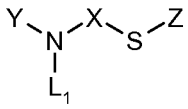
Thiol derivative dyes

The present invention relates to novel thiol derivative dyes, compositions thereof, to processes for their preparation and to their use for the dyeing of organic materials, such as keratin fibers, wool, leather, silk, cellulose or polyamides, especially keratin-containing fibers, cotton or nylon, and preferably hair, more preferably human hair.

It is known, for example, from WO 95/01772 that cationic dyes can be used for the dyeing of organic material, for example keratin, silk, cellulose or cellulose derivatives, and also synthetic fibers, for example polyamides. Cationic dyes exhibit very brilliant shades. A disadvantage is their unsatisfactory fastness to washing.

The technical problem is to provide dyes that are distinguished by deep dyeing having good fastness properties with respect to washing, light, shampooing and rubbing.

Accordingly, the present invention relates to compounds of formula

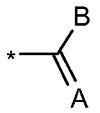
(1)  , wherein

L_1 is hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl;

X is C_1-C_{12}alkylene, C_2-C_{12}alkenylene, C_5-C_{10}cycloalkylene, C_5-C_{10}arylene, or C_5-C_{10}arylene-C_1-C_{10}alkylene, which may by interrupted by -O-, -NH-, -S-, -CO-, o -SO_2-;

Y is the residue of an organic dye

Z is a group of formula

(1b)  ; or -CΞN; wherein

A is O; S; or N-L_2;

B is L_3; -OL_3; -NL_3L_4; or -SL_3; and

L_2, L_3 and L_4, independently from each other are hydrogen; C_1-C_{12}alkyl; C_6-C_{12}aryl; or C_6-C_{12}aryl-C_1-C_{12}alkyl.

C_1-C_{14}alkyl is for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2'-dimethylpropyl, cyclopentyl, cyclohexyl, n-hexyl, n-octyl, 1,1',3,3'-tetramethylbutyl or 2-ethylhexyl, nonyl, decyl, undecyl or dodecyl.

C_1-C_{12}alkylene is for example methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, tert-butylene, n-pentylene, 2-pentylene, 3-pentylene or 2,2'-dimethylpropylene, n-hexylene, n-octylene, 1,1',3,3'-tetramethylbutylene, 2-ethylhexylene, nonylene, decylene, undecylene or dodecylene.

Alkylene may be straight-chain, branched, or, from C_5alkyl upwards, monocyclic or polycyclic, and may be interrupted by hetero atoms, such as such as O, S, -CO-, N, NH, $NR_{54,}$ -OCO-, -CO(OR_4)-, -$CONR_4$-, -(R_5)NC(O)-; for example C_1-C_{10}alkylene may be a resisue such as: $-CH_2CH_2$-O-CH_2CH_2-O-CH_2CH_2-, -CH_2CH_2-O-CH_2CH_2-, -CH_2CH_2-O-CH_2-, -CH_2-O-CH_2-, $-CH_2CH_2$-CH_2CH_2-O-CH_2-CH_2-, -CH_2CH_2-CH($N(CH_3)_2$)-CH_2-CH_2-, CH_2-NH_2-CH_2-CH_2, $-CH_2CH_2$-NH-CH_2CH_2-, $-CH_2CH_2$-NCH_3-CH_2CH_2-, –CO-CH_2-, -CH_2CO-, -CH_2CH_2-NHCO-CH_2CH_2-, $-CH_2CH_2$-CONH-CH_3-CH_2CH_2-, $-CH_2CH_2$-NCH_3CO-CH_2CH_2-, -CH_2CH_2-CONCH_3-CH_3-CH_2CH_2-, $-CH_2$-NHCO-CH_2CH_2-, or $-CH_2CH_2$-NHCO-CH_2-, -CH_2CH_2-CONH-CH_2- or -CH_2-CONH-CH_2CH_2-.

C_5-C_{10}cycloalkylene is for example cyclopentylene, cyclohexylene, cycloheptylene, cyclo-octylene, cyclononylene or cyclodecylene.

C_5-C_{10}arylene is for example phenylene or naphthylene.

Aryl-alkylene is for example C_5-C_{10}aryl-C_1-C_{10}alkylene.

Alkyl-arylene is for example C_1-C_{10}alkyl-C_5-C_{10}arylene.

Preferably, in the compounds of formula (1)

X is C_1-C_{12}alkylene.; and more preferably

X is ethylene.

Preferably, in the compounds of formula (1)

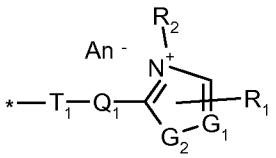
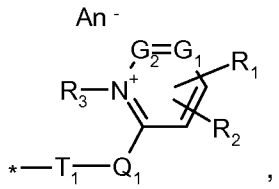
Y is selected from are selected from the group of anthraquinone, acridine, azo, azo-methine, dioxaxin, hydrazomethine, benzodifuranone, coumarine, diketopyrrolopyrrol, dioxaxine, diphenylmethane, formazane, indigoid, indophenol, naphtalimide, naphtha-quinone, nitroaryl, merocyanine, methine, oxazine, perinone, perylene, pyrenequinone,

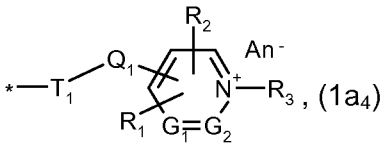
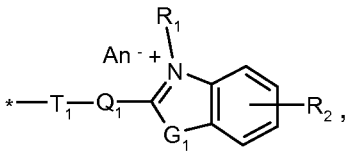
phtalocyanine, phenazine, quinoneimine, quinacridone, quinophtalone, triphenylmethane, xanthene, thiazine dye, thioxanthene and direct dyes.

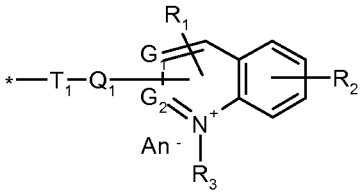
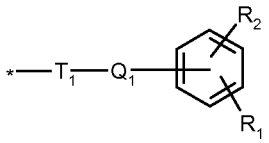
More preferably,

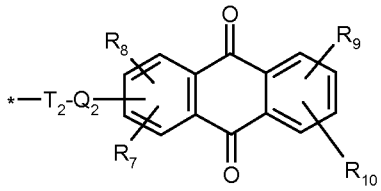
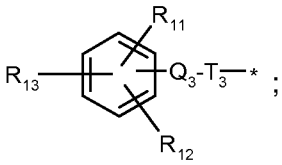
Y is selected from a nitroaryl, an anthraquinone, a naphthoquinone, a pyrenequinone, a phathylocyanine, formazan, a methine, an azomethine, a dioxacin, a phenazine, an azo, an indophenol, a triphenylmethane, a xanthene, a thioxanthene and a cationic direct dye.

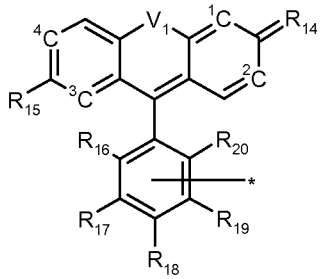
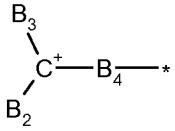
In particular,

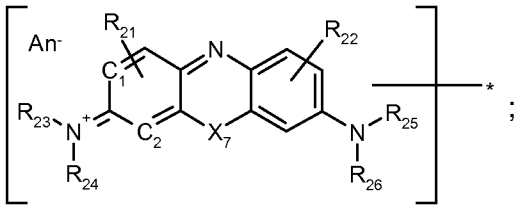
Y is a radical of formula (1a$_1$)  ; (1a$_2$)  ,

(1a$_3$)  , (1a$_4$)  ,

(1a$_5$)  ; (1a$_6$) 

(1b)  ; (1c)  ;

(1d)  ; (1e)  ; or

(1f)  ;

wherein the mixture comprisies at least two compounds of formula (1), and/or at least two compounds of formula (2) and/or at least one compound of formula (1) and at least one compound of formula (2), wherein

R_1, R_2 and R_3 independently from each other hydrogen; halogen; C_1-C_{16}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; phenyl, which substituted or unsubstituted; a carboxylic acid radical; sulfonic acid radical; hydroxy; nitrile; C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; halogen; sulfonylamino; SR_{33}; $NR_{33}R_{34}$; OR_{33}; SO_2; $COOR_{33}$; $NR_{33}COR_{34}$; or $CONR_{33}$;

Q_1 is a bivalent radical selected from -N=N-; $-CR_d=N-$; $-N=CR_d-$; $-NR_d-N=CR_e-$; and $-R_dC=N-NR_e-$;

T_1 is a bivalent radical of an aromatic or heteroaromatic substituted or unsubstituted compound;

R_d and R_e independently from each other are hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1 C_{10}alkyl-C_5-C_{10}aryl; or C_5-C_{10}aryl-C_1-C_{10}alkyl;

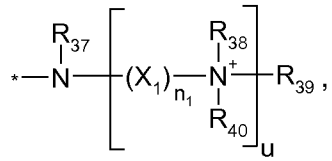
R_{33} and R_{34} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, $-NH_2$, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, $-NO_2$, carboxy or hydroxy;

R_4, R_5 and R_6 independently from each other are hydrogen; C_1-C_{20}alkyl or C_1-C_{20}alkoxy, which may be substituted by one or more C_1-C_5alkoxy, halogen, $-NH_2$, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, $-NO_2$ or hydroxy; C_3-C_6cycloalkyl; -C(O)H; -C(O)-C_1-

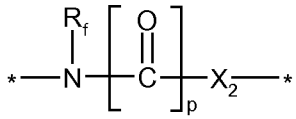
C_5alkyl; halogen; NO_2; OH; phenyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; or a radical of formula -$NR_{35}R_{36}$;

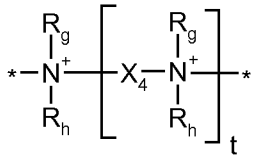
R_{35} and R_{36} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2, carboxy or hydroxy;

R_7, R_8, R_9 and R_{10} independently from each other are hydrogen; C_1-C_{20}alkyl; C_1-C_{20}alkoxy; C_3-C_6cycloalkyl; halogen; NO_2; OH; SH; or a radical of formula

(1c$_1$) 

X_1 is C_1-C_{18}alkylene; -(CO)-C_1-C_{18}alkylene C_1-C_{18}arylene; C_6-C_{18}arylene-C_1-C_{12}alkylene; or -$(OCH_2CH_2)_{n2}$-O-;

T_2 is a radical of formula (1c$_2$)  ; or -O-$(X_3)_s$;

Q_2 is a cationic biradical of a saturated, aromatic or heteroaromatic group; or a radical of formula (1c$_3$) 

R_f, R_g and R_h independently from each other are hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

X_2, X_3 and X_4 independently from each other are C_1-C_{18}alkylene; -(CO)-C_1-C_{18}alkylene-C_1-C_{18}arylene; C_6-C_{18}arylene-C_1-C_{12}alkylene; or -$(OCH_2CH_2)_{n1}$-O-;

p is 0; or 1

R_{37} is hydrogen; or C_1-C_{20}alkyl;

R_{38}, R_{39} and R_{40} independently from each other are hydrogen, C_1-C_{20}alkyl, C_4-C_{12}cycloalkyl, C_6-C_{13}aralkyl; phenyl-C_1-C_5alkyl; or R_{38} and R_{39} together with the linking nitrogen atom form a C_4-C_{12}-membered heterocyclic ring which may be interrupted by one or more than one –O- or –NH- goups;

u is 0 or 1;

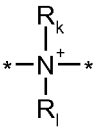
n_1 and n_2 independently from each other are a number from 1 to 5;

s is 0; or 1;

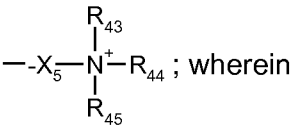
t is 0; or 1;

R_{11}, R_{12} and R_{13} independently from each other are hydrogen; C_1-C_{20}alkyl or C_1-C_{20}alkoxy, which may be substituted by one or more C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkyl-amino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; C_3-C_6cycloalkyl; -C(O)H; -C(O)-C_1-C_5alkyl; -C(O)OH; -C(O)O-C_1-C_5alkyl; halogen; NO_2; OH; SH; phenyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; or a radical -$NR_{41}R_{42}$;

Q_3 is is –C(O)-; -C(O)O-; -OCO-; -N(R_i)-X_5-; -CON(R_i)-; -(R_i)NC(O)-; –O-; -S-; -S(O)-; or -$S(O)_2$-;

T_3 is the direct bond;  ; or a cationic biradical of a saturated, aromatic or heteroaromatic group;

R_i, R_k, R_l independently from each other are C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

R_{41} and R_{42} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2, carboxy or hydroxy; or a radical of formula  ; wherein at least one of the radicals R_{11}, R_{12} or R_{13} is NO_2;

R_{43}, R_{44} and R_{45} independently from each other are hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

X_5 is the direct bond; C_1-C_{10}alkylene; C_5-C_{10}cycloalkylene; C_5-C_{10}arylene; or C_5-C_{10}arylene-(C_1-C_{10}alkylene);

R_{14} is $N^+R_{46}R_{47}$;

R_{46} and R_{47} independently from each other are hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl; or

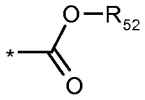
R_{46} and/or R_{47} are a bivalent C_3-C_6alkylene radical which is linked to the carbon atoms C^1 or C^2 in formula (1e) respectively and, together with the linking nitrogen atom form a 6 to 16-membered carbocyclic ring;

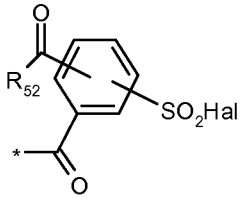
R_{15} is is $NR_{48}R_{49}$; or OR_{48};

R_{48} and R_{49}, independently from each other are hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl; or

R_{48} and R_{49} are a bivalent C_3-C_6alkylene radical which is linked to the carbon atoms C^3 or C^4 in formula (1e) respectively and, together with the linking nitrogen or oxygen atom form a 6 to 16-membered carbocyclic ring; or

R_{48} and R_{49} together with the linking nitrogen atom form a 4 to 8 membered carbocyclic ring;

R_{16}, R_{17}, R_{18}, R_{19} and R_{20} independently form each other are hydrogen; C_1-C_{12}alkyl; halogen; $NR_{50}R_{51}$; or a radical of formula ($1e_1$) ;

