'), 18 parts of dye (2'), 3 parts of the following dye:



and 22 parts of the following dye:



(the remainder (ad 100 parts) consists of a commercially available dispersant based on

5 lignin sulphonate)

After the usual reduction clearing (see Example 4) a fabric which had been dyed a level deep black and had good fastnesses was obtained

Example 4

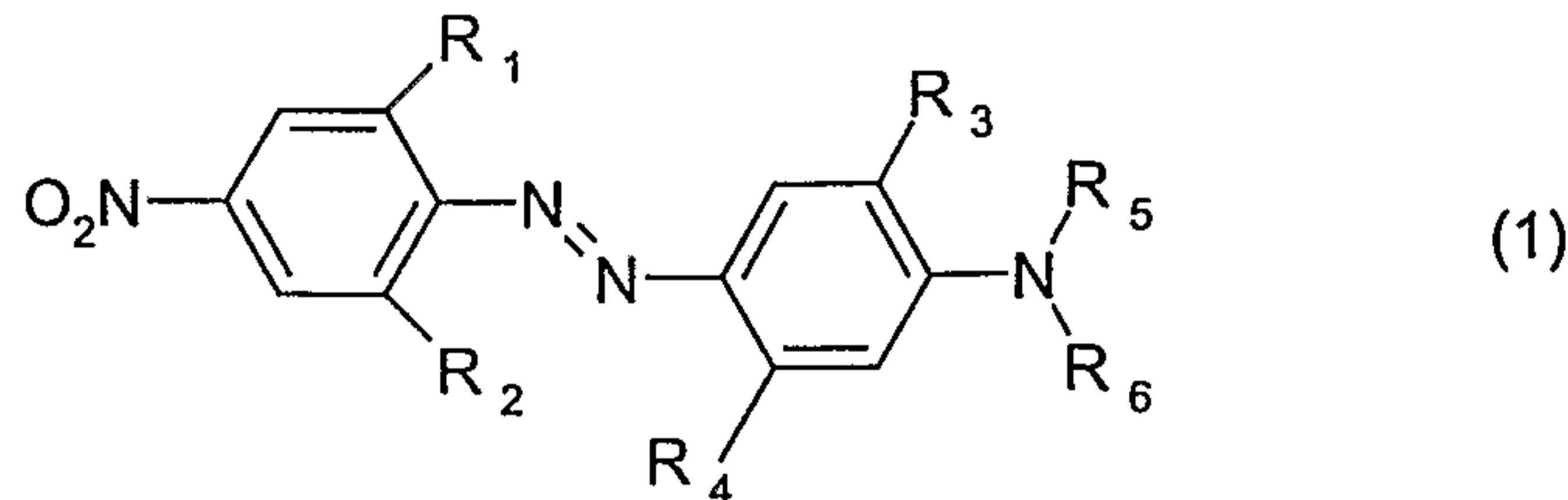
10

A mixture from of dyes as per Example 1 was used for dyeing polyester according to the HT process. To this end, the dyebath at 60°C was admixed with the customary dyeing chemicals and after 10 minutes heated to 130°C at a rate of 1.5°C per minute.

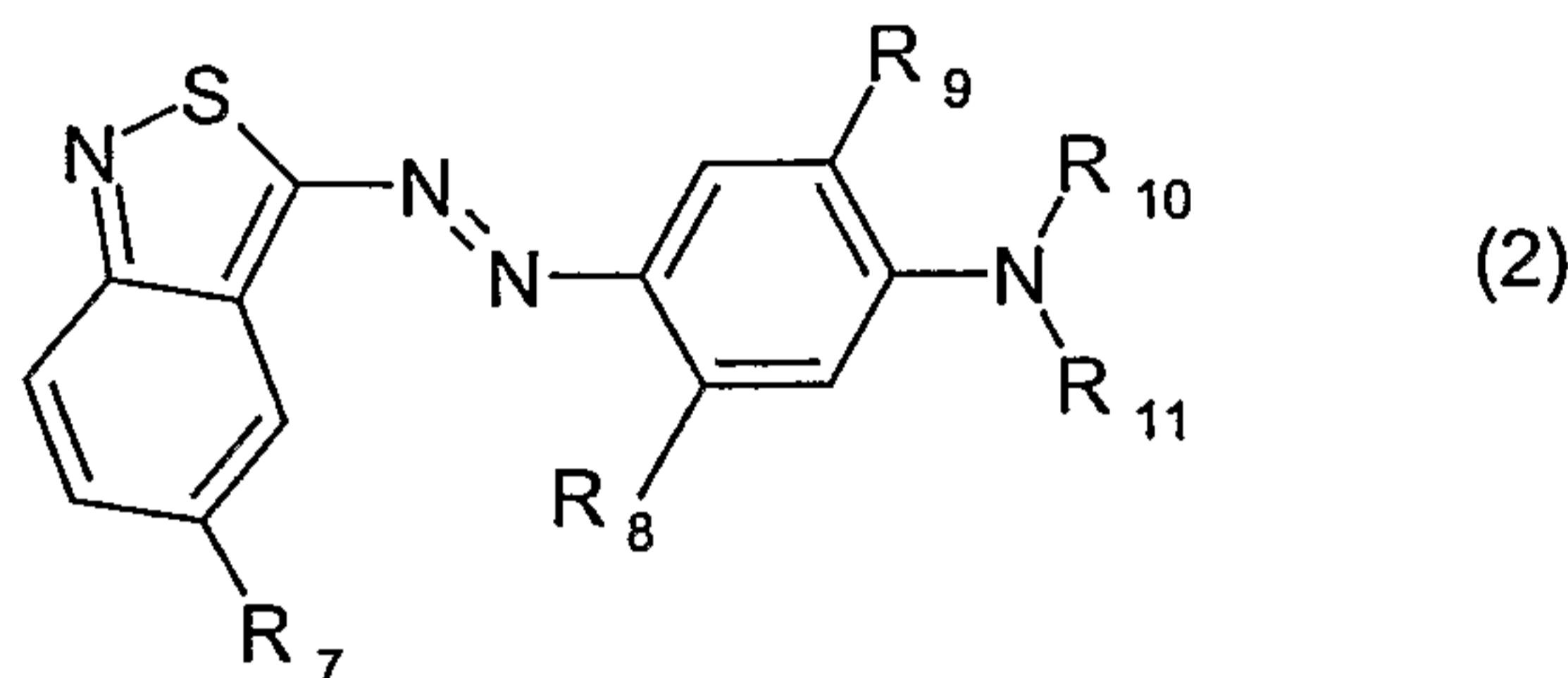
15 The dyebath is held at 130°C for 10 minutes. Thereafter, the bath is cooled down and the textile material is rinsed cold and hot and reduction cleared with a mixture of 3 g/l hydrosulphite, 2.5 g/l of solid NaOH (6 ml/l NaOH 36°Be), 0.5 ml/l of Ekaline F Liquid, then again rinsed cold and hot. The polyester fabric obtained had been dyed a level brilliant blue and possessed good perspiration fastness and good light fastnesses.

