



HEAT STABILIZER FOR ORGANIC PEROXIDES

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The present invention relates to a heat stabilizer for organic peroxides. Another subject
5 matter of the invention is a composition comprising organic peroxides which is stable on storage and stable toward heat.

The use of a solvent, miscible with a (lower) alkyl ketone peroxide and exhibiting a boiling point of
10 between approximately 185 and 225°C, for thermally stabilizing organic peroxide has been disclosed in the document FR 1 594 180. This document teaches that the solvent is chosen from esters, aldehydes, ketones, hydrocarbons, halogenated hydrocarbons and epoxides. It
15 also teaches that, in addition to the heat-desensitizing solvent, pyrrolidine stabilizers can be used to render the ketone peroxides stable on storage.

French Application FR 2 792 321 discloses a process for the manufacture of a controlled-rheology
20 resin from a homopropylene or propylene copolymer in which, in place of the peroxides of the state of the art or in addition to the latter, stable free radicals, such as nitroxides, are incorporated in the resin to be modified, introduced, for example, into the molten zone
25 of an extruder.

Nitroxyl radicals are highly stable radical entities having an N-O[•] functional group. Reference may be made to the publication by D. Griller and K. Ingold



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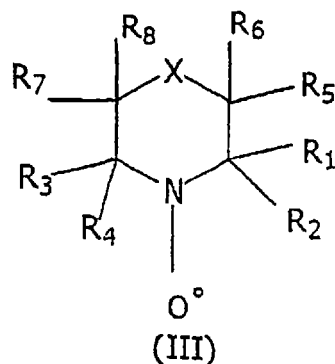
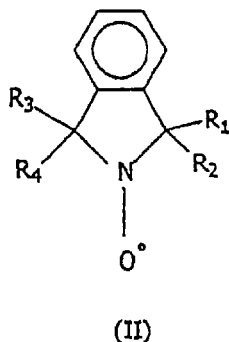
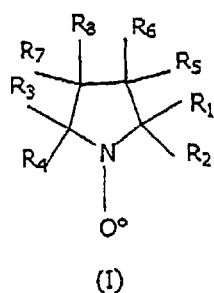
in Accounts of Chemical Research, 1976, 9, 13-19, or to that by A. Forrester et al. "Organic Chemistry of Stable Free Radicals" in Academic Press, 1968, for the definition.

5 These radicals have the property of reacting very rapidly with carbonaceous radicals resulting from the decomposition of initiators or resulting from radical processes, such as radical polymerizations. This reactivity has been taken advantage of by
10 incorporating these nitroxyl radicals in radical polymerization processes, such as the polymerization of styrene or acrylates, or processes for the copolymerization, decomposition or modification of polypropylene.

15 The Applicant Company has just found that nitroxyl radicals can thermally stabilize peroxides and make it possible optionally to increase the stability of the latter on storage.

 A first subject matter of the present
20 invention is a heat stabilizer for organic peroxides, characterized in that it includes at least one nitroxyl radical in its molecule. Preferably, the heat stabilizer for organic peroxides is an N-heterocyclic compound with the nitrogen atom of the nitroxyl radical
25 forming part of the ring.

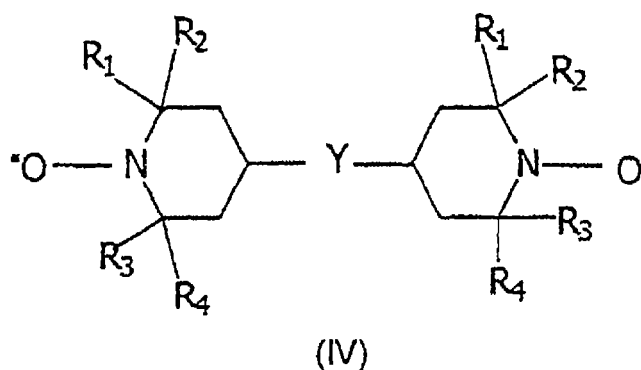
 Mention may in particular be made, as heat stabilizer, of the compounds represented by the formulae (I), (II) and (III):