R_{50} and R_{51} independently from each other are hydrogen; C_1-C_{12}alkyl; phenyl-C_1-C_4alkyl; or a radical of formula ($1e_2$) ;

V_1 is -O-; or -NR_{53};

R_{52} and R_{53} independently from each other are hydrogen; or C_1-C_5alkyl;

Hal is a halogen atom; and wherein at least one of R_{16}, R_{17}, R_{18}, R_{19} and R_{20} is hydrogen;

B_2 and B_3, independently from each other are C_6-C_{10}aryl; or a 5-7-membered heterocyclic compound, which may be substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, phenyl, hydroxy, halogen, sulfonic acid, carboxylate, or by the radical -$NR_{54}R_{55}$ or -OR_{56};

B_4 is C_6-C_{10}arylene, or a bivalent radical of a 5-7-membered heterocyclic compound, which may be substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, phenyl, hydroxy, halogen, sulfonic acid, carboxylate, or by the radical -$NR_{54}R_{55}$ or -OR_{56};

R_{54}, R_{55} and R_{56} independently from each other are hydrogen; or C_1-C_{12}alkyl, which may be substituted by hydroxy or C_6-C_{10}aryl; or

R_{54} and R_{55} together with the linking nitrogen atom form a 5 to 7 membered heterocyclic ring;

R_{21} and R_{22} independently from each other are hydrogen; C_1-C_{20}alkyl; C_1-C_{20}alkoxy; C_3-C_6cycloalkyl; C_5-C_{10}aryl; anellated aromatic groups; carboxylate; or sulfonate groups;

R_{23}, R_{24}, R_{25} and R_{26} each independently from each other are hydrogen; unsubstituted or substituted, straight-chain or branched, monocyclic or polycyclic, interrupted or uninterrupted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, C_6-C_{10}aryl, C_6-C_{10}aryl-C_1-C_{10}alkyl or C_5-C_{10}alkyl(C_5-C_{10}aryl); or

R_{23} and R_{24} and/or R_{25} and R_{26} together with the linking nitrogen atom form a 5 to 7 membered carbocyclic ring which may contain one or more than one hetero atom; or

R_{23} is linked to C_1 together with N^+ forming a 5-7 membered carbocyclic ring; or

R_{24} is linked to C_2 together with N^+ forming a 5-7 membered carbocyclic ring;

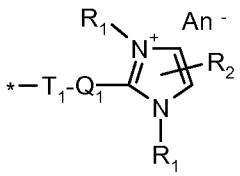
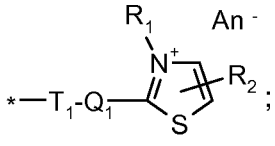
G_1 and G_2 independently from each other are N; -O-; -S-; or a radical of CR_{64};

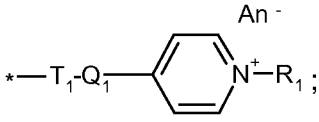
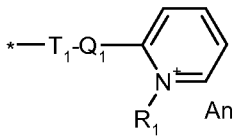
R_{57} is hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_5-C_{10}aryl-(C_1-C_{10}alkyl) ; or -C_1-C_{10}alkyl(C_5-C_{10}aryl);

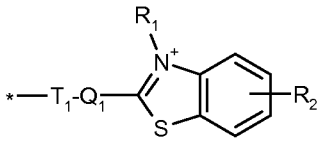
r is 0; or 1; and

An is an anion

Most preferably,

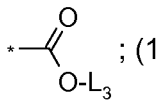
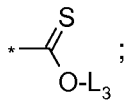
Y is a radical of formula ($1a_7$)  ; ($1a_8$)  ;

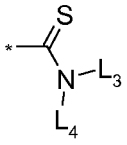
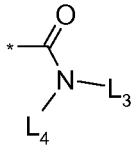
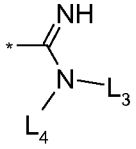
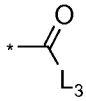
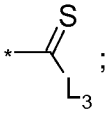
($1a_9$)  ; ($1a_{10}$)  ; or

($1a_{11}$)  ; wherein

R_1, R_2, Q_1 and T_1 independently from each other are defined as in formula (1).

Preferably, in the compounds of formula (1)

Z is selected from the radicals of formulae ($1b_1$)  ; ($1b_2$)  ;

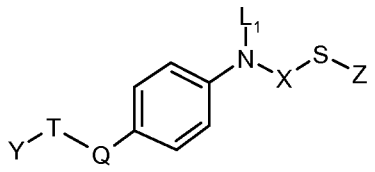
($1b_3$)  ; ($1b_4$)  ; ($1b_5$)  ; ($1b_6$)  ; ($1b_7$)  ;

or ($1b_8$) *-CΞN; wherein

L_3 and L_4 are defined as in formula (1).

Examples of compounds of the present invention are represented In the table 1 below:

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

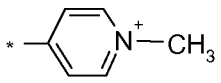
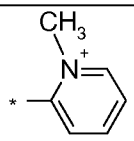
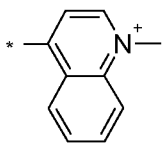
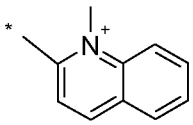
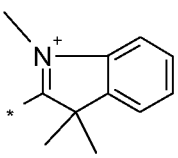
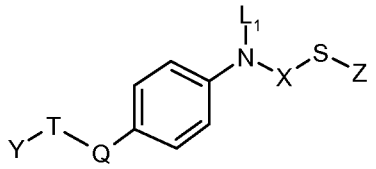
Compound of formula	Y	L_1	X	Z
(3)		H CH_3 C_2H_5	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$ $-(CO)C_6H_5$
(4)		CH_3	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$
(5)		CH_3	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$
(6)		CH_3	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$
(7)		CH_3	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

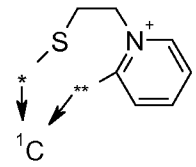
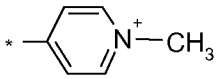
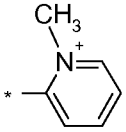
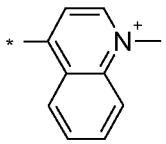
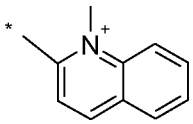
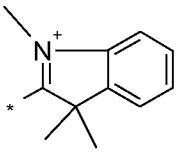
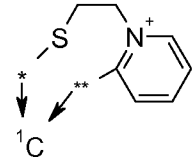
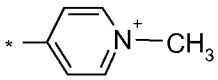
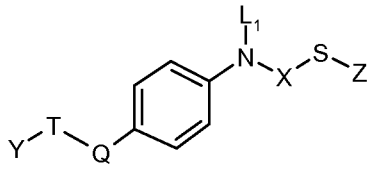
Compound of formula	Y	L_1	X	Z
(8)		CH_3	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$
(9)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(10)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(11)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(12)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(13)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(14)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(15)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

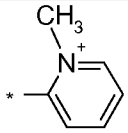
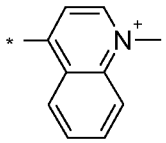
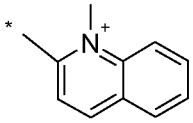
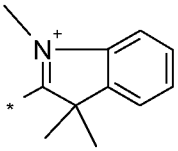
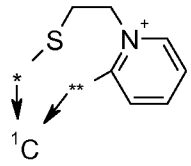
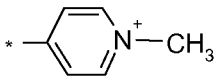
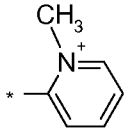
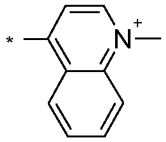
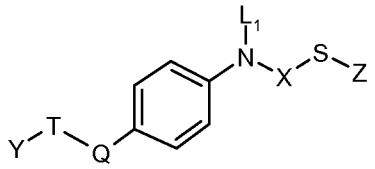
Compound of formula	Y	L_1	X	Z
(16)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(17)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(18)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(19)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(20)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(21)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(22)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(23)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

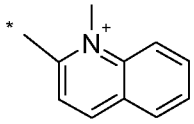
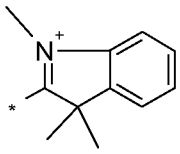
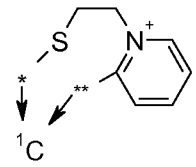
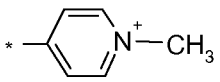
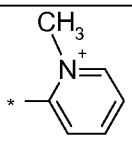
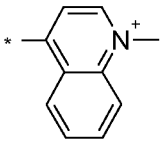
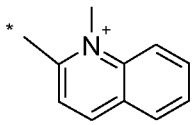
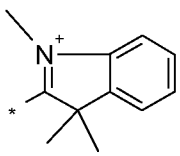
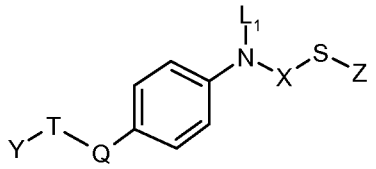
Compound of formula	Y	L_1	X	Z
(24)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(25)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(26)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(27)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(28)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(29)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(30)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(31)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

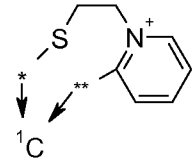
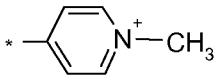
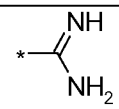
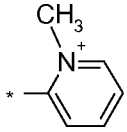
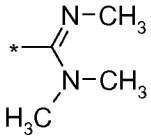
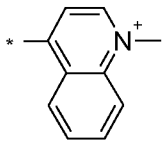
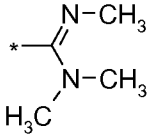
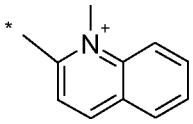
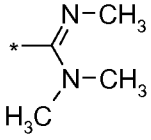
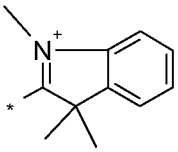
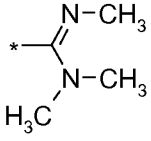
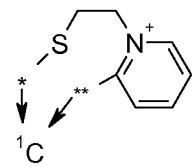
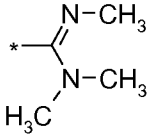
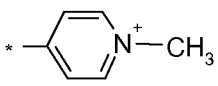
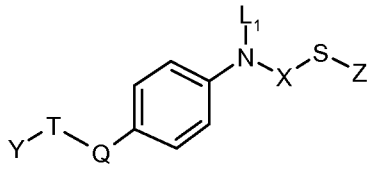
Compound of formula	Y	L_1	X	Z
(32)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(33)		CH_3	$-CH_2-CH_2-$	
(34)		CH_3	$-CH_2-CH_2-$	
(35)		CH_3	$-CH_2-CH_2-$	
(36)		CH_3	$-CH_2-CH_2-$	
(37)		CH_3	$-CH_2-CH_2-$	
(38)		CH_3	$-CH_2-CH_2-$	
(39)		CH_3	$-CH_2-CH_2-$	*—C≡N

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

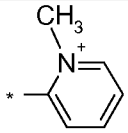
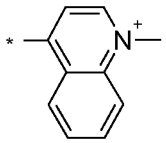
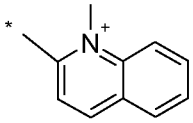
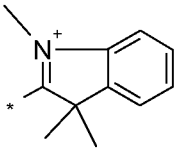
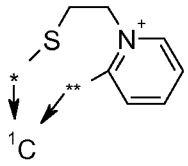
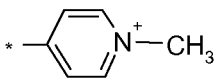
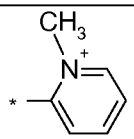
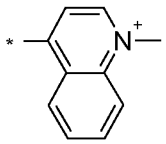
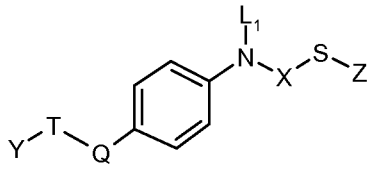
Compound of formula	Y	L_1	X	Z
(40)		CH_3	$-CH_2-CH_2-$	*—C≡N
(41)		CH_3	$-CH_2-CH_2-$	*—C≡N
(42)		CH_3	$-CH_2-CH_2-$	-C≡N
(43)		CH_3	$-CH_2-CH_2-$	-C≡N
(44)		CH_3	$-CH_2-CH_2-$	-C≡N
(45)		CH_3	$-CH_2-CH_2-$	$-(CO)O-C_2H_5$
(46)		CH_3	$-CH_2-CH_2-$	$-(CO)O-CH_3$
(47)		CH_3	$-CH_2-CH_2-$	$-(CO)O-CH_3$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

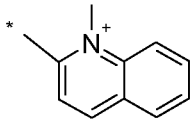
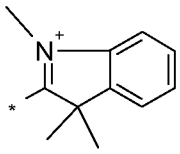
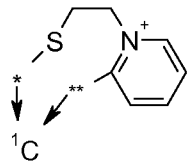
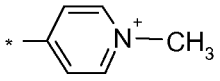
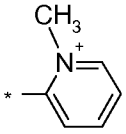
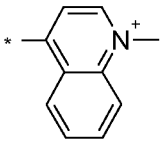
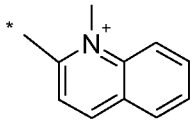
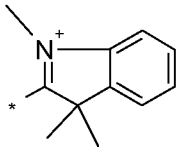
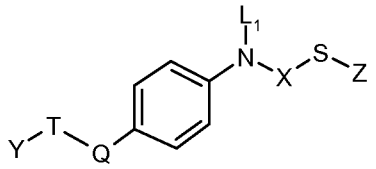
Compound of formula	Y	L_1	X	Z
(48)		CH_3	$-CH_2-CH_2-$	$-(CO)O-CH_3$
(49)		CH_3	$-CH_2-CH_2-$	$-(CO)O-CH_3$
(50)		CH_3	$-CH_2-CH_2-$	$-(CO)O-CH_3$
(51)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(52)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(53)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(54)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(55)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