Claims

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



5 and at least one dye of the formula (2)



where

R₁ is hydrogen, halogen, nitro or cyano

R₂ is hydrogen, halogen, nitro or cyano

10 R₃ is hydrogen, halogen, C₁-C₄-alkoxy or C₁-C₄-alkyl

R₄ is hydrogen, C₁-C₄-alkyl

R₅ is hydrogen, unsubstituted or hydroxyl-, cyano-, C₁-C₄-alkylcarbonyloxy-, substituted C₁-C₄-alkyl or C₁-C₄-alkenyl

R₆ is unsubstituted or hydroxyl-, cyano-, C₁-C₄-alkylcarbonyloxy-, C₁-C₄-alkoxycarbonyl-substituted C₁-C₄-alkyl or C₁-C₄-alkenyl,

15 R₇ is nitro, C₁-C₄-alkoxy or the radical -SO₂CH₃

R₈ is hydrogen or C₁-C₄-alkyl,

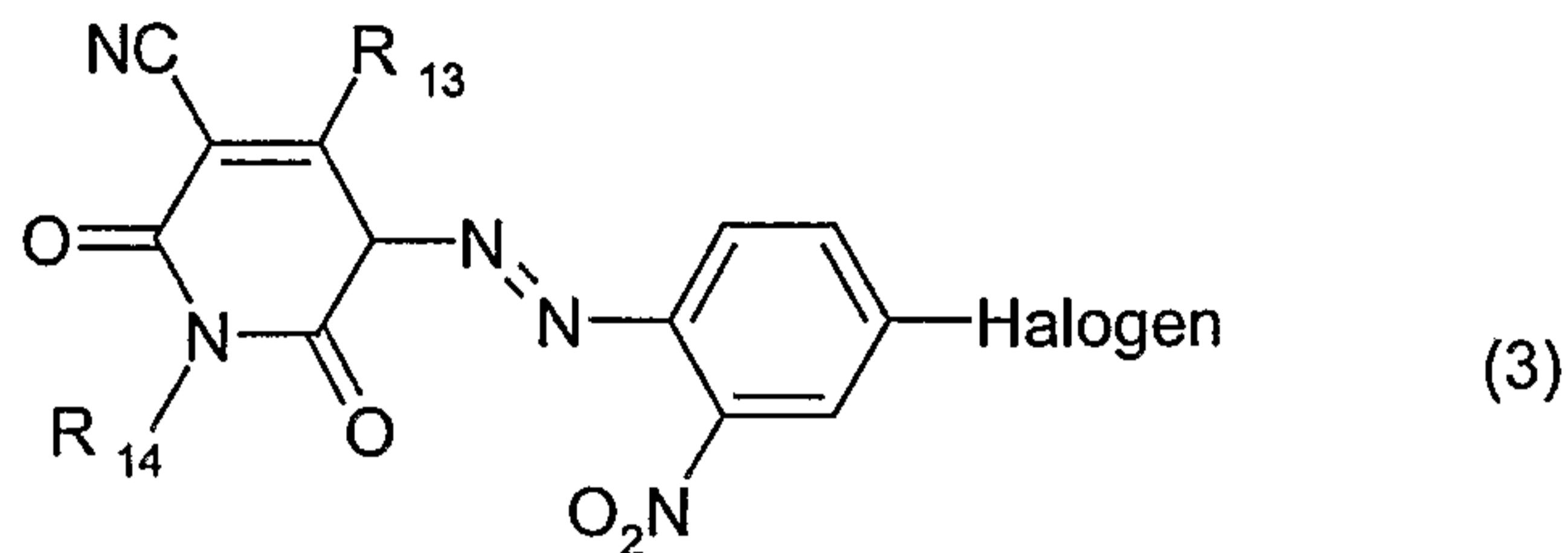
R₉ is hydrogen or C₁-C₄-alkyl,

R₁₀ is unsubstituted or hydroxyl- or cyano-substituted C₁-C₄-alkyl,

20 R₁₁ is unsubstituted C₁-C₄-alkyl or is C₁-C₄-alkyl which is substituted by the radical -O-COR₁₂, where R₁₂ is C₁-C₄-alkyl.

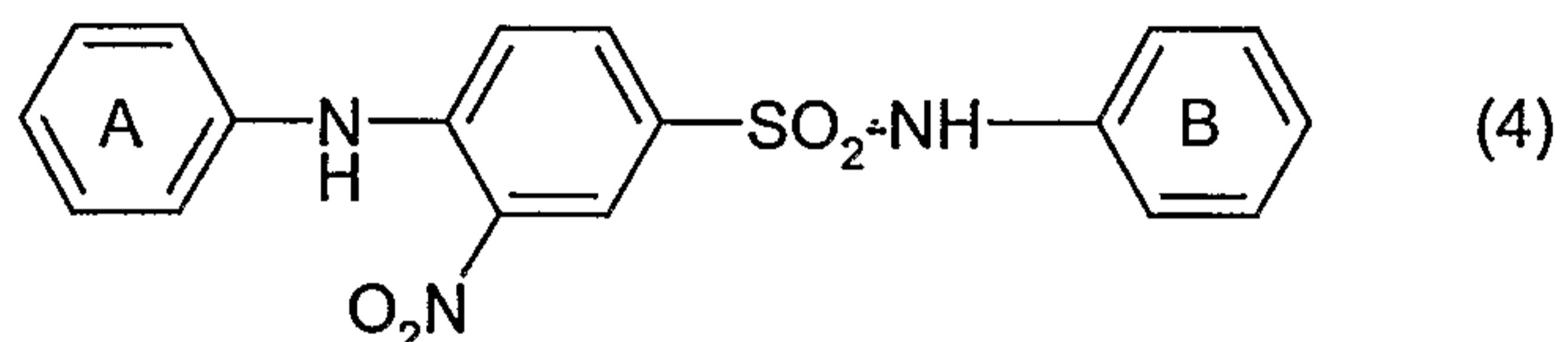
2. Dye mixtures as per Claim 1, characterized in that they contain up to 60% of a dye as per the formula (1) based on the sum total of the dyes (1) and (2).

