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(54) Title: 2-ACYLAMINO OR 2-SULFONYLAMINO-1, 3-THIAZOLES AS COUPLERS FOR THE OXIDATION DYEING OF
KERATIN FIBRES

(57) Abstract: The invention relates to thiazole derivatives of formula (I) that are useful as couplers for the oxidation dyeing of
keratin fibres. The invention also relates to a dye composition containing at least one oxidation base and at least one thiazole derivative
as coupler, to the use of this composition for dyeing keratin fibres and to the dyeing process using this composition.



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2-ACYLAMINO OR 2-SULFONYLAMINO-1,3-THIAZOLES AS COUPLERS FOR THE OXIDATION DYEING OF KERATIN FIBRES

The invention relates to novel thiazole derivatives that are useful as couplers for the oxidation dyeing of keratin fibres.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols, heterocyclic compounds such as diaminopyrazole derivatives, pyrazolo[1,5-a]pyrimidine derivatives, pyrimidine derivatives, pyridine derivatives, 5,6-dihydroxyindole derivatives and 5,6-dihydroxyindoline derivatives, which are generally known as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds that, when combined with oxidizing products, can give rise to coloured compounds or dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases may be varied by combining them with couplers or coloration modifiers, the latter being chosen especially from meta-phenylenediamines, meta-aminophenols, meta-hydroxyphenols and certain heterocyclic compounds such as, for example, pyrazolo-[1,5-b]-1,2,4-triazole derivatives, pyrazolo[3,2-c]-1,2,4-triazole derivatives, pyrazolo[1,5-a]pyrimidine

derivatives, pyridine derivatives, pyrazol-5-one derivatives, indoline derivatives and indole derivatives.

The variety of molecules used as oxidation
5 bases and couplers allows a wide range of colours to be obtained.

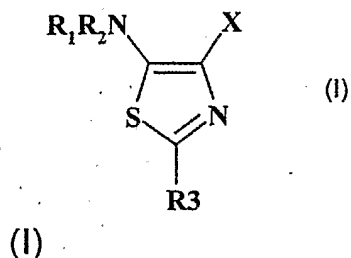
The "permanent" coloration obtained with these oxidation dyes must moreover satisfy a certain number of requirements. Thus, it must have no
10 toxicological drawbacks, it must allow shades to be obtained in the desired intensity, and it must show good resistance to external agents such as light, bad weather, washing, permanent-waving, perspiration and rubbing.

15 The dyes must also allow white hairs to be covered and, finally, they must be as unselective as possible, i.e. they must produce the smallest possible colour differences along the same length of keratin fibre, which may in fact be differently sensitized
20 (i.e. damaged) between its end and its root. They must also show good chemical stability in the formulations, and must have a good toxicological profile.

The aim of the present invention is to provide novel couplers for obtaining an even wider
25 range of shades and also dye compositions that produce powerful, uniform dyeing results between the root and the end of the hairs, which have good chromaticity, are

sparingly selective and are particularly fast, while at the same time being capable of generating strong colorations in varied shades, in particular in the fundamental shades.

5 This aim is achieved with the present invention, one subject of which is a thiazole derivative of formula (I) below, and the addition salts thereof with an acid or a base:



10 in which:

- R_1 and R_2 , which may be identical or different, represent:

- a hydrogen atom;
- a phenyl radical optionally substituted with one or more radicals chosen from halogens, hydroxyl,
- 15 C_1 - C_4 alkoxy, carboxyl, mono- or di(C_1 - C_4)alkyl-carboxamido ($AlkNHCO$ - or $(Alk)_2NCO$), C_1 - C_4 thio-ether, (C_1 - C_4)alkylsulphonyl ($-SO_2alkyl$), sulphonic ($-SO_3H$), alkyl sulphoxide ($-SO-alkyl$), alkyl-
- 20 sulphonamido ($(C_1-C_4)alkylSO_2NH$ -) and $NR_{13}R_{14}$ radicals, or a C_1 - C_4 alkyl radical optionally substituted with one or more hydroxyl, C_1 - C_4 alkoxy, carboxyl, mono- or di(C_1 - C_4)alkyl-carboxamido, (C_1 - C_4)alkylsulphonyl, sulphonic,

alkyl sulphoxide, alkylsulphonamido or $\text{NR}_{13}\text{R}_{14}$;

- a linear or branched $\text{C}_1\text{-C}_8$ alkyl radical optionally substituted with one or more hydroxyl, $\text{C}_1\text{-C}_2$ alkoxy, carboxyl, mono- or di($\text{C}_1\text{-C}_4$)alkyl-carboxamido, (5 $\text{C}_1\text{-C}_4$)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or $\text{NR}_{13}\text{R}_{14}$ radicals,

- R_1 and R_2 may form, with the nitrogen atom to which they are attached, a 5- to 8-membered
10 heterocycle, one or more carbon atoms of the carbon-based ring of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO_2 group, the carbon atoms of the ring possibly being substituted with a radical R_4 and the ring not
15 comprising a peroxide bond or diazo or nitroso radicals;

- R_4 represents:

- a halogen atom;

- a $\text{C}_1\text{-C}_4$ alkyl radical optionally substituted
20 with one or more hydroxyl, carboxyl, $\text{C}_1\text{-C}_4$ alkoxy, carbonyl, $\text{C}_1\text{-C}_4$ alkoxy or NR_5R_6 radicals;

- a carboxyl radical;

- a mono- or di($\text{C}_1\text{-C}_4$)alkylcarboxamido radical;

25 - a ($\text{C}_1\text{-C}_4$)alkylsulphonyl radical;

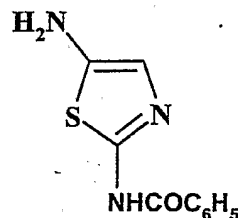
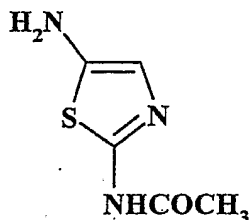
- an alkylsulphonamido radical;

- a hydroxyl radical;

- a C₁-C₄ alkoxy radical;
 - a C₂-C₄ hydroxyalkoxy radical;
 - an aminosulphonyl radical;
 - a C₁-C₄ thioether radical;
 - 5 - a (C₁-C₄)alkyl sulphoxide radical;
 - a (C₁-C₄)alkylsulphonyl radical;
 - a radical NR₇R₈;
- R₃ represents a radical R₉SO₂NH- or a radical R₁₀C(O)NH- with R₉ and R₁₀, which may be identical or
- 10 different, representing:
- a phenyl radical or a 5- or 6-membered aromatic heterocycle, these radicals optionally being substituted with one or more radicals chosen from halogens, hydroxyl, C₁-C₄ alkoxy, carboxyl, C₁-C₄ alkoxy carbonyl, mono- or di(C₁-C₄)alkylcarboxamido, 15 (C₁-C₄)alkylsulphonyl, sulphonic, (C₁-C₄)alkyl sulphoxide, C₁-C₄ thioether, alkylsulphonamido or NR₁₁R₁₂ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, 20 C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄,
 - a linear or branched C₁-C₈ alkyl radical optionally substituted with one or more hydroxyl, 25 OR₁₅, carboxyl, C₁-C₄ alkoxy carbonyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, (C₁-C₄)alkyl sulphoxide, alkyl-

- sulphonamido or $\text{NR}_{16}\text{R}_{17}$ radicals;
with R_{15} representing a $\text{C}_1\text{-C}_4$ alkyl radical
optionally substituted with one or more radicals
chosen from hydroxyl, $\text{C}_1\text{-C}_2$ alkoxy, amino,
5 (di) $(\text{C}_1\text{-C}_4)$ alkylamino and (poly)hydroxy $(\text{C}_2\text{-C}_4)$ -
alkylamino radicals;
- R_5 , R_6 , R_7 , R_8 , R_{11} , R_{12} , R_{13} , R_{14} , R_{16} and R_{17} , which may
be identical or different, represent a hydrogen atom, a
 $(\text{C}_1\text{-C}_4)$ alkylsulphonyl or $(\text{C}_1\text{-C}_4)$ alkyl-CO radical, a mono-
10 or di $(\text{C}_1\text{-C}_4)$ alkylcarboxamido radical, or a $\text{C}_1\text{-C}_4$ alkyl
radical optionally substituted with one or more
hydroxyl, $\text{C}_1\text{-C}_4$ alkoxy, $(\text{C}_1\text{-C}_4)$ alkylsulphonyl, $(\text{C}_1\text{-C}_4)$ -
alkylsulphonamido, carboxyl, mono- or (di) $(\text{C}_1\text{-C}_4)$ alkyl-
carboxamido, $(\text{C}_1\text{-C}_4)$ alkyl sulphoxide, amino, (di) $(\text{C}_1\text{-C}_4)$ -
15 alkylamino or (poly)hydroxy $(\text{C}_2\text{-C}_4)$ alkylamino;
- R_7 and R_8 may also form, with the nitrogen atom that
bears them, a 5- to 8-membered ring optionally
substituted with one or more radicals chosen from
halogens and hydroxyl, $\text{C}_1\text{-C}_2$ alkoxy, carboxyl, alkyl-
20 sulphonamido and $\text{NR}_{13}\text{R}_{14}$ radicals, or a $\text{C}_1\text{-C}_4$ alkyl
radical optionally substituted with one or more
hydroxyl, $\text{C}_1\text{-C}_4$ alkoxy, carboxyl, mono- or di $(\text{C}_1\text{-C}_4)$ -
alkylcarboxamido or $\text{NR}_{13}\text{R}_{14}$;
- X represents a hydrogen atom; a halogen atom (such as
25 fluorine, chlorine or bromine); a $\text{C}_1\text{-C}_4$ alkoxy radical;
a phenoxy radical optionally substituted with one or
more radicals chosen from halogens and hydroxyl, $\text{C}_1\text{-C}_4$

alkoxy, carboxyl, C₁-C₄ alkoxy carbonyl, mono- or
 di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl,
 sulphonic, alkyl sulphoxide, C₁-C₄ thioether, alkyl-
 sulphonamido, NR₁₃R₁₄ and C₁-C₄ alkyl radicals; a C₁-C₄
 5 thioether radical optionally substituted with a
 hydroxyl, C₁-C₂ alkoxy, carboxyl, sulphonic or amino
 radical,
 with the exception of the derivatives



10 A subject of the present invention is also a
 dye composition comprising, in a medium that is
 suitable for dyeing,
 - at least one oxidation base, and
 - as coupler, at least one thiazole derivative of
 15 formula (I) as defined above.