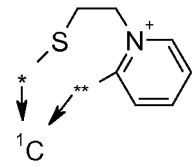
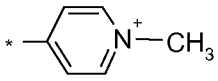
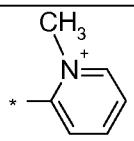
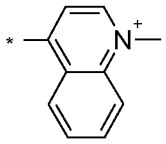
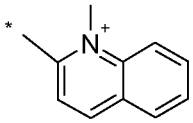
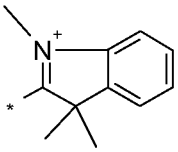
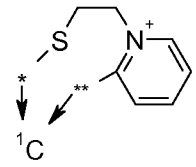
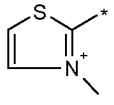
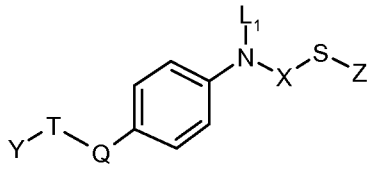
Compound of formula	Y	L_1	X	Z
(56)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(57)		CH_3	$-CH_2-CH_2-$	$-(CS)S-C_2H_5$
(58)		CH_3	$-CH_2-CH_2-$	$-(CS)S-CH_3$
(59)		CH_3	$-CH_2-CH_2-$	$-(CS)S-CH_3$
(60)		CH_3	$-CH_2-CH_2-$	$-(CS)S-CH_3$
(61)		CH_3	$-CH_2-CH_2-$	$-(CS)S-CH_3$
(62)		CH_3	$-CH_2-CH_2-$	$-(CS)S-CH_3$
(63)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

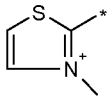
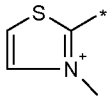
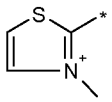
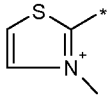
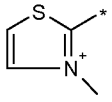
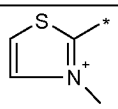
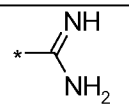
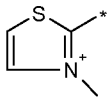
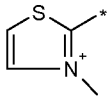
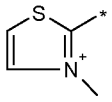
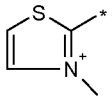
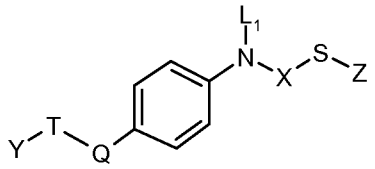
Compound of formula	Y	L_1	X	Z
(64)		H CH_3 C_2H_5	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$ $-(CO)C_6H_5$
(65)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(66)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(67)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(68)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(69)		CH_3	$-CH_2-CH_2-$	
(70)		CH_3	$-CH_2-CH_2-$	-C≡N
(71)		CH_3	$-CH_2-CH_2-$	$-(CO)O-C_2H_5$
(72)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$
(73)		CH_3	$-CH_2-CH_2-$	$-(CS)S-C_2H_5$

Table 1: Exemplified compounds of the present invention



T, Q = -N- or -CH-

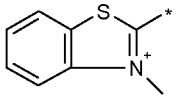
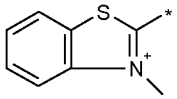
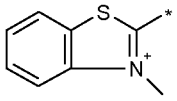
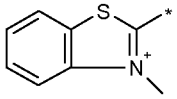
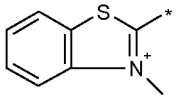
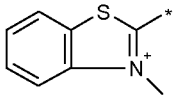
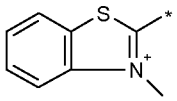
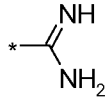
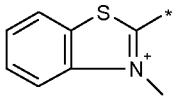
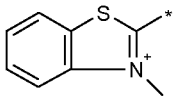
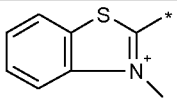
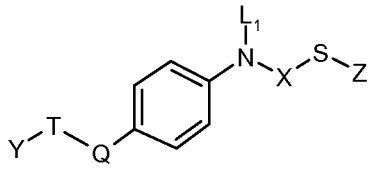
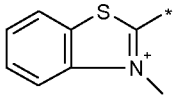
Compound of formula	Y	L_1	X	Z
(74)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(75)		H CH_3 C_2H_5	$-CH_2-CH_2-$	-(CO)H $-(CO)CH_3$ $-(CO)C_6H_5$
(76)		CH_3	$-CH_2-CH_2-$	-(CS)H $-(CS)CH_3$
(77)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(78)		CH_3	$-CH_2-CH_2-$	$-(CS)N(CH_3)_2$
(79)		CH_3	$-CH_2-CH_2-$	$-(CO)N(CH_3)_2$
(80)		CH_3	$-CH_2-CH_2-$	
(81)		CH_3	$-CH_2-CH_2-$	-CΞN
(82)		CH_3	$-CH_2-CH_2-$	$-(CO)O-C_2H_5$
(83)		CH_3	$-CH_2-CH_2-$	$-(CS)O-CH_3$

Table 1: Exemplified compounds of the present invention

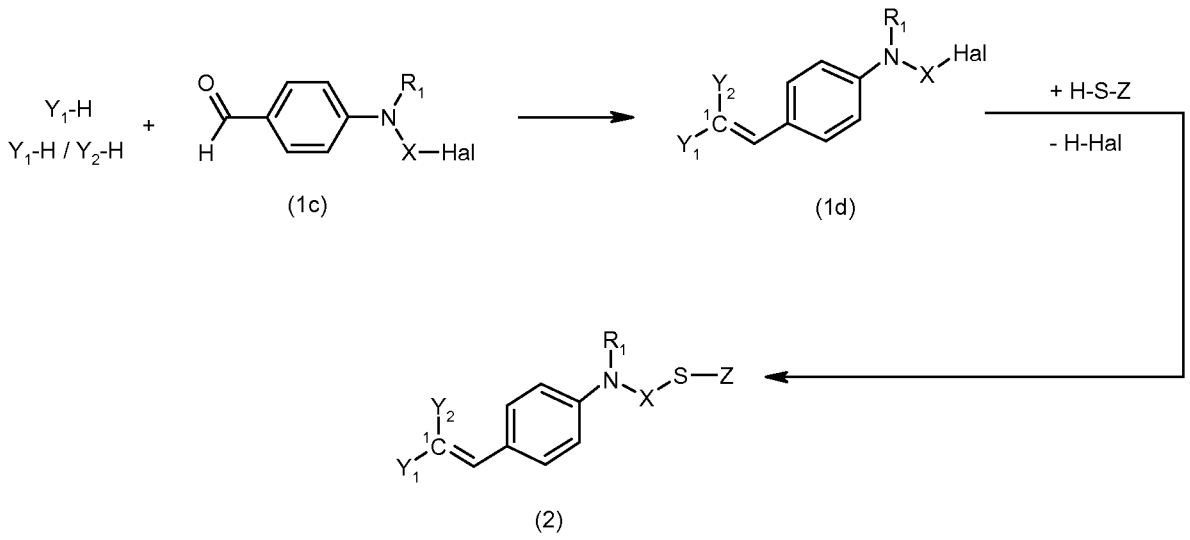


T, Q = -N- or -CH-

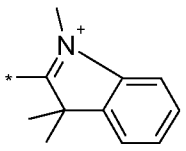
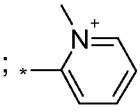
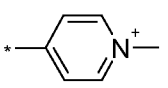
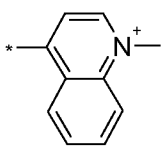
Compound of formula	Y	L_1	X	Z
(84)		CH_3	$-CH_2-CH_2-$	$-(CS)S-C_2H_5$

A further enbodiment of the present inveintion relates to processes for the preparation of the dyes of formula (1).

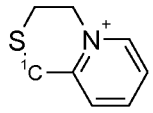
Generally, the process comprises condensating the methylenic compound Y_1 with the amino benzophenone compound of formula (1c) to the compound of formula (1d) and subsequently-reacting this compound to give the compound of formula (2) according to the following reaction scheme:



wherein

Y_1 is selected from  ;  ;  ; and  ;

and Y_2 is simultaneously hydrogen; or

Y_1 and Y_2 togeher with the linked carbon atom ^1C of formula (2) form a condensed carbocyclic ring of formula  ;

Hal is a halogen atom; and

R_1, X and Z are definded as in formula (1).

The reaction is generally initiated by contacting, for example by mixing together the starting compounds or by dropwise addition of one starting compound to the other.

Customary, the temperature is in the range of 250 to 400 K, preferably in the range of 270 to 300 K during the mixing of the starting compounds.

The reaction time is generally dependent on the reactivity of the starting compounds, on the selected reaction temperature and on the desired conversion. The reaction time is usually in the range from 3 hours to 3 days.

The selected reaction pressure is generally in the range from 50 kPa to 3 MPa, especially from 100 kPa to 1 MPa, and is more especially atmospheric pressure.

Preferably the reaction is carried out in the presence of a catalyst.

The molar ratio of compound of formula (1b) to the catalyst is generally selected in the range from 10:1 to 1:5, especially in the range from 10:1 to 1:1.

Preferred are basic catalysts as tertiary amines or acid catalysts, HA and Lewis acids like Ag^+.

In addition, the reaction may be carried out with or without a solvent, but is preferably carried out in the presence of a solvent, preferably organic solvents or solvent mixtures.

Preferred solvents are alcohols like methanol, ethanol, propanol, 2-propanol or butanol; nitriles like acetonitril or propionitril; amides like dimethylformamide, dimethylacetamide or N-methylpyrolidone; halogenated hydrocarbons like chloroform, methylenechloride, trichloro-

ethylene or chlorobenzene; or other solvents like dimethylsulfoxide or water or mixtures of the mentioned solvents.

The product prepared according to the process of the present invention may advantageously be worked up and isolated, and if desired be purified.

Customary, the work up starts by decreasing the temperature of the reaction mixture in the range from 350 to 273 K, especially in the range from 320 to 273 K.

It may be advantageous to decrease the temperature slowly over a period of several hours.

In general, the reaction product is filtered off and then subsequently dried.

Filtration is normally carried out in standard filtering equipment, for example Büchner funnels, filter presses, pressurised suction filters, preferably in vacuo.

The temperature for the drying is dependent on the pressure applied. Drying is usually carried out in vacuo at 50-200 mbar.

The drying is usually carried out at a temperature in the range from 313 to 363 K, especially from 323 to 353 K, and more especially in the range from 328 to 348 K.

Advantageously the product is purified by recrystallisation after isolation.

The dyes of formula (1) according to the invention are suitable for dyeing organic materials, such as keratin-containing fibers, wool, leather, silk, cellulose or polyamides, cotton or nylon, and preferably human hair. The dyeings obtained are distinguished by their depth of shade and their good fastness properties to washing, such as, for example, fastness to light, shampooing and rubbing. The stability, in particular the storage stability of the dyes according to the invention are excellent.

Gernerally, hair dyeing agents on a synthetic base may be classiefied itnto three groups:

- temporary dyeing agents
- semipermanent dyeing agents, and

- permanent dyeing agents.

The multiplicity of shades of the dyes can be increased by combination with other dyes.

Therefore the dyes of formula (1) of the present invention may be combined with dyes of the same or other classes of dyes, especially with direct dyes, oxidation dyes; dye precursor combinations of a coupler compound as well as a diazotized compound, or a capped diazotized compound; and/or cationic reactive dyes.

Direct dyes are of natural origin or may be prepared synthetically. They are uncharged, cationic or anionic, such as acid dyes.

The dyes of formula (1) may be used in combination with at least one single direct dye different from the dyes of formula (1).

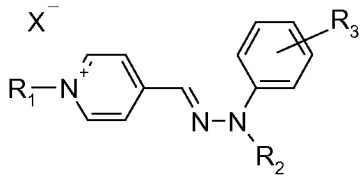
Direct dyes do not require any addition of an oxidizing agent to develop their dyeing effect. Accordingly the dyeing results are less permanent than those obtained with permanent dyeing compositions. Direct dyes are therefore preferably used for semipermanent hair dyeings.

Examples of direct dyes are described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, and in "Europäisches Inventar der Kosmetikrohstoffe", 1996, published by The European Commission, obtainable in diskette form from the Bundesverband der deutschen Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim.

More preferred direct dyes which are useful for the combination with at least one single dye of formula (1), especially for semi permanent dyeing, are: 2-amino-3-nitrophenol, 2-amino-4-hydroxyethylamino-anisole sulfate, 2-amino-6-chloro-4-nitrophenol, 2-chloro-5-nitro-N-hydroxyethylene-p-phenylendiamine, 2-hydroxyethyl-picramic acid, 2,6-diamino-3-((pyridine-3yl)-azo)pyridine, 2-nitro-5-glyceryl-methylaniline, 3-methylamino-4-nitro-phenoxyethanol, 4-amino-2-nitrodiphenyleneamine-2'-carboxilic acid, 6-nitro-1,2,3,4,-tetrahydroquinoxaline, 4-N-ethyl-1,4-bis(2'-hydroxyethylamino-2-nitrobenzene hydrochloride, 1-methyl-3-nitro-4-(2'-

hydroxyethyl)-aminobenzene, 3-nitro-p-hydroxyethyl-aminophenol, 4-amino-3-nitrophenol, 4-hydroxypropylamine-3-nitrophenol, hydroxyanthrylaminopropylmethyl morpohlino methosulfate, 4-nitrophenyl-aminoethylurea, 6-nitro-p-toluidine, Acid Blue 62, Acid Blue 9, Acid Red 35, Acid Red 87 (Eosin), Acid Violet 43, Acid Yellow 1, Basic Blue 3, Basic Blue 6, Basic Blue 7, Basic Blue 9, Basic Blue 12, Basic Blue 26, Basic Blue 99, Basic Brown 16, Basic Brown 17, Basic Red 2, Basic Red 22, Basic Red 76, Basic Violet 14, Basic Yellow 57, Basic Yellow 9, Disperse Blue 3, Disperse Orange 3, Disperse Red 17, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Fast Green FCF, HC Blue 2, HC Blue 7, HC Blue 8, HC Blue 12, HC Orange 1, HC Orange 2, HC Red 1, HC Red 10-11, HC Red 13, HC Red 16, HC Red 3, HC Red BN, HC Red 7, HC Violet 1, HC Violet 2, HC Yellow 2, HC Yellow 5, HC Yellow 5, HC Yellow 6, HC Yellow 7, HC Yellow 9, HC Yellow 12, HC Red 8, hydroxyethyl-2-nitro-p-toluidine, N,N-Bis-(2-Hydroxyethyl)-2-nitro-p-phenylendiamine, HC Violet BS, Picramic Acid, Solvent Green 7.

