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(21) International Application Number: PCT/EP99/07981 (22) International Filing Date: 21 October 1999 (21.10.99) (30) Priority Data: 60/106,634 2 November 1998 (02.11.98) US (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): HÜGLIN, Dietmar [DE/DE]; Dorfstrasse 3, D-79591 Eimeldingen (DE). EHLIS, Thomas [DE/DE]; Ferdinand-Weiss-Strasse 30, D-79106 Freiburg (DE). KRAMER, Erich [AT/CH]; Jägerstrasse 10, CH-4058 Basel (CH). LUPIA, Joseph, Anthony [US/US]; 8511 Quail Creek Drive, Colfax, NC 27235 (US). (74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STABILISATION OF BODY-CARE AND HOUSEHOLD PRODUCTS (57) Abstract <p>A description is given of the use of phenolic antioxidants of formulae (1) and/or (2) and/or (3) for stabilising body-care and household products.</p>		

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Stabilisation of body-care and household products

The present invention relates to the use of phenolic antioxidants for stabilising body-care and household products.

The product trend of recent years towards increasingly using natural substances based on oil and fat in cosmetic formulations and household products also increases the problem of the oxidative degradation of fats and oils, resulting in rancidity. Natural oils or unsaturated fatty acids are hardly ever absent from emulsions. Oxidative changes may sometimes produce reactive metabolites, for example ketones, aldehydes, acids, epoxides and lipoperoxides.

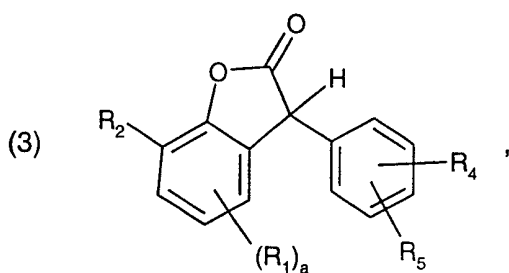
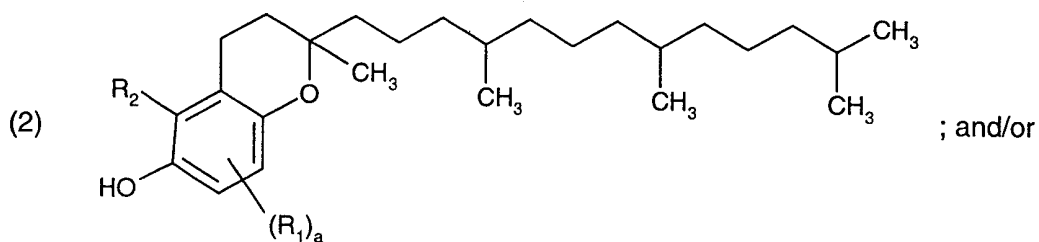
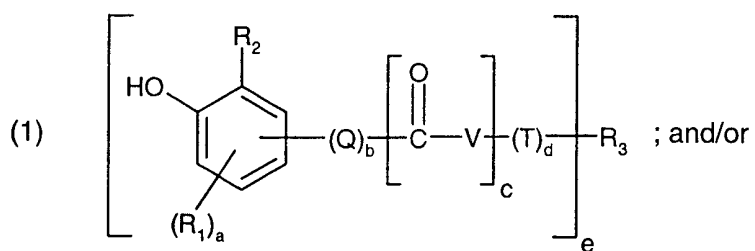
As a result there is on the one hand an undesirable change in the smell of the products and on the other hand substances may be obtained which may alter the skin tolerance. The uncontrolled formation of free radicals on the skin contributes primarily to the initiation and progression of a multitude of pathophysiological modulations, for example inflammation, cancerogenesis and the like.

However, oxidative degradation processes are not only found in the case of natural substances based on oil and fat. They are also found in a number of other cosmetic ingredients, such as fragrances and odoriferous substances, vitamins, colourants and the like.

To prevent oxidative degradation processes (photooxidation, autooxidation), so-called antioxidants (AO) are therefore used in cosmetic and food products. These antioxidants may be classified into compounds which prevent oxidation (complex formers, reducing agents and the like) and into compounds which interrupt the free radical chain reactions, for example butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), gallates, such as propylgallate (PG), or t-butylhydroquinone (TBHQ). However, the latter compounds often do not meet the requirements with respect to pH stability as well as to light and temperature stability.

Surprisingly, it has been found that certain phenolic antioxidants meet these requirements.

Accordingly, this invention relates to the use of phenolic antioxidants of formula

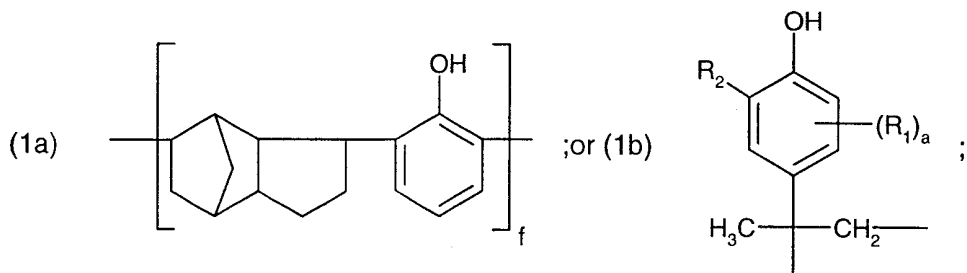


wherein in formulae (1), (2) and (3)

R_1 is hydrogen; $\text{C}_1\text{--C}_{22}$ alkyl; $\text{C}_1\text{--C}_{22}$ alkylthio; $\text{C}_5\text{--C}_7$ cycloalkyl; phenyl; $\text{C}_7\text{--C}_9$ phenylalkyl; or SO_3M ;

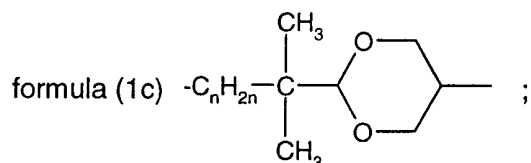
R_2 is $\text{C}_1\text{--C}_{22}$ alkyl; $\text{C}_5\text{--C}_7$ cycloalkyl; phenyl; or $\text{C}_7\text{--C}_9$ phenylalkyl;

Q is $\text{--C}_m\text{H}_{2m}\text{--}$; --CH-- ; $\text{--C}_m\text{H}_{2m}\text{--NH}$; a radical of formula

$$\begin{array}{c} \text{C}_m\text{H}_{2m+1} \\ | \\ \text{--CH--} \end{array}$$


- 3 -

T is $-C_nH_{2n}-$; $-(CH_2)_n-O-CH_2-$; $-C_nH_{2n}-NH-C(=O)-$; or a radical of



V is $-O-$; or $-NH-$;

a is 0; 1; or 2;

b, c and d are each independently of one another 0; or 1;

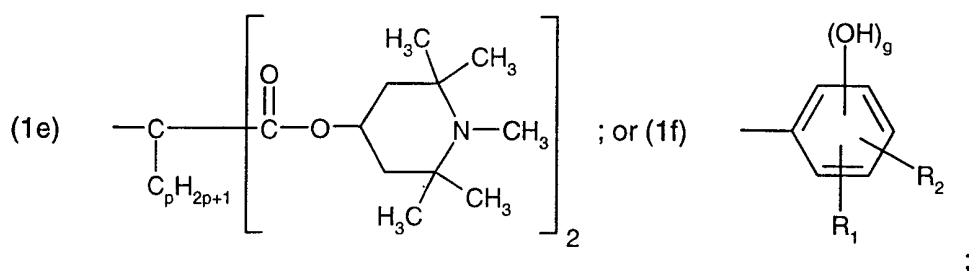
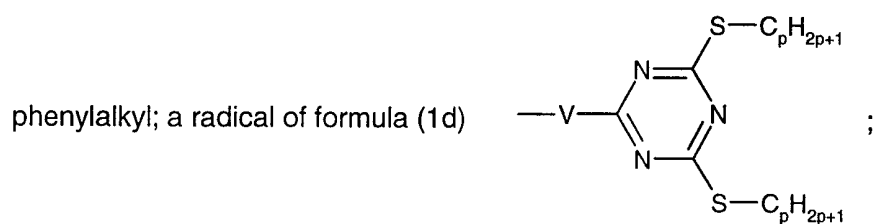
e is an integer from 1 to 4;

f is an integer from 1 to 3; and

m, n and p are each independently of one another an integer from 1 to 3;

if $e = 1$, then

R_3 is hydrogen; M; C_1-C_{22} alkyl; C_5-C_7 cycloalkyl; C_1-C_{22} alkylthio; C_2-C_{18} alkenyl; C_1-C_{18} -



M is alkali; ammonium;

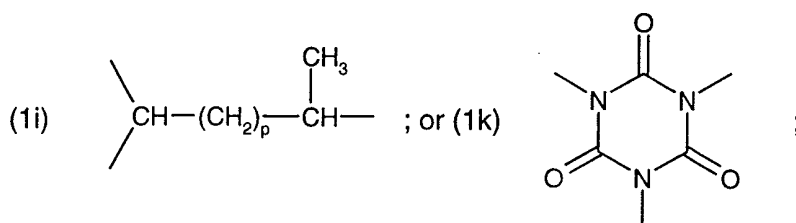
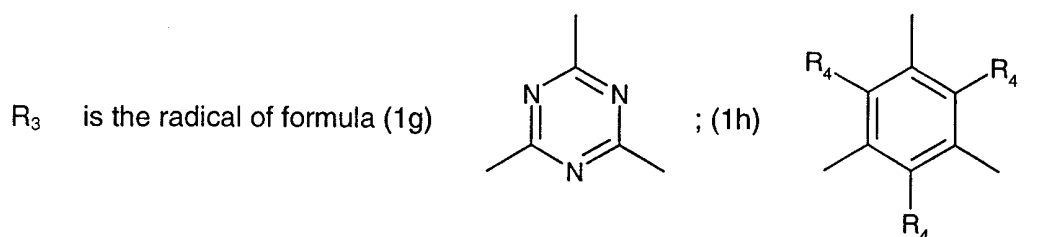
if $e = 2$, then

R_3 is a direct bond; $-CH_2-$; $-CH(CH_3)-(CH_2)_p-CH_3$; $-O-$; or $-S-$;

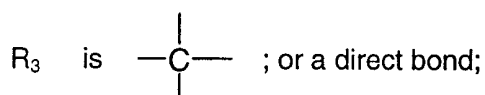
if

$e = 3$, then

- 4 -



if

 $e = 4$, then

R_4 and R_5 are each independently of the other hydrogen; or C_1 - C_{22} alkyl;
for stabilising body-care and household products.

C_1 - C_{22} Alkyl is straight-chain or branched alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-amyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl or eicosyl.

C_1 - C_{22} Alkylthio is straight-chain or branched alkylthio radicals, such as methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, sec-butylthio, tert-butylthio, amylthio, heptylthio, octylthio, isooctylthio, nonylthio, decylthio, undecylthio, dodecylthio, tetradecylthio, pentadecylthio, hexadecylthio, heptadecylthio, octadecylthio or eicosylthio.

C_2 - C_{18} Alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

C_5 - C_7 Cycloalkyl is cyclopentyl, cycloheptyl or, preferably, cyclohexyl.

C₇-C₉Phenylalkyl is phenylpropyl, phenylethyl and, preferably, benzyl.

