

**COMPOSITION COMPRISING A NITROXIDE, A PROMOTER
AND OPTIONALLY A FREE-RADICAL INITIATOR**

The present invention relates to the prevention of scorching before crosslinking of a thermoplastic and/or elastomeric composition with peroxides or azo compounds.

Premature crosslinking (scorching) during the preparatory phase is a major difficulty in the use of peroxides and azo compounds in crosslinking (curing) applications of elastomeric and/or thermoplastic materials. The preparatory phase consists in general in blending the constituents and optionally extruding them at temperatures that are often high. The operating conditions of this preparatory phase quite often lead to decomposition of the peroxide or azo initiator, thus inducing the crosslinking reaction with formation of gel particles in the bulk of the blend. The presence of these gel particles leads to imperfections (inhomogeneity or surface roughness) of the final product. Excessive scorching reduces the plastic properties of the material, such that the said material can no longer be converted, leading to loss of the entire batch. In addition, excessive scorching may lead to the total stoppage of the extrusion operation.

Several solutions have been proposed to overcome this drawback. Thus, it has been proposed to use an initiator with a half-life of 10 hours at high

temperature. The drawbacks of this approach are the low production efficiency due to a long curing time and the high energy costs.

It has also been proposed to incorporate
5 certain additives in order to reduce the scorch
tendency. Thus, the use of organic hydroperoxides as
scorch inhibitors for polyethylene-based compositions
crosslinked with a peroxide was described in British
patent GB 1 535 039. The use of vinyl monomers was the
10 subject of patent US 3 954 907. The use of nitrites was
described in patent US 3 202 648. Patent US 3 335 124
describes the use of aromatic amines, phenolic
compounds, mercaptothiazole compounds, sulphides,
hydroquinones and dialkyl dithiocarbamate compounds.

15 Very recently, the use of 2,2,6,6-tetramethyl-
piperidyloxy (TEMPO) and 4-hydroxy-2,2,6,6-tetramethyl-
piperidyloxy (4-hydroxy TEMPO) was the subject of a
Japanese patent application JP 11-49865.

However, the use of the additives of the
20 prior art cited above to increase the scorch-resistance
time has a harmful effect on the curing time and/or on
the final crosslinking density. It leads, therefore, to
a reduction in the production efficiency and/or
properties of the final product.

25 The present invention eliminates the
drawbacks of the prior art since it makes it possible
to improve the scorch resistance or the crosslinking

density without this having a negative impact on the crosslinking time. This is achieved by using a nitroxide in combination with at least one crosslinking promoter (promoter) chosen from group (P) consisting of 5 compounds containing at least one double bond, which may be difunctional or polyfunctional. Mention may be made, by way of example, of difunctional vinyl monomers, difunctional allylic monomers, polyfunctional vinyl monomers and polyfunctional allylic monomers.

The aim of the present invention is to provide a scorch-retardant composition comprising a nitroxide and at least one promoter chosen from the group (P). In an aspect of the present invention, there is provided a scorch-retardant composition comprising a nitroxide and at least one promoter chosen from the group (P) consisting of compounds containing at least one double bond.

In another aspect of the present invention, there is provided composition as defined in the above aspect, characterized in that the nitroxide is used in weight proportions ranging from 1:0.2 to 1:5 relative to the amount of promoter present.

The nitroxide is preferably used in weight proportions ranging from 1:0.2 to 1:5 and advantageously between 1:0.5 and 1:2 relative to the amount of promoter present.

One aim of the present invention is also to provide a scorch-retardant curing/crosslinking composition (A), comprising a free-radical initiator
20 chosen from the group consisting of organic peroxides, azo compounds and mixtures thereof, a nitroxide and at least one promoter chosen from the group (P). The free-radical initiator is preferably used in weight proportions of from 1:0.02 to 1:1 and advantageously
25 from 1:0.1 to 1:0.5 relative to the amount of nitroxide present.

The free-radical initiator is preferably used

in weight proportions of from 1:0.02 to 1:1 and advantageously from 1:0.1 to 1:0.5 relative to the amount of promoter used.