Furthermore, the dyes of formula (1) may be combined with at least one cationic azo dye, for example the compounds disclosed in GB-A-2 319 776 as well as the oxazine dyes described in DE-A-299 12 327 and mixtures thereof with the other direct dyes mentioned therein, and even more preferred with cationic dyes such as Basic Yellow 87, Basic Orange 31 or Basic Red 51, or with cationic dyes as described in WO 01/66646, especially example 4, or with cationic dyes as described in WO 02/31056, especially example 6 (compound of formula 106); or the cationic dye of formula (3) as described in EP-A-714,954, or with a yellow cationic dye of formula

(DD1)  , wherein

R_1 and R_2 are each independently of the other a C_1-C_8alkyl; or an unsubstituted or substituted benzyl;

R_3 is hydrogen; C_1-C_8alkyl; C_1-C_8alkoxy; cyanide; or halide; preferably hydrogen; and

X^- is an anion; and preferably a compound of formula (DD1), wherein

R_1 is methyl; R_2 is benzyl; R_3 is hydrogen; and X^- is an anion; or wherein

R_1 is benzyl; R_2 is benzyl; R_3 is hydrogen; and X^- is an anion; or wherein

R_1 is benzyl; R_2 is methyl; R_3 is hydrogen; and X^- is an anion.

Furthermore, cationic nitroaniline and anthraquinone dyes are useful for a combination with a dye of formula (1), for example the dyes as described in the following patent specifications: US-5 298 029, especially in col 2, l. 33 to col 5, l. 38; US-5 360 930, especially in col 2, l. 38 to col 5, l. 49; US-5 169 403, especially in col 2, l. 30 to col 5, l. 38; US-5 256 823, especially in col 4, l. 23 to col 5, l. 15; US-5 135 543, especially in col 4, l. 24 to col 5, l. 16; EP-A-818 193, especially on p. 2, l. 40 to p. 3, l. 26; US-5 486 629, especially in col 2, l. 34 to col 5, l. 29; and EP-A-758 547, especially on p. 7, l. 48 to p. 8, l. 19.

The dyes of formula (1) may also be combined with acid dyes, for example the dyes which are known from the international names (Color index), or trade names.

Preferred acid dyes which are useful for the combination with a dye of formula (1) are described in US Patent 6,248,314. They include Red Color No. 120, Yellow Color No. 4, Yellow Color No. 5, Red Color No. 201, Red Color No. 227, Orange Color No. 205, Brown Color No. 201, Red Color No. 502, Red Color No. 503, Red Color No. 504, Red Color No. 506, Orange Color No. 402, Yellow Color No. 402, Yellow Color No. 406, Yellow Color No. 407, Red Color No. 213, Red Color No. 214, Red Color No. 3, Red Color No. 104, Red Color No. 105(1), Red Color No. 106, Green Color No. 2, Green Color No. 3, Orange Color No. 207, Yellow Color No. 202(1), Yellow Color No. 202(2), Blue Color No. 202, Blue Color No. 203, Blue Color No. 205, Blue Color No. 2, Yellow Color No. 203, Blue Color No. 201, Green Color No. 201, Blue Color NO. 1, Red Color No. 230(1), Red Color No. 231, Red Color No. 232, Green Color No. 204, Green Color No. 205, Red Color No. 401, Yellow Color No. 403(1), Green Color No. 401, Green Color No. 402, Black Color No. 401 and Purple Color No. 401, especially Black Color No. 401, Purple Color 401, Orange Color No. 205.

These acid dyes may be used either as single component or in any combination thereof.

Hair dye compositions comprising an acid dye are known. They are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, especially on p. 253 and 254.

Hair dye compositions which comprise an acid dye have a pH of 2-6, preferably 2-5, more preferably 2.5-4.0.

The dyes of formula (1) according to the present invention may also readily be used in combination with acid dyes and/or adjuvants, for example

- acid dyes and an alkylene carbonate, as described in US patent 6,248,314, especially in examples 1 and 2;
- acid hair dye compositions comprising various kinds of organic solvents represented by benzyl alcohol as a penetrant solvent have good penetrability into hair, as described in Japanese Patent Application Laid-Open Nos. 210023/1986 and 101841/1995;
- acid hair dye compositions with a water-soluble polymer or the like to prevent the drooping of the hair dye composition, as described for example in Japanese Patent Application Laid-Open Nos. 87450/1998, 255540/1997 and 245348/1996;
- acid hair dye compositions with a water-soluble polymer of aromatic alcohols, lower alkylene carbonates, or the like as described in Japanese Patent Application Laid-Open No. 53970/1998 and Japanese Patent Invention No. 23911/1973.

The dyes of formula (1) may also be combined with uncharged dyes, for example selected from the group of the nitroanilines, nitrophenylenediamines, nitroaminophenols, anthraquinones, indophenols, phenazines, phenothiazines, bispyrazolons, ~~or~~ bispyrazol aza derivatives and methines.

Furthermore, the dyes of formula (1) may also be used in combination with oxidation dye systems.

Oxidation dyes, which, in the initial state, are not dyes but dye precursors are classified according to their chemical properties into developer and coupler compounds.

Suitable oxidation dyes are described for example in

- DE 19 959 479, especially in col 2, l. 6 to col 3, l. 11;
- "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 8, on p. 264 - 267 (oxidation dyes);

Preferred developer compounds are for example primary aromatic amines, which are substituted in the para- or ortho- position with a substituted or unsubstituted hydroxy- or amino residue, or diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazol

derivatives, 2,4,5,6-tetraaminopyrimidine derivatives, or unsaturated aldehydes as described in DE 19 717 224, especially on p. 2, l. 50 to l. 66 and on p. 3 l. 8 to l. 12, or cationic developer compounds as described in WO 00/43367, especially on p., 2 l. 27 to p. 8, l. 24, in particular on p. 9, l. 22 to p. 11, l. 6.

Furthermore, developer compounds in their physiological compatible acid addition salt form, such as hydrochloride or sulfate can be used. Developer compounds, which have aromatic OH radicals are also suitable in their salt form together with a base, such as alkali metal-phenolates.

Preferred developer compounds are disclosed in DE 19959479, p. 2, l. 8 – 29.

More preferred developer compounds are p-phenylendiamine, p-toluylendiamine, p-, m- o-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulfate, 2-amino-4-hydroxy-ethylaminoanisole sulfate, hydroxyethyl-3,4-methylenedioxyaniline, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 2,6-dimethoxy-3,5-diamino-pyridine, hydroxypropyl-bis-(N-hydroxyethyl-p-phenylenediamine) hydrochloride, hydroxyethyl-p-phenylenediamine sulfate, 4-amino-3-methylphenol, 4-methylaminophenol sulfate, 2-aminomethyl-4-aminophenol, 4,5-diamino-1-(2-hydroxyethyl)-1H- pyrazol, 4-amino-m-cresol, 6-amino-m-cresol, 5-amino-6-chloro-cresol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine or 4-hydroxy-2,5,6-triaminopyrimidine sulfate.

Preferred coupler compounds are m-phenylendiamine derivatives, naphthole, resorcine and resorcine derivatives, pyrazolone and m-aminophenol derivatives, and most preferably the coupler compounds disclosed in DE 19959479, p.1, l. 33 to p. 3, l. 11.

The dyes of formula (1) may also be used together with unsaturated aldehydes as disclosed in DE 19 717 224 (p. 2, l. 50 to l. 66 and on p. 3 l. 8 to l. 12) which may be used as direct dyes or, alternatively together with oxidation dye precursors.

Further preferred for a combination with a dye of formula (1) are the following oxidation dye precursors:

- the developer/-coupler combination 2,4,5,6-tetraaminopyrimidine and 2-methylresorcine for assessing of red shades;

- p-toluenediamine and 4-amino-2-hydroxytoluene for assessing of blue-violet shades;
- p-toluenediamine and 2-amino-4-hydroxyethylaminoanisole for assessing of blue shades;
- p-toluenediamine and 2,4-diamino-phenoxyethynol for assessing of blue shades;
- methyl-4-aminophenol and 4-amino-2-hydroxytloluene for assessing of orange shades;
- p-toluenediamine and resorcine for assessing of brown-green shades;
- p-toluenediamine and 1-naphthol for assessing of blue-violet shades, or
- p-toluenediamine and 2-methylresorcine for assessing of brown-gold shades.

Furthermore, autooxidizable compounds may be used in combination with the dyes of formula (1).

Autooxidizable compounds are aromatic compounds with more than two substituents in the aomatic ring, which have a very low redox potential and will therefore be oxidized when exposed to the air. The dyeings obtained with these compounds are very stable and resistant to shampoo.

Autooxidizable compounds are for example benzene, indol, or indoline, especially 5,6-dihydroxyindol or 5,6-dihydroxyindoline derivatives as described in WO 99/20234, especially on p. 26, l. 10 to p. 28, l. 15, or in WO 00/28957 on p. 2, third paragraph.

Preferred autooxidizable benzene derivatives are 1,2,4-trihydroxybenzene, 1-methyl-2,4,5-trihydroxybenzene, 2,4-diamnio-6-methylphenol, 2-amino-4-methylaminophenol, 2,5-diamino-4-methyl-phenol, 2,6-diamino-4-diethylaminophenol, 2,6-diamino-1,4-dihydroxybenzene, and the salts of these compounds, which are accessible with acid.

Preferred autooxidizable indol derivatives are 5,6-dihydroxyindol, 2-methyl-5,6-dihydroxyindol, 3-methyl-5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindol, 2,3-dimethyl-5,6-dihydroxyindol, 5-methoxy-6-dihydroxyindol, 5-acetoxy-6-hydroixyindol, 5,6-diacetoxyindol, acid of 5,6-dihydroxyindol-2-carbon acid, and the salts of these compounds, which are accessible with acid.

The dyes of formula (1) may also be used in combination with naturally occurring dyes, such as henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea,

Rhamnus frangula bark, sage, campeche wood, madder root, catechu, sedre and alkanet root. Such dyeings are described, for example, in EP-A-404 868, especially on p. 3, l. 55 to p. 4, l. 9.

Furthermore, the dyes of formula (1) may also be used in combination with capped dia-zotised compounds.

Suitable diazotised compounds are for example the compounds of formulae (1) – (4) in WO 2004/019897 (bridging pages 1 and 2) and the corresponding watersoluble coupling components (I) –(IV) as disclosed in the same reference.

Further preferred dyes or dye combinations which are useful for the combination with a dye of formula (1) according to the present invention are described in

(DC-01): WO 95/01772, wherein mixtures of at least two cationic dyes are disclosed, especially p. 2, l. 7 to p. 4, l. 1, preferably p. 4, l. 35 to p. 8, l. 21; formulations p. 11, last § - p. 28, l. 19;

(DC-02): US 6,843,256, wherein cationic dyes are disclosed, especially the compounds of formulae (1), (2), (3) and (4) (col. 1, l. 27 – col. 3, l. 20, and preferably the compounds as prepared in the examples 1 to 4 (col. 10, l.42 to col. 13, l. 37; formulations col. 13, l. 38 to col. 15, l. 8;

(DC-03): EP 970 685, wherein direct dyes are described, especially p. 2, l. 44 to p. 9, l. 56 and preferably p. 9, l. 58 to p. 48, l. 12; processes for dyeing of keratin-containing fibers especially p. 50, l. 15 to 43; formulations p. 50, l. 46 to p. 51, l. 40;

(DC-04): DE-A-19 713 698, wherein direct dyes are described, especially p. 2, l. 61 to p. 3, l. 43; formulations p. 5, l. 26 to 60;

(DC-05): US 6,368,360, wherein directed dyes (col. 4, l. 1 to col. 6, l. 31) and oxidizing agents (col. 6, l. 37 –39) are disclosed; formulations col. 7, l. 47 to col. 9, l. 4;

(DC-06): EP 1 166 752, wherein cationic dyes (p. 3, l. 22 – p. 4, l. 15) and anionic UV-absorbers (p. 4, l. 27 – 30) are disclosed; formulations p. 7, l. 50 – p. 9, l. 56;

(DC-07): EP 998,908, wherein oxidation dyeings comprising a cationic direct dye and pyra-zolo-[1,5-a]-pyrimidines (p. 2, l. 48 – p. 4, l. 1) are disclosed; dyeing formulations p. 47, l. 25 to p. 50, l. 29;

(DC-08): FR-2788432, wherein combinations of cationic dyes with Arianors are disclosed, especially p. 53, l. 1 to p. 63, l. 23, more especially p. 51 to 52, most especially Basic

Brown 17, Basic brown 16, Basic Red 76 and Basic Red 118, and/or at least one Basic Yellow 57, and/or at least one Basic Blue 99; or combinations of arianors and/or oxidative dyes, especially p. 2, l. 16 to p. 3, l. 16; dyeing formulations on p. 53, l. 1 to p. 63, l. 23;

(DC-09): DE-A-19 713 698, wherein the combinations of direct dyes and permanent-wave fixing comprising an oxidation agent, an oxidation dye and a direct dye are disclosed; especially p. 4, l. 65 to p. 5, l. 59;

(DC-10): EP 850 638, wherein developer compounds and oxidizing agents are disclosed; especially p. 2, l. 27 to p. 7, l. 46 and preferably p. 7, l. 20 to p. 9, l. 26; dyeing formulations p. 2, l. 3-12 and l. 30 to p. 14, and p. 28, l. 35 - p. 30, l. 20; preferably p. 30, l. 25 - p. 32, l. 30;

(DC-11): US 6,190,421 wherein extemporaneous mixtures of a composition (A) containing one or more oxidation dye precursors and optionally one or more couplers, of a composition (B), in powder form, containing one or more direct dyes (col. 5, l. 40 – col. 7, l. 14), optionally dispersed in an organic pulverulent excipient and/or a mineral pulverulent excipient, and a composition (C) containing one or more oxidizing agents are disclosed; formulations col. 8, l. 60 – col. 9, l. 56;

(DC-12): US 6,228,129, wherein a ready-to-use composition comprising at least one oxidation base, at least one cationic direct dye and at least one enzyme of the 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme are disclosed; especially col. 8, l. 17 – col. 13, l. 65; dyeing formulations in col. 2, l. 16 to col. 25, l. 55, a multi-compartment dyeing device is described in col. 26, l. 13 - 24;

(DC-13): WO 99/20235, wherein compositions of at least one cationic dye and at least one nitrated benzene dye with cationic direct dyes and nitro benzene direct dyes are described; on p. 2, l. 1 to p. 7, l. 9, and p. 39, l. 1 to p. 40 l. 11, preferably p. 8, l. 12 to p. 25 l. 6, p. 26, l. 7 to p. 30, l. 15; p. 1, l. 25 to p. 8, l. 5, p. 30, l. 17 to p. 34 l. 25, p. 8, l. 12 to p. 25 l. 6, p. 35, l. 21 to 27, especially on p. 36, l. 1 to p. 37;

(DC-14): WO 99/20234, wherein compositions comprising at least one direct cationic dye and at least one autooxidisable dye, especially benzene, indol and indoline derivatives are described, preferably direct dyes on p. 2, l. 19 to p. 26, l. 4, and autooxidisable dyes as dislosed especially on p. 26, l. 10 to p. 28, l. 15; dyeing formulations especially on p. 34, l. 5 to p. 35, li 18;

(DC-15): EP 850 636, wherein oxidation dyeing compositions comprising at least one direct dye and at least one meta-aminophenol derivative as coupler component and at least

one developer compound and an oxidizing agent are disclosed, especially p. 5, l. 41 to p. 7, l. 52, dyeing formulations p. 19, l. 50 - p. 22, l. 12;

(DC-16): EP-A-850 637, wherein oxidation dyeing compositions comprising at least one oxidation base selected from para-phenylenediamines and bis(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler selected from meta-diphenols, and the acid-addition salts thereof, at least one cationic direct dye, and at least one oxidizing agent are disclosed, especially p. 6, l. 50 to p. 8, l. 44 are discloseded; dyeing formulations p. 21, l. 30 - p. 22, l. 57;

(DC-17): WO 99/48856, wherein oxidation dyeing compositions comprising cationic couplers are disclosed, especially p. 9, l. 16 - p. 13, l. 8, and p. 11, l. 20 - p. 12, l. 13; dyeing formulations p. 36, l. 7 – p. 39, l. 24;

(DC-18): DE 197 172 24, wherein dyeing agents comprising unsaturated aldehydes and coupler compounds and primary and secondary amino group compounds, nitrogen-containing heterocyclic compounds, amino acids, oligopeptids, aromatic hydroxy compounds, and/or at least one CH-active compound are disclosed p. 3, l. 42 - p. 5 l. 25; dyeing formulations p. 8, l. 25 – p. 9, l. 61.