It is preferred to use antioxidants of formula (1), wherein

Q is -C_mH_{2m}- and, preferably, a methylene or ethylene radical, and
m has the meaning given in formula (1).

V in formula (1) is preferably -O-.

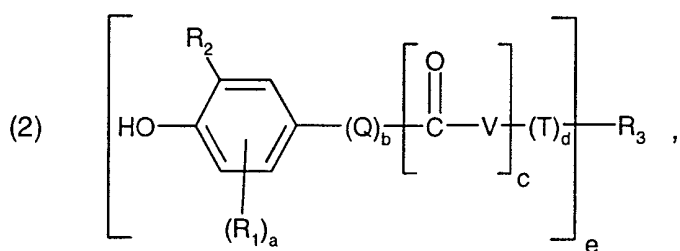
Particularly interesting compounds of formula (1) are those, wherein

R₁ and R₂ are each independently of the other C₁-C₁₈alkyl and, in particular, C₁-C₅alkyl.

Other important compounds of formula (1) are those, wherein

a is 1.

Very particularly interesting compounds are those of formula



wherein

R₁ and R₂ are each independently of the other C₁-C₅alkyl,

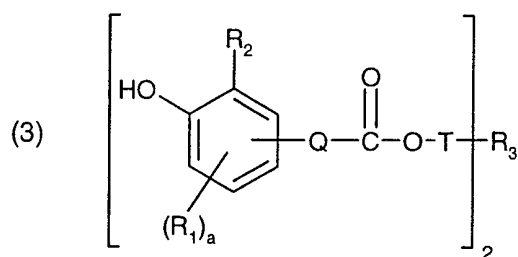
a is 1 or 2; and

R₃, Q, V, T, b, c, d and e have the meanings cited for formula (1).

Preferred compounds are those of formula (1), wherein R₁ and R₂ are the tert-butyl radical;
and

a is 1.

It is also preferred to use antioxidants of formula



wherein

R_1 and R_2 are each independently of the other $\text{C}_1\text{-C}_5$ alkyl;

Q is $-\text{C}_m\text{H}_{2m}-$; or $-\text{C}_m\text{H}_{2m}-\text{NH}-$;

R_3 is a direct bond; $-\text{O}-$; $-\text{S}-$; $-\text{CH}_2-$; or $-\text{CH}(\text{CH}_3)-$;

a is 1 or 2;

m is 1 to 5; and

T has the meaning cited in formula (1).

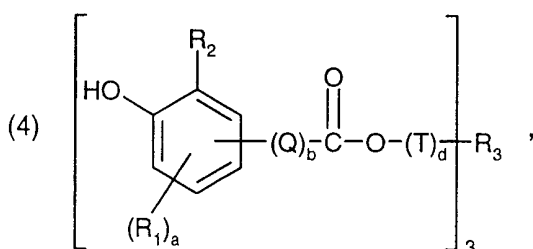
Interesting compounds of formula (1) are those, wherein

Q is ethylene; or $-\text{CH}(\text{CH}_3)-$;

R_3 is a direct bond; and

R_1 , R_2 , T and a have the meanings given in formula (3).

Likewise preferred are compounds of formula



wherein

Q is $-\text{C}_m\text{H}_{2m}-$;

T is $-\text{C}_n\text{H}_{2n}-$;

R_1 and R_2 are each independently of the other C_1 - C_5 alkyl;

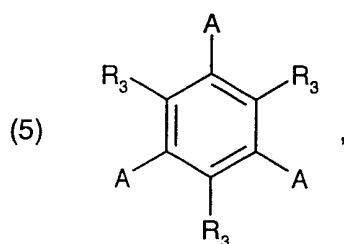
R_3 is the radical of formula (1g); (1h); (1i); or (1k);

m and n are each independently of the other 1 to 3;

a is 1 or 2; and

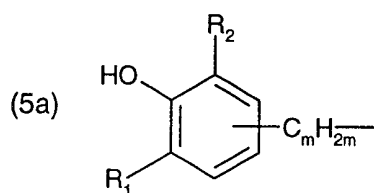
b and d are each independently of the other 0 or 1.

Other antioxidants which are preferably used conform to formula



wherein

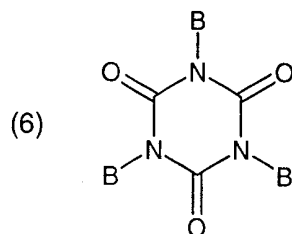
A is a radical of formula



R_1 , R_2 and R_3 are each independently of one another C_1 - C_5 alkyl; and

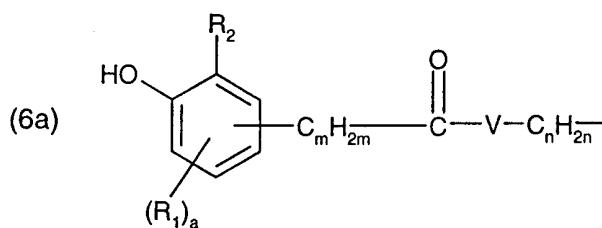
m is 1 to 3.

Other preferred antioxidants are those of formula



wherein

B is a radical of formula



R_1 and R_2 are each independently of the other C_1 - C_5 alkyl;

V is -O-; or -NH-;

a is 1; or 2;

m is 1 to 3; and

n is 0 to 3.

Examples of antioxidants used according to this invention are listed in Table 1:

Table 1:	
compound of formula	
(7)	
(8)	

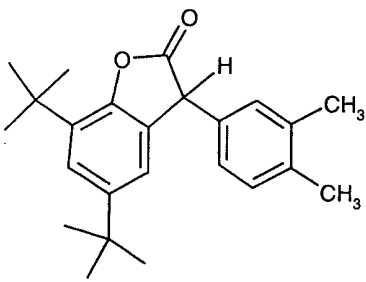
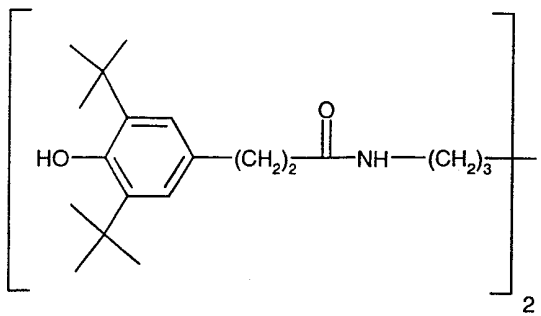
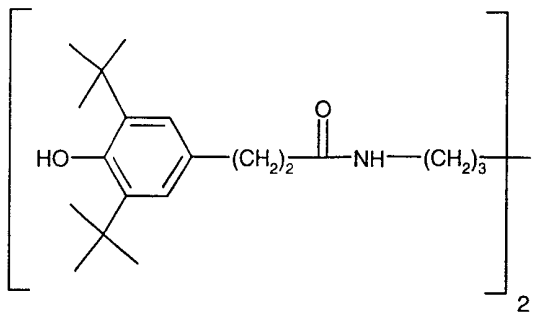
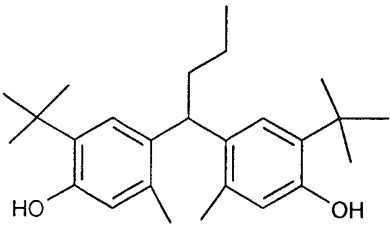
Table 1:	
compound of formula	
(9)	
(10)	
(11)	
(12)	

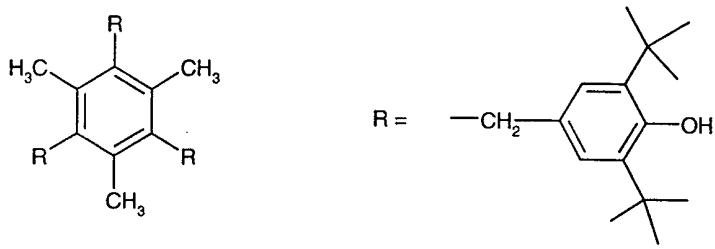
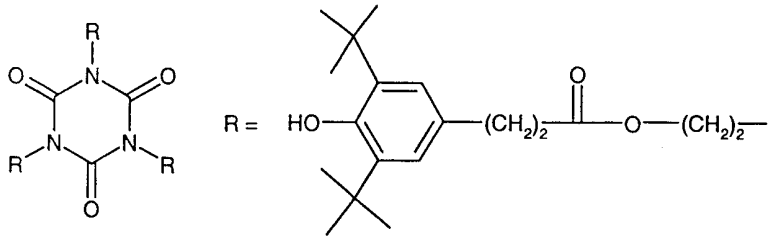
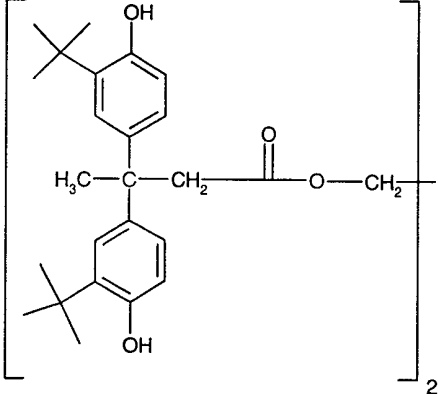
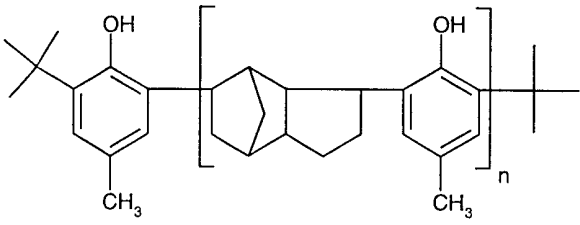
Table 1:	
compound of formula	
(13)	
(14)	
(15)	
(16)	 <p style="text-align: center;">n = 1-3</p>

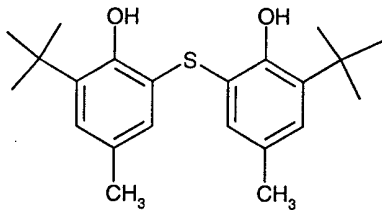
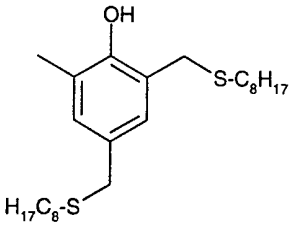
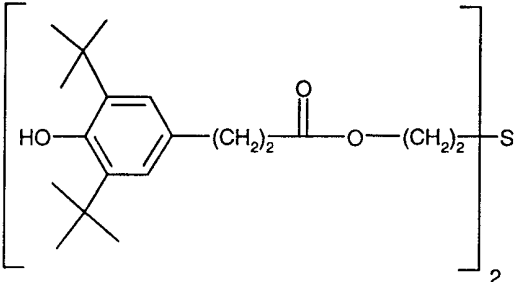
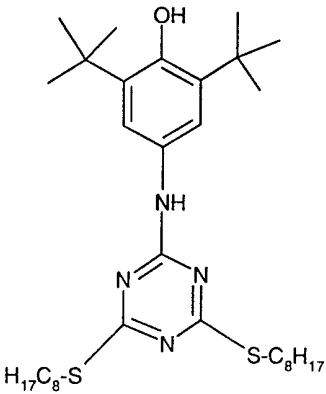
Table 1:	
compound of formula	
(17)	
(18)	
(19)	
(20)	

Table 1:

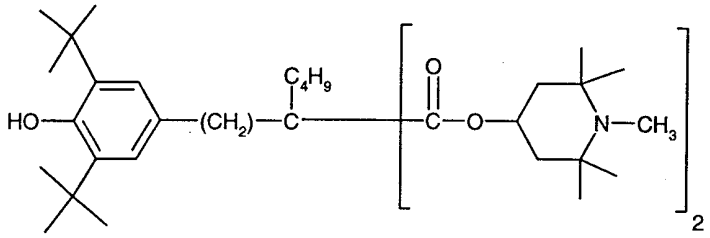
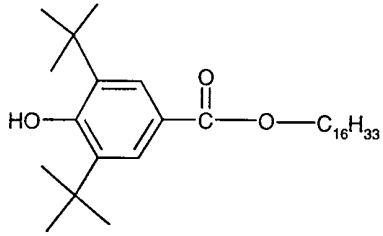
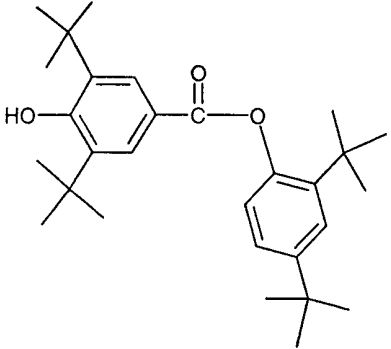
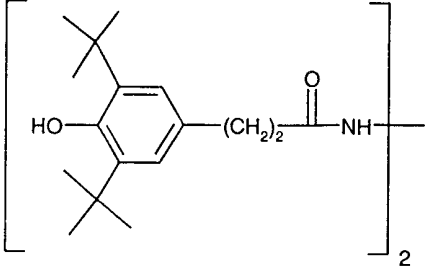
compound of formula	
(21)	
(22)	
(23)	
(24)	

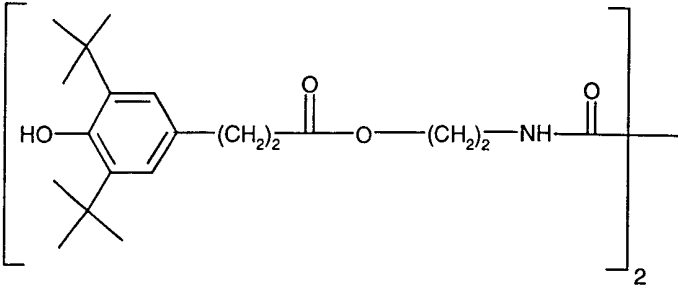
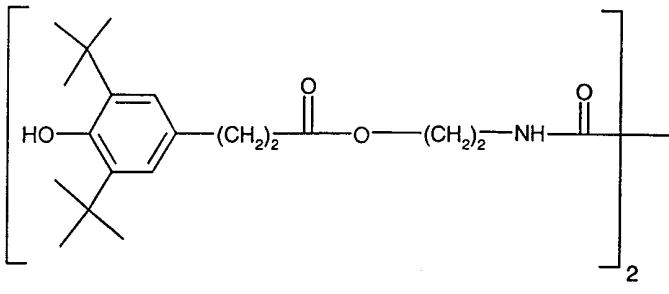
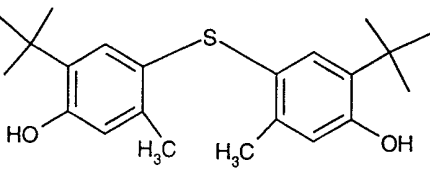
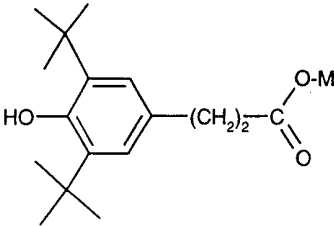
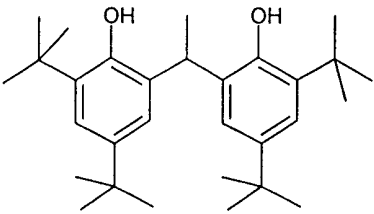
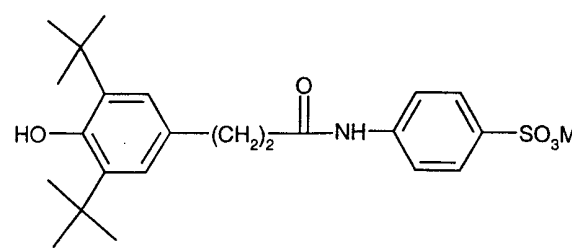
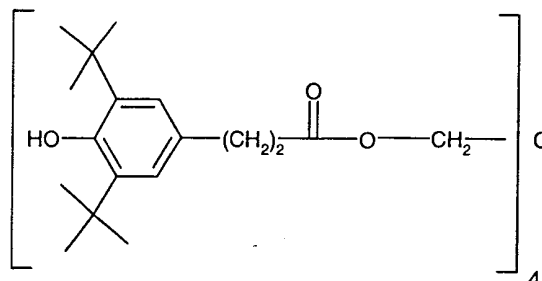
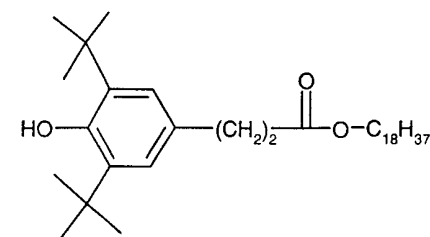
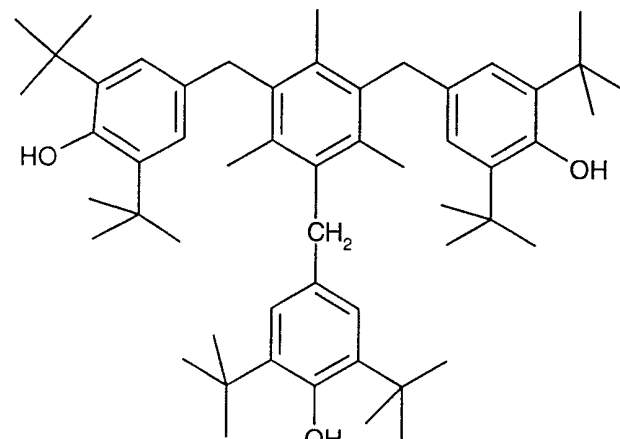
Table 1:	
compound of formula	
(25)	
(26)	
(27)	
(28)	 <p data-bbox="1013 1545 1252 1579">M = H, ammonium, alkali</p>
(29)	

Table 1:

compound of formula	
(30)	 <p style="text-align: center;">$M = H, Na$</p>
(31)	
(32)	
(33)	

The phenolic antioxidants of formulae (1), (2) and (3) can be used as individual compounds or as mixtures of several individual compounds.

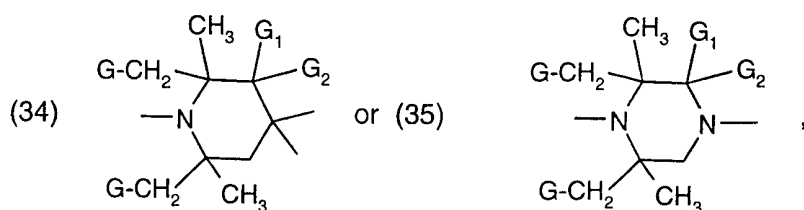
The antioxidants used according to this invention have pronounced reactivity and can therefore be advantageously used at low temperatures. They furthermore have good hydrolytic stability, in particular in alkaline medium. Owing to their good solubility, they can be easily incorporated into the respective formulations.

The phenolic antioxidants of formulae (1), (2) and (3) can also be used together with tocopherol and/or tocopherol acetate.

The phenolic antioxidants of formulae (1), (2) and (3) can furthermore also be used together with light stabilisers.

Suitable light stabilisers are, for example, sterically hindered amines.

These include preferably a 2,2,6,6-tetraalkylpiperidine derivative containing at least one group of formula

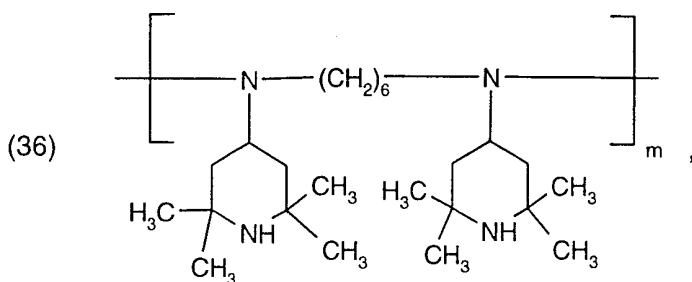


wherein G, G₁ and G₂ are each independently of one another hydrogen or methyl, preferably hydrogen.

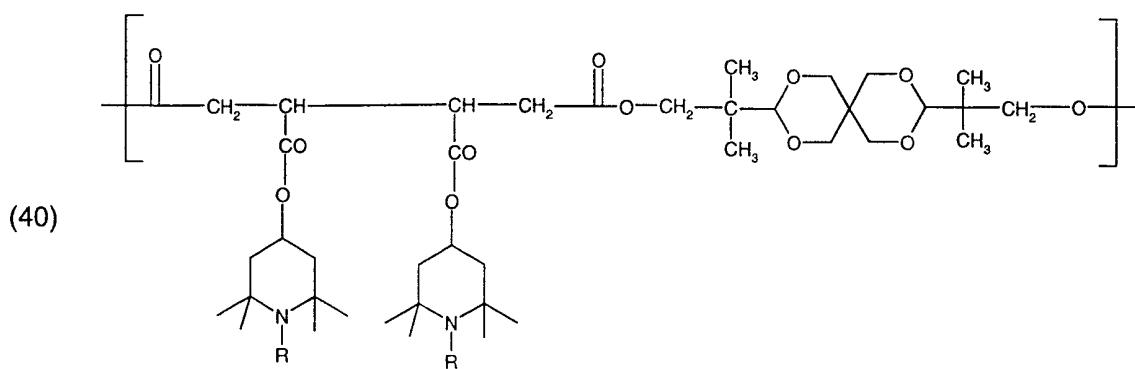
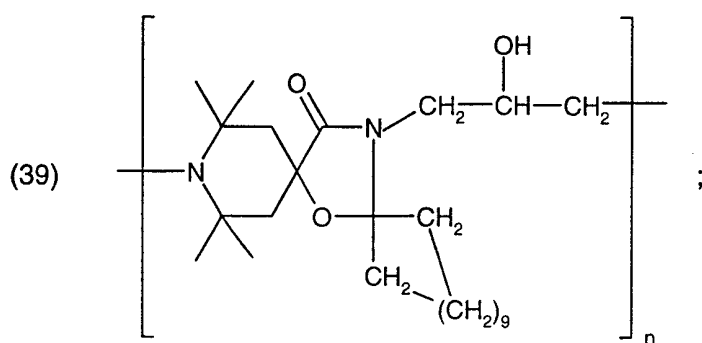
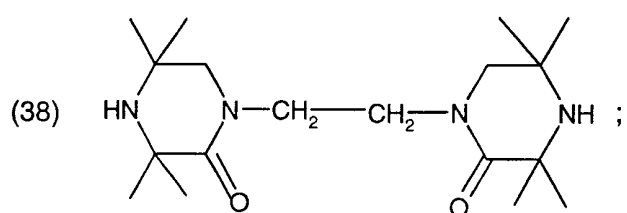
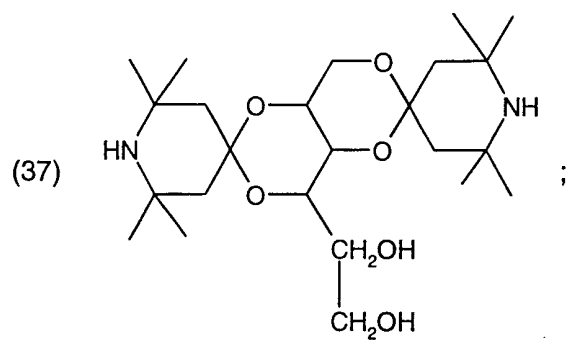
Examples of tetraalkylpiperidine derivatives which can be used according to this invention are to be found in EP-A-356677, pages 3-17, paragraphs a) to f). The cited paragraphs of this EP-A are regarded as part of the present description. It is particularly useful to employ the following tetraalkylpiperidine derivatives:

bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonic acid-bis(1,2,2,6,6-pentamethylpiperidyl)ester, the condensate of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-

piperidine and succinic acid, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)-pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS reg. No. [136504-96-6]); (2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, (1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, the reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane and epichlorohydrin, tetra(2,2,6,6-tetramethylpiperidin-4-yl)-butane-1,2,3,4-tetracarboxylate, tetra(1,2,2,6,6-pentamethylpiperidin-4-yl)-butane-1,2,3,4-tetracarboxylate, 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro[5.1.11.2] -heneicosan, 8-acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4,5] -decane-2,4-dione, or a compound of formulae