A subject of the invention is also dyeing
 processes using this composition.

Another subject of the invention is the use
 of the derivatives of formula (I) for the oxidation
 20 dyeing of keratin fibres, in particular human keratin
 fibres such as the hair.

Not only are the thiazole derivatives of
 formula (I) of the invention suitable for use as
 couplers for the oxidation dyeing of keratin fibres,

but also they produce particularly strong and sparingly selective colorations. Furthermore, they make it possible to obtain dye compositions which produce colorations that show good fastness with respect to the various attacking factors to which the hair may be subjected, such as light, bad weather, washing or perspiration. The oxidation dye compositions in accordance with the invention furthermore make it possible to obtain shades in a very wide range of colours.

In the radicals defined above bearing an alkyl group, and unless otherwise indicated, the alkyl radical may be linear or branched and optionally substituted with a hydroxyl, alkoxy or carboxyl. Furthermore, when the molecule contains several radicals of the same name, for example $NR_{13}R_{14}$, these radicals may be identical or different.

Examples that may be mentioned for the radicals R_1 and R_2 of formula (I) include hydrogen and a methyl, ethyl, (iso)propyl, 2-hydroxyethyl, 1-hydroxyethyl, 2-carboxyethyl, 2-aminoethyl, 2-(dimethylamino)ethyl, 2-(acylamino)ethyl, 2-methoxyethyl, 1,2-dihydroxyethyl, 1-hydroxy-2-aminoethyl, 2-hydroxy-1-aminoethyl, acetyl or phenyl radical.

According to one particular embodiment, R_1 and R_2 , which may be identical or different, represent:

- a hydrogen atom;

- a phenyl radical optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, C₁-C₄ thioether, 5 alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)-alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄;
- 10 - a linear or branched C₁-C₆ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, carboxyl, (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄ radicals.
- 15 According to one preferred embodiment, R₁ and R₂, which may be identical or different, represent a hydrogen atom; a phenyl radical; a linear or branched C₁-C₄ alkyl radical, optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, amino, di(C₁-C₄)alkylamino, 20 carboxyl, (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonamido or NR₁₃R₁₄ radicals in which R₁₃ and R₁₄, which may be identical or different, represent a hydrogen atom, (C₁-C₄)alkyl-CO or a C₁-C₂ alkyl radical optionally substituted with a hydroxyl or a C₁-C₂ 25 alkoxy.

Preferably, R₁ and R₂, which may be identical or different, represent a hydrogen atom or an

optionally substituted alkyl radical, for example methyl, 2-hydroxyethyl, 2-carboxyethyl or 1,2-dihydroxyethyl, or phenyl.

According to another embodiment, R_1 and R_2 form, with the nitrogen atom to which they are attached, a 5- to 8-membered heterocycle chosen from pyrrolidine, piperidine, homopiperidine, piperazine and homopiperazine, the said rings possibly being substituted with one or more radicals R_4 .

As examples of this particular embodiment, R_1 and R_2 form, together with the nitrogen atom to which they are attached, a heterocycle chosen from pyrrolidine, 2,5-dimethylpyrrolidine, proline, 3-hydroxyproline, 4-hydroxyproline, 2,4-dicarboxypyrrolidine, 3-hydroxy-2-hydroxymethylpyrrolidine, 2-carboxamidopyrrolidine, 3-hydroxy-2-carboxamidopyrrolidine, 2-(diethylcarboxamido)pyrrolidine, 2-hydroxymethylpyrrolidine, 3,4-dihydroxy-2-hydroxymethylpyrrolidine, 3-hydroxypyrrolidine, 3,4-dihydroxypyrrolidine, 3-amino-pyrrolidine, 3-methylaminopyrrolidine, 4-amino-3-hydroxypyrrolidine, 3-hydroxy-4-(2-hydroxyethyl)-aminopyrrolidine, piperidine, 2,6-dimethylpiperidine, 2-carboxypiperidine, 2-carboxamidopiperidine, 2-hydroxymethylpiperidine, 3-hydroxy-2-hydroxymethylpiperidine, 3-hydroxypiperidine, 4-hydroxypiperidine, 3-hydroxymethylpiperidine, homopiperidine, 2-carboxy-

homopiperidine, 2-carboxamidohomopiperidine, homopiperazine, N-methylhomopiperazine and N- β -hydroxyethylhomopiperazine, and the addition salts thereof.

Preferably, R_1 and R_2 form, together with the
5 nitrogen atom to which they are attached, a heterocycle
chosen from pyrrolidine, 3-hydroxypyrrolidine, 3-amino-
pyrrolidine, proline, 3-hydroxyproline, piperidine,
3-hydroxypiperidine, 4-hydroxypiperidine, homo-
piperidine, homopiperazine, N-methylhomopiperazine and
10 N- β -hydroxyethylhomopiperazine, and the addition salts
thereof.

Examples that may be mentioned for R_3 include
the radicals R_9SO_2NH- or a radical $R_{10}C(O)NH-$ with R_9 and
 R_{10} , which may be identical or different, chosen from a
15 methyl, methyl, ethyl, (iso)propyl, 2-hydroxyethyl,
1-hydroxyethyl, 2-carboxyethyl, 2-aminoethyl, 2-(di-
methylamino)ethyl, 2-(acylamino)ethyl, 2-methoxyethyl,
phenyl, 4-aminophenyl, 4-hydroxyphenyl, 4-diethyl-
aminophenyl, pyrazolyl, thiazolyl, pyridyl or thienyl.

20 According to one particular embodiment, when
 R_3 is an aromatic heterocycle, it is preferably chosen
from pyridyl, pyrimidinyl, pyrazolyl, thiazolyl, furyl,
imidazolyl and thienyl heterocycles.

According to one preferred embodiment, R_3
25 represents a radical R_9SO_2NH- or a radical $R_{10}C(O)NH-$;
with R_9 and R_{10} , which may be identical or different,
representing:

- a phenyl radical or a 5- or 6-membered aromatic heterocycle such as pyridyl, pyrimidinyl, pyrazolyl, thiazolyl, furyl, imidazolyl or thienyl, these radicals being optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido or NR₁₁R₁₂ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido or NR₁₃R₁₄ radicals;
- a linear or branched C₁-C₈ alkyl radical substituted with one or more radicals chosen from hydroxyl, C₁-C₂ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, (C₁-C₄)alkyl sulphoxide, alkylsulphonamide and NR₁₆R₁₇ radicals;
- R₁₁, R₁₂, R₁₃, R₁₄, R₁₆ and R₁₇, which may be identical or different, represent a hydrogen atom, acyl, a carboxamido or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, (C₁-C₄)alkylsulphonyl, (C₁-C₄)alkylsulphonamido, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkyl sulphoxide, amino, (di)(C₁-C₄)alkylamino or (poly)hydroxy(C₂-C₄)alkylamino radicals.

According to one particular embodiment, R₃

represents a radical R_9SO_2NH- or a radical $R_{10}C(O)NH-$ with R_9 and R_{10} , which may be identical or different, chosen from an alkyl radical, a phenyl radical, a pyrazolyl radical, a thiazolyl radical, a pyridyl radical or a thienyl radical, these radicals possibly being substituted. Preferably, R_{10} represents a methyl, ethyl, 2-hydroxyethyl, 2-carboxyethyl, phenyl, pyrazolyl, thienyl or pyridyl radical and R_9 represents a methyl, phenyl or tolyl radical.

10 In formula (I) above, X preferably represents a hydrogen atom, a chlorine atom or an alkoxy radical, for example methoxy.