The present invention also provides a
5 crosslinkable composition (B) comprising a thermoplastic polymer and/or an elastomeric polymer which may be crosslinked by means of a peroxide or an azo compound, a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds
10 and mixtures thereof, a nitroxide and at least one promoter chosen from group (P). The free-radical initiator preferably represents between 0.2 and 5 parts and advantageously between 0.5 and 3 parts per
100 parts by weight of polymer. The proportions of
15 nitroxide and of promoter used relative to the free-radical initiator are preferably in the region of those used for composition (A).

The present invention also provides a process for crosslinking a crosslinkable composition comprising
20 a thermoplastic polymer and/or an elastomeric polymer which may be crosslinked using a peroxide or an azo compound, in which the said polymer is mixed with a free-radical initiator chosen from the group consisting of organic peroxides, azo compounds and mixtures
25 thereof, in the presence of a nitroxide combined with at least one promoter chosen from the group (P).

In yet another aspect of the present invention, there is provided a crosslinking process comprising a thermoplastic and/or elastomeric polymer, in which the said polymer is mixed in the presence of a free-radical initiator, a nitroxide and a promoter chosen from the group (P).

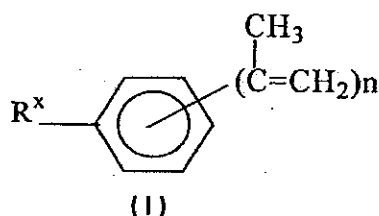
In still another aspect of the present invention, there is provided a process according to the above aspect characterized in that the conversion into moulded or extruded articles is carried out during or after crosslinking.

In further aspect of the present invention, there is provided a moulded or extruded articles which may be obtained according to the above aspect.

The present invention also provides moulded

or extruded articles such as wires and electrical cables obtained from a crosslinkable composition (B).

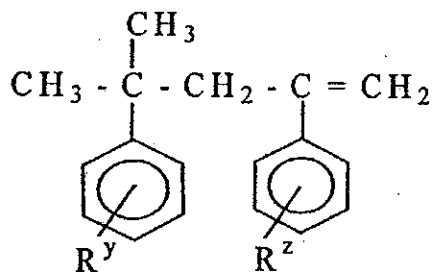
Advantageously, the promoters chosen from the group (P) are trans-stilbene, divinylbenzene,
 5 trans,trans-2,6-dimethyl-2,4,6-octatriene,
 dicyclopentadiene, 3,7-dimethyl-1,3,6-octatriene
 (OCIMENE), the compounds represented by the general formula (I):



10

in which R^x represents a hydrogen atom or an alkyl group of 1 to 9 carbon atoms and n is an integer between 1 and 3,

15 - and the compounds represented by the general formula (II):



(II)

in which R^Y and R^Z , which may be identical or different, represent an alkyl group of 1 to 4 carbon atoms.

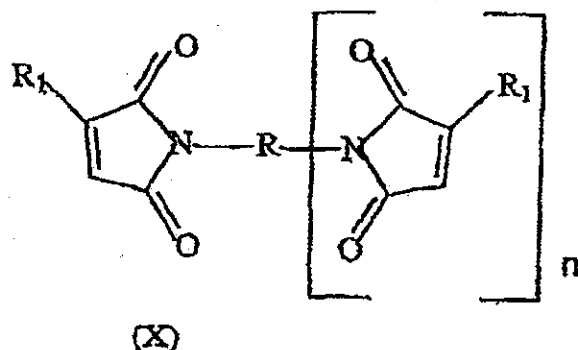
As compounds represented by the general
5 formula (I), mention may be made of α -methylstyrene,
ortho-, meta- and para-diisopropenylbenzene,
1,2,4-triisopropenylbenzene, 1,3,5-triisopropenyl-
benzene, 3-isopropyl-ortho-diisopropenylbenzene,
4-isopropyl-ortho-diisopropenylbenzene, 4-isopropyl-
10 m-diisopropenylbenzene, 5-isopropyl-m-diisopropenyl-
benzene and 2-isopropyl-p-diisopropenylbenzene.