3. Dye mixture as per Claim 1 characterized in that it contains at least one further one of the following dyes:



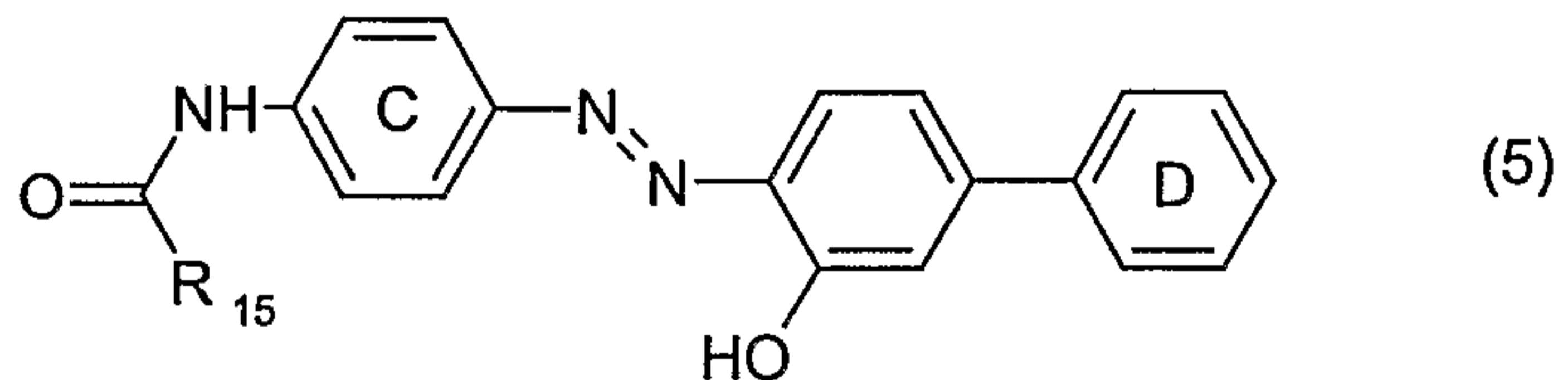
5 where

R_{13} is C_1 - C_4 -alkyl, R_{14} is C_1 - C_4 -alkyl and Halogen denotes the halogen atoms,



