

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION
EN MATIÈRE DE BREVETS (PCT)(19) Organisation Mondiale de la Propriété
Intellectuelle
Bureau international(43) Date de la publication internationale
21 novembre 2002 (21.11.2002)

PCT

(10) Numéro de publication internationale
WO 02/092561 A1(51) Classification internationale des brevets⁷ :
C07C 409/00LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN,
YU, ZA, ZM, ZW.(21) Numéro de la demande internationale :
PCT/FR02/01500

(22) Date de dépôt international : 30 avril 2002 (30.04.2002)

(25) Langue de dépôt : français

(26) Langue de publication : français

(84) États désignés (régional) : brevet ARIPO (GH, GM, KE,
LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), brevet
eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet
européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR,
IE, IT, LU, MC, NL, PT, SE, TR), brevet OAPI (BF, BJ,
CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG).(30) Données relatives à la priorité :
01/06526 17 mai 2001 (17.05.2001) FR

Déclarations en vertu de la règle 4.17 :

— relative au droit du déposant de demander et d'obtenir un
brevet (règle 4.17.ii)) pour les désignations suivantes AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, 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, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD,
SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ,
VN, YU, ZA, ZM, ZW, brevet ARIPO (GH, GM, KE, LS, MW,
MZ, SD, SL, SZ, TZ, UG, ZM, ZW), brevet eurasiatique (AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT,
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG)
— relative à la qualité d'inventeur (règle 4.17.iv)) pour US
seulement(71) Déposant (pour tous les États désignés sauf US) : ATO-
FINA [FR/FR]; 4-8, cours Michelet, F-92800 Puteaux
(FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants (pour US seulement) :
GRIMALDI, Sandra [FR/FR]; 29, rue du Brulet,
F-69110 Sainte Foy-les-Lyon (FR). GUERRET, Olivier
[FR/FR]; 6, route du Lac, F-64230 Mazerol (FR). COU-
TURIER, Jean-Luc [FR/FR]; 26, rue Lieutenant-Colonel
Prévost, F-69006 Lyon (FR). DEBAUD, Fabien [FR/FR];
50, avenue du Point du Jour, F-69005 Lyon (FR).(74) Mandataire : DANG, Doris; ATOFINA, Département
Propriété Industrielle, 4-8, Cours Michelet, La Défense 10,
F-92091 Paris la Défense Cedex (FR).

Publiée :

— avec rapport de recherche internationale

(81) États désignés (national) : AE, AG, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ,
DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,En ce qui concerne les codes à deux lettres et autres abrégia-
tions, se référer aux "Notes explicatives relatives aux codes et
abréviations" figurant au début de chaque numéro ordinaire de
la Gazette du PCT.

(54) Title: ORGANIC PEROXIDE HEAT STABILISER

(54) Titre : STABILISATEUR THERMIQUE DE PEROXYDES ORGANIQUES

(57) Abstract: The invention concerns a heat stabiliser of organic peroxides characterised in that it contains at least a nitroxyl radical in its molecule. The invention also concerns a storage-stable and heat-stable organic peroxide composition, the method for preparing same and uses thereof for modifying polymers.

(57) Abrégé : La présente invention concerne un stabilisateur thermique de peroxydes organiques caractérisé en ce qu'il renferme au moins un radical nitroxyle dans sa molécule. Elle a également pour objet une composition de peroxyde organique stable au stockage et stable thermiquement, son procédé de préparation ainsi que ses utilisations dans la modification des polymères.

HEAT STABILIZER FOR ORGANIC PEROXIDES

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

-2-

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.

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 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.

10 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.

According to a first aspect, the present invention provides the use of an N-heterocyclic heat-stabilizing compound including at least one nitroxyl radical with the N atom of the nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabilizer being > the temperature of the beginning of decomposition of the solution not comprising the stabilizer.

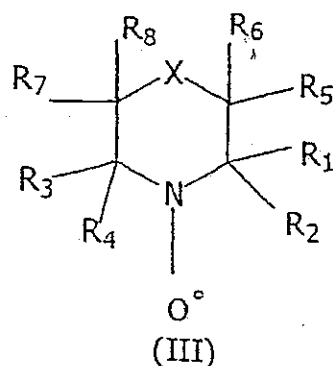
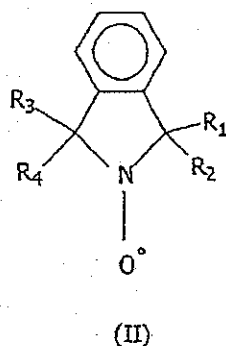
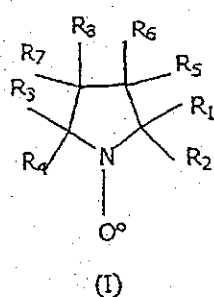
According to a second aspect, the present invention provides a composition comprising organic peroxide(s) which is/are stable on storage and stable towards heat, which composition comprises at least one organic peroxide and at least one N-heterocyclic heat-stabilizing compound including at least one nitroxyl radical with the N atom of the nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabiliser being > the temperature of the beginning of decomposition of the solution not comprising the stabilizer.