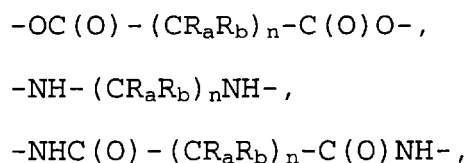
in which R_1 , R_2 , R_3 and R_4 , which can be identical or different, represent a hydrogen atom, a halogen atom, such as fluorine, chlorine, bromine or iodine, a saturated or unsaturated and linear, branched or cyclic hydrocarbonaceous group, such as an alkyl or phenyl radical, a polymer chain, which can, for example, be a chain of poly(alkyl (meth)acrylate), such as poly(methyl methacrylate), of polydiene, of polyolefin or of polystyrene, or a functional group, such as a cyano group $-CN$, an ester group $-COOR$, an amide group $-CON(R)_2$, an alkoxyl group $-OR$ or a phosphonate group $-PO(OR)_2$ in which R represents a hydrocarbonaceous chain having from 1 to 9 carbon atoms, and in which R_5 , R_6 , R_7 and R_8 , which can be identical or different, can be chosen from the same family of group as that which has just been envisaged for R_1 , R_2 , R_3 and R_4 and, furthermore, can represent a hydroxyl group $-OH$ or an acid group, such as $-COOH$ or $-PO(OH)_2$ or $-SO_3H$. Furthermore, X in the formula (III) represents a divalent group chosen from methylene $-CH_2-$, $-C(OR^o)(OR')$, carbonyl $-C(O)-$, oxy $-O-$ and $-CHZ-$, with Z representing a monovalent residue chosen from cyano:

-CN, hydroxyl: -OH, amino: -NR^oR', alkoxy: -OR^o,
 iminoyl: -N=CR^oR', carboxylate: -OC(O)-R^o or amide:
 -NHR^o-C(O)R' groups, in which R^o and R', which are
 identical or different, represent a hydrogen atom, a
 5 linear or branched alkyl group having a number of
 carbon atoms ranging from 1 to 20, or a benzyl or
 phenyl group. In the formula (III), X can also
 represent a phosphonate group: -OP(O)R''R'''- with R'' and
 R''' having the same meaning as Z.

10 The compounds represented by the general
 formula (IV)



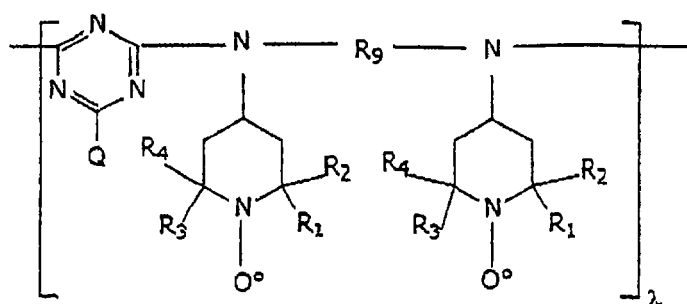
in which R₁, R₂, R₃ and R₄, which can be identical or
 different, have the same meaning as those used for the
 15 formulae (I) to (III) and Y represents a divalent group
 chosen from:



20 -S-, -O-; R_a and R_b, which are identical or
 different, represent a hydrogen atom or a linear or
 branched alkyl radical having a number of carbon atoms

ranging from 1 to 10, and n represents an integer ranging from 0 to 20, may also be suitable as heat stabilizer.

According to the invention, in addition to the compounds of general formula (IV), other compounds including several nitroxyl radicals, such as, for example, those represented by the general formula (V), may also be suitable as heat stabilizer:



(V)

in which R_1 , R_2 , R_3 and R_4 , which can be identical or different, have the same meaning as those of the preceding formulae (I) to (IV), λ is an integer between 1 and 20, R_9 represents an alkylene group having a number of carbon atoms ranging from 2 to 12 which can be interrupted by an $-O-$ or $-NR_{10}-$ with R_{10} denoting a hydrogen atom, an alkyl group having a number of carbon atoms of between 1 and 12, or a cycloalkyl group, and Q represents an $-OR_{11}$, $-NHR_{12}$ or $-NR_{12}R_{13}$ radical where R_{11} represents a linear or branched alkyl radical having a number of carbon atoms ranging from 1 to 12, a C_3-C_{12} alkoxyalkyl radical, a cyclohexyl radical, a benzyl