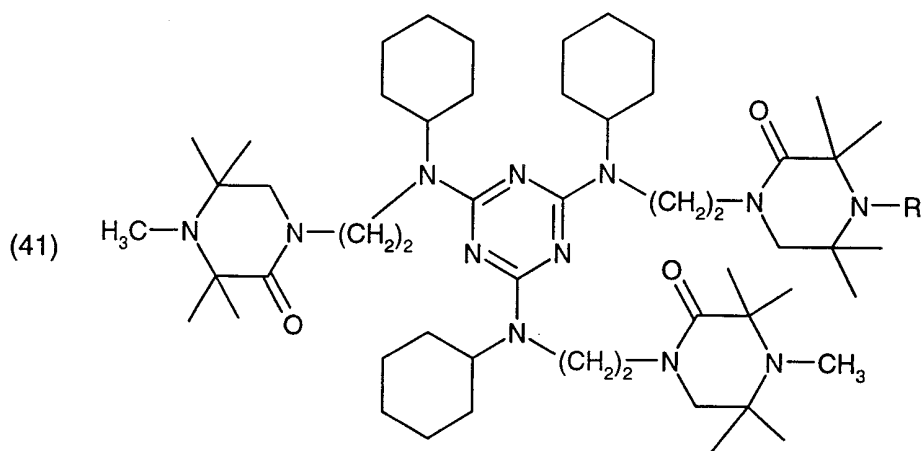


wherein m has a value of 5-50,



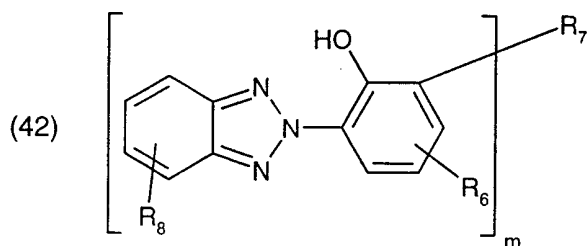
R = H or CH₃

or



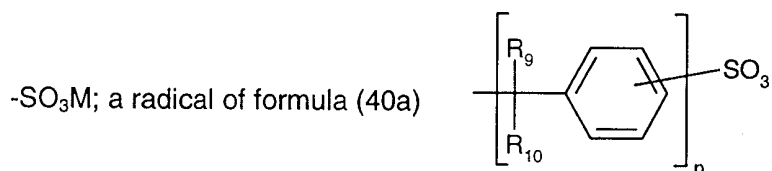
R = H or CH₃

It is also possible to use the inventive antioxidants of formulae (1), (2) and (3) together with benzotriazoles of formula



In formula (42),

R₆ is C₁-C₁₂alkyl; C₁-C₅alkoxy; C₁-C₅alkoxycarbonyl; C₅-C₇cycloalkyl; C₆-C₁₀aryl; aralkyl;



R₈ is hydrogen; C₁-C₅alkyl; C₁-C₅alkoxy; halogen, preferably Cl; or hydroxy

R₉ and R₁₀ are each independently of the other hydrogen; or C₁-C₅alkyl;

m is 1 or 2;

n is 0 or 1;

if $m = 1$, then

R_7 is hydrogen; unsubstituted or phenyl-substituted C_1 - C_{12} alkyl; C_6 - C_{10} aryl;

A

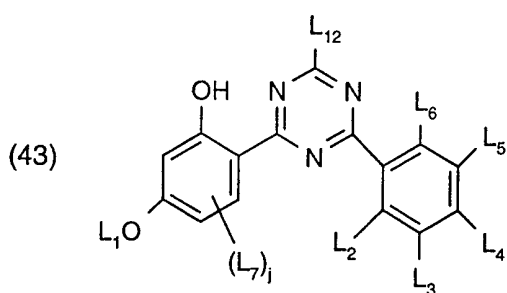
B

if $m = 2$, then

R_7 is a direct bond; $-(CH_2)_p$; and

p is 1 to 3.

The inventive antioxidants of formulae (1), (2) and (3) can also be used together with hydroxyphenyltriazine compounds of formula



wherein

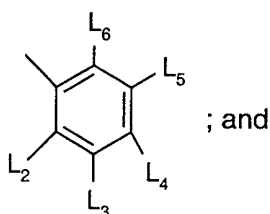
L_1 is C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl or C_5 - C_7 cycloalkyl;

L_2 and L_6 are each independently of the other H, OH, halogen, C_1 - C_{22} alkyl, halomethyl;

L_3 , L_5 and L_7 are each independently of one another H, OH, OL_1 , halogen, C_1 - C_{22} alkyl, halomethyl;

L_4 is H, OH, OL_1 , halogen, C_1 - C_{22} alkyl, phenyl, halomethyl;

L_{12} is C_1 - C_{22} alkyl, phenyl C_1 - C_5 alkyl, C_5 - C_7 cycloalkyl, OL_1 or, preferably a group of formula



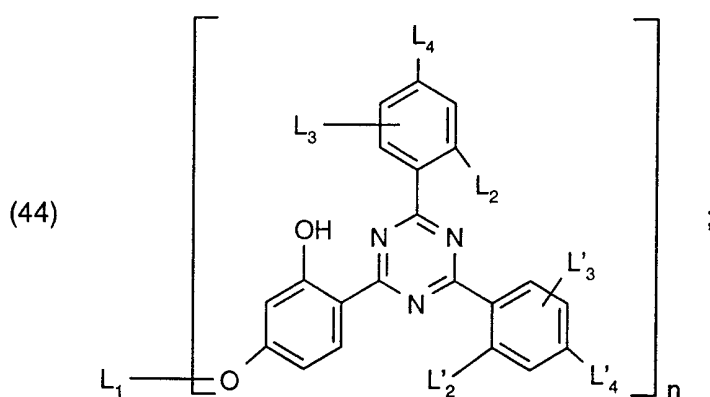
j is 0, 1, 2 or 3.

If L-substituents are defined as alkyl or alkenyl, or if they are aromatic or aliphatic ring systems, then these contain within the scope of the cited meanings usually 1 to 50 carbon atoms and can be interrupted once or several times by O, S, NR' , SO_2 , CO, phenylene,

cyclohexylene, COO, OCO, $-(\text{SiR}_p\text{R}_q\text{O})-$ and/or substituted once or several times by OH, OR', NR'R'', halogen, -CN, alkenyl, phenyl, $-\text{SiR}_p\text{R}_q\text{R}_r$ or COOH, where R' and R'' are each independently of the other H, alkyl, alkenyl or acyl, and R_p, R_q and R_r are each independently of the other H, alkyl, alkenyl, phenyl, alkoxy, acyl or acyloxy.

The above groups can also carry further substituents. Dimers or polymers are also possible.

Preferred 2-hydroxyphenyltriazines of this class are, for example, those of formulae



wherein in formula (44)

n is 1 or 2, and

L₁, where n = 1, is alkyl or alkyl which is interrupted by one or several O and/or substituted by one or several of the radicals OH, glycidyloxy, alkenoxy, COOH, COOR^e, O-CO-R^f; or alkenyl, cycloalkyl; phenylalkyl which is unsubstituted or substituted by OH, Cl or CH₃; COR^g; SO₂-R^h; CH₂CH(OH)-Rⁱ; where

R^e is alkyl; alkenyl; hydroxyalkyl; alkyl or hydroxyalkyl which is interrupted by one or several O; cycloalkyl; benzyl; alkylphenyl; phenyl; phenylalkyl; furfuryl; or CH₂CH(OH)-Rⁱ;

R^f, R^g are each independently of the other alkyl, alkenyl or phenyl;

R^h is alkyl, aryl or alkylaryl;

Rⁱ is aralkyl or CH₂OR^k;

R^k is cyclohexyl, phenyl, tolyl, benzyl; and

L₁, where n = 2, is alkylene; alkenylene; xylylene; alkylene or hydroxyalkylene which is interrupted by one or several -O-; hydroxyalkylene;

L₂ and L'₂ are each independently of the other H, alkyl or OH;

L₄ and L'₄ are each independently of the other H, alkyl, OH, alkoxy, halogen and, where n = 1, OL₁;

L_3 and L'_3 are each independently of the other H, alkyl or halogen.

L_1 , L_2 , L'_2 , L_3 , L'_3 , L_4 , L'_4 can within the scope of the cited meanings carry additional substituents, for example an ethylenically unsaturated polymerisable group. Dimers or polymers are also possible.