According to a third aspect, the present invention provides a process for the manufacture of such a composition comprising organic peroxide(s) which is/are stable on storage and stable towards heat, in which process at least one N-heterocyclic heat-stabilizing compound including at least one nitroxyl radical with

-2a-

the N atom of the nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabilizer being > the temperature of the beginning of decomposition of the solution not comprising the stabilizer, is added
5 to the organic peroxide.

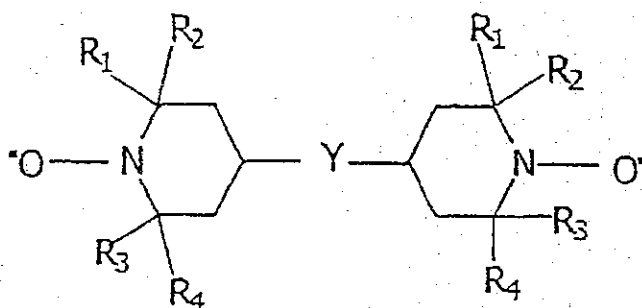
Mention may in particular be made, as heat stabilizer, of the compounds represented by the formulae (I), (III) and (III):



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 $-\text{CN}$, an ester group $-\text{COOR}$, an amide group $-\text{CON}(\text{R})_2$, an alkoxy group $-\text{OR}$ or a phosphonate group $-\text{PO}(\text{OR})_2$ 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 $-\text{OH}$ or an 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:

-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)



(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:

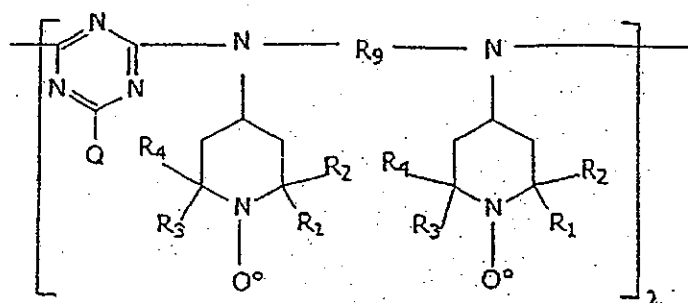
-OC(O)-(CR_aR_b)_n-C(O)O-,
 -NH-(CR_aR_b)_nNH-,
 -NHC(O)-(CR_aR_b)_n-C(O)NH-,

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)

10

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

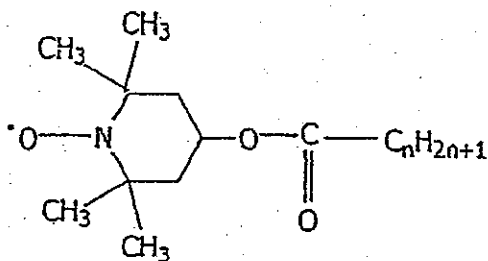
radical, a phenyl radical, a tolyl radical or a 2,2,6,6-tetrapiperidinyloxy residue and R_{12} and R_{13} have the same meaning as R_{11} and, furthermore, can also form, together and with the nitrogen atom which carries them, a 5-, 6- or 7-membered heterocyclic radical which can additionally comprise 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 $-N(O^\bullet)-C_8H_{11}$ 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.

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 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 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-butylperoxyisopropyl)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 peroxyesters, of tert-butyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 00-tert-butyl 0-(2-ethylhexyl) monoperoxycarbonate, 00-tert-butyl 0-isopropyl monoperoxycarbonate, 00-tert-

amyl O-(2-ethylhexyl) monoperoxycarbonate, 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, α -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(hydroxyperoxy)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-hydroperoxideprop-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-butylperoxy)-3,5,5-trimethylcyclohexane or 1,1-di(tert-
25 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 peroxyvalate), requiring a storage temperature below ambient temperature are advantageously chosen.