In the dye combinations disclosed in the references (DC-01 – DC-18) above, the dyes of formula (1) according to the present invention may be added to the dye combinations or dyeing formulations or may be replaced with at least one dye of formula (1).

The present invention also releates to formulations, which are used for the dyeing of organic materials, preferably keratin-containing fibers, and most preferably human hair, comprising at least one dye of formula (1).

Preferably the dyes of formula (1) are incorporated into the composition for treating organic material, preferably for dyeing in amounts of 0.001 - 5% b.w. (hereinafter indicated merely by "%"), particularly 0.005 - 4%, more particularly 0.2 - 3%, based on the total weight of the composition.

The formulations may be applied on the keratin-containing fiber, preferably the human hair in different technical forms.

Technical forms of formulations are for example a solution, especially a thickened aqueous or aqueous alcoholic solution, a cream, foam, shampoo, powder, gel, or emulsion.

Customary the dyeing compositions are applied to the keratin-containing fiber in an amount of 50 to 100 g at a temperature from 15 to 50°C, preferably from 20 to 40°C.

Preferred forms of formulations are ready-to-use compositions or multi-compartment dyeing devices or 'kits' or any of the multi-compartment packaging systems with compartments as described for example in US 6,190,421, col 2, l. 16 to 31.

The pH value of the ready-to-use dyeing compositions is usually from 2 to 11, preferably from 5 to 10.

Preferably the dyeing compositions, which are not stable to reduction, are prepared with oxidizing agent free compositions just before the dyeing process.

One preferred embodiment of the present invention relates to the formulation of dyes, wherein the dyes of formula (1) are in powder form.

Powder formulations are preferably used if stability and/or solubility problems as for example described in DE 197 13 698, p. 2, l. 26 to 54 and p. 3, l. 51 to p. 4, l. 25, and p. 4, l. 41 to p. 5 l. 59.

Suitable cosmetic hair-care formulations are hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pre-treatment preparations or leave-on products such as sprays, creams, gels, lotions, mousses and oils, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colorants, preparations containing self-oxidizing dyes, or natural hair colorants, such as henna or camomile.

For use on human hair, the dyeing compositions of the present invention can usually be incorporated into an aqueous cosmetic carrier. Suitable aqueous cosmetic carriers include, for example W/O, O/W, O/W/O, W/O/W or PIT emulsions and all kinds of microemulsions, creams, sprays, emulsions, gels, powders and also surfactant-containing foaming solutions, e.g. shampoos or other preparations, that are suitable for use on keratin-containing fibers. Such forms of use are described in detail in Research Disclosure 42448 (August 1999). If necessary, it is also possible to incorporate the dyeing compositions into anhydrous carriers, as described, for example, in US-3 369 970, especially col 1, l. 70 to col 3, l. 55. The dyeing compositions according to the invention are also excellently suitable for the dyeing method described in DE-A-3 829 870 using a dyeing comb or a dyeing brush.

The constituents of the aqueous carrier are present in the dyeing compositions of the present invention in the customary amounts, for example emulsifiers may be present in the dyeing compositions in concentrations from 0.5 to 30 % b.w. and thickeners in concentrations from 0.1 to 25 % b.w. of the total dyeing composition.

Further carriers for dyeing compositions are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, especially on p. 243, l. 1 to p. 244, l. 12.

A shampoo has, for example, the following composition:
0.01 to 5 % b.w. of a dye of formula (1);
8 % b.w of disodium PEG-5 laurylcitrate Sulfosuccinate, Sodium Laureth Sulfate;
20 % b.w. of sodium cocoamphoacetate;
0.5 % b.w. of methoxy PEG/PPG-7/3 aminopropyl dimethicone;
0.3 % b.w. of hydroxypropyl guar hydroxypropytrimonium chloride;
2.5 % b.w. of PEG-200 hydrogenated glyceryl palmate; PEG-7 glyceryl cocoate;
0.5 % b.w. of PEG-150 distearate;
2.2. % b.w of citric acid;
perfume, preservatives; and
water ad 100 %.

The dyes of formula (1) may be stored in a liquid to paste-like preparation (aqueous or non-aqueous) or in the form of a dry powder.

When the dyes and adjuvants are stored together in a liquid preparation, the preparation should be substantially anhydrous in order to reduce reaction of the compounds.

The dyeing compositions according to the invention may comprise any active ingredients, additives or adjuvants known for such preparations, like surfactants, solvents, bases, acids, perfumes, polymeric adjuvants, thickeners and light stabilisers.

The following adjuavents are preferably used in the hair dyeing compositions of the present invention:

- non-ionic polymers, for example vinylpyrrolidone/vinyl acrylate copolymers, polyvinyl-pyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes;
- cationic polymers, such as quaternised cellulose ethers, polysiloxanes having quaternary groups, dimethyldiallylammonium chloride polymers, copolymers of dimethyldiallyl-ammonium chloride and acrylic acid, as available commercially under the name Merquat® 280 and the use thereof in hair dyeing as described, for example, in DE-A-4 421 031, especially p. 2, l. 20 to 49, or EP-A-953 334;
- acrylamide/dimethyldiallylammonium chloride copolymers, diethyl-sulfate-quaternised dimethylaminoethyl methacrylate/vinylpyrrolidone copolymers, vinylpyrrolidone/-imidazolinium methochloride copolymers;
- quaternised polyvinyl alcohol:
- zwitterionic and amphoteric polymers, such as acrylamido-propyltrimethylammonium chloride/acrylate copolymers and octylacrylamide/methyl methacry-late/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers;
- anionic polymers, such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinylpyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert-butyl acrylamide terpolymers;
- thickeners, such as agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean flour, linseed gums, dextrans, cellulose derivatives, e.g. methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such amylose, amylopectin and dextrins, clays, e.g. bentonite or fully synthetic hydro-colloids such as, for example, polyvinyl alcohol;

- structuring agents, such as glucose and maleic acid;
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin, cephalins, silicone oils, and conditioning compounds, such as those described in DE-A-19 729 080, especially p. 2, l. 20 to 49, EP-A-834 303, especially p. 2, l. 18 - p. 3, l. 2, or EP-A-312 343, especially p. 2, l. 59 - p. 3, l. 11;
- protein hydrolysates, especially elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolysates, condensation products thereof with fatty acids and also quaternised protein hydrolysates;
- perfume oils, dimethyl isosorbitol and cyclodextrins,
- solubilisers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- anti-dandruff active ingredients, such as piroctones, olamines and zinc Omadine,
- substances for adjusting the pH value;
- panthenol, pantothenic acid, allantoin, pyrrolidonecarboxylic acids and salts thereof, plant extracts and vitamins;
- cholesterol;
- light stabilisers and UV absorbers as listed in Table below:

Table 2: UV absorbers which may be use in the dyeing compositions of the present invention

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo-[2.2.1]heptan-2-one	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
8	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
9	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione	70356-09-1
10	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate	118-56-9
11	Isopentyl p-methoxycinnamate	71617-10-2

Table 2: UV absorbers which may be use in the dyeing compositions of the present invention

No.	Chemical Name	CAS No.
12	Menthyl-o-aminobenzoate	134-09-8
13	Menthyl salicylate	89-46-3
14	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate	6197-30-4
15	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
16	2- ethylhexyl 4- methoxycinnamate	5466-77-3
17	2- ethylhexyl salicylate	118-60-5
18	Benzoic acid, 4,4',4"-(1, 3,5- triazine-2,4,6-triyltriimino)tris-tris(2-ethylhexyl)ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine	88122-99-0
19	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
20	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
21	Triethanolamine salicylate	2174-16-5
22	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-butyl)-phenol]	103597-45-1
23	2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxy-phenyl)-(1,3,5)-triazine (Tinosorb S)	187393-00-6
24	Benzoic acid, 4,4'-[[6-[[4-[[(1,1-dimethylethyl)amino]carbonyl]-phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)-ester	154702-15-5
25	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-	155633-54-8
26	Dimethicodiethylbezalmalonate	207574-74-1
27	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester	302776-68-7
28	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
29	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
30	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
31	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
32	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7
33	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1

Table 2: UV absorbers which may be use in the dyeing compositions of the present invention		
No.	Chemical Name	CAS No.
34	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
35	Anthralinic acid, p-menth-3-yl ester	134-09-8
36	1,3,5-Triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N''-(2-ethylhexyl)- or Uvasorb K2A	288254-16-0
37	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
38	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts	56039-58-8
39	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate;	52793-97-2
40	4- aminobenzoic acid	150-13-0
41	2- phenyl- 1H- benzimidazole- 5- sulphonic acid	27503-81-7
42	3,3'-(1,4-phenylenedimethylene)bis[7,7-dimethyl-2-oxo-bicyclo-[2.2.1]heptane-1-methanesulfonic acid]	90457-82-2
43	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
44	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt	92484-48-5
45	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]propyl]N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1)	156679-41-3
46	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
48	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethyl-ethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
49	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neoheliopan AP	349580-12-7,

The use of UV absorbers can effectively protect natural and dyed hair from the damaging rays of the sun and increase the wash fastness of dyed hair.

Furthermore, the following UV absorbers or combinations may be used in the dyeing compositions according to the invention:

- cationic benzotriazole UV absorbers as for example described in WO 01/36396 especially on p. 1, l. 20 to p. 2, l. 24, and preferred on p. 3 to 5, and on p. 26 to 37;
- cationic benzotriazole UV in combination with antioxidants as described in WO 01/36396, especially on p. 11, l. 14 to p. 18;
- UV absorbers in combination with antioxidants as described in US Patent 5 922 310, especially in col 2, l. 1 to 3;
- UV absorbers in combination with antioxidants as described in US Patent 4 786 493, especially in col 1, 42 to col 2, l. 7, and preferred in col 3, 43 to col 5, l. 20;
- combination of UV absorbers as described in US Patent 5 830 441, especially in col 4, l. 53 to 56;
- combination of UV absorbers as described in WO 01/36396, especially on p. 11, l. 9 to 13; or
- triazine derivatives as described in WO 98/22447, especially on p. 1, l. 23 to p. 2, l. 4, and preferred on p. 2, l. 11 to p. 3, l. 15 and most preferred on p. 6 to 7, and 12 to 16.

Suitable cosmetic preparations may usually contain 0.05 to 40 % b.w., preferably from 0.1 to 20 % b.w., based on the total weight of the composition, of one or more UV absorbers;

- consistency regulators, such as sugar esters, polyol esters or polyol alkyl ethers;
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters;
- fatty alkanolamides;
- polyethylene glycols and polypropylene glycols having a molecular weight from 150 to 50 000, for example such as those described in EP-A-801 942, especially p. 3, l. 44 to 55,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration substances, such as polyols and polyol ethers, as listed extensively, for example, in EP-A-962 219, especially p. 27, l. 18 to 38, for example glycerol, propylene glycol, propylene glycol monoethyl ether, butyl glycol, benzyl alcohol, carbonates, hydrogen carbonates, guanidines, ureas and also primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole;
- opacifiers, such as latex;

- pearlising agents, such as ethylene glycol mono- and di-stearate;
- propellants, such as propane-butane mixtures, N_2O, dimethyl ether, CO_2 and air;
- antioxidants; preferably the phenolic antioxidants and hindered nitroxyl compounds disclosed in ip.com (IPCOM # 000033153D);
- sugar-containing polymers, as described in EP-A-970 687;
- quaternary ammonium salts, as described in WO 00/10517;
- Bacteria inhibiting agents, like preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monolaurate has also proved to be a bacteriostatic agent. The amount of the additional bacteria-inhibiting agents present is usually from 0.1 to 2 % b.w., based on the solids content of the preparations;

The dyeing compositions according to the present invention generally comprise at least one surfactant.

Suitable surfactants are zwitterionic or ampholytic, or more preferably anionic, non-ionic and/or cationic surfactants.