Examples of such compounds are, inter alia,

2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine,

2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine,

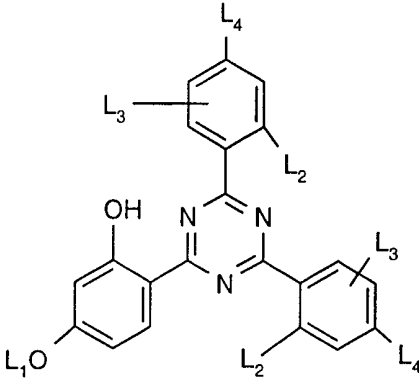
2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine,

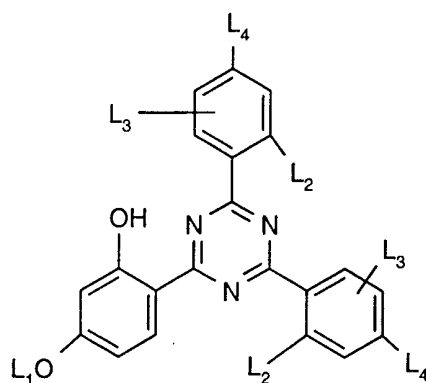
2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

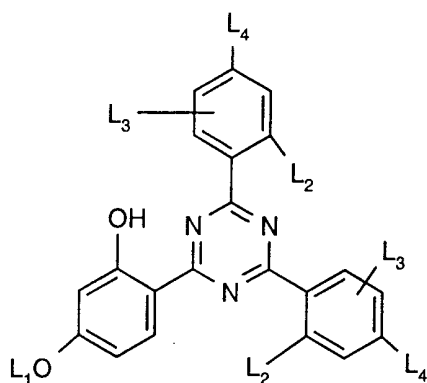
2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2-[2-hydroxy-4-(2-hydroxy-3-tridecyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; and compounds of the following formulae:

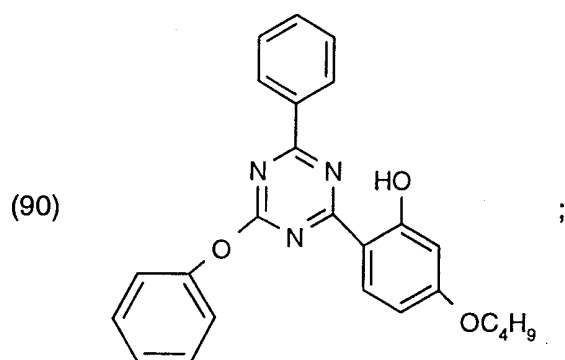
				
compound of formula	L_1	L_2	L_4	L_3
(45)	$\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$	CH_3	CH_3	H
(46)	$\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OC}_{12}\text{H}_{25}/\text{C}_{13}\text{H}_{27}$ (mixture)	CH_3	CH_3	H
(47)	$\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\text{C}_4\text{H}_9$ (n)	CH_3	CH_3	H
(48)	$\text{CH}_2\text{COO}-\text{C}_{18}\text{H}_{37}$	H	H	m- CF_3



compound of formula	L_1	L_2	L_4	L_3
(49)	C_8H_{17}	CH_3	CH_3	H
(50)	$CH_2CH(OH)CH(C_2H_5)-C_4H_9(n)$	CH_3	CH_3	H
(51)	H	CH_3	CH_3	H
(52)	CH_2CH_2OH	H	H	H
(53)	C_6H_{13}	H	H	H
(54)	$C_{18}H_{37}$	CH_3	CH_3	o- CH_3
(55)	$CH_2CH(OH)CH_2O-C_4H_9(n)$	H	H	H
(56)	$CH(OH)-C_5H_{11}(n)$	CH_3	CH_3	o- CH_3
(57)	C_8H_{17}	H	Cl	H
(58)	$CH(CH_3)-COO-C_2H_5$	CH_3	CH_3	o- CH_3
(59)	$CH_2CH(OCOCH_3)CH(C_2H_5)-C_4H_9(n)$	H	H	H
(60)	$CH_2CH(OH)CH(C_2H_5)-C_4H_9(n)$	H	H	H
(61)	$CH_2CH_2-O-CO-C(CH_3)_3$	H	H	H
(62)	H	H	H	H
(63)	$(CH_2)_{10}COO-C_2H_5$	H	Cl	H
(64)	$(CH_2)_5COOH$	H	H	H
(65)	$CH_2CH(C_2H_5)-C_4H_9(n)$	H	H	H
(66)	$CH_2CH(OH)CH_2O-C_4H_9(n)$	H	H	t- C_4H_9H
(67)	$CH_2CH(OH)CH_2O-C_4H_9(n)$	H	H	O CH_3H
(68)	$(CH_2)_3-Si(CH_3)_3$	H	H	H
(69)	cyclohexyl			
(70)	$CH_2CH(OH)CH_2O-2\text{-butyl}/2\text{-pentyl (mixture)}$			
(71)	$CH_2CH(OH)CH_2O-C_4H_9(n)$			



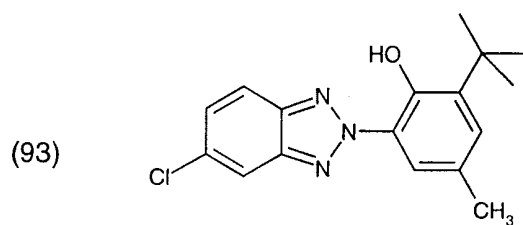
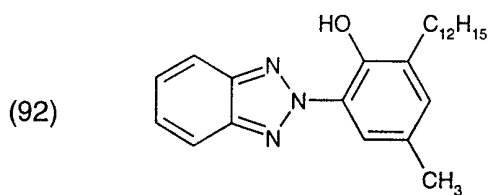
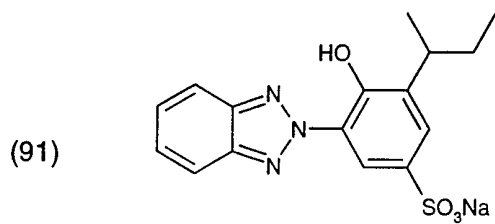
<u>compound of formula</u>	<u>L₁</u>	<u>L₂</u>	<u>L₄</u>	<u>L₃</u>
(72)	(CH ₂) ₁₀ COO-C ₂ H ₅			
(73)	C ₄ H ₉			
(74)	CH ₂ CH(OH)CH(C ₂ H ₅)-C ₄ H ₉ (n)			
(75)	CH(C ₃ H ₇) ₂			
(76)	cyclopentyl			
(77)	C(CH ₃) ₂ -COO-C ₂ H ₅			
(78)	CH(CH ₃)-COO-C ₂ H ₅			
(79)	(CH ₂) ₅ -CH ₃			
(80)	CH ₃	OCH ₃		
(81)	CH ₂ CH(OCOCH ₃)CH(C ₂ H ₅)-C ₄ H ₉ (n)	OCH ₂ CH ₂ OC ₂ H ₅		
(82)	CH ₂ CH ₂ CH ₂ -O-CO-C ₂ H ₅	OCH ₃		
(83)	CH ₂ CH(OH)CH ₂ -O-C ₄ H ₉ (n)	CH ₃		
(84)	CH ₂ CH(OH)CH ₂ -O-C ₄ H ₉ (n)	OCH ₃		
(85)	<div><div>n-C₁₀H₂₁</div><div>-CH₂-CH₂-CH</div><div>n-C₁₂H₂₅</div></div>			
(86)	iso-C ₈ H ₁₈			
(87)	<div><div>n-C₆H₁₃</div><div>-CH₂-CH₂-CH</div><div>n-Octyl</div></div>			
(88)	n-C ₁₈ H ₃₇			
(89)	2-ethylhexyl			

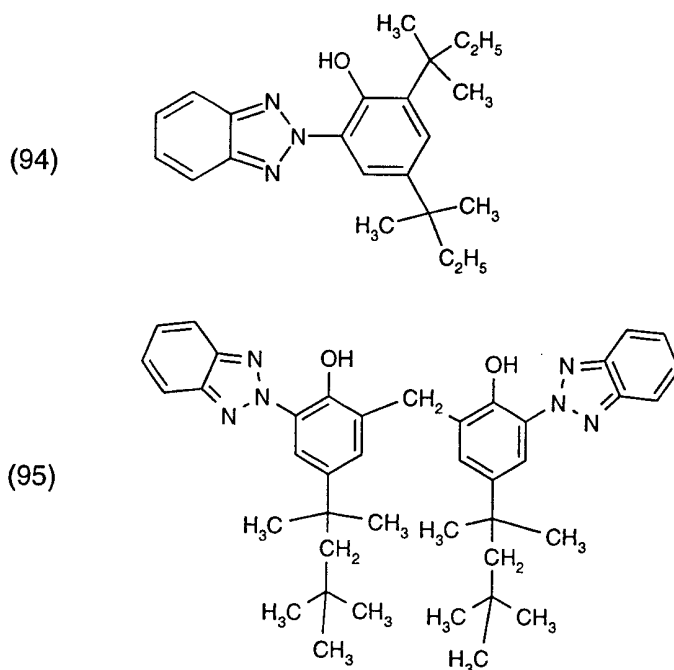


Abbreviations used in the above formulae:

i = isomeric mixture; n = straight-chain radical; t = tertiary radical; o-, m-, p- designate the position of the radical relative to the triazine ring.

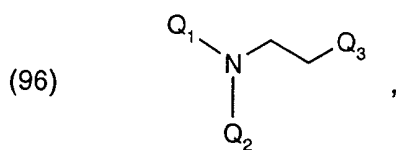
Examples of benzotriazole compounds which may be used in accordance with this invention:





In addition, the inventive antioxidants of formulae (1), (2) and (3) can also be used together with complex formers, in particular nitrogen-containing complex formers, for example ethylenediaminetetracetic acid (EDTA), nitrilotriacetic acid (NTA), β -alaninediacetic acid (EDETA) or ethylenediaminedisuccinic acid (EDDS).

Other suitable complex formers conform to formula



wherein

Q_1 , is Carb₁; Carb₂; or a radical of formula $-(CH_2)_{m_1}-OH$

Q_2 is hydrogen or Carb₂; and

Q_3 is Carb₃; an amino acid radical; or a radical of formula (96a)

wherein Carb₁, Carb₂ and Carb₃ are each independently of one another the radical of a C₁-C₈ mono- or dicarboxylic acid; and

m₁ is 1 to 5.

Particularly preferred compounds are those of formula (96), wherein

Q₁ is a monocarboxylic acid; or a radical of formula (96b) $-(CH_2)_{m_1}-OH$;

Q₂ is hydrogen or a monocarboxylic acid; and

Q₃ is formula (96b); or a monocarboxylic acid.

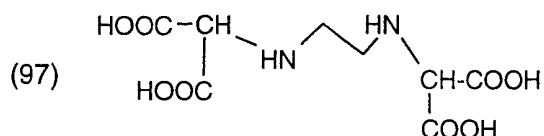
Particularly interesting complex formers are those of formula (96), wherein Carb₂ and Carb₃ are each independently of the other the radical of formula

(96c) $-(CH_2)_{n_1}-COOH$,

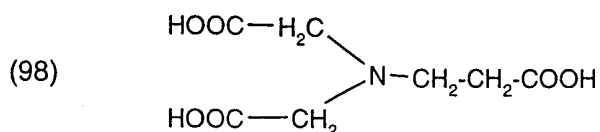
wherein

n₁ is 0 to 5.

Complex formers which are important in practice are those conforming to formula

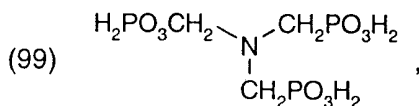


or to formula

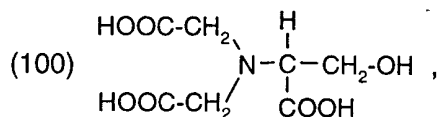


Nitrilotriacetic acid (NTA) is also suitable for use.