Among the derivatives of formula (I) that are useful in the present invention, in particular in the composition of the invention, mention may be made of the following compounds:

5-amino-2-methylsulphonylaminothiazole
5-amino-2-phenylsulphonylaminothiazole
5-amino-2-tolylsulphonylaminothiazole
20 5-amino-2-thiazolylsulphonylaminothiazole
5-amino-2-pyridylsulphonylaminothiazole
5-amino-2-phenacylaminothiazole
5-amino-2-(pyrid-2-yl)acylaminothiazole
5-amino-2-(pyrid-3-yl)acylaminothiazole
25 5-amino-2-(pyrid-4-yl)acylaminothiazole
5-amino-2-acetylaminothiazole
5-amino-2-isopropylacylaminothiazole

- 5-amino-2-(thien-2-yl)acylaminothiazole
- 5-methylamino-2-methylsulphonylaminothiazole
- 5-methylamino-2-phenylsulphonylaminothiazole
5. 5-methylamino-2-tolylsulphonylaminothiazole
- 5-methylamino-2-thiazolylsulphonylaminothiazole
- 5-methylamino-2-pyridylsulphonylaminothiazole
- 5-methylamino-2-phenacylaminothiazole
- 5-methylamino-2-(pyrid-2-yl)acylaminothiazole
- 10 5-methylamino-2-(pyrid-3-yl)acylaminothiazole
- 5-methylamino-2-(pyrid-4-yl)acylaminothiazole
- 5-methylamino-2-acetylaminothiazole
- 5-methylamino-2-isopropylacylaminothiazole
- 5-methylamino-2-(thien-2-yl)acylaminothiazole
- 15
- 5-(2-hydroxyethyl)amino-2-methylsulphonylaminothiazole
- 5-(2-hydroxyethyl)amino-2-phenylsulphonylaminothiazole
- 5-(2-hydroxyethyl)amino-2-tolylsulphonylaminothiazole
- 5-(2-hydroxyethyl)amino-2-thiazolylsulphonylamino-
- 20 thiazole
- 5-(2-hydroxyethyl)amino-2-pyridylsulphonylaminothiazole
- 5-(2-hydroxyethyl)amino-2-phenacylaminothiazole
- 5-(2-hydroxyethyl)amino-2-(pyrid-2-yl)acylaminothiazole
- 5-(2-hydroxyethyl)amino-2-(pyrid-3-yl)acylaminothiazole
- 25 5-(2-hydroxyethyl)amino-2-(pyrid-4-yl)acylaminothiazole
- 5-(2-hydroxyethyl)amino-2-acetylaminothiazole
- 5-(2-hydroxyethyl)amino-2-isopropylacylaminothiazole

- 5-(2-hydroxyethyl)amino-2-(thien-2-yl)acylaminothiazole
5-amino-4-chloro-2-methylsulphonylaminothiazole
5-amino-4-chloro-2-phenylsulphonylaminothiazole
5-amino-4-chloro-2-tolylsulphonylaminothiazole
5 5-amino-4-chloro-2-thiazolylsulphonylaminothiazole
5-amino-4-chloro-2-pyridylsulphonylaminothiazole
5-amino-4-chloro-2-phenacylaminothiazole
5-amino-4-chloro-2-(pyrid-2-yl)acylaminothiazole
5-amino-4-chloro-2-(pyrid-3-yl)acylaminothiazole
10 5-amino-4-chloro-2-(pyrid-4-yl)acylaminothiazole
5-amino-4-chloro-2-acetylaminothiazole
5-amino-4-chloro-2-isopropylacylaminothiazole
5-amino-4-chloro-2-(thien-2-yl)acylaminothiazole

15 5-methylamino-4-chloro-2-methylsulphonylaminothiazole
5-methylamino-4-chloro-2-phenylsulphonylaminothiazole
5-methylamino-4-chloro-2-tolylsulphonylaminothiazole
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thiazole
20 5-methylamino-4-chloro-2-pyridylsulphonylaminothiazole
5-methylamino-4-chloro-2-phenacylaminothiazole
5-methylamino-4-chloro-2-(pyrid-2-yl)acylaminothiazole
5-methylamino-4-chloro-2-(pyrid-3-yl)acylaminothiazole
5-methylamino-4-chloro-2-(pyrid-4-yl)acylaminothiazole
25 5-methylamino-4-chloro-2-acetylaminothiazole
5-methylamino-4-chloro-2-isopropylacylaminothiazole
5-methylamino-4-chloro-2-(thien-2-yl)acylaminothiazole

- 5-(2-hydroxyethyl)amino-4-chloro-2-methylsulphonyl-aminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-phenylsulphonyl-aminothiazole
- 5 5-(2-hydroxyethyl)amino-4-chloro-2-tolylsulphonyl-aminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-thiazolylsulphonyl-aminothiazole
- 10 5-(2-hydroxyethyl)amino-4-chloro-2-pyridylsulphonyl-aminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-phenacylamino-thiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-(pyrid-2-yl)acyl-aminothiazole
- 15 5-(2-hydroxyethyl)amino-4-chloro-2-(pyrid-3-yl)acyl-aminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-(pyrid-4-yl)acyl-aminothiazole
- 20 5-(2-hydroxyethyl)amino-4-chloro-2-acetylaminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-isopropylacyl-aminothiazole
- 5-(2-hydroxyethyl)amino-4-chloro-2-(thien-2-yl)acyl-aminothiazole
- 25 5-(pyrrolidin-1-yl)-2-methylsulphonylaminothiazole
- 5-(pyrrolidin-1-yl)-2-phenylsulphonylaminothiazole

- 5-(pyrrolidin-1-yl)-2-tolylsulphonylaminothiazole
5-(pyrrolidin-1-yl)-2-thiazolylsulphonylaminothiazole
5-(pyrrolidin-1-yl)-2-pyridylsulphonylaminothiazole
5-(pyrrolidin-1-yl)-2-phenacylaminothiazole
5 5-(pyrrolidin-1-yl)-2-(pyrid-2-yl)acylaminothiazole
5-(pyrrolidin-1-yl)-2-(pyrid-3-yl)acylaminothiazole
5-(pyrrolidin-1-yl)-2-(pyrid-4-yl)acylaminothiazole
5-(pyrrolidin-1-yl)-2-acetylaminothiazole
5-(pyrrolidin-1-yl)-2-isopropylacylaminothiazole
10 5-(pyrrolidin-1-yl)-2-(thien-2-yl)acylaminothiazole

5-(pyrrolidin-1-yl)-4-chloro-2-methylsulphonylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-phenylsulphonylamino-
15 thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-tolylsulphonylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-thiazolylsulphonyl-
aminothiazole
20 5-(pyrrolidin-1-yl)-4-chloro-2-pyridylsulphonylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-phenacylaminothiazole
5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-2-yl)acylamino-
thiazole
25 5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-3-yl)acylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-4-yl)acylamino-

thiazole

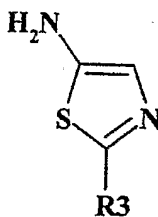
5-(pyrrolidin-1-yl)-4-chloro-2-acetylaminothiazole

5-(pyrrolidin-1-yl)-4-chloro-2-isopropylacylamino-
thiazole

5 5-(pyrrolidin-1-yl)-4-chloro-2-(thien-2-yl)acylamino-
thiazole

and also the addition salts thereof with an acid or a
base.

According to one particular embodiment, the
10 thiazole derivative corresponds to formula (Ib)



(Ib)

in which R₃ is as defined above.

A derivative of formula (I) of the invention
that is more particularly preferred is 5-(pyrrolidin-
15 1-yl)-2-(thien-2-yl)acylaminothiazole and the addition
salts thereof.

Another subject of the invention is a dye
composition comprising, in a suitable medium, at least
one oxidation base and, as coupler, at least one
20 thiazole derivative of formula (I).

The composition of the present invention is
particularly useful for the oxidation dyeing of keratin
fibres and in particular of human keratin fibres.

The oxidation bases that may be used in the composition of the present invention are the oxidation bases conventionally used in oxidation dyeing. By way of example, these oxidation bases are chosen from

5 oxidation bases, for example para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof with an acid or a base.

Among the para-phenylenediamines that may be
10 mentioned, are para-phenylenediamine, para-tolylene-diamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylene-diamine, 2,6-diethyl-para-phenylenediamine, 2,5-di-methyl-para-phenylenediamine, N,N-dimethyl-para-
15 phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, N,N-diethyl-3-methyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-2-methyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-
20 2-chloro-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-
25 phenylenediamine, N-ethyl-N-(β -hydroxyethyl)-para-phenylenediamine, N-(β,γ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-

phenylenediamine, N-phenyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2- β -acetylaminoethyloxy-para-phenylenediamine, N-(β -methoxyethyl)para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-
5 para-phenylenediamine, 2- β -hydroxyethylamino-5-amino-toluene, and the addition salts thereof with an acid or a base.

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-tolylenediamine,
10 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-
15 phenylenediamine, 2-chloro-para-phenylenediamine and 2- β -acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid or a base, are particularly preferred.

Among the bis(phenyl)alkylenediamines that
20 may be mentioned, for example, are N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4-amino-
25 phenyl)tetramethylenediamine, N,N'-bis(4-methylamino-phenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis-

(2,5-diaminophenoxy)-3,6-dioxaoctane, and the addition salts thereof with an acid or a base.

Among the para-aminophenols that may be mentioned, for example, are para-aminophenol, 4-amino-
5 3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the
10 addition salts thereof with an acid or a base.

Among the ortho-aminophenols that may be mentioned, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an
15 acid or a base.

Among the heterocyclic bases that may be mentioned, for example, are pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives that may be
20 mentioned are the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β -methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diamino-
25 pyridine, and the addition salts thereof with an acid or a base.