Suitable anionic surfactants in the dyeing compositions according to the present invention include all anionic surface-active substances that are suitable for use on the human body. Such substances are characterised by an anionic group that imparts water solubility, for example a carboxylate, sulfate, sulfonate or phosphate group, and a lipophilic alkyl group having approximately 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide groups and also hydroxy groups may be present in the molecule. The following are examples of suitable anionic surfactants, each in the form of sodium, potassium or ammonium salts or mono-, di- or tri-alkanolammonium salts having 2 or 3 carbon atoms in the alkanol group:

- linear fatty acids having 10 to 22 carbon atoms (soaps),

- ether carboxylic acids of formula R-O-(CH_2-CH_2-O)$_x$-CH_2-COOH, in which R is a linear alkyl group having 10 to 22 carbon atoms and x = 0 or from 1 to 16,
- acyl sarcosides having 10 to 18 carbon atoms in the acyl group,
- acyl taurides having 10 to 18 carbon atoms in the acyl group,
- acyl isothionates having 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic mono- and di-alkyl esters having 8 to 18 carbon atoms in the alkyl group and sulfosuccinic monoalkylpolyoxyethyl esters having 8 to 18 carbon atoms in the alkyl group and from 1 to 6 oxyethyl groups,
- linear alkane sulfonates having 12 to 18 carbon atoms,
- linear α-olefin sulfonates having 12 to 18 carbon atoms,
- α-sulfo fatty acid methyl esters of fatty acids having12 to 18 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates of formula R'-O(CH_2-CH_2-O)$_{x'}$-SO_3H, in which R' is a preferably linearar alkyl group having 10 to 18 carbon atoms and x' = 0 or from 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-3 725 030;
- sulfated hydroxyalkylpolyethylene and/or hydroxyalkylenepropylene glycol ethers according to DE-A-3 723 354, especially p. 4, l. 42 to 62,
- sulfonates of unsaturated fatty acids having 12 to 24 carbon atoms and 1 to 6 double bonds according to DE-A-3 926 344, especially p. 2, l. 36 to 54,
- esters of tartaric acid and citric acid with alcohols which are addition products of approximately from 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols having from 8 to 22 carbon atoms, or
- anionic surfactants, as described in WO 00/10518, especially p. 45, l. 11 to p. 48, l. 3.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids having 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule, and also especially salts of saturated and especially unsaturated C_8-C_{22}carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Surface-active compounds that carry at least one quaternary ammonium group and at least one $-COO^-$ or $-SO_3^-$ group in the molecule are terminated zwitterionic surfactants. Preference is given the so-called betaines, such as the N-alkylN,N-dimethylammonium glycinates, for example cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinates, for example cocoacylaminopropyldimethylammonium glycinate, and 2-alkyl-3-

carboxymethyl-3-hydroxyethylimidazoline having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name cocoamidopropyl betaine.

Ampholytic surfactants are surface-active compounds that, in addition to a C_8-C_{18}-alkyl or -acyl group and contain at least one free amino group and at least one -COOH or -SO_3H group in the molecule and are capable of forming internal salts. Examples of suitable ampholytic surfactants include N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids, each having approximately from 8 to 18 carbon atoms in the alkyl group. Ampholytic surfactants to which special preference is given are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C_{12}-C_{18}acylsarcosine.

Suitable non-ionic surfactants are described in WO 00/10519, especially p. 45, l. 11 to p. 50, l. 12. Non-ionic surfactants contain as hydrophilic group, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups. Such compounds are, for example:

- addition products of 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide with linearar fatty alcohols having 8 to 22 carbon atoms, with fatty acids having 12 to 22 carbon atoms and with alkylphenols having 8 to 15 carbon atoms in the alkyl group,
- C_{12}-C_{22} fatty acid mono- and di-esters of addition products of 1 to 30 mol of ethylene oxide with glycerol,
- C_8-C_{22}alkyl-mono- and -oligo-glycosides and ethoxylated analogues thereof,
- addition products of 5 to 60 mol of ethylene oxide with castor oil and hydrogenated castor oil,
- addition products of ethylene oxide with sorbitan fatty acid esters,
- addition products of ethylene oxide with fatty acid alkanolamides.

The surfactants which are addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of such addition products may either be products having a "normal" homologue distribution or products having a restricted homologue distribution. "Normal" homologue distribution are mixtures of homologues obtained in the reaction of fatty alcohol

and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. Restricted homologue distributions, on the other hand, are obtained when, for example, hydrotalcites, alkali metal salts of ether carboxylic acids, alkali metal oxides, hydroxides or alcoholates are used as catalysts.

The use of products having restricted homologue distribution may be preferred.

Examples of cationic surfactants that can be used in the dyeing compositions according to the invention are especially quaternary ammonium compounds. Preference is given to ammonium halides, such as alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethy-lammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride. Further cationic surfactants that can be used in accordance with the invention are quaternised protein hydrolysates.

Also suitable are cationic silicone oils, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilised trimethylsilylamodimethicone), Dow Corning 929 emulsion (comprising a hydroxylamino-modified silicone, which is also referred to as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and also Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, quaternium-80), or silicones, as described in WO 00/12057, especially p. 45, l. 9 to p. 55, l. 2.

Alkylamidoamines, especially fatty acid amidoamines, such as the stearylamidopropyldimethylamine obtainable under the name Tego Amid® 18 are alos preffered as surfactants in the present dyeing compositions. They are distinguished not only by a good conditioning action but also especially by their good biodegradability.

Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyldialkoyloxyalkylammonium methosulfates marketed under the trademark Stepantex®, are also very readily biodegradable.

An example of a quaternary sugar derivative that can be used as cationic surfactant is the commercial product Glucquat®100, according to CTFA nomenclature a "lauryl methyl gluceth-10 hydroxypropyl dimonium chloride".

The alkyl-group-containing compounds used as surfactants may be single substances, but the use of natural raw materials of vegetable or animal origin is generally preferred in the preparation of such substances, with the result that the substance mixtures obtained have different alkyl chain lengths according to the particular starting material used.

The dyes of formula (1) are suitable for the dyeing of organic material, perferably keratin-containig fibers.

A further preferred embodiment of the present invention relates to a method of treating keratin-containig fibers with a thiol dye of formula (1).

The process comprises

(a) contacting the keratin fiber with at least a compound of formula (1),
(b) leaving the fibers to stand, and
(c) then rinsing the fiber.

The process for dyeing is for example described in WO 01/66646 on page 15, line 32 to page 16, line 2.

A further preferred method comprises treating the hair in the presence of a reduction agent.

Preferred reduction agents are for example thioglycol acid or salts therof, gycerine monothioglycolat, cystein, 2-mercaptopropionic acid, 2-mercaptoethylamine, thiolactic acid, thioglycerine, sodium sulfite, dithionithe, ammonium sulfite, sodium bisulfite, sodium metabisulfite or hydrochinon.

Furthermore, the present invention relates to a process, comprising treating the hair with

(a) optionally a reduction agent,
(b) at least one single thiol dye of formula (1) as defined above, and
(c) with an oxidizing agent.

The sequence of the reaction steps is generally not important, the reduction agent can be applied first or in a final step.

Usally, the oxidizing agent is applied together with an acid or a base.

The acid is for example citric acid, phosphoric acid or tartrate acid.

The base is for example sodium hydroxide, ammonia or monoethanolamine.

The dyes of formula (1) are suitable for all-over dyeing of the hair, that is to say when dyeing the hair on a first occasion, and also for re-dyeing subsequently, or dyeing of locks or parts of the hair.

The dyes of formula (1) are applied on the hair for example by massage with the hand, a comb, a brush, or a bottle, or a bottle, which is combined with a comb or a nozzle.

Further preferred is a process for dyeing keratin-containing fibers which comprises treating the keratin-containing fiber with at least one dye of formula (1), a base and an oxidizing agent.

The oxidation dyeing process usually involves lightening, that is to say that it involves applying to the keratin-containing fibers, at basic pH, a mixture of bases and aqueous hydrogen peroxide solution, leaving the applied mixture to stand on the hair and then rinsing the hair. It allows, particularly in the case of hair dyeing, the melanin to be lightened and the hair to be dyed.

Lightening the melanin has the advantageous effect of creating a unified dyeing in the case of grey hair, and, in the case of naturally pigmented hair, of bringing out the color, that is to say of making it more visible.

In general, the oxidizing agent containing composition is left on the fiber for 0 to 15 minutes, in particular for 0 to 5 minutes at 15 to 45°C, usually in amounts of 30 to 200 g.

Oxidizing agents are for example persulfate or dilute hydrogen peroxide solutions, hydrogen peroxide emulsions or hydrogen peroxide gels, alkaline earth metal peroxides, organic peroxides, such as urea peroxides, melamine peroxides, or alkalimetalbromat fixations are also applicable if a shading powder on the basis of semi-permanent, direct hair dyes is used.

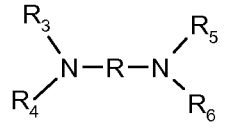
Further preferred oxidizing agents are

- oxidizing agents to achieve lightened coloration, as described in WO 97/20545, especially p. 9, l. 5 to 9,
- oxidizing agents in the form of permanent-wave fixing solution, as described in DE-A-19 713 698 , especially p. 4, l. 52 to 55, and l. 60 and 61 or EP-A-1062940, especially p. 6, l. 41 to 47 (and in the equivalent WO 99/40895).

Most preferred oxidizing agent is hydrogen peroxide, preferably used in a concentration from about 2 to 30 %, more preferably about 3 to 20% by, and most preferably from 6 to 12% b.w. the corresponding composition.

The oxidizing agents may be present in the dyeing compositions according to the invention preferably in an amount from 0.01 % to 6 %, especially from 0.01 % to 1 %, based on the total dyeing composition.

In general, the dyeing with an oxidative agent is carried out in the presence of a base, for example ammonia, alkali metal carbonates, earth metal (potassium or lithium) carbonates, alkanol amines, such as mono-, di- or triethanolamine, alkali metal (sodium) hydroxides, earth metal hydroxides or compounds of the formula



, wherein

R is a propylene residue, which may be substituted with OH or C_1-C_4alkyl,
R_3, R_4, R_5 and R_6 are independently or dependently from each other hydrogen, C_1-C_4alkyl or hydroxy-(C_1-C_4)alkyl.

The pH-value of the oxidizing agent containing composition is usually about 2 to 7, and in particular about 2 to 5.

One preferred method of applying formulations comprising the dyes of formula (1) on the keratin-containing fiber, preferably the hair is by using a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, as described for example in WO 97/20545 on p. 4, l. 19 to l. 27.

The first compartment contains for examle at least one dye of formula (1) and optionally furhter direct dyes and a basifying agent, and in the second compartment an oxidizing agent; or in the first compartment at least one dye of formula (1) and optionally futhter direct dyes, in the second compartment a basifiying agent and in the third compartment an oxidizing agent.

A further preferred embodiment of the present invention relates to a method of dyeing hair with oxidative dyes, which comprises

(a) mixing at least one dye of formula (1) and optionally at least one coupler compound and at least one developer compound, and an oxidizing agent, which optionally contains at least one further dye, and
(b) contacting the keratin-containing fibers with the mixture as prepared in step (a).

The pH-value of the oxidizing agent free composition is usually from 3 to 11, and in particular from 5 to 10, and most particular about 9 to 10.

Preferably, a ready-to-use composition is prepared according to a first preferred embodiment by a process which comprises a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines and bis(phenyl)-alkylenediamines, and the acid-addition salts thereof, at least one coupler, especially selected from meta-phenylenediamines and the acid-addition salts thereof, and at least one dye of formula (1), on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent and mixing (A) and (B) together immediately before applying this mixture to the keratin-containing fibers.

According to a second preferred embodiment for the preparation of the ready-to-use dye composition, the process includes a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines and bis-

(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler compound, especially selected from meta-phenylenediamines and the acid-addition salts thereof; on the other hand, a composition (A') comprising, in a medium which is suitable for dyeing, at least one dye of formula (1), and, finally, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent as defined above, and mixing them together at the time of use immediately before applying this mixture to the keratin-containing fibers.

The composition (A') used according to this second embodiment may optionally be in powder form, the dye(s) of formula (1) (themselves) constituting, in this case, all of the composition (A') or optionally being dispersed in an organic and/or inorganic pulverulent excipient.

When present in the composition A', the organic excipient may be of synthetic or natural origin and is selected in particular from crosslinked and non-crosslinked synthetic polymers, polysaccharides such as celluloses and modified or unmodified starches, as well as natural products such as sawdust and plant gums (guar gum, carob gum, xanthan gum, etc.).

When present in the composition (A'), the inorganic excipient may contain metal oxides such as titanium oxides, aluminium oxides, kaolin, talc, silicates, mica and silicas.

A~~n~~ very suitable excipient in the dyeing compositions according to the invention is sawdust.

The powdered composition (A') may also contain binders or coating products in an amount which preferably does not exceed approximately 3% b.w. relative to the total weight of composition (A'). These binders are preferably selected from oils and liquid fatty substances of inorganic, synthetic, animal or plant origin.

Furthermore, the present invention relates to a process of dyeing of keratin-containig fibers of the dyes of formula (1) with autooxidable compounds and optionally further dyes.

Furthermore, the present invention relates to a process for dyeing keratin-containig fibers with the dyes of formula (1) and capped diazotised compounds, which comprises,

(a) treating the keratin-containing fibers under alkaline conditions with at least one capped diazotised compound and a coupler compound, and optionally a developer compound

ad optionally an oxidizing agent, and optionally in the presence of a further dye, and optionally with at least one dye of formula (1); and

(b) adjusting the pH in the range of 6 to 2 by treatment with an acid, optionally in the presence of a further dye, and optionally at least one dye of formula (1),

with the proviso that at least in one step (a) or (b) at least one dye of formula (1) is present.

The capped diazotised compound and coupler compound and optionally the oxidizing agent and developer compound can be applied in any desired order successively, or simultaneously.

Preferably, the capped diazotised compound and the coupler compound are applied simultaneously, in a single composition.

"Alkaline conditions" denotes a pH in the range from 8 to 10, preferably 9-10, especially 9.5-10, which are chieved by the addition of bases, for example sodium carbonate, ammonia or sodium hydroxide.

The bases may be added to the hair, to the dye precursors, the capped diazotised compound and/or the water-soluble coupling component, or to the dyeing compositions comprising the dye precursors.

Acids are for example tartaric acid or citric acid, a citric acid gel, a suitable buffer solution with optionally an acid dye.

The ratio of the amount of alkaline dyeing composition applied in the first stage to that of acid dyeing composition applied in the second stage is preferably about from 1:3 to 3:1, especially about 1:1.

Furthermore, the present invention relates to a process for dyeing keratin-containig fibers with the dyes of formula (1) and at least one acid dye.

The following Examples serve to illustrate the processes for dyeing without limiting the processes thereto. Unless specified otherwise, parts and percentages relate to weight. The amounts of dye specified are relative to the material being coloured.

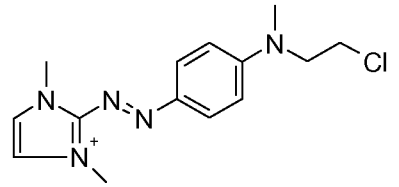
t, s, d, q and J, wherein t is a triplett, s is singulett, d is duplett, q is a quartett, and J is a coupling constant, define the NMR spectra values.