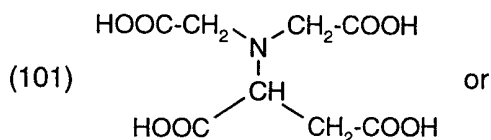
Other examples of complex formers which may be used according to this invention are aminotrimethylenephosphoric acid (ATMP) conforming to formula



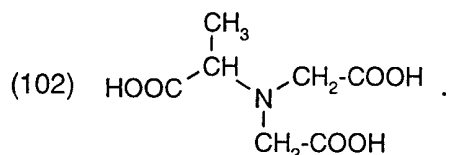
serinediacetic acid (SDA) conforming to formula



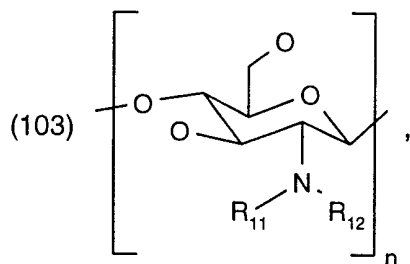
asparaginediacetic acid conforming to formula



methylglycinediacetic acid (MGDA) conforming to formula

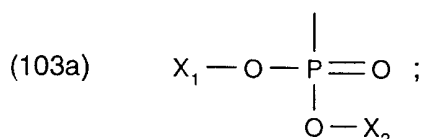


Other suitable complex formers are polyanionically-derived natural polysaccharides, for example containing phosphate, phosphonate or methylphosphonate groups, such as chitin derivatives, e.g. sulfochitin, carboxymethylchitin, phosphochitin, chitosan derivatives, for example sulfochitosan, carboxymethylchitosan or, very particularly preferably, phosphochitosan, which conform to formula



wherein

R_{11} is hydrogen or a radical of formula



R_{12} is a radical of formula (1a);

X_1 and X_2 are each independently of the other hydrogen, C_1 - C_5 alkyl or an alkali ion or ammonium ion; and
 n is 10 to 4000.

The antioxidants of formulae (1), (2) and (3) as well as mixtures of these compounds with light stabilisers or complex formers are particularly suitable for stabilising body-care products, in particular used for skin-care products, bath and shower additives, preparations containing fragrances and odoriferous substances, hair-care products, dentifrices, deodorising and antiperspirant preparations, decorative preparations, light protection formulations and preparations containing active ingredients.

Suitable skin-care products are, in particular, body oils, body lotions, body gels, treatment creams, skin protection ointments, shaving preparations, such as shaving foams or gels, skin powders, such as baby powder, moisturising gels, moisturising sprays, revitalising body sprays, cellulite gels and peeling preparations.

Preparations containing fragrances and odoriferous substances are in particular scents, perfumes, toilet waters and shaving lotions (aftershave preparations).

Suitable hair-care products are, for example, shampoos for humans and animals, in particular dogs, hair conditioners, products for styling and treating hair, perming agents, hair sprays and lacquers, hair gels, hair fixatives and hair dyeing or bleaching agents.

Suitable dentifrices are in particular tooth creams, toothpastes, mouth-washes, mouth rinses, anti-plaque preparations and cleaning agents for dentures.

Suitable decorative preparations are in particular lipsticks, nail varnishes, eye shadows, mascaras, dry and moist make-up, rouge, powders, depilatory agents and suntan lotions.

Suitable cosmetic formulations containing active ingredients are in particular hormone preparations, vitamin preparations, vegetable extract preparations and antibacterial preparations.

The cited body-care products can be in the form of creams, ointments, pastes, foams, gels, lotions, powders, make-ups, sprays, sticks or aerosols. They preferably contain the antioxidants of formulae (1) and/or (2) and/or (3) and, optionally, the above light stabilisers in the oil phase or in the aqueous or aqueous/alcoholic phase.

This invention therefore also relates to a body-care product containing at least one phenolic antioxidant of formula (1) and/or (2) and/or (3).

The antioxidant(s) are usually present in the novel body-care product in a concentration of 50 to 1000 ppm.

Creams are oil-in-water emulsions containing more than 50 % of water. The oil-containing base used therein is usually mainly fatty alcohols, for example lauryl, cetyl or stearyl alcohol, fatty acids, for example palmitic or stearic acid, liquid to solid waxes, for example isopropylmyristate or beeswax and/or hydrocarbon compounds, such as paraffin oil. Suitable emulsifiers are surfactants having primarily hydrophilic properties, such as the corresponding non-ionic emulsifiers, for example fatty acid esters of polyalcohols of ethylene oxide adducts, such as polyglycerol fatty acid ester or polyoxyethylenesorbitan fatty acid ether (Tween trademarks); polyoxyethylene fatty alcohol ether or their esters or the corresponding ionic emulsifiers, such as the alkali metal salts of fatty alcohol sulfonates, sodium cetyl sulfate or sodium stearyl sulfate, which are usually used together with fatty alcohols, such as cetyl alcohol or stearyl alcohol. In addition, creams contain agents which reduce water loss during evaporation, for example polyalcohols, such as glycerol, sorbitol, propylene glycol, and/or polyethylene glycols.

Ointments are water-in-oil emulsions which contain up to 70 %, preferably not more than 20 to 50 %, of water or of an aqueous phase. The oil-containing phase contains predominantly hydrocarbons, such as paraffin oil and/or solid paraffin which preferably contains hydroxy compounds, for example fatty alcohol or their esters, such as cetyl alcohol or wool wax for improving the water absorption. Emulsifiers are corresponding lipophilic substances, such as sorbitan fatty acid ester. In addition, the ointments contain moisturisers such as polyalcohols, for example glycerol, propylene glycol, sorbitol and/or polyethylene glycol as well as preservatives.

Rich creams are anhydrous formulations and are produced on the basis of hydrocarbon compounds, such as paraffin, natural or partially synthetic fats, for example coconut fatty acid triglycerides or, preferably, hardened oils and glycerol partial fatty acid esters.

Pastes are creams and ointments containing powdered ingredients which absorb secretions, for example metal oxides, such as titanium dioxide or zinc oxide, and also tallow and/or aluminium silicates which bind the moisture or the absorbed secretion.

Foams are liquid oil-in-water emulsions in aerosol form. Hydrocarbon compounds are used, inter alia, for the oil-containing phase, for example paraffin oil, fatty alcohols, such as cetyl alcohol, fatty acid esters, such as isopropylmyristate and/or waxes. Suitable emulsifiers are, inter alia, mixtures of emulsifiers having predominantly hydrophilic properties, for example polyoxyethylenesorbitan fatty acid ester, and also emulsifiers having predominantly lipophilic properties, for example sorbitan fatty acid ester. Commercially available additives are usually additionally employed, for example preservatives.

Gels are, in particular, aqueous solutions or suspensions of active substances in which gel formers are dispersed or swelled, in particular cellulose ethers, such as methyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose or vegetable hydrocolloids, for example sodium alginate, tragacanth or gum arabic. The gels preferably additionally contain also polyalcohols, such as propylene glycol or glycerol as moisturisers and wetting agents, such as polyoxyethylenesorbitan fatty acid ester. The gels furthermore contain commercially available preservatives, such as benzyl alcohol, phenethyl alcohol, phenoxyethanol and the like.

The following Table lists typical examples of body-care products of this invention and their ingredients:

<u>Body-care product</u>	<u>Ingredients</u>
moisturising cream	vegetable oil, emulsifier, thickener, perfume, water, antioxidant
shampoo	surfactant, emulsifier, preservatives, perfume, antioxidant
toothpaste	cleaning agent, thickener, sweetener, flavour, colourant, antioxidant, water

lip-care stick vegetable oil, wax, TiO₂, antioxidant

The novel body-care products have high stability towards colour changes and chemical degradation of the ingredients present in these products. This is to be attributed to the effectiveness, colour stability, ease of incorporation and hydrolytic stability of the antioxidants used.

The phenolic antioxidants are also used in household cleaning and treatment agents, for example in liquid scouring agents, glass detergents, neutral cleaners (all-purpose cleaners), acid household cleaners (bath), WC cleaners, preferably in washing, rinsing and dishwashing agents, clear rinsing agents, dishwasher detergents, shoe polishes, polishing waxes, floor detergents and polishes, metal, glass and ceramic cleaners, textile-care agents, agents for removing rust, colour and stains (stain remover salt), furniture and multipurpose polishes and leather dressing agents (leather sprays).

Typical examples of novel household cleaning and treating agents are:

<u>Household cleaners/household treating agents</u>	<u>Ingredients</u>
detergent concentrate	surfactant mixture, ethanol, antioxidant, water
shoe polish	wax, wax emulsifier, antioxidant, water, preservative
wax-containing floor cleaning agent	emulsifier, wax, sodium chloride, antioxidant, water, preservative

The antioxidant(s) are usually incorporated by dissolution in an oil phase or alcoholic or water phase, where required at elevated temperature. Details can be found in the Examples.

The phenolic antioxidants of formulae (1), (2) and (3) also have pronounced antimicrobial action.

The following Examples illustrate the invention.

Preparation of stabilised formulations of body-care productsExample 1a: Preparation of a moisturiser cream

<u>Phase</u>	<u>Ingredients</u>	<u>(w/w) %</u>
A	passionflower oil	8
	glyceryl dioleate	4
	dicapryl ether	4
	isopropylisostearate	4
	antioxidant of formula (31)	0.05
B	water, demin.	ad. 100
	EDTA	0.1
C	carbomer	0.15
D	sodium hydroxide	10%
		0.20
E	perfume; preservative	q.s.

Preparation: The components (A) are thoroughly mixed in a homogeniser for 10 min at 75-80°C. The water (B), likewise heated to 75-80°C beforehand, is slowly added and the mixture is homogenised for 1 min. The mixture is cooled, with stirring, to 40°C and then (C) and (E) are added and the mixture is homogenised for 1 min. Subsequently, (D) is added and the mixture is homogenised for 1/2 min and cooled, with stirring, to room temperature.

Alternatively to the antioxidant of the formulae (31) the following antioxidants can be applied (0.05 %):

- Example 1b: antioxidant of the formula (7)
 Example 1c: antioxidant of the formula (32)
 Example 1d: antioxidant of the formula (33)

Example 2: Preparation of a toilet water (w/w) %

<u>Ingredients</u>	<u>(w/w) %</u>
ethanol, 96%	60
d-limonene	5
cedrene	1.5

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citronellol	0.5
savin	0.5
antioxidant of formula (29)	0.08
UV absorber of formula (91)	0.1
S,S-EDDS	0.005
colourant (D&C Yellow No.5)	0.02
water	ad. 100

Preparation: The components are thoroughly mixed in the cited sequence at 50°C, a clear homogeneous solution being obtained.

Example 3: Preparation of a hair styling spray

Ingredients

	<u>(w/w) %</u>
alcohol, anhydrous	96.21
octylacrylamide/acrylate/butylaminoethylmethacrylate copolymer	2.52
hydroxypropyl cellulose	0.51
aminomethylpropanol (95%)	0.46
antioxidant of formula (33)	0.05
benzophenone-4	0.05
perfume oil	0.20

Preparation: The hydroxypropyl cellulose is first predissolved in half of the alcohol (Vortex mixer) and is charged with the aminomethylpropanol. The other components - with the exception of the acrylate resin - are dissolved in alcohol and this solution is added, with stirring, to the hydroxypropyl cellulose. Subsequently, the acrylate resin is added and stirred until completely dissolved.

Example 4: Preparation of a shampoo for greasy hair

Ingredients

	<u>(w/w) %</u>
sodium myreth sulfate	50.00
TEA abietoyl collagen hydrolysate	3.50
laureth-3	3.00
colourant (D&C Red No. 33)	0.20
antioxidant of formula (29)	0.05

UV absorber of formula (92)	0.15
phosphonomethylchitosan, sodium salt	0.01
perfume oil	0.10
water	ad. 100

Preparation: The components are mixed, with stirring, at room temperature until they are completely dissolved. The pH is 6.5.