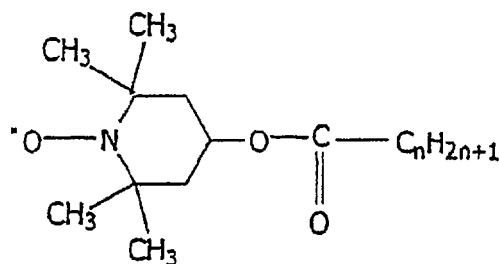
radical, a phenyl radical, a tolyl radical or a 2,2,6,6-tetrapiperidinyloxy residue and R_{12} and R_{13} have the same meaning as R_{11} and, furthermore, can also form, together and with the nitrogen atom which carries them, a 5-, 6- or 7-membered heterocyclic radical which can additionally comprise an oxygen.

The compounds of general formula (V) generally used are those obtained by oxidation of amines sold by Ciba under the name Chimasorb 944, where R_1 , R_2 , R_3 and R_4 each denoting a methyl group, R_5 an alkylene group comprising 6 carbon atoms, Q representing an $-N(O^\bullet)-C_6H_{11}$ radical and λ being an integer between 2 and 4.

The preferred compounds of general formula (III) are those for which R_1 , R_2 , R_3 and R_4 each denote a methyl group, R_5 , R_6 , R_7 and R_8 each represent a hydrogen atom and X a $-CH_2-$ group.

In particular, mention may be made, as compounds of general formula (III), of 2,2,6,6-tetramethyl-1-piperidinyloxy, generally sold under the name TEMPO, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy, sold under the name 4-hydroxy-TEMPO, 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy, commonly referred to as 4-methoxy-TEMPO, or 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, generally referred to as 4-oxo-TEMPO.

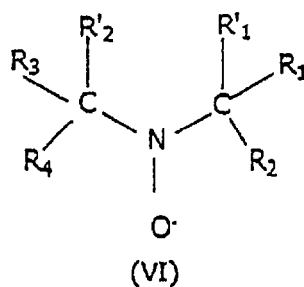
The compounds of general formula (III) which are particularly preferred are those represented by the following formula:



with n being able to vary from 1 to 20.

The compounds such as 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, sold under the trade name PROXYL, 1-piperidinyloxy-2,2,6,6-tetramethyl-4-[(1-oxooctadecyl)oxy], 1-piperidinyloxy-4,4'-((1,10-decanediyl)-bis(oxy)bis(2,2,6,6-tetramethyl) nitroxide, sold under the trade name CXA 5415 by Ciba Specialty Chemical, 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl mono-phosphonate or 3-carboxy-2,2,5,5-tetramethyl-pyrrolidinyloxy (commonly referred to a 3-carboxy-Proxyl) are also preferred.

Noncyclic compounds, such as those represented by the general formula (VI), may also be suitable as heat stabilizers:



in which R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , which can be identical or different, have the same meaning as R_1 , R_2 , R_3 and R_4 of the preceding general formulae.

A second subject matter of the invention is a composition comprising organic peroxide which is stable on storage and stable toward heat, characterized in that it comprises at least one organic peroxide and at least one heat stabilizer according to the first
5 subject matter of the present invention.

The amount of heat stabilizer present in the stable organic peroxide composition according to the invention is preferably between 0.1 and 99% by weight
10 and advantageously between 0.2 and 30%.

Mention may in particular be made, as organic peroxides, of dialkyl peroxides, hydroperoxides and their salts, peroxyketals and peroxyesters. Dialkyl peroxides, in particular cyclic dialkyl peroxides
15 deriving from the oxidation of ketones, peroxyketals and hydroperoxides are particularly preferred.

Mention may be made, as examples of dialkyl peroxides, of 2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne, di(tert-butyl) peroxide, di(tert-amyl) peroxide, tert-butyl cumyl peroxide, di(tert-butylperoxyiso-
20 propyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, dicumyl peroxide or 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane.

Mention may be made, as examples of
25 peroxyesters, of tert-butyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, OO-tert-butyl O-(2-ethylhexyl) monoperoxycarbonate, OO-tert-butyl O-isopropyl monoperoxycarbonate, OO-tert-

amyl O-(2-ethylhexyl) monoperoxy carbonate, tert-butyl
 peroxyisobutyrate, tert-butyl peroxy-2-ethylhexanoate,
 tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-
 2-ethylhexanoate (Luperox 575), 2,5-dimethyl-
 5 2,5-di(2-ethylhexanoylperoxy)hexane (Luperox 256),
 3,6,9-triethyl-1,4,7-triperoxonane, tert-butyl
 peroxy-pivalate (Luperox 11M75), tert-amyl
 peroxy-pivalate, tert-butyl peroxyneodecanoate, tert-
 amyl peroxyneodecanoate, β -cumyl peroxyneodecanoate or
 10 3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate.