where the rings A and B may be further substituted,

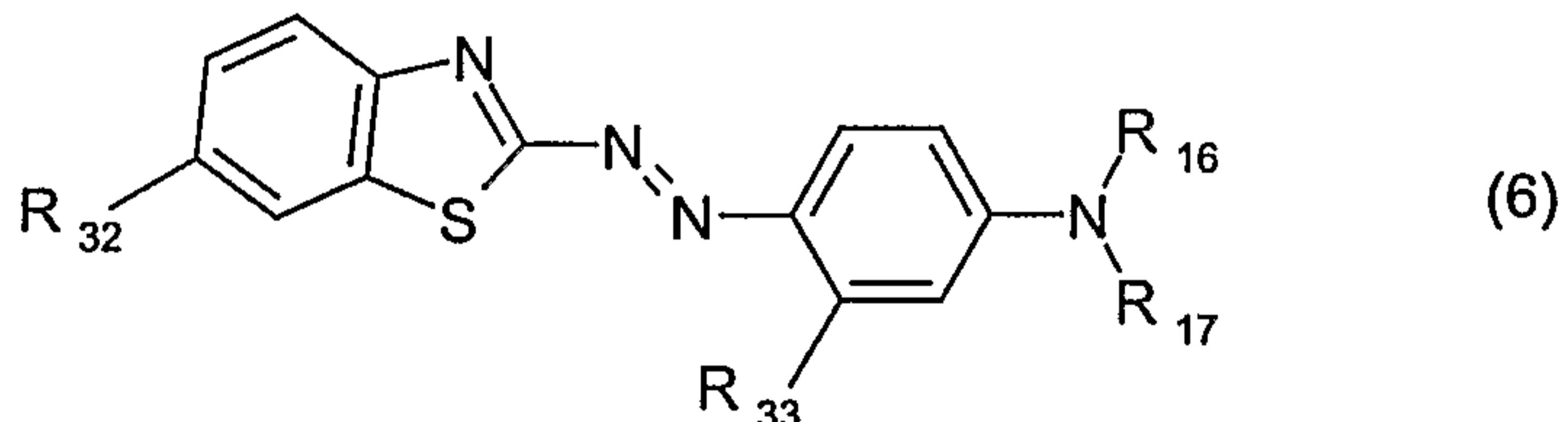
10



where

R_{15} is C_1 - C_4 -alkyl and the rings C and D may be further substituted,

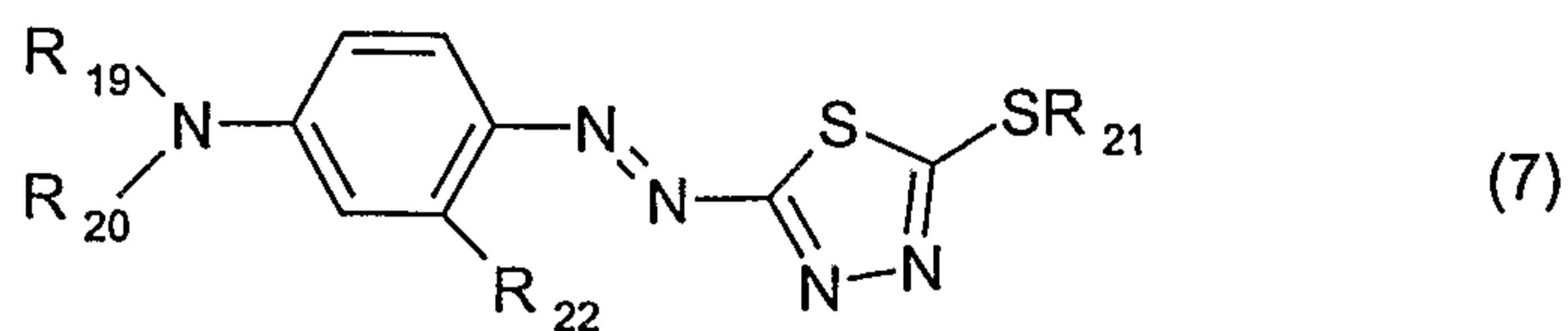
15



where

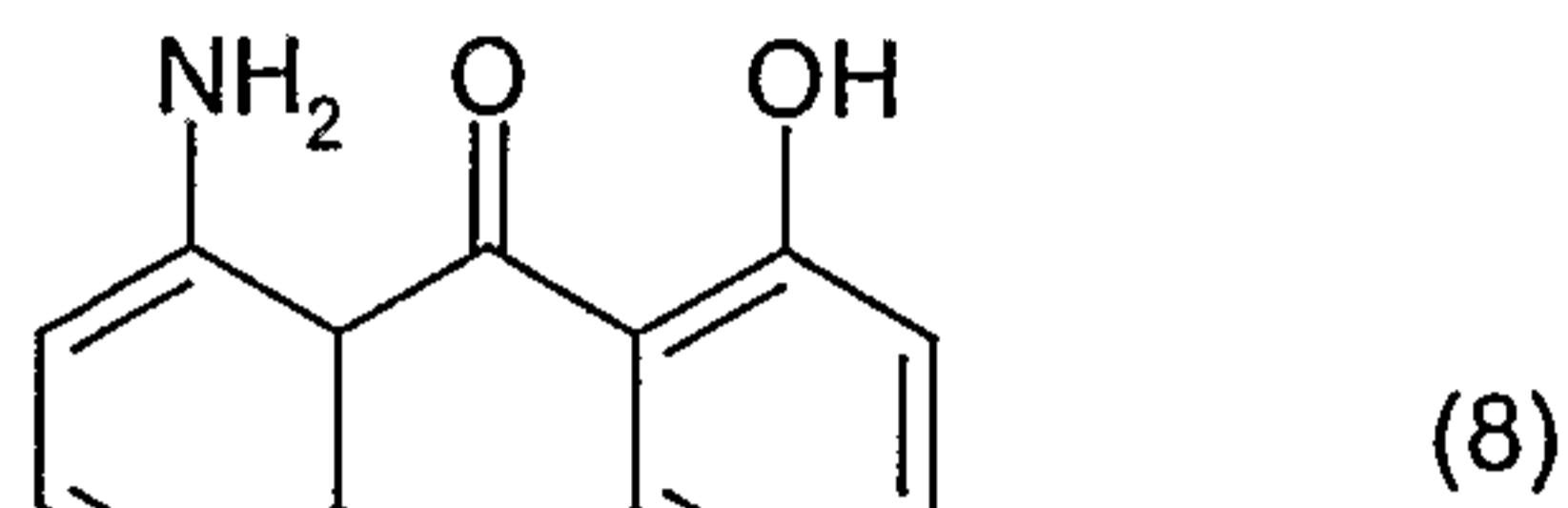
R_{16} is unsubstituted or hydroxyl- or cyano-substituted C_1 - C_4 -alkyl, R_{17} is unsubstituted C_1 - C_4 -alkyl or C_1 - C_4 -alkyl which is substituted by the radical $-O-COR_{18}$, where R_{18} is

20 C_1 - C_4 -alkyl, R_{32} is nitro, C_1 - C_4 -alkoxy or the radical $-SO_2CH_3$ and R_{33} is hydrogen or C_1 - C_4 -alkyl,