The organic peroxide composition according to the second aspect 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 aspect of the invention, of the composition comprising the disodium salt of 1,3- and 1,4-bis(2-hydroxyperoxyprop-2-yl)benzene, a stabilizer used according to the present invention, in particular TEMPO, and a metal-sequestering agent, such as EDTA.

The process for the preparation of the organic peroxide composition according to the second subject matter of the invention may comprise adding a sufficient amount of the heat stabilizer(s) to the organic peroxide to be stabilized.

The composition according to

of the invention may be used 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

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 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 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
 5 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
 10 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
 15 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

TABLE II

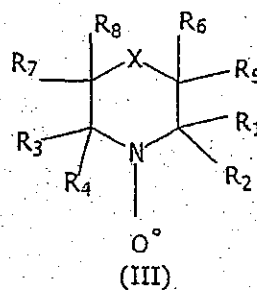
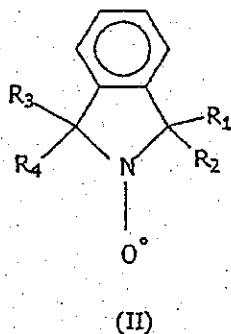
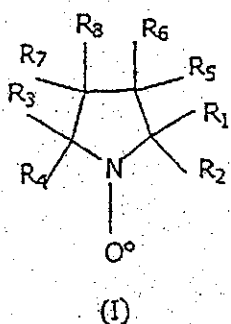
The incorporation of a composition based on organic peroxide and on nitroxide, such as TEMPO, makes

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. The use of an N-heterocyclic heat-stabilizing compound including at least one nitroxyl radical with the N atom of the nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabilizer being > the temperature of the beginning of decomposition of the solution not comprising the stabilizer.

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



in which R₁, R₂, R₃ and R₄, 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

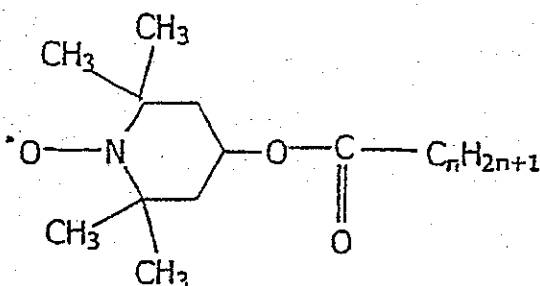
hydrocarbonaceous group, such as an alkyl or phenyl radical, a polymer chain or a functional group, such as a cyano group $-\text{CN}$, an ester group $-\text{COOR}$, an amide group $-\text{CON}(\text{R})_2$, an alkoxyl group $-\text{OR}$ or a phosphonate group $-\text{PO}(\text{OR})_2$, with R representing a hydrocarbonaceous chain having from 1 to 9 carbon atoms;

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 for R_1 , R_2 , R_3 and R_4 and, furthermore, can represent a hydroxyl group $-\text{OH}$ or an acid group, such as $-\text{COOH}$ or $-\text{PO}(\text{OH})_2$ or $-\text{SO}_3\text{H}$;

X in the formula (III) representing:

- 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 ($-\text{CN}$), 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 and with R° and R' , which are identical or different, representing a hydrogen atom, a linear or branched alkyl group having a number of carbon atoms ranging from 1 to 20, or a benzyl or phenyl group, or
- a phosphonate group $-\text{OP}(\text{O})\text{R}''\text{R}'''$ with R'' and R''' having the same meaning as Z .

3. The use as claimed in claim 2, characterized in that the heat stabilizer is represented by the following formula:



5

with n being able to vary from 1 to 20.

4. The use as claimed in claim 2, characterized in that the heat stabilizer 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, 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, 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 or 3-carboxy-2,2,5,5-tetramethylpyrrolidinyloxy.

5. A composition comprising organic peroxide(s) which is/are stable on storage and stable toward heat, characterized in that it comprises at least one organic peroxide and at least one N-heterocyclic heat-stabilizing compound including at least one nitroxyl radical with the N atom of the

nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabilizer being > the
5 temperature of the beginning of decomposition of the solution not comprising the stabilizer.

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

7. 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-
15 hydroxyperoxideprop-2-yl)benzene.

8. A process for the manufacture of a composition as claimed in one of claims 5 to 7, characterized in that at least one N-heterocyclic heat-stabilizing compound including at least one nitroxyl
20 radical with the N atom of the nitroxyl radical forming part of the ring for preparing a thermally stable solution of organic peroxide, the temperature of the beginning of decomposition of said solution comprising the stabilizer being > the temperature of the beginning
25 of decomposition of the solution not comprising the stabilizer, is added to the organic peroxide.