Preparation of stabilised household productsExample 5: Preparation of a leather dressing and cleaning agent

<u>Ingredients</u>	<u>(w/w) %</u>
synthetic soap (Zetesap 813)	7.85
glycerol	6.00
anionic surfactant (Lumorol 4192; Mulsifan RT 13)	22.00
Vaseline	11.00
paraffin 52/54	20.00
talcum	2.00
orange terpene	4.00
antioxidant of formula (33)	0.02
water	27.13

Preparation: The antioxidant is predissolved in the terpene. The components are then stirred in the cited sequence at about 65°C until homogeneous. The mixture is then cooled to room temperature.

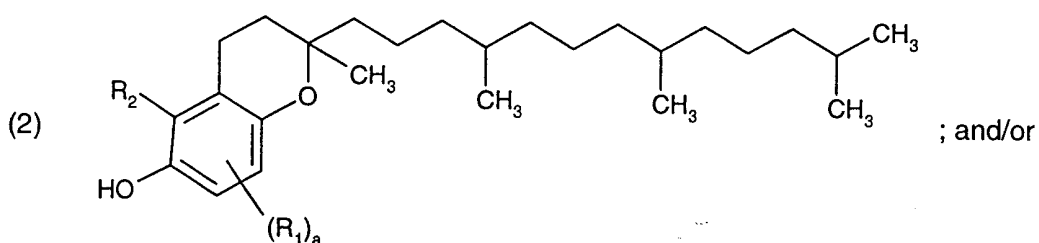
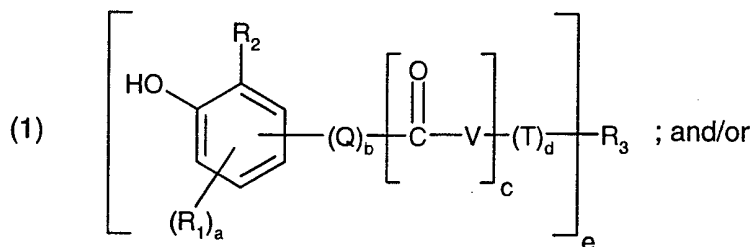
Example 6: Preparation of a glass detergent

<u>Ingredients</u>	<u>(w/w) %</u>
anionic / amphoteric surfactants (Lumorol RK)	0.7
butyl glycol	5.0
isopropanol	20.0
d-limonene	4.00
antioxidant of formula (32)	0.02
water, demin.	ad. 100

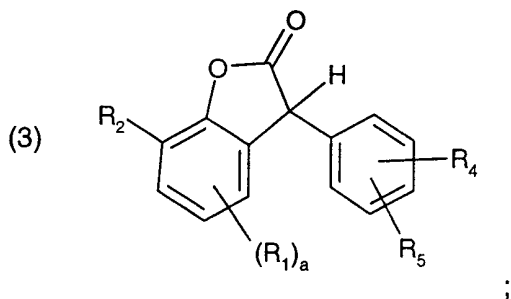
Preparation: The antioxidant is predissolved in the terpene. The components are then dissolved in the cited sequence until a clear homogeneous mixture is obtained.

What is claimed is:

1. Use of phenolic antioxidants of formulae



(a₂) an antioxidant of formula

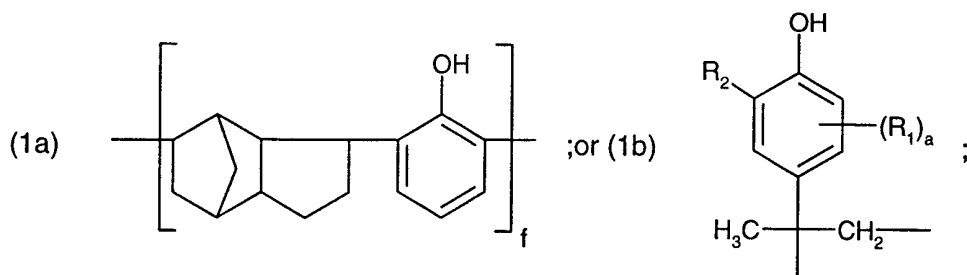


wherein in formulae (1), (2) and (3)

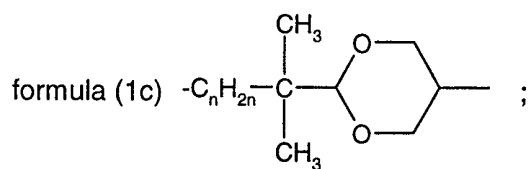
R₁ is hydrogen; C₁-C₂₂alkyl; C₁-C₂₂alkylthio; C₅-C₇cycloalkyl; phenyl; C₇-C₉phenylalkyl; or SO₃M;

R₂ is C₁-C₂₂alkyl; C₅-C₇cycloalkyl; phenyl; or C₇-C₉phenylalkyl;

Q is $-C_mH_{2m}-$; $-\underset{\substack{| \\ C_mH_{2m+1}}}{CH}-$; $-C_mH_{2m}-NH$; a radical of formula



T is $-C_nH_{2n}-$; $-(CH_2)_n-O-CH_2-$; $-C_nH_{2n}-NH-C(=O)-$; or a radical of



V is $-O-$; or $-NH-$;

a is 0; 1; or 2;

b, c and d are each independently of one another 0; or 1;

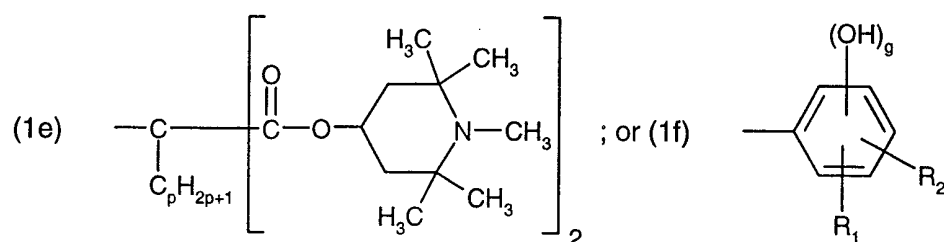
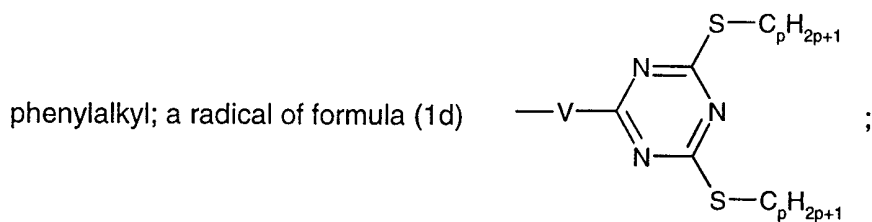
e is an integer from 1 to 4;

f is an integer from 1 to 3; and

m, n and p are each independently of one another an integer from 1 to 3;

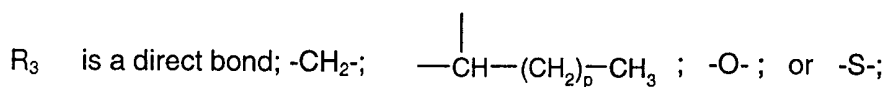
if e = 1, then

R_3 is M; hydrogen; C_1 - C_{22} alkyl; C_5 - C_7 cycloalkyl; C_1 - C_{22} alkylthio; C_2 - C_{18} alkenyl; C_1 - C_{18} -



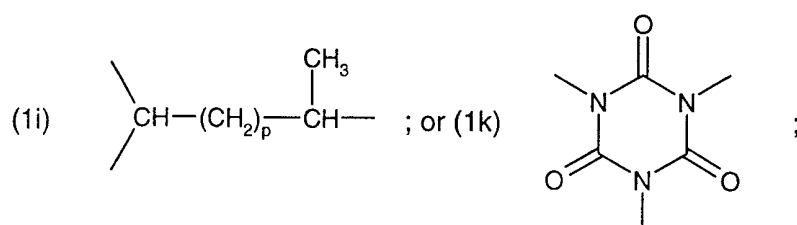
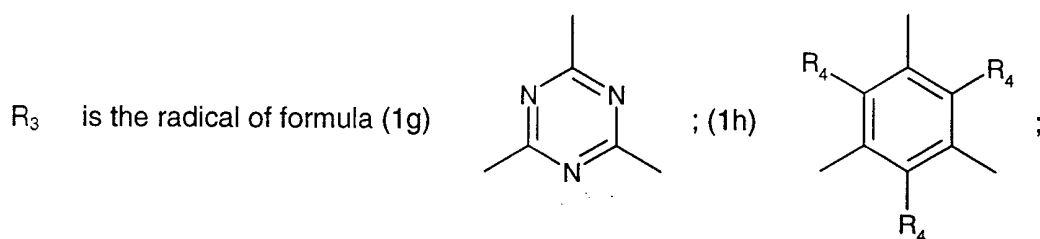
M is alkali; ammonium;

if $e = 2$, then



if

$e = 3$, then



if

$e = 4$, then

R_3 is $\begin{array}{c} | \\ -C- \\ | \end{array}$; or a direct bond;

R_4 and R_5 are each independently of the other hydrogen; or C_1 - C_{22} alkyl;
for stabilising body-care and household products.

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

Q is $-C_mH_{2m-}$,

wherein

m has the meaning cited in claim (1).

3. Use according to either claim 1 or claim 2, wherein

Q is a methylene or ethylene radical.

4. Use according to any one of claims 1 to 3, wherein

V is $-O-$.

5. Use according to any one of claims 1 to 4, wherein

R_1 and R_2 are each independently of the other C_1 - C_{18} alkyl.

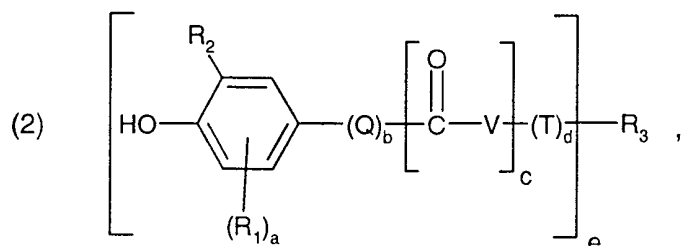
6. Use according to claim 5, wherein

R_1 and R_2 are each independently of the other C_1 - C_5 alkyl.

7. Use according to either claim 1, claim 5 or claim 6, wherein

a is 1.

8. Use according to claim 1, which comprises using an antioxidant of formula



wherein

R_1 and R_2 are each independently of the other C_1 - C_5 alkyl,

a is 1 or 2; and

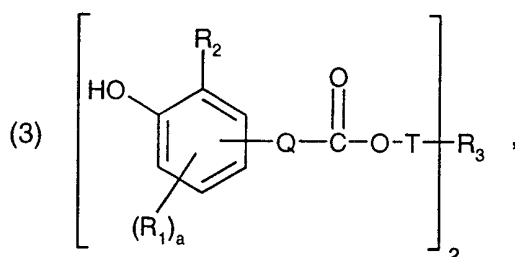
R_3 , Q , V , T , b , c , d and e have the meanings cited in claim 1.

9. A composition according to claim 8, wherein

R_1 and R_2 are the tert-butyl radical; and

a is 1.

10. Use according to claim 1, which comprises using an antioxidant of formula



wherein

R_1 and R_2 are each independently of the other C_1 - C_5 alkyl;

Q is $-C_mH_{2m}-$; or $-C_mH_{2m}-NH-$;

R_3 is a direct bond; $-O-$; $-S-$; $-CH_2-$; or $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}- \end{array}$;

a is 1 or 2;

m is 1 to 5; and

T has the meaning cited in claim 1.