5

Examples

A. Preparation Examples

Example A-1: Preparation of the compound of formula (101)

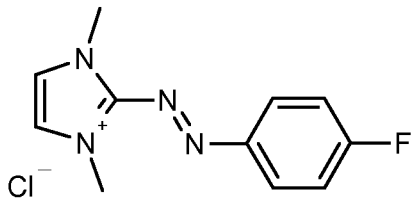


A-1.1 monoazo

62 g 4-fluoroanilin is added to a stirred solution of 125ml water and 12 ml of 32% hydrochloric acid at 295K. Then the reaction mixture is cooled to 273K and 95ml 36% sodium nitrite solution are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276K. After the addition of the sodium nitrite solution the mixture is stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide paper), further amounts of sodium nitrite solution are added. After this one hour the remaining excess of nitrite is reduced with sulfamic acid. Then the obtained diazo-solution is dropped to a 273K cold solution of 38g imidazole in 30ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% sodium hydroxide solution. After completing the diazo addition the obtained suspension is warmed up to 295K, the pH is adjusted to 10.5 with 36% sodium hydroxide solution. After one hour stirring at this pH and temperature, the suspension is filtered off and then washed twice with 250ml water to obtain 250g of the humid product.

This humid product is introduced into a reaction vessel 500ml of water, the filter cake is added from the previous step and suspended by stirring. Dimethyl sulphate (DMS) and sodium hydroxide are added, maintaining the pH at 10-10.3 and the temperature at 25-30°C. 2.6 equivalent of dimethyl sulphate (DMS) are added withhin ca. 5 hours. Temperature is maintained for one more hour to finish the hydrolysis of excess of DMS. The disappearance of DMS is controlled. Then 100 g of sodium chloride and 50 g of potassium chloride are added and cooled to 0°C. After 16 hours the product is separated by filtration and washed with a cold solution of sodium /potassium chloride.

Ca. 200g cake mole product is obtained with the following formula

(101b) 

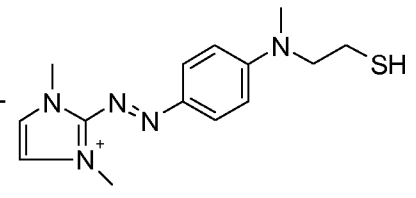
19.9 g of N-methyl-2-chlorethylamin are added at 293K, under nitrogen atmosphere, with stirring to 120g isopropanol and 22g of the foregoing compound.

Then the temperature is raised then to 333K, and viscosity of the reaction mixture decreases. The reaction mixture is stirred at this temperature during 5h. Then the reaction mass is stirred for 4h while the temperature is decreased to 295K. The reaction mass is filtered off and the filter residue is washed with 45ml isopropanole. Then the material is dried in vacuum to obtain 26g of product.

The product is characterized by the following data:

1H-NMR data in deuterated chloroform (128 scans)/ 360MHz

8,003	d	6,7	2,00	Phe
7,576	s		2,01	imidazol
7,026	d	6,9	2,01	Phe
4,072	s		6,00	methyl
4,002	t	6	2,03	ethylene
3,855	t	6	2,05	ethylene
2,289	s		3,087	methyl(amine)

Example A-2: Preparation of the compound of formula (102) 

A-2.1 Alkylation

One equivalent (6.0g) of thiourea is dissolved to 30g of the foregoing alkylating dye using absolute ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 48 hours.

A-2.2 Hydrolysis

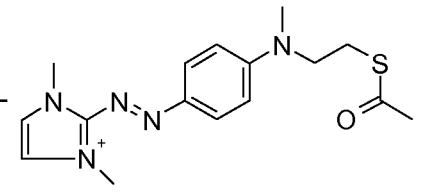
One equivalent (4,0 g) of sodium hydroxide is dissolved to the foregoing substance with absolute ethanol as solvent. The temperature is maintained at 80°C during the following 4h. The product is crystallized by cooling to room temperature under mixing, than separated by filtration, washed and dryed in vacuum dryer.

The product is characterized by the following data:

1H-NMR data in deuterated chloroform (128 scans)/360MHz

8,003	d	6,7	2,00	Phe
7,576	s		2,01	imidazol
7,000	d	6,9	2,01	Phe
4,060	s		6,00	methyl
4,002	t	6	2,03	ethylene
3,343	s		3,08	methyl(amine)
2,703	t	6	2,05	ethylene

Example A-3: Preparation of the compound of formula (103)



A-3.1 Alkylation

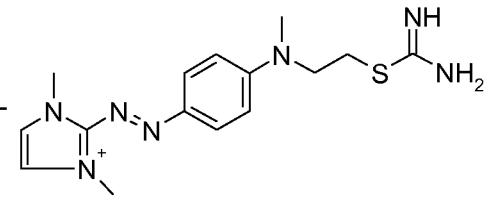
One equivalent (10.0g) of potasium thioacetate is dissolved to 30g of the foregoing alkylating dye with 75ml ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 4h.

The product is characterized by the following data:

1H-NMR data in deuterated chloroform (128 scans)/ 360MHz

8,003	d	6,7	2,00	Phe
7,578	s		2,01	imidazol
7,060	d	6,9	2,01	Phe
4,074	s		6,00	methyl
3,352	t	6	2,03	ethylene
3,085	t	6	2,05	ethylene
2,289	s		3,087	acetate

Example A-4: Preparation of the compound of formula

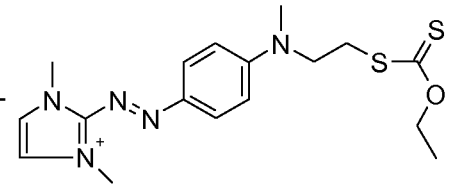
(104) 

A-4.1 Alkylation

One equivalent (8.0g) of thiourea is dissolved to 30g of the foregoing alkylating dye with absolute ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 48h.

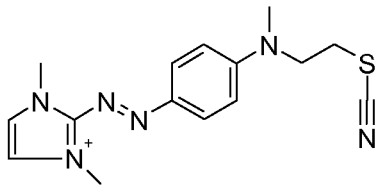
The product is crystallized by cooling to room temperature under mixing, than separated by filtration, washed and dried in vacuum dryer.

The product is characterized by NMR data.

Example A-5: Preparation of the compound of formula (105) 

One equivalent (14.0g) of ethyl xantogenate is dissolved to the foregoing alkylating dye with absolute ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 2 hours. The product is crystallized by cooling to room temperature under mixing than separated by filtration, washed and dryed in the vacuum dryer.

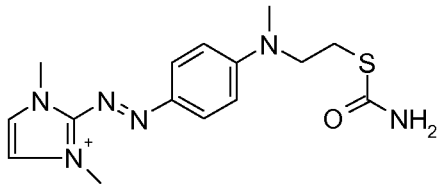
The product is characterized by 1H-NMR data in deuterated chloroform (128 scans)/ 360MHz.

Example A-6: Preparation of the compound of formula (106) 

A-6-1. Alkylation

One equivalent (10.0g) of potasium thiocyanate is dissolved to 30g of the foregoing alkylating dye with 75ml ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 4h.

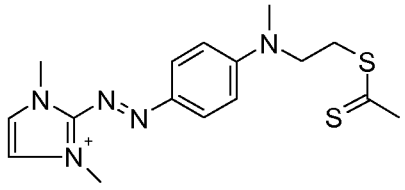
The product is characterized by 1H-NMR data in deuterated chloroform (128 scans)/360MHz.

Example A-7: Preparation of the compound of formula (107) 

A-7.1. Alkylation

One equivalent (10.0g) of potasium thiocyanate is dissolved to 30g of the foregoing alkylating dye with 75 ml ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 4h. Then sulfuric acid and water are added and the hydrolysis to the thiocarbamate is performed.

The product is characterized by 1H-NMR data in deuterated chloroform (128 scans)/ 360MHz

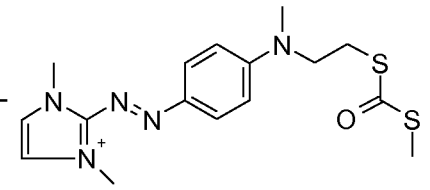
Example A-8: Preparation of the compound of formula (108) 

A-8.1 Alkylation

One equivalent (13.0g) of potasium dithioacetate is dissolved to 30g of the foregoing alkylating dye with 75ml ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 3h.

The product is characterized by the following data:
1H-NMR data in deuterated chloroform (128 scans)/ 360MHz

Example A-9: Preparation of the compound of formula (109)



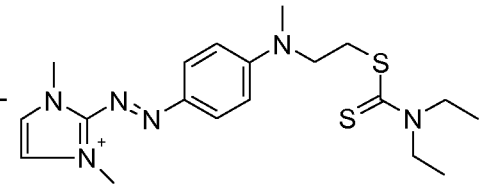
A-9.1 Alkylation

One equivalent (15.0g) of potasium methylthiocarbonate is dissolved to 30g of the foregoing alkylating dye with 75ml ethanol as solvent. The temperature was raised to reflux andwas maintained at 80°C during the following 4h.

The product is characterized by the following data:
1H-NMR data in deuterated chloroform (128 scans)/ 360MHz

Example A-10: Preparation of the compound of formula compound of formula

(110)



A-10.1 Alkylation

One equivalent (15.0g) of potasium diethylaminodithiocarbamate is dissolved to 30g of the foregoing alkylating dye with 75ml ethanol as solvent. The temperature is raised to reflux and maintained at 80°C during the following 4h.

The product is characterized by 1H-NMR data in deuterated chloroform
(128 scans)/360MHz.

B. Application Examples

The washing fastness of the dyed hair is analyzed by the Grey scale according to Industrial organic pigments by Herbst&Hunger, 2nd ed. engl. S. 61) Nr 10: DIN 54 001-8-1982, „Herstellung und Bewertung der Aenderung der Farbe“, ISO 105-A02-1993.

In the following application examples compositions within the below given definitions are used:

Solution 1 (permanent lotion, pH 8.2):

Aqua, Ammonium Thioglycolate, Ammonium Bicarbonate, Ethoxydiglycol, Hexylene Glycol, Thioglycolic Acid; Thiolactic Acid, PEG-60 Hydrogenated Castor Oil, Glycine, Etidronic Acid, Isoceteth-20, Polysilicone-9, Styrene/PVP Copolymer, Trideceth-12, Amodimethicone, Cetrimonium Chloride, Ammonium Hydroxide, Polyquaternium-6, Isopropyl Alcohol, Alcohol denat., Simethicone, Parfum

Solution 2 (permanent fixation, pH 3.9):

Based on:

Aqua, Hydrogen Peroxide, Propylene Glycol, Lauryldimonium Hydroxypropyl Hydrolyzed Wheat Protein, PEG-5 Cocamide, Sodium Cocoamphoacetate, Polyquaternium-35, Coco-Betaine, Acetaminophen, Phosphoric Acid, Sodium Chloride, Parfum

Solution 3 (dyeing solution):

0.1 % of the dye is dissolved in a 10 % solution of a non-ionic surfactant (Plantacare 200UP, Henkel) adjusted to pH 9.5 using citric acid or monoethanolamine.

Example B1:

50mg of the compound of formula (103) is dissolved in 2 g ethanol and then 30g of water is added: This red dyeing solution is applied on the dry hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20min at room temperature. Then the strands are rinsed under tap water and dried for 12h.

Washing fastness: 10x washed with shampoo

Results:		
Strand	Colour result	Washing fastness
blond	Pink/good	2-3
middelblond	Pink/good	3-4
damaged	Pink/good	3

Example B2:

The 0.1%, by weight colouring material solution of example B1 is applied on the dry hair (two blond, two middle blond, and two damaged hair strands) and allowed to stand for 20min at room temperature. Then the strands are rinsed and the towel dry strands are treated with the solution 2 (permanent fixation) and allowed to stand for 10min.

Then the strands are rinsed under tap water and dried for 12h at room temperature.

Washing fastness: 10x washed with shampoo.

Results:		
Strand	Colour result	Washing fastness
blond	Pink/good	2-3
middelblond	Pink/good	3-4
damaged	Pink/good	3

Example B3:

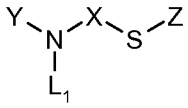
A solution 1 (permanent lotion) is applied on shampooed hair at room temperature (two blond, two middle blond, and two damaged hair strands) and allowed to stand for 10min. Then the strands are rinsed under tap water and the towel dry strands are treated with the 0.1%, by weight colouring material solution of example B1 allowed to stand for 20min and then rinsed. Then the towel dry strands are treated with the solution 2 (permanent fixation) at room temperature and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12h at room temperature.

Washing fastness: 10x washed with shampoo

Results:		
Strand	Colour	Washing fastness
blond	Pink/good	3-4
middelblond	Pink/good	3-4
damaged	Pink/good	2-3

Claims

1. Compounds of formula

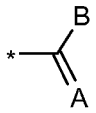
(1)  , wherein

L_1 is hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl;

X is C_1-C_{12}alkylene, C_2-C_{12}alkenylene, C_5-C_{10}cycloalkylene, C_5-C_{10}arylene, or C_5-C_{10}arylene-C_1-C_{10}alkylene, which may by interrupted by -O-, -NH-, -S-, -CO-, o -SO_2-;

Y is the residue of an organic dye

Z is a group of formula

(1b)  ; or -C≡N; wherein

A is O; S; or N-L_2;

B is L_3; -OL_3; -NL_3L_4; or -SL_3; and

L_2, L_3 and L_4, independently from each other are hydrogen; C_1-C_{12}alkyl; C_6-C_{12}aryl; or C_6-C_{12}aryl-C_1-C_{12}alkyl.

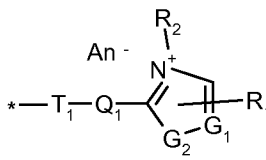
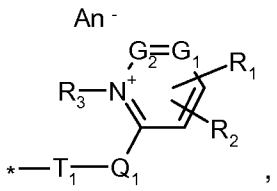
2. Compounds according to claim 1, wherein in formula (1)

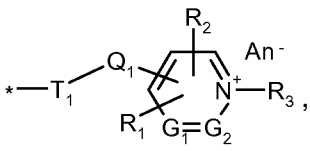
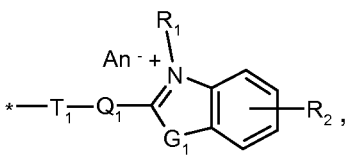
X is C_1-C_{12}alkylene.