As compounds represented by the general
formula (II), mention may be made of
2,4-bis(3-isopropylphenyl)-4-methyl-1-pentene,
15 2,4-bis(4-isopropylphenyl)-4-methyl-1-pentene,
2-(3-isopropylphenyl)-4-(4-isopropylphenyl)-4-methyl-
1-pentene, 2-(4-isopropylphenyl)-4-(3-isopropylphenyl)-
4-methyl-1-pentene, 2,4-bis(3-methylphenyl)-4-methyl-
1-pentene and 2,4-bis(4-methylphenyl)-4-methyl-
20 1-pentene.

Methyl methacrylate, lauryl methacrylate,
allyl methacrylate, trimethylolpropane triacrylate,
triallyl cyanurate (TAC), triallyl isocyanurate (TAIC),
triallyl phosphate, tetraallyloxyethane,
25 diallyldiglycol carbonate, triallyl trimellitate,
triallyl citrate, diallyl adipate, diallyl
terephthalate, diallyl oxalate, diallyl fumarate,

ethylene glycol dimethacrylate and 2-hydroxyethyl methacrylate may also be suitable as promoters.

Compounds suitable as promoters from the group (P) may also include the compounds represented by
 5 the general formula (X)



in which n is 1 or 2 and R is divalent or trivalent and
 10 is selected from the group consisting of aliphatic acyclic groups having 2 to 16 carbon atoms, aliphatic cyclic groups having 5 to 20 carbon atoms, aromatic groups having 6 to 18 carbon atoms and alkyl aromatic (alkylaryl) groups having 7 to 24 carbon atoms, and
 15 these divalent or trivalent groups may contain one or more oxygen, nitrogen and/or sulphur heteroatoms in replacement of one or more carbon atoms, and each R_1 is identical and represents a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.

20 Among the compounds of general formula (X) the bismaleimides and the biscitraconimides are advantageously selected.

As bismaleimide mention may be made of

N,N'-m-phenylenebismaleimide, N,N'-ethylene-
bismaleimide, N,N'-hexamethylenebismaleimide,
N,N'-dodecamethylenebismaleimide, N,N'-(2,2,4-tri-
5 methylhexamethylene)bismaleimide, N,N'-(oxydi-
propylene)bismaleimide, N,N'-(aminodipropylene)-
bismaleimide, N,N'-(ethylenedioxydipropylene)-
bismaleimide, N,N'-(1,4-cyclohexylene)bismaleimide,
N,N'-(1,3-cyclohexylene)bismaleimide, N,N'-(methylene-
10 1,4-dicyclohexylene)bismaleimide, N,N'-(isopropylidene-
1,4-dicyclohexylene)bismaleimide, N,N'-(oxy-
1,4-dicyclohexylene)bismaleimide, N,N'-p-(phenylene)-
bismaleimide, N,N'-(o-phenylene)bismaleimide,
N,N'-(1,3-naphthylene)bismaleimide,
15 N,N'-(1,4-naphthylene)bismaleimide,
N,N'-(1,5-naphthylene)bismaleimide,
N,N'-(3,3'-dimethyl-(4,4-diphenylene)bismaleimide,
N,N'-(3,3-dichloro-4,4-biphenylene)bismaleimide,
N,N'-(2,4-pyridyl)bismaleimide, N,N'-(2,6-pyridyl)-
20 bismaleimide, N,N'-(1,4-anthraquinonediy1)bismaleimide,
N,N'-(m-tolylene)bismaleimide, N,N'-(p-tolylene)-
bismaleimide, N,N'-(4,6-dimethyl-1,3-phenylene)-
bismaleimide, N,N'-(2,3-dimethyl-1,4-phenylene)-
bismaleimide, N,N'-(4,6-dichloro-1,3-phenylene)-
25 bismaleimide, N,N'-(5-chloro-1,3-phenylene)-
bismaleimide, N,N'-(5-hydroxy-1,3-phenylene)-
bismaleimide, N,N'-(5-methoxy-1,3-phenylene)-