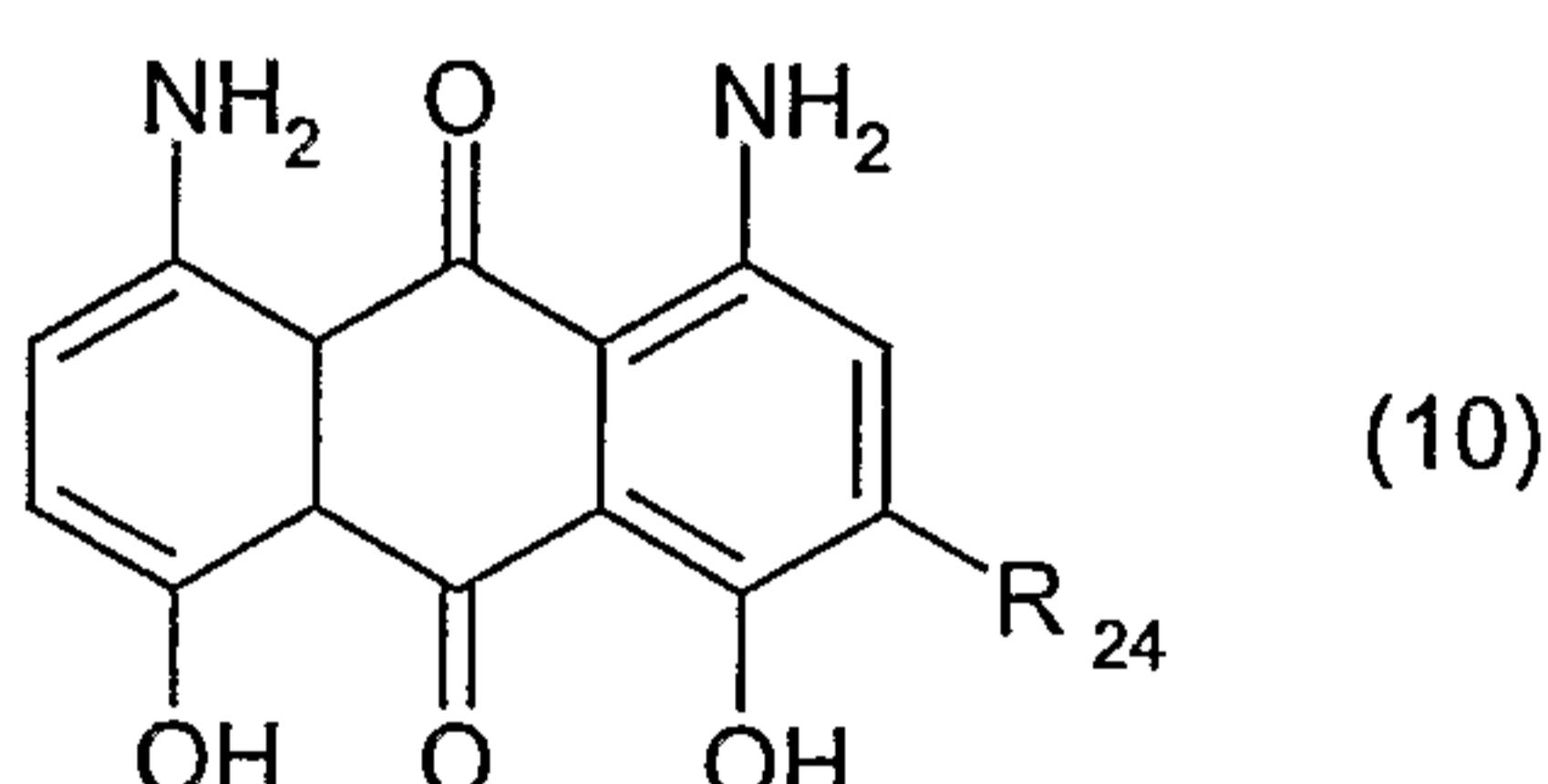
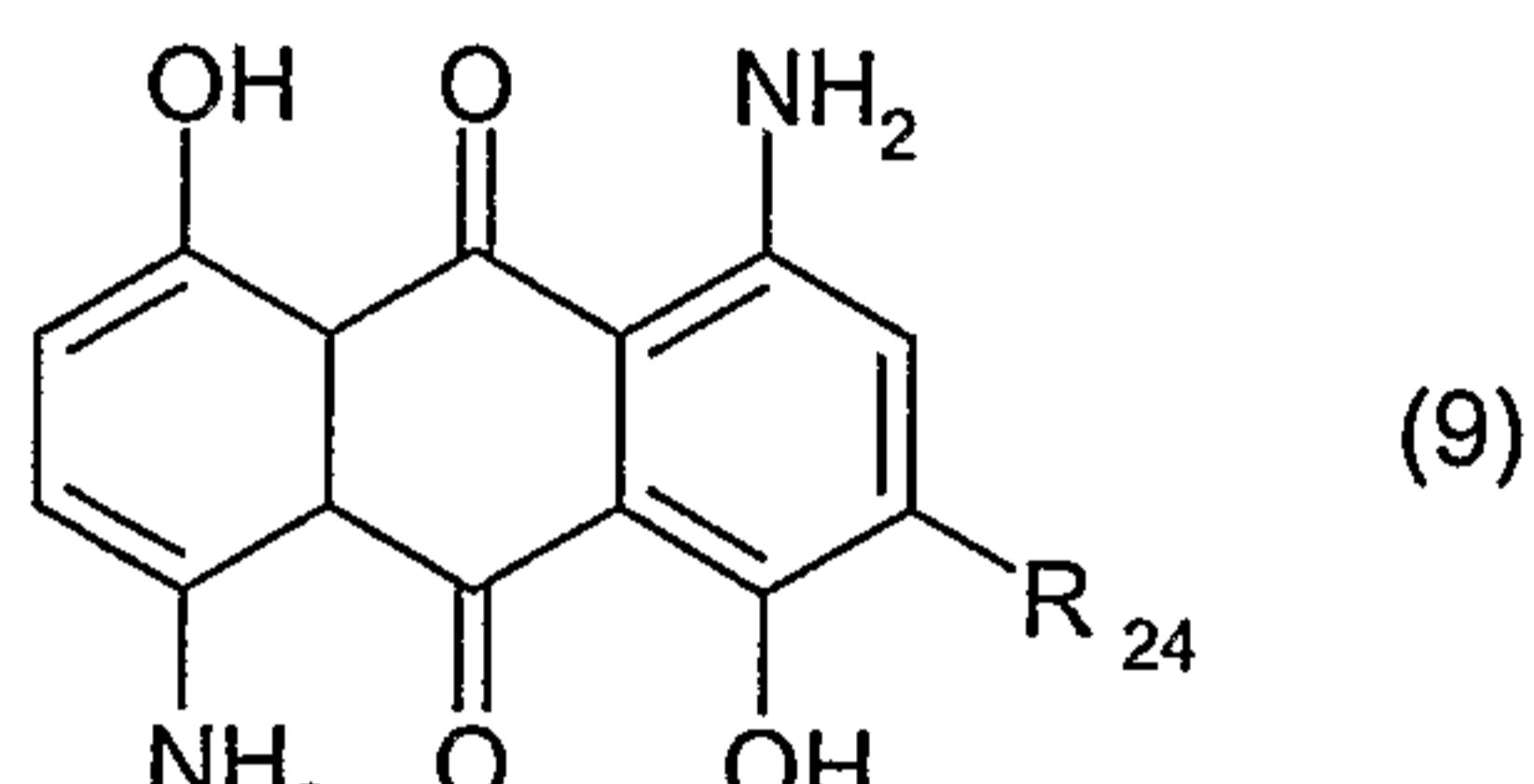


where

R₁₉ is C₁-C₄-alkyl, R₂₀ is C₁-C₄-alkyl, R₁₅ is C₁-C₄-alkyl and R₂₂ is C₁-C₄-alkyl or the radical -NHCOR₂₃, where R₂₃ is C₁-C₄-alkyl,