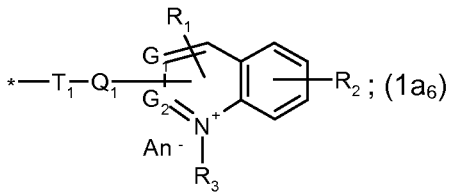
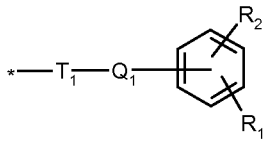
3. Compounds according to claim 2, wherein

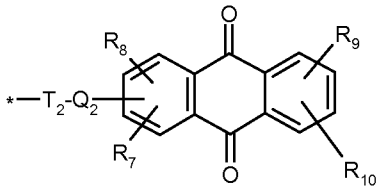
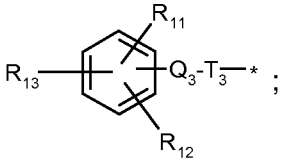
X is ethylene.

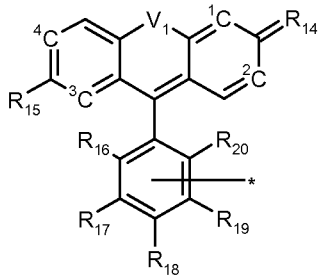
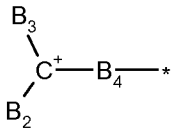
4. Compounds according to any of claims 1 to 3, wherein

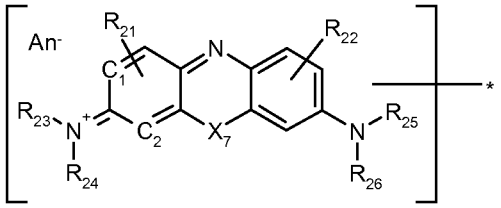
Y is a radical of formula ($1a_1$)  ; ($1a_2$)  ,

($1a_3$)  , ($1a_4$)  ,

(1a$_5$)  ; (1a$_6$) 

(1b)  ; (1c)  ;

(1d)  ; (1e)  ; or

(1f)  ; wherein

R_1, R_2 and R_3 independently from each other hydrogen; halogen; C_1-C_{16}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; phenyl, which substituted or unsubstituted; a carboxylic acid radical; sulfonic acid radical; hydroxy; nitrile; C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; halogen; sulfonylamino; SR_{33}; $NR_{33}R_{34}$; OR_{33}; SO_2; $COOR_{33}$; $NR_{33}COR_{34}$; or $CONR_{33}$;

Q_1 is a bivalent radical selected from -N=N-; -CR_d=N-; -N=CR_d-; -NR_d-N=CR_e-; and -R_dC=N-NR_e-;

T_1 is a bivalent radical of an aromatic or heteroaromatic substituted or unsubstituted compound;

R_d and R_e independently from each other are hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1 C_{10}alkyl-C_5-C_{10}aryl; or C_5-C_{10}aryl-C_1-C_{10}alkyl;

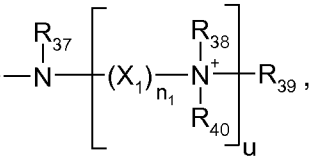
R_{33} and R_{34} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be

substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2, carboxy or hydroxy;

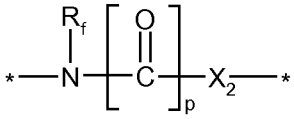
R_4, R_5 and R_6 independently from each other are hydrogen; C_1-C_{20}alkyl or C_1-C_{20}alkoxy, which may be substituted by one or more C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; C_3-C_6cycloalkyl; -C(O)H; -C(O)-C_1-C_5alkyl; halogen; NO_2; OH; phenyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; or a radical of formula -$NR_{35}R_{36}$;

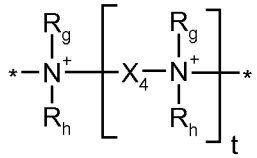
R_{35} and R_{36} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2, carboxy or hydroxy;

R_7, R_8, R_9 and R_{10} independently from each other are hydrogen; C_1-C_{20}alkyl; C_1-C_{20}alkoxy; C_3-C_6cycloalkyl; halogen; NO_2; OH; SH; or a radical of formula

(1c$_1$) 

X_1 is C_1-C_{18}alkylene; -(CO)-C_1-C_{18}alkylene C_1-C_{18}arylene; C_6-C_{18}arylene-C_1-C_{12}alkylene; or -$(OCH_2CH_2)_{n2}$-O-;

T_2 is a radical of formula (1c$_2$)  ; or -O-$(X_3)_s$;

Q_2 is a cationic biradical of a saturated, aromatic or heteroaromatic group; or a radical of formula (1c$_3$) 

R_f, R_g and R_h independently from each other are hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

X_2, X_3 and X_4 independently from each other are C_1-C_{18}alkylene; -(CO)-C_1-C_{18}alkylene-C_1-C_{18}arylene; C_6-C_{18}arylene-C_1-C_{12}alkylene; or -$(OCH_2CH_2)_{n1}$-O-;

p is 0; or 1

R_{37} is hydrogen; or C_1-C_{20}alkyl;

R_{38}, R_{39} and R_{40} independently from each other are hydrogen, C_1-C_{20}alkyl, C_4-C_{12}cycloalkyl, C_6-C_{13}aralkyl; phenyl-C_1-C_5alkyl; or R_{38} and R_{39} together with the linking nitrogen atom form a C_4-C_{12}-membered heterocyclic ring which may be interrupted by one or more than one –O- or –NH- goups;

u is 0 or 1;

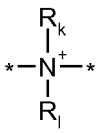
n_1 and n_2 independently from each other are a number from 1 to 5;

s is 0; or 1;

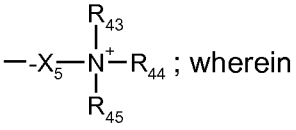
t is 0; or 1;

R_{11}, R_{12} and R_{13} independently from each other are hydrogen; C_1-C_{20}alkyl or C_1-C_{20}alkoxy, which may be substituted by one or more C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkyl-amino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; C_3-C_6cycloalkyl; -C(O)H; -C(O)-C_1-C_5alkyl; -C(O)OH; -C(O)O-C_1-C_5alkyl; halogen; NO_2; OH; SH; phenyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2 or hydroxy; or a radical -$NR_{41}R_{42}$;

Q_3 is is –C(O)-; -C(O)O-; -OCO-; -N(R_i)-X_5-; -CON(R_i)-; -(R_i)NC(O)-; –O-; -S-; -S(O)-; or -$S(O)_2$-;

T_3 is the direct bond;  ; or a cationic biradical of a saturated, aromatic or heteroaromatic group;

R_i, R_k, R_l independently from each other are C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

R_{41} and R_{42} independently from each other are hydrogen; C_1-C_{12}alkyl, which may be substituted by one or more C_1-C_5alkyl, C_1-C_5-alkoxy, hydroxy or -(CO)-H; -(CO)-C_1-C_5alkyl; phenyl or phenyl-C_1-C_4alkyl, wherein the phenyl moiety may be substituted by one or more C_1-C_5alkyl, C_1-C_5alkoxy, halogen, -NH_2, mono-C_1-C_5alkylamino, di-C_1-C_5alkylamino, -NO_2, carboxy or hydroxy; or a radical of formula  ; wherein at least one of the radicals R_{11}, R_{12} or R_{13} is NO_2;

R_{43}, R_{44} and R_{45} independently from each other are hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);

X_5 is the direct bond; C_1-C_{10}alkylene; C_5-C_{10}cycloalkylene; C_5-C_{10}arylene; or C_5-C_{10}arylene-(C_1-C_{10}alkylene);

R_{14} is $N^+R_{46}R_{47}$;

R_{46} and R_{47} independently from each other are hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl; or

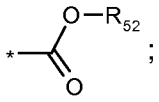
R_{46} and/or R_{47} are a bivalent C_3-C_6alkylene radical which is linked to the carbon atoms C^1 or C^2 in formula (1e) respectively and, together with the linking nitrogen atom form a 6 to 16-membered carbocyclic ring;

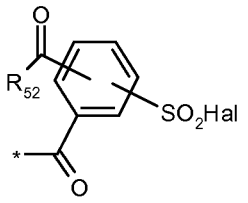
R_{15} is is $NR_{48}R_{49}$; or OR_{48};

R_{48} and R_{49}, independently from each other are hydrogen; C_1-C_{12}alkyl; or phenyl-C_1-C_4alkyl; or

R_{48} and R_{49} are a bivalent C_3-C_6alkylene radical which is linked to the carbon atoms C^3 or C^4 in formula (1e) respectively and, together with the linking nitrogen or oxygen atom form a 6 to 16-membered carbocyclic ring; or

R_{48} and R_{49} together with the linking nitrogen atom form a 4 to 8 membered carbocyclic ring;

R_{16}, R_{17}, R_{18}, R_{19} and R_{20} independently form each other are hydrogen; C_1-C_{12}alkyl; halogen; $NR_{50}R_{51}$; or a radical of formula ($1e_1$) ;

R_{50} and R_{51} independently from each other are hydrogen; C_1-C_{12}alkyl; phenyl-C_1-C_4alkyl; or a radical of formula ($1e_2$) ;

V_1 is -O-; or -NR_{53};

R_{52} and R_{53} independently from each other are hydrogen; or C_1-C_5alkyl;

Hal is a halogen atom; and wherein at least one of R_{16}, R_{17}, R_{18}, R_{19} and R_{20} is hydrogen;

B_2 and B_3, independently from each other are C_6-C_{10}aryl; or a 5-7-membered heterocyclic compound, which may be substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, phenyl, hydroxy, halogen, sulfonic acid, carboxylate, or by the radical -$NR_{54}R_{55}$ or -OR_{56};

B_4 is C_6-C_{10}arylene, or a bivalent radical of a 5-7-membered heterocyclic compound, which may be substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, phenyl, hydroxy, halogen, sulfonic acid, carboxylate, or by the radical -$NR_{54}R_{55}$ or -OR_{56};

R_{54}, R_{55} and R_{56} independently from each other are hydrogen; or C_1-C_{12}alkyl, which may be substituted by hydroxy or C_6-C_{10}aryl; or

R_{54} and R_{55} together with the linking nitrogen atom form a 5 to 7 membered heterocyclic ring;

R_{21} and R_{22} independently from each other are hydrogen; C_1-C_{20}alkyl; C_1-C_{20}alkoxy; C_3-C_6cycloalkyl; C_5-C_{10}aryl; anellated aromatic groups; carboxylate; or sulfonate groups;

R_{23}, R_{24}, R_{25} and R_{26} each independently from each other are hydrogen; unsubstituted or substituted, straight-chain or branched, monocyclic or polycyclic, interrupted or uninterrupted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, C_6-C_{10}aryl, C_6-C_{10}aryl-C_1-C_{10}alkyl or C_5-C_{10}alkyl(C_5-C_{10}aryl); or

R_{23} and R_{24} and/or R_{25} and R_{26} together with the linking nitrogen atom form a 5 to 7 membered carbocyclic ring which may contain one or more than one hetero atom; or

R_{23} is linked to C_1 together with N^+ forming a 5-7 membered carbocyclic ring; or

R_{24} is linked to C_2 together with N^+ forming a 5-7 membered carbocyclic ring;

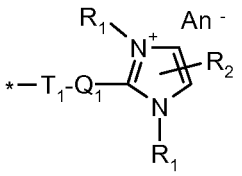
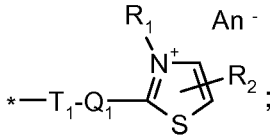
G_1 and G_2 independently from each other are N; -O-; -S-; or a radical of CR_{64};

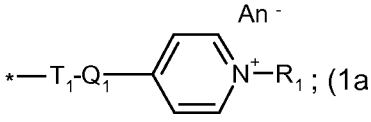
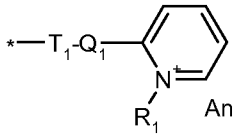
R_{57} is hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_5-C_{10}aryl-(C_1-C_{10}alkyl) ; or -C_1-C_{10}alkyl(C_5-C_{10}aryl);

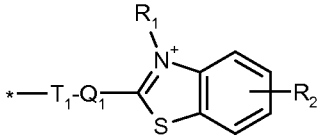
r is 0; or 1; and

An is an anion

5. Compounds according to claim 4, wherein

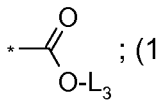
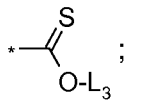
Y is a radical of formula ($1a_7$)  ; ($1a_8$)  ;

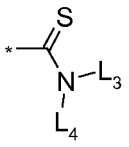
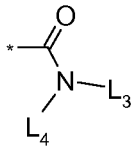
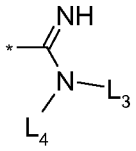
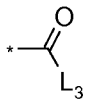
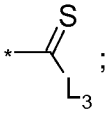
($1a_9$)  ; ($1a_{10}$)  ; or

($1a_{11}$)  ; wherein

R_1, R_2, Q_1 and T_1 independently from each other are defined as in claim 1.

6. Compounds according to any of claims 1 to 5, wherein

Z is selected from the radicals of formulae ($1b_1$)  ; ($1b_2$)  ;

($1b_3$)  ; ($1b_4$)  ; ($1b_5$)  ; ($1b_6$)  ; ($1b_7$)  ;

or ($1b_8$) *-CΞN; wherein

L_3 and L_4 are defined as in claim 1.

7. A method of dyeing keratin-containing fibers comprising treating the fiber with at least one dye of formula (1) according to claim 1.

8. A method according to claim 7, wherein the dyeing is carried out in the absence of a reducing agent.

9. A method according to claim 7, wherein the dyeing is carried out in presence of a reducing agent.

10. A method according to claim 9, wherein the reducing agent is selected from thioglycol acid or salts therof, gycerine monothioglycolate, cystein, 2-mercaptopropionic acid, 2-mercaptoethylamine, thiolactic acid, thioglycerine, sodium sulfite, dithionithe, ammonium sulfite, sodium bisulfite, sodium metabisulfite and hydrochinon.

11. A method according to any of claims 7 to 10, comprising treating the keratin-containing fiber

(a) optionally with a reduction agent, and

(b) at least one single dye of formula (1) as defined in claim 1, and

(c) optionally with an oxidizing agent.

12. A composition comprising at least one dye of formula (1) as defined in claim 1.

13. A composition according to claim 12 in form of a shampoo, conditioner, gel or emulsion.

14. A composition according to claim 12 or 13 comprising at least one single dye of formula (1) as defined in claim 1, and a direct dye and/or a reactive dye.

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