Among the pyrimidine derivatives that can be

mentioned are the compounds described, for example, in patents DE 2 359 399; JP 88-169 571; JP 05-163 124; EP 0 770 375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triamino-
5 pyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-2 750 048 and among which mention may be made of pyrazolo[1,5-a]-
10 pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-aminopyrazolo-
15 [1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo-
20 [1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 3-amino-5-methyl-7-imidazolylpropylaminopyrazolo[1,5-a]pyrimidine, and the addition salts thereof with an acid
25 and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives that may be

mentioned are the compounds described in patents
DE 3 843 892 and DE 4 133 957 and patent applications
WO 94/08969, WO 94/08970, FR-A-2 733 749 and
DE 195 43 988, such as 4,5-diamino-1-methylpyrazole,
5 4,5-diamino-1-(β -hydroxyethyl)pyrazole, 3,4-diamino-
pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole,
4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-
1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenyl-
pyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole,
10 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-
tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-
3-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)-
3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,
4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
15 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-
(2'-aminoethyl)amino-1,3-dimethylpyrazole,
20 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triamino-
pyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole
and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methyl-
pyrazole, and the addition salts thereof with an acid
or a base.

25 The oxidation base(s) is (are) each generally
present in an amount of between 0.001% and 10% and
preferably between 0.005% and 6% by weight

approximately relative to the total weight of the dye composition.

The composition according to the invention may also contain one or more couplers conventionally used for oxidation dyeing of human keratin fibres. Among these additional couplers, mention may be made especially of meta-phenylenediamines, meta-amino-phenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers other than the thiazole derivatives of formula (I) of the invention, and the addition salts thereof with an acid or a base.

Examples that may be mentioned include 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 6-chloro-2-methyl-5-aminophenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1- β -hydroxyethylamino-3,4-methylenedioxybenzene, α -naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β -hydroxyethyl)amino-3,4-methylenedioxybenzene and 2,6-bis(β -hydroxyethylamino)toluene and the addition salts thereof with an

acid or a base.

In the composition of the present invention, the coupler(s) is (are) each generally present in an amount ranging from 0.001% to 10% by weight approximately, and more preferably from 0.005% to 6% by weight, relative to the total weight of the dye composition.

In general, the addition salts of the oxidation bases and couplers that may be used in the context of the invention are chosen especially from the addition salts with an acid, such as the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzene-sulphonates, phosphates and acetates, and the addition salts with a base, such as sodium hydroxide, potassium hydroxide, ammonia, amines or alkanolamines.

The dye composition according to the invention may also contain one or more direct dyes, which may be chosen in particular from nitrobenzene dyes, azo direct dyes and methine direct dyes. These direct dyes may be of nonionic, anionic or cationic nature.

The medium that is cosmetically suitable for dyeing, also known as the dye support, generally consists of water or a mixture of water and at least one organic solvent to dissolve the compounds that would not be sufficiently soluble in water. As organic

solvent, mention may be made, for example, of C₁-C₄ lower alkanols, such as ethanol and isopropanol, polyols and polyol ethers, such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, 5 diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, and mixtures thereof.

The solvents are preferably present in proportions of between 1% and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5% and 30% by weight approximately.

The dye composition in accordance with the invention may also contain various adjuvants 15 conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, mineral or organic 20 thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, for instance volatile or non- 25 volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and opacifiers.

The above adjuvants are generally present in an amount for each of between 0.01% and 20% by weight relative to the weight of the composition.

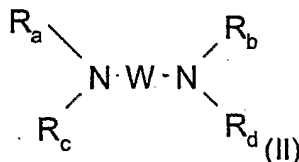
Needless to say, a person skilled in the art
5 will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the oxidation dye composition in accordance with the invention are not, or are not substantially, adversely affected by
10 the envisaged addition(s).

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately. It may be adjusted to the desired value
15 by means of acidifying or basifying agents usually used for dyeing keratin fibres, or alternatively using standard buffer systems.

Among the acidifying agents that may be mentioned, for example, are mineral or organic acids,
20 for instance hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid or lactic acid, and sulphonc acids.

Among the basifying agents that may be
25 mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as monoethanolamine, diethanolamine and triethanolamine and derivatives

thereof, sodium hydroxide, potassium hydroxide and the derivatives of formula (II) below:



in which W is a propylene residue optionally

5 substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R_a, R_b, R_c and R_d, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

The dye composition according to the
10 invention may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, and especially human hair.

The process of the present invention is a
15 process in which the composition according to the present invention as defined above is applied to the fibres, in the presence of an oxidizing agent for a time which is sufficient to obtain the desired coloration. The colour may be revealed at acidic,
20 neutral or alkaline pH and the oxidizing agent may be added to the composition of the invention just at the time of use, or it may be introduced using an oxidizing composition containing it, applied simultaneously with or sequentially to the composition of the invention.

25 According to one particular embodiment, the

composition according to the present invention is mixed, preferably at the time of use, with a composition containing, in a medium that is suitable for dyeing, at least one oxidizing agent, this
5 oxidizing agent being present in an amount that is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibres. After a leave-in time of 3 to 50 minutes approximately and preferably 5 to 30 minutes approximately, the keratin
10 fibres are rinsed, washed with shampoo, rinsed again and then dried.

The oxidizing agents conventionally used for the oxidation dyeing of keratin fibres are, for example, hydrogen peroxide, urea peroxide, alkali metal
15 bromates, persalts such as perborates and persulphates, peracids, and oxidase enzymes, among which mention may be made of peroxidases, 2-electron oxidoreductases such as uricases, and 4-electron oxygenases, for instance laccases. Hydrogen peroxide is particularly preferred.

20 The oxidizing composition may also contain various adjuvants conventionally used in hair dye compositions and as defined above.

The pH of the oxidizing composition containing the oxidizing agent is such that, after
25 mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and

even more preferably between 5 and 11. It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres and as defined above.

5 The ready-to-use composition that is finally applied to the keratin fibres may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, and especially human hair.

10 A subject of the invention is also a multi-compartment device or dyeing "kit", in which a first compartment contains the dye composition defined above and a second compartment contains an oxidizing agent. This device may be equipped with a means for applying
15 the desired mixture to the hair, such as the devices described in patent FR 2 586 913 in the name of the Applicant.

 Using this device, it is possible to dye keratin fibres using a process that involves mixing a
20 dye composition comprising at least one oxidation base of formula (I) with an oxidizing agent, and applying the mixture obtained to the keratin fibres for a time that is sufficient to develop the desired coloration.

 The derivatives of formula (I) may be
25 obtained according to the synthetic methods known in the field of heterocyclic synthesis. Reference may be made, for example, to the publications EP 1256578,

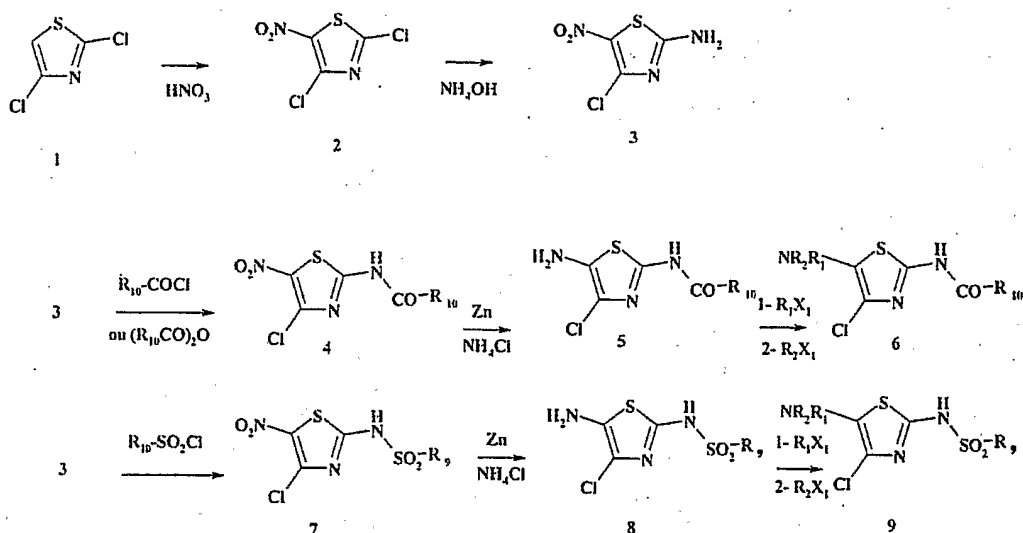
US 61143665, WO 97/47299, EP 402716, DE 3842970,
DE 3518520, Khimico Farmaberticheskii Zhurnal 1983,
17(11), 1340-2, J. Org. Chem., 1975, 40(9), 1275-8.

The derivatives of the present invention are
5 obtained, for example, from thiazole reagents
substituted with a nitro radical, which are reduced via
standard reduction methods.