Mention may be made, as hydroperoxides, of
 tert-butyl hydroperoxide, tert-amyl hydroperoxide,
 cumyl hydroperoxide, 2,5-dimethyl-2,5-di(hydroxy-
 peroxy)hexane, diisopropylbenzene monohydroperoxide,
 15 diisopropylbenzene dihydroperoxide or para-menthyl
 hydroperoxide.

Mention may be made, as hydroperoxide salts,
 of the disodium salt of 1,3- and 1,4-bis(2-hydro-
 peroxideprop-2-yl)benzene.

20 Mention may be made, as peroxyketals, of
 ethyl 3,3-di(tert-butylperoxy)butyrate, ethyl 3,3-
 di(tert-amylperoxy)butyrate, n-butyl 4,4-di(tert-
 butylperoxy)valerate, 2,2-di(tert-butylperoxy)butane,
 1,1-di(tert-butylperoxy)cyclohexane, 1,1-di(tert-
 25 butylperoxy)-3,5,5-trimethylcyclohexane or 1,1-di(tert-
 amylperoxy)cyclohexane.

Peroxyesters, such as Luperox 575 (tert-amyl
 peroxy-2-ethylhexanoate), Luperox 256 (2,5-dimethyl-
 2,5-di(2-ethylhexanoylperoxy)hexane) and Luperox 11M75

(tert-butyl peroxy-pivalate), requiring a storage temperature below ambient temperature are advantageously chosen.

The organic peroxide composition according to the second subject matter of the invention can also comprise conventional diluents, such as plasticizers, liquid phlegmatizers, organic solvents, polymeric carriers or organic carriers. This organic peroxide composition can additionally comprise one or more additives, such as anticaking agents, antioxidants, pigments or dyes, and metal-sequestering agents, such as DTPA (sodium diethylenetriaminepentaacetate) or EDTA (sodium ethylenediaminetetraacetate).

Mention may be made, as example of composition according to the second subject matter of the invention, of the composition comprising the disodium salt of 1,3- and 1,4-bis(2-hydroxyperoxyprop-2-yl)benzene, a stabilizer according to the first subject matter, in particular TEMPO, and a metal-sequestering agent, such as EDTA.

A third subject matter of the invention is a process for the preparation of the organic peroxide composition according to the second subject matter of the invention. This process consists in adding a sufficient amount of the heat stabilizer(s) according to the first subject matter of the invention to the organic peroxide to be stabilized.

A fourth subject matter of the invention is the use of the composition according to the second

subject matter of the invention for modifying polymers. Mention may in particular be made of the decomposition of polymers, in particular of polypropylene, and the grafting of polymers, such as, for example, the

5 grafting of polypropylene with maleic anhydride.

EXPERIMENTAL PART

Luperox 101 = 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane

10 Luperox 802 = 1,4-bis(tert-butylperoxyisopropyl)benzene

Luperox 331M50 = 1,1-di(tert-butylperoxy)

Luperox TBH70X* = tert-butyl hydroperoxide

TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy

AF845: 1-piperidinyloxy-2,2,6,6-tetramethyl-4-[(1-oxo-

15 octadecyl)oxy]

CXA 5415: 1-piperidinyloxy-4,4'-((1,10-decanediyl)-bis(oxy)bis(2,2,6,6-tetramethyl) nitroxide

* 14% solution in isododecane

The beneficial effect of the stabilizers

20 (TEMPO, AF845 and CXA 5415) on the decomposition temperature of the various organic peroxides is illustrated in table I.