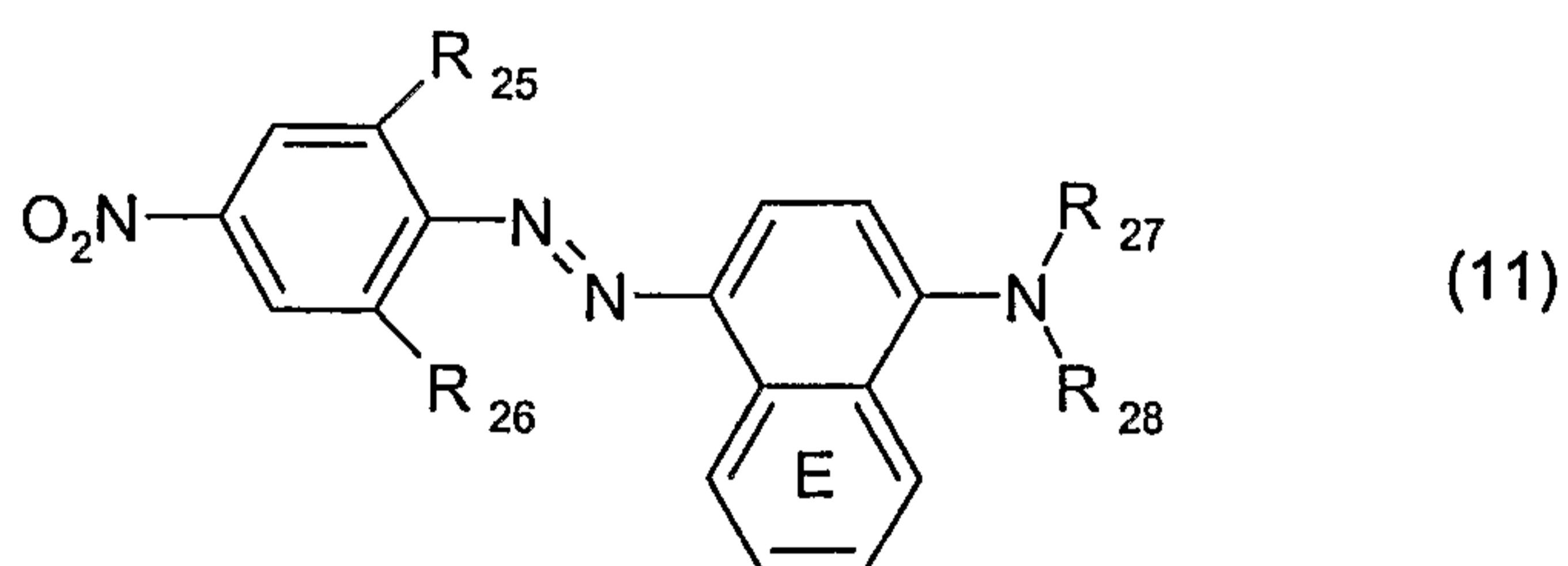


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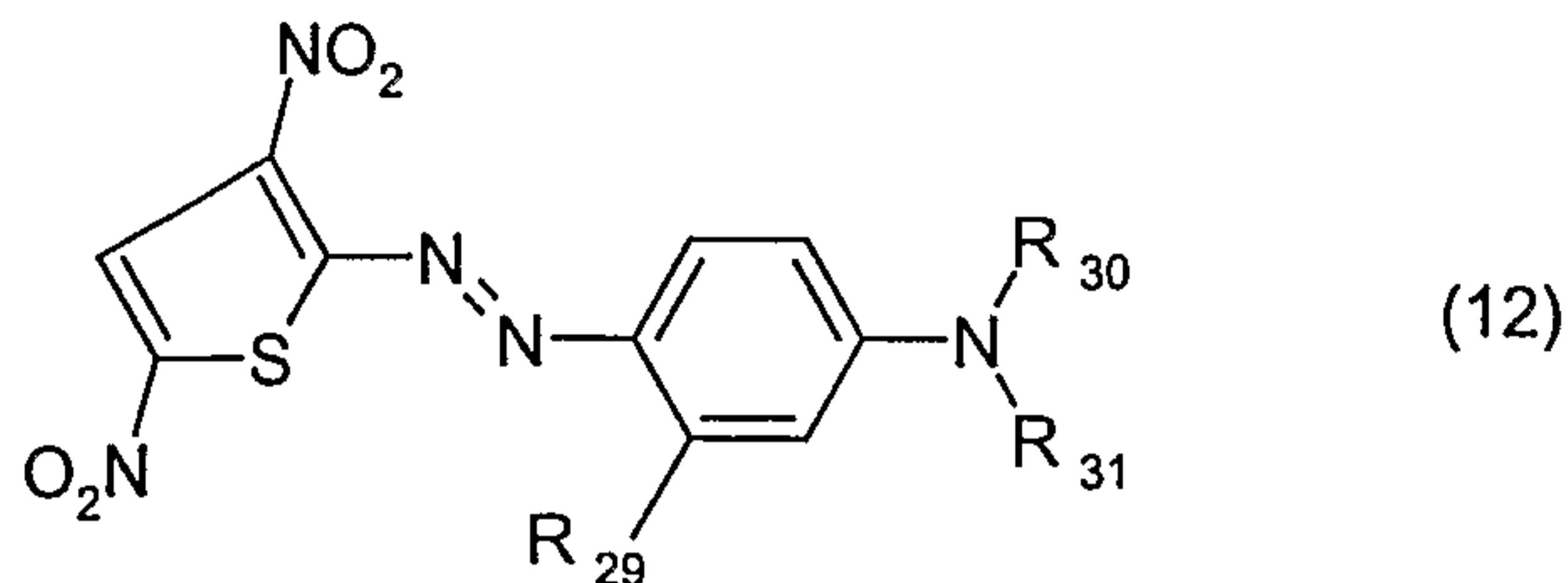
where R₂₄ is halogen,

10



where

R₂₅ is cyano, nitro or halogen, R₂₆ is halogen, R₂₇ is unsubstituted or hydroxyl-substituted C₁-C₄-alkyl and R₂₈ is unsubstituted or hydroxyl-substituted C₁-C₄-alkyl and the naphthalen ring E may be further substituted,
15 and/or