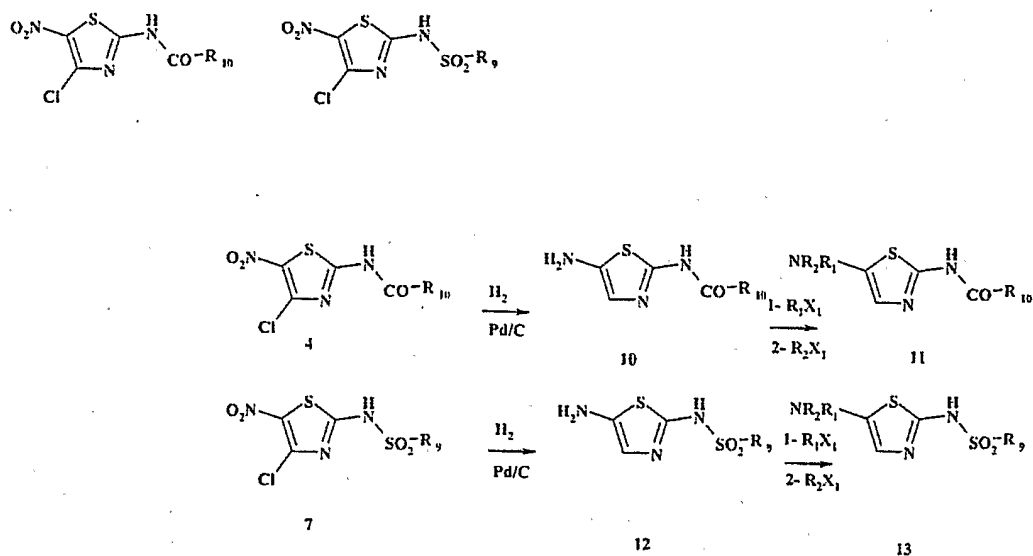
A first method consists in treating 2,4-di-
chlorothiazole with nitric acid to give 5-nitro-2,4-di-
10 chlorothiazole **2**, which reacts at temperatures of
between 0°C and 130°C in a polar solvent, with primary,
secondary or tertiary amines, and in particular with
ammonia, to give the 2-amino-4-chloro-5-nitrothiazole
compounds **3**. The acylation reaction of the amine in
15 position 2 is performed according to the standard
methods (for example, refer to *Advanced Organic
Chemistry, 3rd edition, J. March, Willey Interscience*)
with an acyl chloride $R_{10}-COCl$ or an anhydride
($R_{10}-CO$)₂-O, in aprotic solvents with a boiling point of
20 between 45°C and 180°C, to give the compounds of
formulae **4**. The nitro group is then reduced via the
action of a metal such as iron, tin or zinc and in the
catalytic presence of an acid such as protic acids, for
instance HCl, HBr or NH₄Cl, to give the 5-amino-4-
25 chloro-2-acylaminothiazoles **5**. This product is then
subjected to a standard alkylation reaction (for
example, refer to *Advanced Organic Chemistry, 3rd*

edition, J. March, Willey Interscience) with alkyl halides or alkyl O-sulphonates to give the desired compounds 6.

The compounds of formula 7 are obtained by reaction of alkyl or arylsulphonyl halides with the amine 3, in aprotic solvents with a boiling point of between 45°C and 180°C. The reactions for reduction of the nitrothiazole group 7 and then for alkylation of the amine 8 thus obtained are performed as mentioned above.



The compounds 10 (or 12, respectively) are obtained by heterogeneous catalytic hydrogenation of the compounds 4 (or 7, respectively), the catalyst possibly being, for example, palladium-on-charcoal, Raney nickel or palladium dihydroxide, in a polar solvent with a boiling point of between 60°C and 180°C. The 5-aminothiazole derivatives 10 and 12 are then reacted with electrophiles (halides, O-sulphonates, etc.) to give the desired compounds 11 and 13.

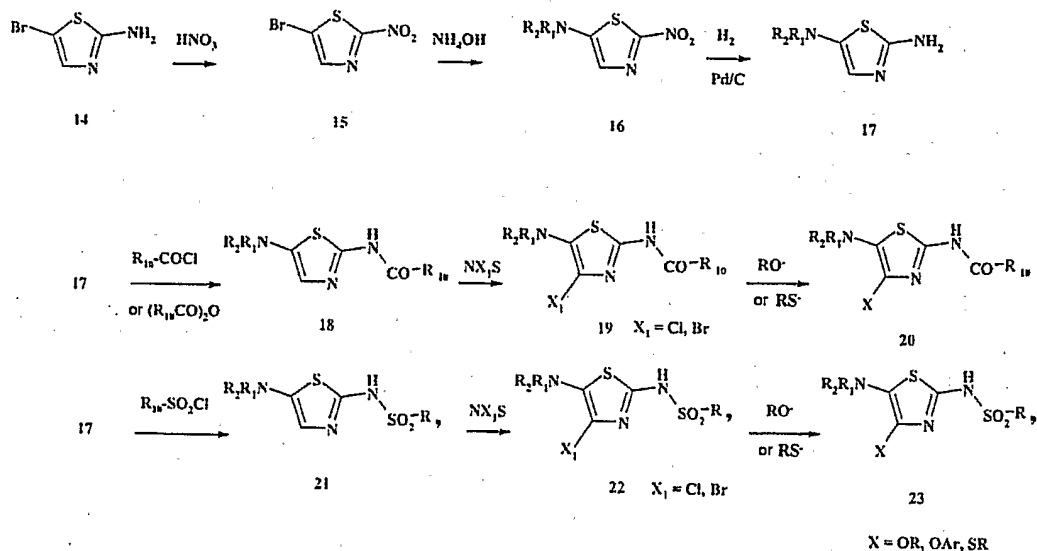


A second method consists in reacting commercial 2-amino-5-bromothiazole 14 with nitric acid in the presence of tetrafluoroboric acid and copper to give the nitro derivative 15. The bromine becomes labile and is reacted with amines NHR_1R_2 in polar solvents with boiling points of between 65°C and 180°C , to give the 2-nitro-5-aminothiazole derivatives 16. The reduction of the nitro group via standard methods (Reduction in Organic Chemistry, M. Hudlicky, Ellis Horwood series chemical Science), for example via heterogeneous catalytic hydrogenation with $\text{Pd}(0)$ or $\text{Pd}(\text{II})$ on charcoal, gives the diamine compounds 17. The acylation reaction of the amine in position 2 is performed according to the standard methods (for example, refer to *Advanced Organic Chemistry*, 3rd edition, J. March, Willey Interscience) with an acyl chloride $\text{R}_{10}-\text{COCl}$ or an anhydride $(\text{R}_{10}-\text{CO})_2-\text{O}$, in aprotic solvents with a boiling point of between 45°C and

180°C, to give the compounds of formula 18. The compounds of formula 21 are obtained via reaction of alkyl or arylsulphonyl halides with the amine 17 in aprotic solvents with a boiling point of between 45°C and 180°C.

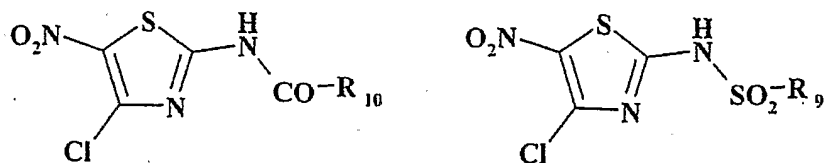
The introduction of the halogen atom into position 4 of the thiazole derivatives 18 and 21 is performed via the action of N-chlorosuccinimide or N-bromosuccinimide according to the standard methods, and allows access to compounds 19 and 22.

The introduction of an alkoxy, aryloxy or alkylthio group is performed via substitution of the halogen with the corresponding alkoxide or thioalkoxide anion and allows compounds 20 and 23 to be obtained.



15

Finally, a subject of the invention is the intermediate nitro derivatives of formula:



in which R9 and R10 are as defined above.

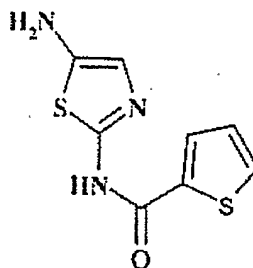
The examples that follow serve to illustrate the invention without, however, being limiting in

5 nature.

EXAMPLES

1 mmol of 5-nitro-2-(thien-2-yl)acylamino-thiazole derivative is added to 10 ml of an aqueous-alcoholic solution (80/20 ethanol/water) containing 10% of protic acid such as hydrochloric acid, ammonium chloride, acetic acid or sulphuric acid, and 0.5 g of zinc in powder form, at a temperature of 80°C. After total consumption of the nitro starting material, the reaction mixture is concentrated until a solid precipitates out, which is filtered off by suction, washed with diisopropyl ether and dried under vacuum to constant weight.

5-Amino-2-(thien-2-yl)acylaminothiazole (C₈H₇N₃OS₂) is thus obtained: 95% yield.



Examples of dyeingExample 1

The compositions below were prepared using the above compound:

5-Amino-2-(thien-2-yl)acylaminothiazole	4×10^{-4} mol
3,7-Diamino-5-methylpyrazolo[1,5-a]-pyrimidine	4×10^{-4} mol
Dye support (1)	(*)
Demineralized water qs	100 g

5	(*) Dye support (1) pH 9.5	
	DMSO	0.18 g
	96° ethyl alcohol	9.3 g
	Methyl alcohol	39.7 g
	Acetic acid	4.4 g
10	Sodium metabisulphite	0.204 g
	Pentasodium salt of diethylene triaminopentaacetic acid, as an aqueous 40% solution	1.1 g
	C ₈ -C ₁₅ alkyl polyglucoside sold as	5.3 g
15	60% solution under the name Oramix CG110 by the company SEPPIC	
	Benzyl alcohol	1.8 g
	Polyethylene glycol containing	2.7 g
	8 mol of EO	
20	pH 9.5 buffer of NH ₄ Cl/aqueous ammonia containing 20% NH ₃	31.0 g

At the time of use, the composition is mixed

with one third of its weight of 20-volumes aqueous hydrogen peroxide solution (6% by weight).

The mixture obtained is applied to a lock of grey hair containing 90% white hairs. After a leave-in time of 30 minutes, the lock is rinsed, washed with a standard shampoo, rinsed again and then dried.

The shade obtained is dark purple.