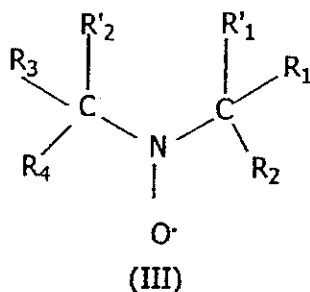
bismaleimide, N,N'-(m-xylylene)bismaleimide,
N,N'-(p-xylylene)bismaleimide, N,N'-(methylenedi-
p-phenylene)bismaleimide, N,N'-(isopropylidenedi-
p-phenylene)bismaleimide, N,N'-(oxydi-p-phenylene)-
5 bismaleimide, N,N'-(thiodi-p-phenylene)bismaleimide,
N,N'-(dithiodi-p-phenylene)bismaleimide,
N,N'-(sulphodi-p-phenylene)bismaleimide,
N,N'-(carbonyldi-p-phenylene)bismaleimide,
 α,α' -bis(4-maleimidophenyl)-meta-diisopropylbenzene,
10 α,α' -bis(4-p-phenylene)bismaleimide and
 α,α' -bis(4-maleimidophenyl)-para-diisopropylbenzene.

As biscitraconimides mention may be made of
the following:

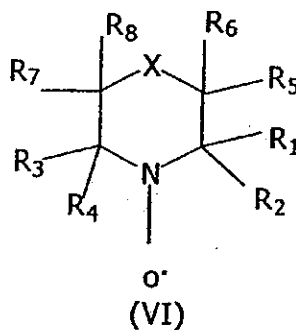
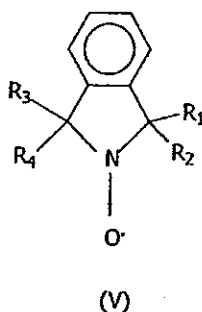
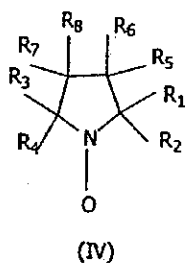
- 1,2-N,N'-dimethylenebiscitraconimide;
 - 15 - 1,2-N,N'-trimethylenebiscitraconimide;
 - 1,5-N,N'-(2-methylpentamethylene)biscitraconimide;
- and
- N,N'-(methylphenylene)biscitraconimide.

The compounds of general formula (X) are
20 preferably selected so as to crosslink the elastomers.

Nitroxides which may be used, for example,
are those represented by the general formula (III):

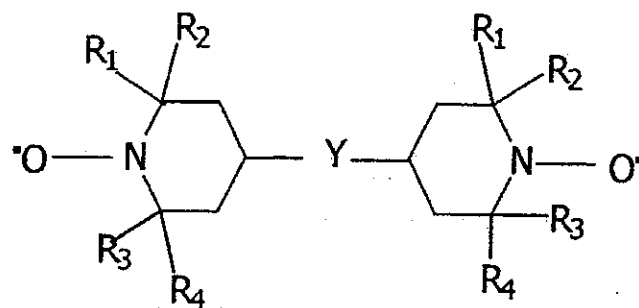


in which R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , which may be identical or different, represent a hydrogen atom, a halogen atom such as fluorine, chlorine, bromine or iodine, a linear, branched or cyclic, saturated or unsaturated hydrocarbon-based group such as an alkyl or phenyl radical, a polymer chain which may be, for example, a polyalkyl (meth)acrylate chain, for instance polymethyl methacrylate, a polydiene, polyolefin or polystyrene chain, a functionalized group such as a cyano $-CN$ group, an ester $-COOR$ group, an amide $-CON(R)_2$ group, an alkoxy $-OR$ group or a phosphonate $-PO(OR)_2$ group in which R represents a hydrocarbon-based chain containing from 1 to 9 carbon atoms. In addition, R'_1 and R'_2 may be linked together to form a ring such as, for example, the nitroxides represented by the following formulae:



in which R_5 , R_6 , R_7 and R_8 , which may be identical or different, may be chosen from the same family of groups as that which has just been envisaged for R_1 , R_2 , R_3 and R_4 and, furthermore, may represent a hydroxyl $-OH$ group, an acid group such as $-COOH$ or $-PO(OH)_2$ or $-SO_3H$. Furthermore, X in formula (VI) represents a divalent group chosen from methylene, $-CH_2-$, $-C(OR)(OR')-$, carbonyl $-C(O)-$, oxy $-O-$ and $-CHZ-$ with Z representing a monovalent residue chosen from cyano: $-CN$, amino: $-NRR'$, alkoxy: $-OR$, iminoyl $-N=CRR'$, carboxylate: $-OC(O)-R$ and amide: $-NHR-C(O)R'$ groups, in which R and R' , which may be identical or different, represent a hydrogen atom, a linear or branched alkyl group containing a number of carbon atoms ranging from 1 to 10, or a benzyl or phenyl group. X in formula (VI) may also represent a phosphonate group: $-OP(O)R''R'''-$ with R'' and R''' having the same meaning as Z .

It is also possible to use the nitroxides represented by the general formula (VII)



(VII)

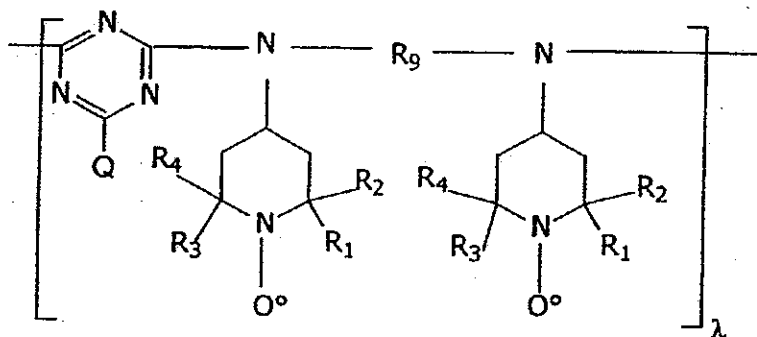
in which R_1 , R_2 , R_3 and R_4 , which may be identical or different, have the same meaning as those used for formulae (III) to (VI) and Y represents a divalent group chosen from:

- 5 $-\text{OC}(\text{O})-(\text{CR}_a\text{R}_b)_n-\text{C}(\text{O})\text{O}-$,
 $-\text{NH}-(\text{CR}_a\text{R}_b)_n\text{NH}-$,
 $-\text{NHC}(\text{O})-(\text{CR}_a\text{R}_b)_n-\text{C}(\text{O})\text{NH}-$,

$-\text{S}-$, $-\text{O}-$; R_a and R_b , which may be identical or different, represent a hydrogen atom or a linear or
 10 branched alkyl radical containing a number of carbon atoms ranging from 1 to 10 and n represents an integer ranging from 0 to 20.

In addition, it is possible to use the nitroxides represented by the general formula (VIII):

15



(VIII)

in which R_1 , R_2 , R_3 and R_4 , which may be identical or different, have the same meaning as those
 20 in the above formulae (III) to (VII), λ is an integer

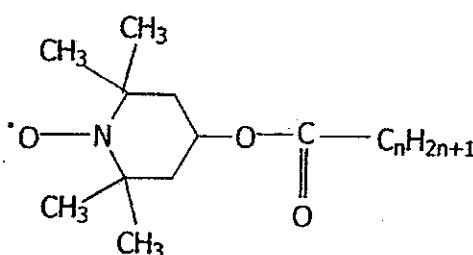
between 1 and 20, R_9 represents an alkylene group containing a number of carbon atoms ranging from 2 to 12 which may be interrupted with an $-O-$ or $-NR_{10}-$ with R_{10} denoting a hydrogen atom, an alkyl group containing
 5 a number of carbon atoms of between 1 and 12, or a cycloalkyl group, and Q represents a radical $-OR_{11}$, $-NHR_{12}$ or $-NR_{12}R_{13}$ in which R_{11} represents a linear or branched alkyl radical containing a number of carbon atoms ranging from 1 to 12, a C_3-C_{12} alkoxyalkyl
 10 radical, a cyclohexyl radical, a benzyl radical, a phenyl radical, a tolyl radical or a 2,2,6,6-tetrapiperidyl residue, R_{12} and R_{13} have the same meaning as R_{11} and may moreover also form, together and with the nitrogen atom which bears them, a 5-, 6- or
 15 7-membered heterocyclic radical which may also contain an oxygen.