Organic peroxide or mixture	Peroxide/ stabilizer ratio by mass	Temperature of the beginning of decomposition (°C)
Luperox 101	-	120
Luperox 101 + TEMPO	10	125
Luperox 101 + AF 845	3	130
Luperox 802	-	120
Luperox 802 + TEMPO	12	130
Luperox 802 + AF 845	4	130
Luperox 802 + CXA 5415	4	130
Luperox 331M50	-	100
Luperox 331M50 + TEMPO	5	115
Luperox TBH70X	-	190
Luperox TBH70X + TEMPO	5	205

TABLE I

Products used for the decomposition

- 5 - Polypropylene with an MFI of 3.3 (230°C/2.16 kg)
- Organic peroxide: 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane - Luperox 101 (peroxide content 95%)
- Stabilizer: TEMPO

10 **Experimental procedure**

The polypropylene is decomposed in a corotating twin-screw extruder of Brabender type. This extruder comprises 4 zones Z1 to Z4, the respective temperatures of which are 200°C/220°C/220°C/180°C. The

15 extrusion rate at the outlet of zone Z4 depends on the screw speed; it typically varies from 4.5 to 5 kg/h. The lace is granulated after cooling. The product is characterized by the MFI value (measured at 230°C, 2.16 kg), by the value of the modulus (measured

20 according to ISO Standard 178) and by the value of the

Charpy impact test (measured at 23°C according to ISO Standard 179/1eA).

The polypropylene is reduced to the form of a powder, on which a solution based on acetone, on organic peroxide and on TEMPO is adsorbed. After adsorption, the acetone is evaporated and the polypropylene-based reactive mixture is introduced via a hopper into zone 1 (Z1).

The results obtained with regard to decomposition of the problem with a stabilizing composition according to the invention are summarized in table II (examples 3 and 4 carried out from organic peroxide and TEMPO compositions, whereas example 5 was carried out by dispersing the peroxide and the TEMPO separately over the polypropylene powder).

Example	Peroxide (ppm)	TEMPO (ppm)	TEMPO/ Peroxide molar ratio	MFI (dg/min)	Modulus (MPa)	Notched Charpy impact Energy at 23°C (kJ/m ²)
1	0	0	-	3.3	1270	3.1
2	500	0	0.0	33.4	1170	2.3
3	500*	25*	0.1	25.8	1170	2.6
4	2000*	1020*	1.0	23.6	1180	2.7
5	2000*	1020	1.0	23.5	1180	2.7

* Use of a composition (premix) based on organic peroxide and on TEMPO

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TABLE II

The incorporation of a composition based on organic peroxide and on nitroxide, such as TEMPO, makes

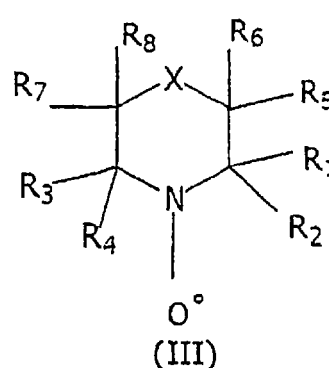
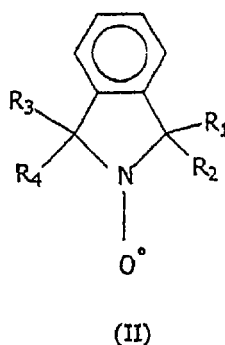
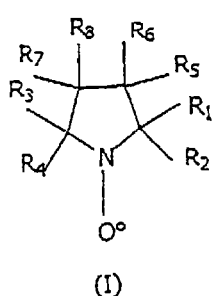
it possible to obtain a polypropylene with a lower flow index and with a better impact property while retaining the same stiffness. Comparison of examples 4 and 5 clearly shows that the use of a premix results in properties identical to those obtained from the constituents used separately.

WHAT IS CLAIMED IS:

1. A heat stabilizer for organic peroxides, characterized in that it includes at least one nitroxyl radical in the molecule.

2. The stabilizer as claimed in claim 1, characterized in that it is an N-heterocyclic compound with the nitrogen atom of the nitroxyl radical forming part of the ring.