Example 2

The compositions below were prepared using the above compound:

5-Amino-2-(thien-2-yl)acylaminothiazole	4×10^{-4} mol
3,7-Diamino-5-methylpyrazolo[1,5-a]-pyrimidine	4×10^{-4} mol
Dye support (2)	(*)
Demineralized water qs	100 g

(*) Dye support (2) pH 7

DMSO	0.18 g
96° ethyl alcohol	9.3 g
Methyl alcohol	39.7 g
Acetic acid	4.4 g
Sodium metabisulphite	0.204 g
Pentasodium salt of diethylene triaminopentaacetic acid, as an aqueous 40% solution	1.1 g
C ₈ -C ₁₅ alkyl polyglucoside sold as 60% solution under the name Oramix CG110 by the company SEPPIC	5.3 g

	Benzyl alcohol	1.8 g
	Polyethylene glycol containing	2.7 g
	8 mol of EO	
	pH 7 buffer of 0.5M ammonium	31.0 g
5	chloride	

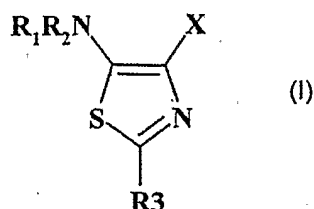
At the time of use, the composition is mixed with one third of its weight of 20-volumes aqueous hydrogen peroxide solution (6% by weight).

The mixture obtained is applied to a lock of
10 grey hair containing 90% white hairs. After a leave-in time of 30 minutes, the lock is rinsed, washed with a standard shampoo, rinsed again and then dried.

The shade obtained is dark purple.

CLAIMS

1. Thiazole derivative of formula (I) below, and the addition salts thereof with an acid or a base:



(I)

5

in which:

• R₁ and R₂, which may be identical or different, represent:

- a hydrogen atom;
- a phenyl radical optionally substituted with one or more radicals chosen from halogens, hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, C₁-C₄ thioether, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄;
- a linear or branched C₁-C₈ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄.

radicals,

- R₁ and R₂ may form, with the nitrogen atom to which they are attached, a 5- to 8-membered heterocycle, one or more carbon atoms of the carbon-based ring of which may be replaced with an oxygen, nitrogen or sulphur atom or with an SO₂ group, the carbon atoms of the ring possibly being substituted with a radical R₄ and the ring not comprising a peroxide bond or diazo or nitroso radicals;

- R₄ represents:

- a halogen atom;
- a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, carboxyl, C₁-C₄ alkoxy, carbonyl, C₁-C₄ alkoxy or NR₅R₆ radicals;
- a carboxyl radical;
- a mono- or di(C₁-C₄)alkylcarboxamido radical;
- a (C₁-C₄)alkylsulphonyl radical;
- an alkylsulphonamido radical;
- a hydroxyl radical;
- a C₁-C₄ alkoxy radical;
- a C₂-C₄ hydroxyalkoxy radical;
- an aminosulphonyl radical;
- a C₁-C₄ thioether radical;
- a (C₁-C₄)alkyl sulfoxide radical;
- a (C₁-C₄)alkylsulphonyl radical;

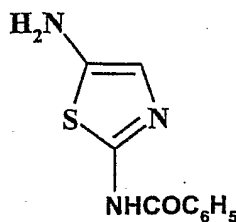
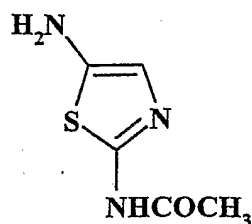
- a radical NR_7R_8 ;

- R_3 represents a radical $\text{R}_9\text{SO}_2\text{NH}-$ or a radical $\text{R}_{10}\text{C}(\text{O})\text{NH}-$ with R_9 and R_{10} , which may be identical or different, representing:

- 5 - a phenyl radical or a 5- or 6-membered aromatic heterocycle, these radicals optionally being substituted with one or more radicals chosen from halogens, hydroxyl, $\text{C}_1\text{-C}_4$ alkoxy, carboxyl, $\text{C}_1\text{-C}_4$ alkoxy carbonyl, mono- or di($\text{C}_1\text{-C}_4$)alkylcarboxamido, (
- 10 ($\text{C}_1\text{-C}_4$)alkylsulphonyl, sulphonic, ($\text{C}_1\text{-C}_4$)alkyl sulphoxide, $\text{C}_1\text{-C}_4$ thioether, alkylsulphonamido or $\text{NR}_{11}\text{R}_{12}$ radicals, or a $\text{C}_1\text{-C}_4$ alkyl radical optionally substituted with one or more hydroxyl, $\text{C}_1\text{-C}_4$ alkoxy, carboxyl, mono- or di($\text{C}_1\text{-C}_4$)alkyl-
- 15 carboxamido, ($\text{C}_1\text{-C}_4$)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or $\text{NR}_{13}\text{R}_{14}$,
- a linear or branched $\text{C}_1\text{-C}_8$ alkyl radical optionally substituted with one or more hydroxyl, OR_{15} , carboxyl, $\text{C}_1\text{-C}_4$ alkoxy carbonyl, mono- or
- 20 di($\text{C}_1\text{-C}_4$)alkylcarboxamido, ($\text{C}_1\text{-C}_4$)alkylsulphonyl, sulphonic, ($\text{C}_1\text{-C}_4$)alkyl sulphoxide, alkyl-sulphonamido or $\text{NR}_{16}\text{R}_{17}$ radicals;
- with R_{15} representing a $\text{C}_1\text{-C}_4$ alkyl radical optionally substituted with one or more radicals
- 25 chosen from hydroxyl, $\text{C}_1\text{-C}_2$ alkoxy, amino, (di) ($\text{C}_1\text{-C}_4$)alkylamino and (poly)hydroxy($\text{C}_2\text{-C}_4$)-alkylamino radicals;

- R₅, R₆, R₇, R₈, R₁₁, R₁₂, R₁₃, R₁₄, R₁₆ and R₁₇, which may be identical or different, represent a hydrogen atom, a (C₁-C₄)alkylsulphonyl or (C₁-C₄)alkyl-CO radical, a mono- or di(C₁-C₄)alkylcarboxamido radical, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, (C₁-C₄)alkylsulphonyl, (C₁-C₄)-alkylsulphonamido, carboxyl, mono- or (di)(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkyl sulphoxide, amino, (di)(C₁-C₄)-alkylamino or (poly)hydroxy(C₂-C₄)alkylamino;
- 10 - R₇ and R₈ may also form, with the nitrogen atom that bears them, a 5- to 8-membered ring optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₂ alkoxy, carboxyl, alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)-alkylcarboxamido or NR₁₃R₁₄;
- X represents a hydrogen atom; a halogen atom; a C₁-C₄ alkoxy radical; a phenoxy radical optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, C₁-C₄ alkoxy carbonyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, C₁-C₄ thioether, alkylsulphonamido, NR₁₃R₁₄ and C₁-C₄ alkyl radicals; a C₁-C₄ thioether radical optionally substituted with a hydroxyl, C₁-C₂ alkoxy, carboxyl, sulphonic or amino radical,

with the exception of the derivatives



2. Derivative according to Claim 1, in which R1 and R2 represent, independently of each other:

- 5 - a hydrogen atom;
- a phenyl radical optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulfoxide, C₁-C₄ thioether,
- 10 alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)-alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulfoxide, alkylsulphonamido or NR₁₃R₁₄;
- 15 - a linear or branched C₁-C₆ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, carboxyl, C₁-C₄ alkoxycarbonyl (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulfoxide, alkylsulphonamido or NR₁₃R₁₄ radicals.

- 20 3. Derivative according to Claim 2, in which R₁ and R₂, which may be identical or different, represent a hydrogen atom; a phenyl radical; a linear or branched C₁-C₄ alkyl radical, optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, amino,

di(C₁-C₄)alkylamino, carboxyl, (C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonamido or NR₁₃R₁₄ radicals in which R₁₃ and R₁₄, which may be identical or different, represent a hydrogen atom, a (C₁-C₄)alkyl-CO or a C₁-C₂ alkyl
5 radical optionally substituted with a hydroxyl or a C₁-C₂ alkoxy.

4. Derivative according to Claim 3, in which R₁ and R₂, which may be identical or different, represent a hydrogen atom, methyl, 2-hydroxyethyl, 2-
10 carboxyethyl or 1,2-dihydroxyethyl, or phenyl.

5. Derivative according to Claim 1, in which R₁ and R₂ form, with the nitrogen atom to which they are attached, a 5- to 8-membered heterocycle chosen from pyrrolidine, piperidine, homopiperidine,
15 piperazine and homopiperazine, the said rings possibly being substituted with one or more radicals R₄.

6. Derivative according to Claim 5, in which R₁ and R₂ form, together with the nitrogen atom to which they are attached, a heterocycle chosen from
20 pyrrolidine, 2,5-dimethylpyrrolidine, proline, 3-hydroxyproline, 4-hydroxyproline, 2,4-dicarboxypyrrolidine, 3-hydroxy-2-hydroxymethylpyrrolidine, 2-carboxamidopyrrolidine, 3-hydroxy-2-carboxamidopyrrolidine, 2-(diethyl-
25 carboxamido)pyrrolidine, 2-hydroxymethylpyrrolidine, 3,4-dihydroxy-2-hydroxymethylpyrrolidine, 3-hydroxypyrrolidine, 3,4-dihydroxypyrrolidine, 3-amino-

pyrrolidine, 3-methylaminopyrrolidine, 4-amino-3-hydroxypyrrolidine, 3-hydroxy-4-(2-hydroxyethyl)-aminopyrrolidine, piperidine, 2,6-dimethylpiperidine, 2-carboxypiperidine, 2-carboxamidopiperidine,
5 2-hydroxymethylpiperidine, 3-hydroxy-2-hydroxymethylpiperidine, 3-hydroxypiperidine, 4-hydroxypiperidine, 3-hydroxymethylpiperidine, homopiperidine, 2-carboxyhomopiperidine, 2-carboxamidohomopiperidine, homopiperazine, N-methylhomopiperazine and N- β -hydroxy-
10 ethylhomopiperazine, and the addition salts thereof.