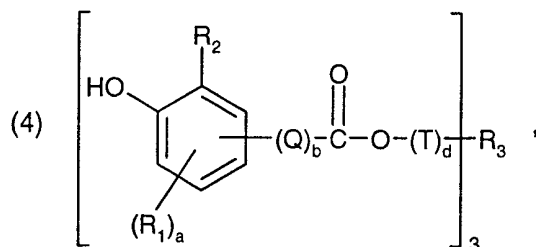
11. Use according to claim 10, wherein the antioxidant is a compound of formula (3), wherein

Q is ethylene; or $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}- \end{array}$;

R_3 is a direct bond; and

R_1 , R_2 , T and a have the meaning given in claim 10.

12. Use according to claim 1, wherein the antioxidant is the compound of formula



wherein

Q is $-\text{C}_m\text{H}_{2m}-$;

T is $-\text{C}_n\text{H}_{2n}-$;

R_1 and R_2 are each independently of the other C_1 - C_5 -alkyl;

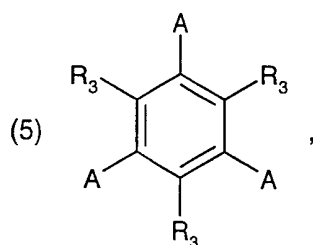
R_3 is the radical of formula (1g); (1h); (1i); or (1k) ;

m and n are each independently of the other 1 to 3;

a is 1 or 2; and

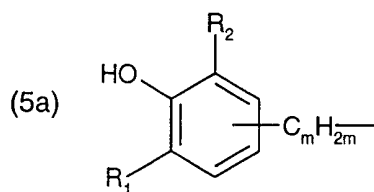
b and d are each independently of the other 0 or 1.

13. Use according to claim 12, wherein the antioxidant is a compound of formula



wherein

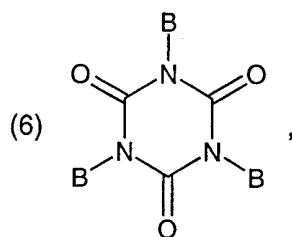
A is a radical of formula



R_1 , R_2 and R_3 are each independently of one another C_1 - C_5 alkyl; and

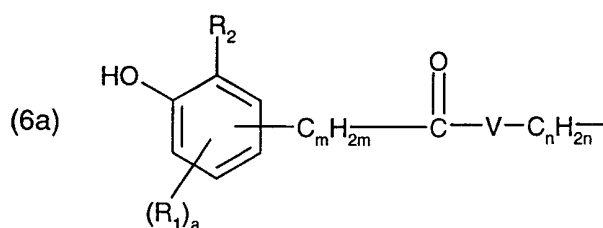
m is 1 to 3.

14. Use according to claim 12, wherein the antioxidant is a compound of formula



wherein

B is a radical of formula



R_1 and R_2 are each independently of the other C_1 - C_5 alkyl;

V is -O-; or -NH-;

a is 1; or 2;

m is 1 to 3; and

n is 0 to 3.

15. Use according to any one of claims 1 to 14, which comprises using the phenolic antioxidants of formulae (1), (2) and (3) as individual compounds or as a mixture of several individual compounds.

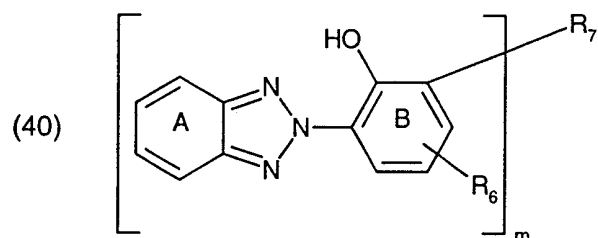
16. Use according to any one of claims 1 to 15, which comprises using the antioxidant or the sum of the antioxidants in a concentration of 50 to 1000 ppm.

17. Use according to any one of claims 1 to 16, which comprises using the antioxidants together with tocopherol and/or tocopherol acetate.

18. Use according to any one of claims 1 to 17, which comprises using the phenolic antioxidants together with light stabilisers.

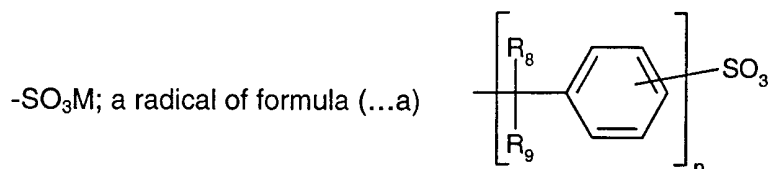
19. Use according to claim 18, wherein the light stabilisers used are sterically hindered amines.

20. Use according to claim 18, wherein the light stabilisers used are benzotriazoles of formula



wherein

R_6 is C_1 - C_{12} alkyl; C_1 - C_5 alkoxy; C_1 - C_5 alkoxycarbonyl; C_5 - C_7 cycloalkyl; C_6 - C_{10} aryl; aralkyl;



R_8 and R_9 are each independently of the other hydrogen; or C_1 - C_5 alkyl;

m is 1 or 2;

n is 0 or 1;

if $m = 1$,

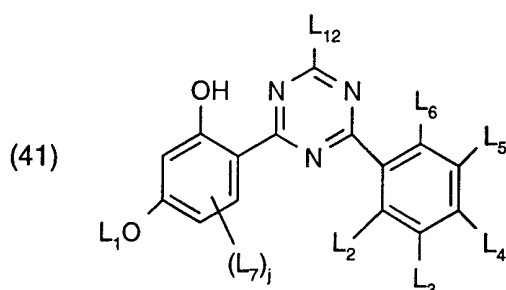
R_7 is hydrogen; unsubstituted or phenyl-substituted C_1 - C_{12} alkyl; C_6 - C_{10} aryl;

if $n = 2$,

R_2 is a direct bond; $-(CH_2)_p$ -; and

p is 1 to 3.

21. Use according to claim 18, wherein the light stabilisers used are 2-hydroxyphenyltriazines of formula



wherein

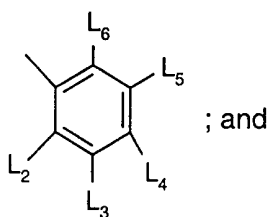
L_1 is C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl or C_5 - C_7 cycloalkyl;

L_2 and L_6 are each independently of the other H, OH, halogen, C_1 - C_{22} alkyl, halomethyl;

L_3 , L_5 and L_7 are each independently of one another H, OH, OL_1 , halogen, C_1 - C_{22} alkyl, halomethyl;

L_4 is H, OH, OL_1 , halogen, C_1 - C_{22} alkyl, phenyl, halomethyl;

L_{12} is C_1 - C_{22} alkyl, phenyl C_1 - C_5 alkyl, C_5 - C_7 cycloalkyl, OL_1 or, preferably, a group of formula



j is 0, 1, 2 or 3.

22. Use of the phenolic antioxidant according to claim 1 in body-care products for the skin and its adnexa.

23. Use according to claim 22, wherein the body-care products are selected from skin-care products, bath and shower additives, preparations containing fragrances and odoriferous substances, hair-care products, dentifrices, deodorising and antiperspirant preparations, decorative preparations, light protection formulations and preparations containing active ingredients.

24. Use according to claim 23, wherein the skin-care products are selected from body oils, body lotions, body gels, treatment creams, skin protection ointments, shaving preparations and skin powders.
25. Use according to claim 23, wherein the preparations containing fragrances and olfactory substances are selected from scents, perfumes, toilet waters and shaving lotions.
26. Use according to claim 23, wherein the hair-care products are selected from shampoos, hair conditioners, agents for styling and treating hair, perming agents, hair sprays and lacquers and hair dyeing or bleaching agents.
27. Use according to claim 23, wherein the decorative preparations are selected from lipsticks, nail varnishes, eye shadows, mascaras, dry and moist make-up, rouge, powders, depilatory agents and suntan lotions.
28. Use according to claim 23, wherein the active ingredient-containing cosmetic formulations are selected from hormone preparations, vitamin preparations, vegetable extract preparations and antibacterial preparations.
29. Use of the phenolic antioxidant according to claim 1 in household cleaning and treating agents.
30. Use according to claim 29, wherein the household cleaning and treating agents are selected from washing, rinsing and dishwashing agents, shoe polishes, polishing waxes, floor detergents and polishes, metal, glass and ceramic cleaners, textile care agents, agents for removing rust, colour and stains (stain remover salt), furniture and multipurpose polishes.
31. A body-care product, which comprises at least one phenolic antioxidant according to claim 1.
32. A household cleaning and treating agent, which comprises a phenolic antioxidant according to claim 1.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 99/07981

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/00 C11D1/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K C11D C08K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 283 252 A (PROCTER & GAMBLE LTD ;PROCTER & GAMBLE (US)) 21 September 1988 (1988-09-21) page 3, line 38 -page 5, line 16 claims 1-21 ---	1-16, 18, 19, 29, 30, 32
X	US 3 356 612 A (D.B.GUNTHRIE) 5 December 1967 (1967-12-05) column 12, line 1 -column 13, line 35 column 18, line 3 - line 33 ---	1-3, 5-9, 15-17, 29, 30, 32
X	US 4 900 469 A (CARTY DANIEL T ET AL) 13 February 1990 (1990-02-13) column 14, line 42 -column 15, line 56 column 20, line 43 - line 44 claims 1-18 --- -/-	1-3, 5-8, 15, 16, 29, 30, 32

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

6 March 2000

Date of mailing of the international search report

14/03/2000

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INTERNATIONAL SEARCH REPORT

Int. Appl. No.

PCT/EP 99/07981

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 13, 30 November 1998 (1998-11-30) & JP 10 204479 A (LION CORP), 4 August 1998 (1998-08-04) abstract	1-3,5-9, 29,30,32
X	WO 97 27839 A (COLGATE PALMOLIVE CO) 7 August 1997 (1997-08-07) abstract; claims 1-26	1-9,15, 16,22, 23,26, 29-32
X	EP 0 287 342 A (KURITA WATER IND LTD) 19 October 1988 (1988-10-19) abstract; claims 1-9	1-3,5-9, 15,16, 22,23, 25,31
X	DE 196 16 570 A (BASF AG) 30 October 1997 (1997-10-30) claims 1-12	1-3,5-9, 13,15, 16,29, 30,32
X	WO 96 03481 A (PROCTER & GAMBLE) 8 February 1996 (1996-02-08) claims 1-10	1-6, 8-10,15, 16,18, 20,29, 30,32
X	GB 1 456 199 A (BEECHAM GROUP LTD) 17 November 1976 (1976-11-17) claims 1-5	1,5,6,8, 15-17, 22,23,31
A	EP 0 453 396 A (CIBA GEIGY AG) 23 October 1991 (1991-10-23) claims 1-27	
A	US 5 688 995 A (LUTHER HELMUT ET AL) 18 November 1997 (1997-11-18) column 17, line 14 - line 16; claims 1-8	
A	WO 94 07946 A (CIBA GEIGY AG ;HOFFMANN KURT (DE); HERBST HEINZ (DE); PFAENDNER RU) 14 April 1994 (1994-04-14) claims 1-30	
A	EP 0 263 524 A (BASF AG) 13 April 1988 (1988-04-13) claims 1-3	
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/07981

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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