The nitroxides of general formula (VIII) usually used are those obtained by oxidation of the amines sold by the company CIBA under the name
 20 Chimasorb 944 in which R_1 , R_2 , R_3 and R_4 each denote a methyl group, R_9 denotes an alkylene group containing 6 carbon atoms, Q represents a radical $-N(O^\bullet)-C_8H_{11}$ and λ is an integer between 2 and 4.

The nitroxides of general formula (VI) that
 25 are preferred 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 represents a group $-CH_2-$.

In particular, nitroxides of general formula (VI) which may be mentioned are 2,2,6,6-tetramethyl-1-piperidyloxy, generally sold under the name TEMPO, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidyloxy, sold under the name 4-hydroxy TEMPO, 4-methoxy-2,2,6,6-tetramethyl-1-piperidyloxy, commonly known as 4-methoxy TEMPO, and 4-oxo-2,2,6,6-tetramethyl-1-piperidyloxy, commonly known as 4-oxo TEMPO.

The nitroxides of general formula (VI) that are particularly preferred are those represented by the following formula:



with n possibly ranging from 1 to 20.

Nitroxides such as 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, sold under the brand name PROXYL, bis(1-oxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, sold under the brand name CXA 5415 by the company Ciba Specialty Chemical, 2,2,6,6-tetramethyl-4-hydroxy-1-piperidyloxy monophosphonate and 3-carboxy-2,2,5,5-tetramethylpyrrolidinyloxy (commonly known as 3-carboxy Proxyl) are also preferred.

According to the present invention, compounds

which may be used as free-radical initiators are azo compounds and/or organic peroxides, which, upon thermal decomposition, produce free radicals which facilitate the curing/crosslinking reaction. Among the free-
5 radical initiators used as crosslinking agents, dialkyl peroxides and diperoxyketal initiators are preferred. A detailed description of these compounds will be found in *Encyclopedia of Chemical Technology*, 3rd edition, vol. 17, pages 27 to 90 (1982).

10 Among the dialkyl peroxides, the preferred initiators are: dicumyl peroxide, di-*t*-butyl peroxide, *t*-butylcumyl peroxide, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane, 2,5-dimethyl-2,5-di(*t*-amylperoxy)hexane, 2,5-dimethyl-2,5-di(*t*-butylperoxy)-3-hexyne,
15 2,5-dimethyl-2,5-di(*t*-amylperoxy)-3-hexyne, α,α -di-[(*t*-butylperoxy)isopropyl]benzene, di-*t*-amyl peroxide, 1,3,5-tri[(*t*-butylperoxy)isopropyl]benzene, 1,3-dimethyl-3-(*t*-butylperoxy)butanol and 1,3-dimethyl-3-(*t*-amylperoxy)butanol, and mixtures thereof.

20 Among the diperoxyketals, the preferred initiators are: 1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(*t*-butylperoxy)cyclohexane, *n*-butyl 4,4-di(*t*-amylperoxy)valerate, ethyl 3,3-di(*t*-butylperoxy)butyrate, 2,2-di(*t*-amylperoxy)propane,
25 3,6,6,9,9-pentamethyl-3-ethoxycarbonylmethyl-1,2,4,5-tetraoxacyclononane, *n*-butyl 4,4-bis(*t*-butylperoxy)valerate and ethyl 3,3-di(*t*-amylperoxy)butyrate,

and mixtures thereof.

Azo compounds which may be mentioned, for example, are 2,2'-azobis(2-acetoxypropane), azobis-isobutyronitrile, azodicarbamide, 4,4'-azobis(cyano-
5 pentanoic acid) and 2,2'-azobismethylbutyronitrile.