7. Derivative according to Claim 5 or 6, in which R_1 and R_2 form, together with the nitrogen atom to which they are attached, a heterocycle chosen from pyrrolidine, 3-hydroxypyrrolidine, 3-aminopyrrolidine,
15 proline, 3-hydroxyproline, piperidine, 3-hydroxypiperidine, 4-hydroxypiperidine, homopiperidine, homopiperazine, N-methylhomopiperazine and N- β -hydroxyethylhomopiperazine, and the addition salts thereof.

8. Derivative according to any one of
20 Claims 1 to 7, in which R_3 represents a pyridyl, pyrimidinyl, pyrazolyl, thiazolyl, furyl, imidazolyl or thienyl aromatic heterocycle.

9. Derivative according to Claims 1 to 8, in which R_3 represents a radical R_9SO_2NH- or a radical
25 $R_{10}C(O)NH-$; with R_9 and R_{10} , which may be identical or different, representing:

- a phenyl radical or a 5- or 6-membered aromatic

heterocycle such as pyridyl, pyrimidinyl, pyrazolyl, thiazolyl, furyl, imidazolyl or thienyl, these radicals being optionally substituted with one or more radicals chosen from

5 halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido or NR₁₁R₁₂ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-

10 carboxamido or NR₁₃R₁₄ radicals;

- a linear or branched C₁-C₈ alkyl radical substituted with one or more radicals chosen from hydroxyl, C₁-C₂ alkoxy, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl,

15 sulphonic, (C₁-C₄)alkyl sulphoxide, alkyl-sulphonamide and NR₁₆R₁₇ radicals;

- R₁₁, R₁₂, R₁₃, R₁₄, R₁₆ and R₁₇, which may be identical or different, represent a hydrogen atom, acyl, a carboxamido or a C₁-C₄ alkyl radical optionally

20 substituted with one or more hydroxyl, C₁-C₄ alkoxy, (C₁-C₄)alkylsulphonyl, (C₁-C₄)alkylsulphonamido, carboxyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkyl sulphoxide, amino, (di)(C₁-C₄)alkylamino or (poly)hydroxy(C₂-C₄)alkylamino radicals.

25 10. Derivative according to Claim 9, in which R₃ represents a radical R₉SO₂NH- or a radical R₁₀C(O)NH- with R₉ and R₁₀, which may be identical or

different, chosen from an alkyl radical, a phenyl radical, a pyrazolyl radical, a thiazolyl radical, a pyridyl radical and a thienyl radical, these radicals possibly being substituted.

5 11. Derivative according to Claim 10, in which R_3 represents a radical $R_{10}C(O)NH-$ in which R_{10} represents a methyl, ethyl, 2-hydroxyethyl, 2-carboxyethyl, phenyl, pyrazolyl, thienyl or pyridyl radical and R_9 represents a methyl, phenyl or tolyl radical.

10 12. Derivative according to any one of Claims 1 to 11, in which X represents a hydrogen atom, chlorine or an alkoxy radical.

 13. Derivative according to any one of Claims 1 to 12, chosen from the following compounds,
15 and the addition salts thereof with an acid or a base:

5-amino-2-methylsulphonylaminothiazole

5-amino-2-phenylsulphonylaminothiazole

5-amino-2-tolylsulphonylaminothiazole

5-amino-2-thiazolylsulphonylaminothiazole

20 5-amino-2-pyridylsulphonylaminothiazole

5-amino-2-(pyrid-2-yl)acylaminothiazole

5-amino-2-(pyrid-3-yl)acylaminothiazole

5-amino-2-(pyrid-4-yl)acylaminothiazole

5-amino-2-isopropylacylaminothiazole

25 5-amino-2-(thien-2-yl)acylaminothiazole

5-methylamino-2-methylsulphonylaminothiazole

- 5-methylamino-2-phenylsulphonylaminothiazole
5-methylamino-2-tolylsulphonylaminothiazole
5-methylamino-2-thiazolylsulphonylaminothiazole
5-methylamino-2-pyridylsulphonylaminothiazole
5 5-methylamino-2-phenacylaminothiazole
5-methylamino-2-(pyrid-2-yl)acylaminothiazole
5-methylamino-2-(pyrid-3-yl)acylaminothiazole
5-methylamino-2-(pyrid-4-yl)acylaminothiazole
5-methylamino-2-acetylaminothiazole
10 5-methylamino-2-isopropylacylaminothiazole
5-methylamino-2-(thien-2-yl)acylaminothiazole

5-(2-hydroxyethyl)amino-2-methylsulphonylaminothiazole
5-(2-hydroxyethyl)amino-2-phenylsulphonylaminothiazole
15 5-(2-hydroxyethyl)amino-2-tolylsulphonylaminothiazole
5-(2-hydroxyethyl)amino-2-thiazolylsulphonylamino-
thiazole

5-(2-hydroxyethyl)amino-2-pyridylsulphonylaminothiazole
5-(2-hydroxyethyl)amino-2-phenacylaminothiazole
20 5-(2-hydroxyethyl)amino-2-(pyrid-2-yl)acylaminothiazole
5-(2-hydroxyethyl)amino-2-(pyrid-3-yl)acylaminothiazole
5-(2-hydroxyethyl)amino-2-(pyrid-4-yl)acylaminothiazole
5-(2-hydroxyethyl)amino-2-acetylaminothiazole
5-(2-hydroxyethyl)amino-2-isopropylacylaminothiazole
25 5-(2-hydroxyethyl)amino-2-(thien-2-yl)acylaminothiazole

5-amino-4-chloro-2-methylsulphonylaminothiazole

- 5-amino-4-chloro-2-phenylsulphonylaminothiazole
5-amino-4-chloro-2-tolylsulphonylaminothiazole
5-amino-4-chloro-2-thiazolylsulphonylaminothiazole
5-amino-4-chloro-2-pyridylsulphonylaminothiazole
5 5-amino-4-chloro-2-phenacylaminothiazole
5-amino-4-chloro-2-(pyrid-2-yl)acylaminothiazole
5-amino-4-chloro-2-(pyrid-3-yl)acylaminothiazole
5-amino-4-chloro-2-(pyrid-4-yl)acylaminothiazole
5-amino-4-chloro-2-acetylaminothiazole
10 5-amino-4-chloro-2-isopropylacylaminothiazole
5-amino-4-chloro-2-(thien-2-yl)acylaminothiazole

5-methylamino-4-chloro-2-methylsulphonylaminothiazole
5-methylamino-4-chloro-2-phenylsulphonylaminothiazole
15 5-methylamino-4-chloro-2-tolylsulphonylaminothiazole
5-methylamino-4-chloro-2-thiazolylsulphonylamino-
thiazole
5-methylamino-4-chloro-2-pyridylsulphonylaminothiazole
5-methylamino-4-chloro-2-phenacylaminothiazole
20 5-methylamino-4-chloro-2-(pyrid-2-yl)acylaminothiazole
5-methylamino-4-chloro-2-(pyrid-3-yl)acylaminothiazole
5-methylamino-4-chloro-2-(pyrid-4-yl)acylaminothiazole
5-methylamino-4-chloro-2-acetylaminothiazole
5-methylamino-4-chloro-2-isopropylacylaminothiazole
25 5-methylamino-4-chloro-2-(thien-2-yl)acylaminothiazole

5-(2-hydroxyethyl)amino-4-chloro-2-methylsulphonyl-

- aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-phenylsulphonyl-
aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-tolylsulphonyl-
5 aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-thiazolylsulphonyl-
aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-pyridylsulphonyl-
aminothiazole
- 10 5-(2-hydroxyethyl) amino-4-chloro-2-phenacylamino-
thiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-(pyrid-2-yl) acyl-
aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-(pyrid-3-yl) acyl-
15 aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-(pyrid-4-yl) acyl-
aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-acetylaminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-isopropylacyl-
20 aminothiazole
- 5-(2-hydroxyethyl) amino-4-chloro-2-(thien-2-yl) acyl-
aminothiazole
- 5-(pyrrolidin-1-yl)-2-methylsulphonylaminothiazole
- 25 5-(pyrrolidin-1-yl)-2-phenylsulphonylaminothiazole
- 5-(pyrrolidin-1-yl)-2-tolylsulphonylaminothiazole
- 5-(pyrrolidin-1-yl)-2-thiazolylsulphonylaminothiazole