3. The stabilizer as claimed in claim 1 or 2, characterized in that it is represented by at least one of the formulae (I), (II) and (III):



15

in which R_1 , R_2 , R_3 and R_4 , which can be identical or different, represent a hydrogen atom, a halogen atom, such as fluorine, chlorine, bromine or iodine, a saturated or unsaturated and linear, branched or cyclic hydrocarbonaceous group, such as an alkyl or phenyl radical, a polymer chain, which can, for example, be a chain of poly(alkyl (meth)acrylate), such as poly(methyl methacrylate), of polydiene, of polyolefin

or of polystyrene, or a functional group, such as a cyano group $-\text{CN}$, an ester group $-\text{COOR}$, an amide group $-\text{CON}(\text{R})_2$, an alkoxyl group $-\text{OR}$ or a phosphonate group $-\text{PO}(\text{OR})_2$ in which R represents a hydrocarbonaceous

5 chain having from 1 to 9 carbon atoms, and in which R_5 , R_6 , R_7 and R_8 , which can be identical or different, can be chosen from the same family of group as that which has just been envisaged for R_1 , R_2 , R_3 and R_4 and, furthermore, can represent a hydroxyl group $-\text{OH}$ or an

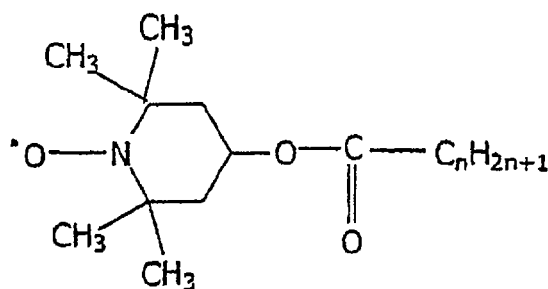
10 acid group, such as $-\text{COOH}$ or $-\text{PO}(\text{OH})_2$ or $-\text{SO}_3\text{H}$. Furthermore, X in the formula (III) represents a divalent group chosen from methylene $-\text{CH}_2-$, $-\text{C}(\text{OR}^\circ)(\text{OR}')-$, carbonyl $-\text{C}(\text{O})-$, oxy $-\text{O}-$ and $-\text{CHZ}-$, with Z representing a monovalent residue chosen from cyano:

15 $-\text{CN}$, hydroxyl: $-\text{OH}$, amino: $-\text{NR}^\circ\text{R}'$, alkoxy: $-\text{OR}^\circ$, iminoyl: $-\text{N}=\text{CR}^\circ\text{R}'$, carboxylate: $-\text{OC}(\text{O})-\text{R}^\circ$ or amide: $-\text{NHR}^\circ-\text{C}(\text{O})\text{R}'$ groups, in which R° and R' , which are identical or different, represent a hydrogen atom, a linear or branched alkyl group having a number of

20 carbon atoms ranging from 1 to 20, or a benzyl or phenyl group. In the formula (III), X can also represent a phosphonate group: $-\text{OP}(\text{O})\text{R}''\text{R}'''-$ with R'' and R''' having the same meaning as Z .

4. The stabilizer as claimed in claim 3,

25 characterized in that it is represented by the following formula:



with n being able to vary from 1 to 20.

5. The stabilizer as claimed in any one of
 5 the preceding claims, characterized in that it is
 chosen from 2,2,6,6-tetramethyl-1-piperidinyloxy,
 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy,
 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy or
 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy.

10 6. The stabilizer as claimed in one of
 claims 1 to 4, characterized in that it is chosen from
 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, bis(1-oxyl-
 2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-
 tetramethyl-4-hydroxypiperidine-1-oxyl monophosphonate
 15 or 3-carboxy-2,2,5,5-tetramethylpyrrolidinyloxy.

7. A composition comprising organic
 peroxide(s) which is stable on storage and stable
 toward heat, characterized in that it comprises at
 least one organic peroxide and at least one stabilizer
 20 as claimed in any one of the preceding claims.

8. The composition as claimed in claim 7,
 characterized in that the organic peroxide is chosen
 from dialkyl peroxides, hydroperoxides and their salts,
 peroxyketals and peroxyesters.

9. The composition as claimed in claim 8, characterized in that the organic peroxide is dicumyl peroxide, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane or the disodium salt of 1,3- and 1,4-bis(2-
5 hydroxyperoxideprop-2-yl)benzene.

10. The composition as claimed in one of claims 7 to 9, characterized in that it additionally comprises diluents and/or additives.

11. A process for the production of a
10 composition as claimed in one of claims 7 to 10, characterized in that at least one heat stabilizer as claimed in one of claims 1 to 6 is added to the organic peroxide.

12. The use of a composition as claimed in
15 one of claims 7 to 10 for modifying polymers.