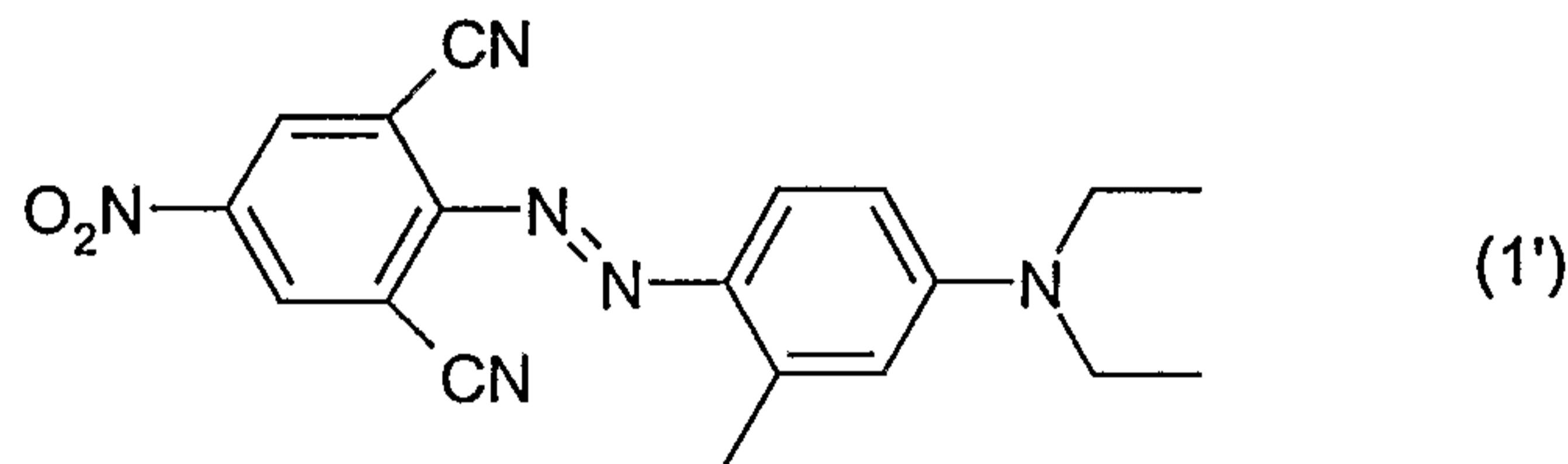


where

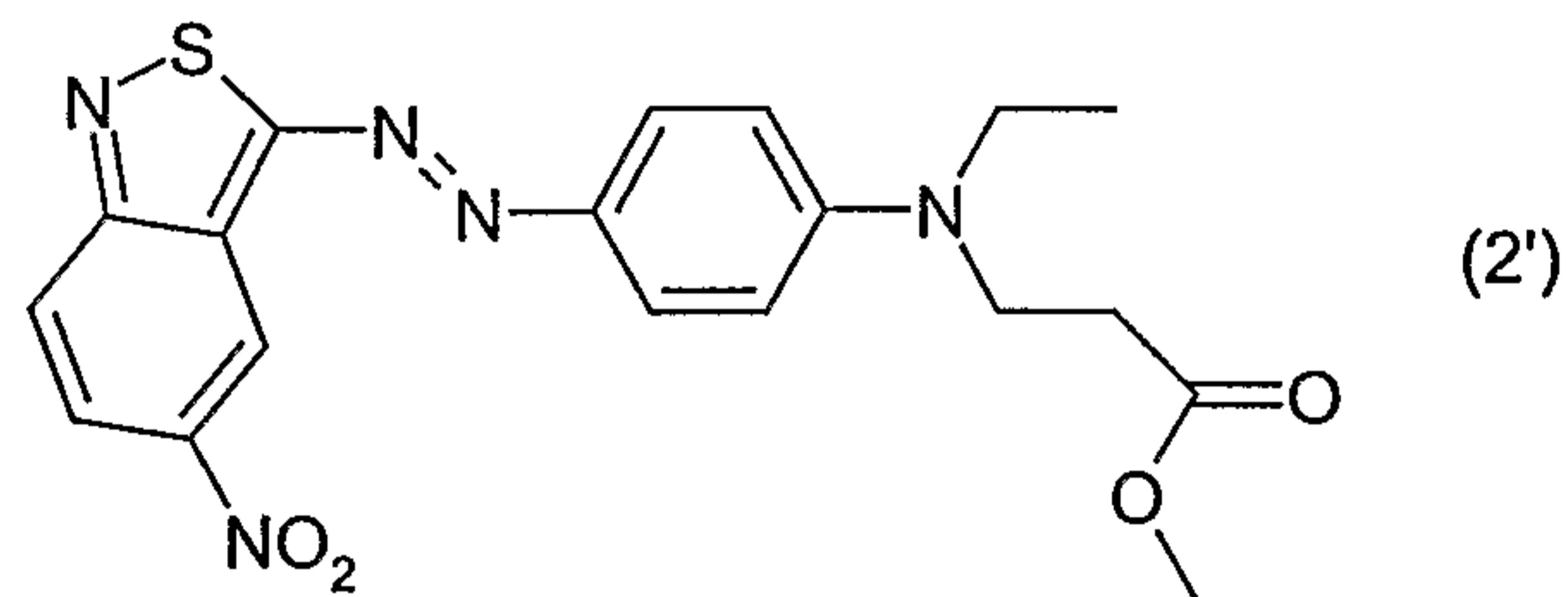
R_{26} is C_1 - C_4 -alkyl or the radical $NHCOR_{17}$, where R_{17} is C_1 - C_4 -alkyl, R_{27} is C_1 - C_4 -alkyl or C_1 - C_4 -alkylcarbonyloxy- C_1 - C_4 -alkyl and R_{28} is C_1 - C_4 -alkyl or C_1 - C_4 -alkylcarbonyloxy- C_1 - C_4 -alkyl.

5

4. Dye mixtures as per Claim 1 characterized in that the at least one dye of the formula (1) the formula (1') and at least one dye of the formula (2'):



10 and the at least one dye of the formula (2) the formula (2')