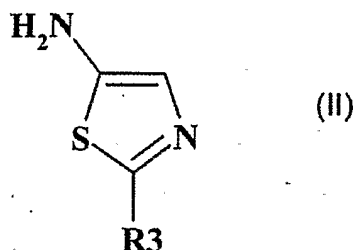
- 5-(pyrrolidin-1-yl)-2-pyridylsulphonylaminothiazole
5-(pyrrolidin-1-yl)-2-phenacylaminothiazole
5-(pyrrolidin-1-yl)-2-(pyrid-2-yl)acylaminothiazole
5-(pyrrolidin-1-yl)-2-(pyrid-3-yl)acylaminothiazole
5 5-(pyrrolidin-1-yl)-2-(pyrid-4-yl)acylaminothiazole
5-(pyrrolidin-1-yl)-2-acetylaminothiazole
5-(pyrrolidin-1-yl)-2-isopropylacylaminothiazole
5-(pyrrolidin-1-yl)-2-(thien-2-yl)acylaminothiazole
10 5-(pyrrolidin-1-yl)-4-chloro-2-methylsulphonylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-phenylsulphonylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-tolylsulphonylamino-
15 thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-thiazolylsulphonyl-
aminothiazole
5-(pyrrolidin-1-yl)-4-chloro-2-pyridylsulphonylamino-
thiazole
20 5-(pyrrolidin-1-yl)-4-chloro-2-phenacylaminothiazole
5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-2-yl)acylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-3-yl)acylamino-
thiazole
25 5-(pyrrolidin-1-yl)-4-chloro-2-(pyrid-4-yl)acylamino-
thiazole
5-(pyrrolidin-1-yl)-4-chloro-2-acetylaminothiazole

5-(pyrrolidin-1-yl)-4-chloro-2-isopropylacylamino-thiazole

5-(pyrrolidin-1-yl)-4-chloro-2-(thien-2-yl)acylamino-thiazole

5 and also the addition salts thereof with an acid or a base.

14. Derivative according to any one of Claims 1 to 12, of formula (II)



10 in which R_3 is as defined above in Claims 1 to 13.

15 15. Derivative according to any one of Claims 1 to 14, chosen from 5-(pyrrolidin-1-yl)-2-(thien-2-yl)acylaminothiazole, and the addition salts thereof.

16. Composition for dyeing keratin fibres, comprising, in a medium that is suitable for dyeing:

- at least one oxidation base, and
- at least one thiazole derivative of formula (I) in which:

20 • R_1 and R_2 , which may be identical or different, represent:

- a hydrogen atom;
- a phenyl radical optionally substituted with one or more radicals chosen from halogens, hydroxyl,

- C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, C₁-C₄ thioether, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl radical
- 5 optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄;
- a linear or branched C₁-C₈ alkyl radical
- 10 optionally substituted with one or more hydroxyl, C₁-C₂ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-carboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄ radicals,
- 15 - R₁ and R₂ may form, together with the nitrogen atom to which they are attached, a 5- to 8-membered heterocycle, one or more carbon atoms of the carbon-based ring of which may be replaced with an oxygen, nitrogen or sulphur atom or with
- 20 an SO₂ group, the carbon atoms of the ring possibly being substituted with a radical R₄ and the ring not comprising a peroxide bond or diazo or nitroso radicals;
- R₄ represents:
- 25 - a halogen atom;
- a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, carboxyl, C₁-C₄

- alkoxycarbonyl, C₁-C₄ alkoxy or NR₅R₆ radicals;
- a carboxyl radical;
 - a mono- or di(C₁-C₄)alkylcarboxamido radical;
- 5 - a (C₁-C₄)alkylsulphonyl radical;
- an alkylsulphonamido radical;
 - a hydroxyl radical;
 - a C₁-C₄ alkoxy radical;
 - a C₂-C₄ hydroxyalkoxy radical;
- 10 - an aminosulphonyl radical;
- a C₁-C₄ thioether radical;
 - a (C₁-C₄)alkyl sulphoxide radical;
 - a (C₁-C₄)alkylsulphonyl radical;
 - a radical NR₇R₈;
- 15 • R₃ represents a radical R₉SO₂NH- or a radical R₁₀C(O)NH- with R₉ and R₁₀, which may be identical or different, representing:
- a phenyl radical or a 5- or 6-membered aromatic heterocycle, these radicals optionally being
- 20 substituted with one or more radicals chosen from halogens, hydroxyl, C₁-C₄ alkoxy, carboxyl, C₁-C₄ alkoxycarbonyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, (C₁-C₄)alkyl sulphoxide, C₁-C₄ thioether, alkylsulphonamido or
- 25 NR₁₁R₁₂ radicals, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)alkyl-

carboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, alkyl sulphoxide, alkylsulphonamido or NR₁₃R₁₄,
- a linear or branched C₁-C₈ alkyl radical optionally substituted with one or more hydroxyl,
5 OR₁₅, carboxyl, C₁-C₄ alkoxy, carbonyl, mono- or di(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkylsulphonyl, sulphonic, (C₁-C₄)alkyl sulphoxide, alkylsulphonamido or NR₁₆R₁₇ radicals;
with R₁₅ representing a C₁-C₄ alkyl radical
10 optionally substituted with one or more radicals chosen from hydroxyl, C₁-C₂ alkoxy, amino, (di)(C₁-C₄)alkylamino and (poly)hydroxy(C₂-C₄)alkylamino radicals;
- R₅, R₆, R₇, R₈, R₁₁, R₁₂, R₁₃, R₁₄, R₁₆ and R₁₇, which may
15 be identical or different, represent a hydrogen atom, a (C₁-C₄)alkylsulphonyl or (C₁-C₄)alkyl-CO radical, a mono- or di(C₁-C₄)alkylcarboxamido radical, or a C₁-C₄ alkyl radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, (C₁-C₄)alkylsulphonyl, (C₁-C₄)alkylsulphonamido, carboxyl, mono- or (di)(C₁-C₄)alkylcarboxamido, (C₁-C₄)alkyl sulphoxide, amino, (di)(C₁-C₄)alkylamino or (poly)hydroxy(C₂-C₄)alkylamino;
20 - R₇ and R₈ may also form, with the nitrogen atom that bears them, a 5- to 8-membered ring optionally
25 substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₂ alkoxy, carboxyl, alkylsulphonamido and NR₁₃R₁₄ radicals, or a C₁-C₄ alkyl

radical optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, mono- or di(C₁-C₄)-alkylcarboxamido or NR₁₃R₁₄;

X represents a hydrogen atom; a halogen atom; a C₁-C₄ alkoxy radical; a phenoxy radical optionally substituted with one or more radicals chosen from halogens and hydroxyl, C₁-C₄ alkoxy, carboxyl, C₁-C₄ alkoxy carbonyl, mono- or di(C₁-C₄)-alkylcarboxamido, (C₁-C₄)-alkylsulphonyl, sulphonic, alkyl sulphoxide, C₁-C₄ thioether, alkylsulphonamido, NR₁₃R₁₄ and C₁-C₄ alkyl radicals; a C₁-C₄ thioether radical optionally substituted with a hydroxyl, C₁-C₂ alkoxy, carboxyl, sulphonic or amino radical.

17. Composition according to Claim 16, in which the oxidation base(s) is(are) chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

18. Composition according to either of Claims 16 and 17, in which the oxidation base(s) is(are) each present in an amount of between 0.001% and 10% by weight relative to the total weight of the dye composition.

19. Composition according to any one of Claims 16 to 18, comprising one or more additional couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based

couplers and heterocyclic couplers other than those of formula (I), and the addition salts thereof.

20. Composition according to any one of Claims 15 to 19, in which the coupler(s) is(are) each
5 present in an amount of between 0.001% and 10% by weight relative to the total weight of the dye composition.

21. Process for the oxidation dyeing of keratin fibres, characterized in that a composition as
10 defined in any one of Claims 16 to 20 is applied to the fibres in the presence of an oxidizing agent for a time that is sufficient to develop the desired colour.

22. Process according to Claim 21, in which the oxidizing agent is chosen from hydrogen peroxide,
15 urea peroxide, alkali metal bromates, persalts, peracids and oxidase enzymes.

23. Process according to Claim 22, in which the oxidizing agent is mixed at the time of use with the composition as defined according to any one of
20 Claims 16 to 19.

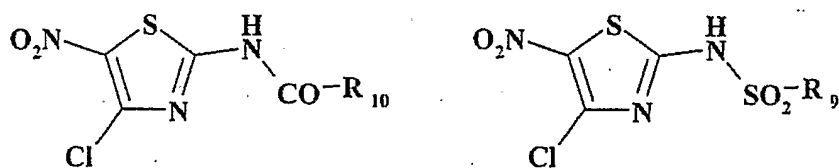
24. Process according to Claim 23, in which the oxidizing agent is applied to the fibres simultaneously with or sequentially to the composition as defined according to any one of Claims 16 to 19, in
25 the form of an oxidizing composition.

25. Multi-compartment device, in which a first dye compartment contains a composition as defined

in any one of Claims 16 to 19 and a second compartment contains an oxidizing agent.

26. Use of at least one thiazole derivative as defined according to any one of Claims 1 to 15, for the oxidation dyeing of keratin fibres.

27. Intermediate nitro derivatives of formula:



in which R₉ and R₁₀ are as defined in Claims 1 to 15.

INTERNATIONAL SEARCH REPORT

Intern Application No
PCT/EP2004/007994

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07D417/12 A61K7/13 A61Q5/10 C07D277/58		
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 7 C07D A61K A61Q 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 practical, search terms used) EPO-Internal, CHEM ABS Data, BEILSTEIN Data		
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° 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 document 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 3 December 2004		Date of mailing of the international search report 13/12/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Schuemacher, A

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