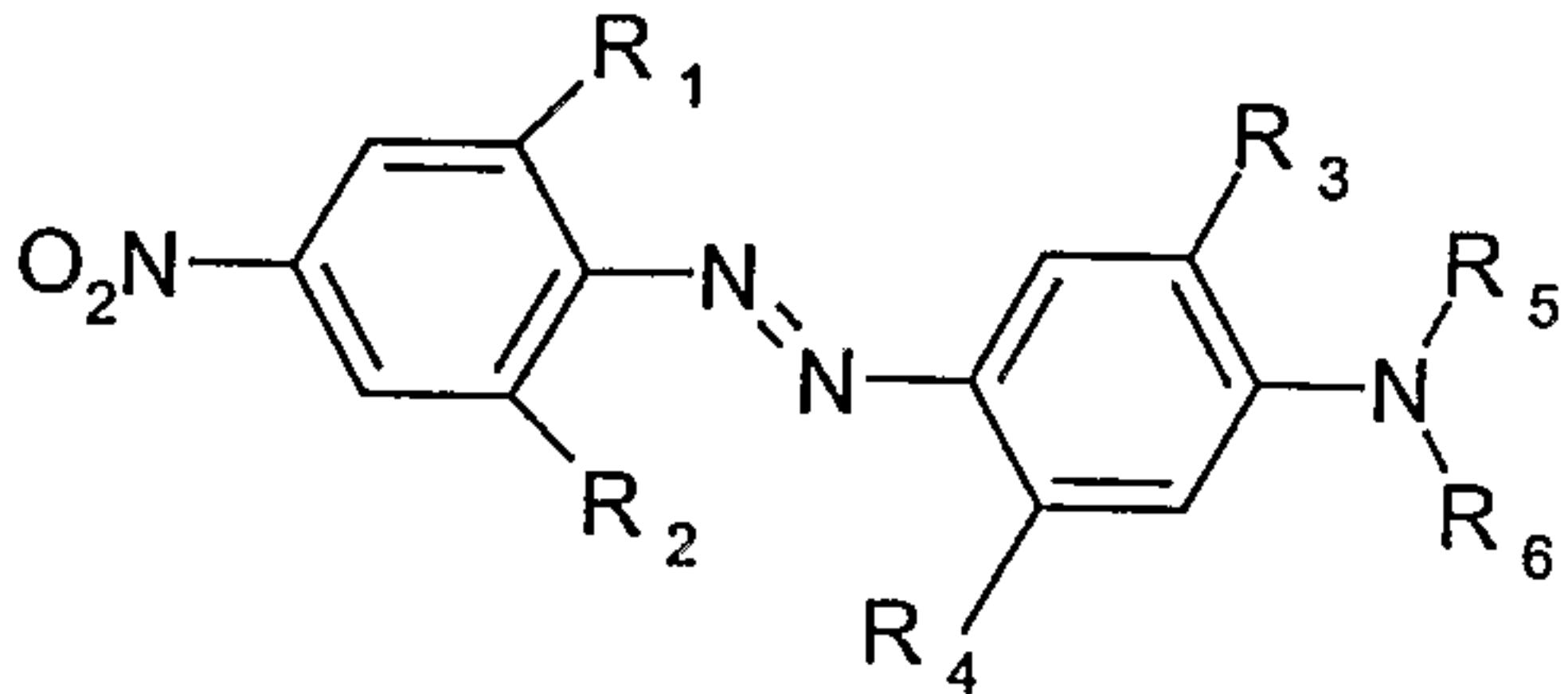
5. Use of dye mixtures as per Claim 1 for dyeing or printing semisynthetic or synthetic hydrophobic fibre materials comprising cellulose acetate.

15

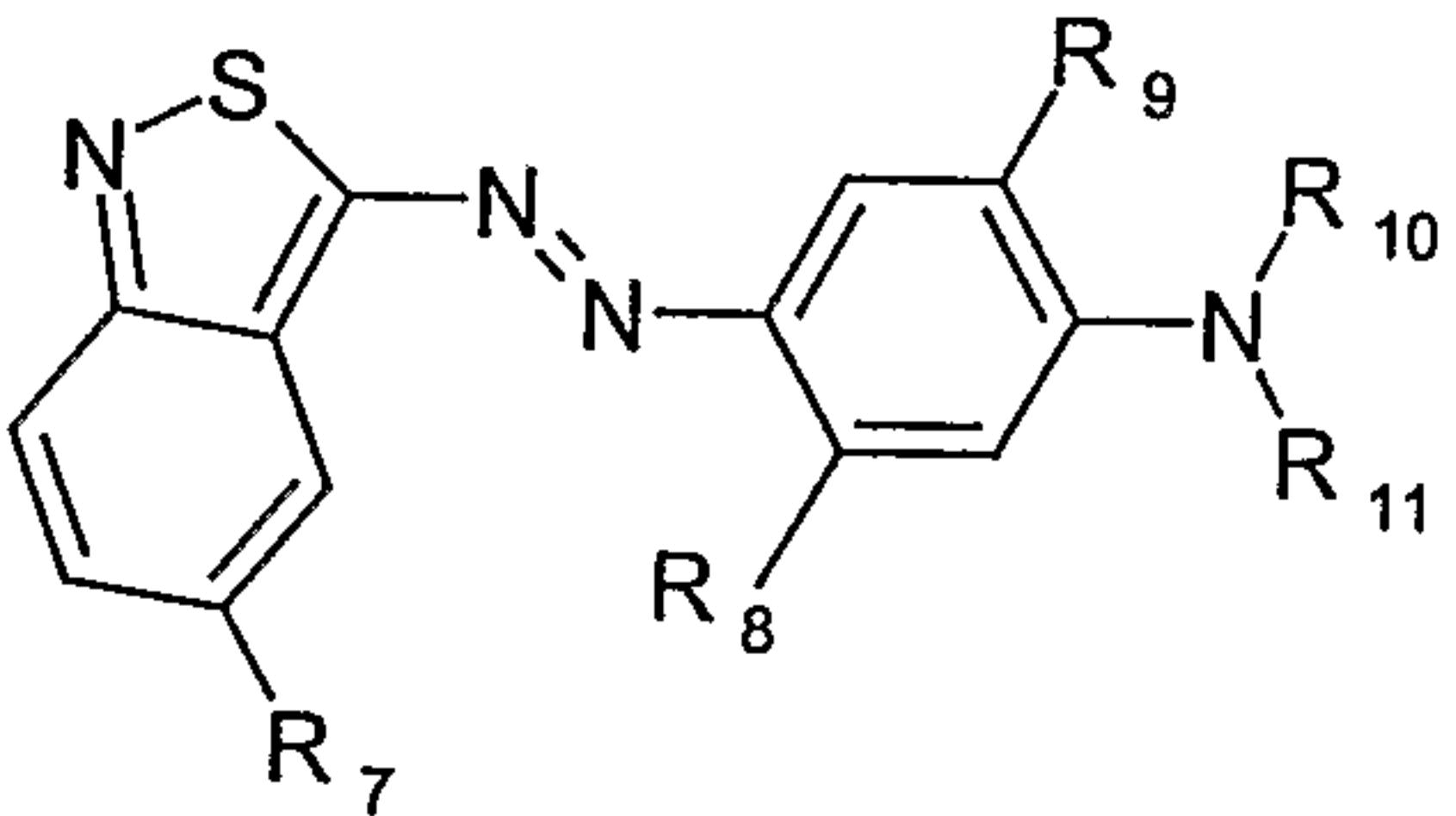
6. Use of dye mixtures as per Claim 1 for dyeing or printing fibrous structures comprising polyester and/or cellulose secondary acetate.

7. Fibrous structures dyed or printed with a dye mixture as per Claim 1.

20



(1)



(2)