Dicumyl peroxide and α,α' -di[(t-butyl-peroxy)isopropyl]benzene are particularly preferred.

The thermoplastic and/or elastomeric polymers taken into consideration in the present invention may
10 be defined as natural or synthetic polymers which have a thermoplastic and/or elastomeric nature and which may be crosslinked (cured) under the action of a crosslinking agent. In *Rubber World*, "Elastomer Crosslinking with Diperoxyketals", October 1983,
15 pages 26-32, and in *Rubber and Plastic News*, "Organic Peroxides for Rubber Crosslinking", 29 September 1980, pages 46-50, the crosslinking action and crosslinkable polymers are described. Polyolefins which are suitable for the present invention are described in *Modern*
20 *Plastics Encyclopaedia* 89, pages 63-67 and 74-75. By way of example of polymers and/or elastomers, mention may be made of linear low density polyethylene, low density polyethylene, high density polyethylene, chlorinated polyethylene, ethylene/propylene/diene
25 terpolymers (EPDM), ethylene/vinyl acetate copolymers, ethylene/propylene copolymers, silicone rubber, natural rubber (NR), polyisoprene (IR), polybutadiene (BR),

acrylonitrile-butadiene copolymers (NBR), styrene-butadiene copolymers (SBR), chlorosulphonated polyethylene and fluoroelastomers.

Mention may also be made of ethylene/methyl (meth)acrylate copolymers and ethylene/glycidyl methacrylate copolymers.

In addition to the constituents mentioned above, the compositions (A) and (B) may comprise antioxidants, stabilizers, plasticizers and inert fillers such as silica, clay or calcium carbonate.

The compositions (A) and (B) may comprise two or more nitroxides (N). They may also comprise two or more free-radical initiators.

According to the process of the present invention, the crosslinking temperature may be between 110 and 220°C and preferably between 140 and 200°C.

Advantageously the process is implemented in the presence of an amount of initiator, nitroxide and promoter such that the initiator/polymer, nitroxide/polymer and promoter/polymer weight ratios are close to the composition (B).

The conversion of the crosslinkable compositions into moulded or extruded articles may be carried out during or after crosslinking.

EXPERIMENTAL SECTION

In the text hereinbelow, the following abbreviations are used:

M_H : the maximum value of the torque
obtained from the curve recorded by the
rheometer.

5 This value determines the crosslinking
density.

T_{90} : crosslinking time, the time required to
reach 90% of the maximum torque.

10 T_{55} : scorch time, the time required at a
given temperature for the torque to
increase by 5 Mooney units.

The crosslinking density (M_H) and the
crosslinking time (T_{90}) of the blend obtained were
measured at 180°C using a Monsanto ODR 2000 E rheometer
(Alpha Technologies, oscillation arc: 3°, oscillation
15 frequency: 100 cycles/min).

The crosslinking time is also determined
using the rheometer used under the same conditions as
above.

The scorch time was measured at 145°C using a
20 Mooney MV 2000 viscometer (Alpha Technologies).

Example 1 (not in accordance with the
invention):

1 000 g of low density polyethylene (Mitene
sold by Ashland), 25 g of dicumyl peroxide (Luperox® DC)
25 and 3 g of 2,2,6,6-tetramethylpiperidylloxy (TEMPO) were
mixed together in a turbomixer at 80°C (nominal
temperature) for 15 minutes (stirring speed = 930 rpm).

The powder was then converted into a sample in the form of a disc by melting at 110°C for 3 min. The sample was then placed in the rheometer or viscometer chamber.

Example 2 (not in accordance with the
5 invention):

Example 1 was repeated without the use of 2,2,6,6-tetramethylpiperidyloxy. The results are given in Table 1. Comparison of Examples 1 and 2 shows that the scorch time is higher in Example 1, but is
10 accompanied by a large reduction in crosslinking density and by a slight increase in the crosslinking time.

Example 3:

Example 1 was repeated, adding 3 g of
15 diisopropylbenzene (DIPB).

Comparison of the results with those obtained in the above examples shows unambiguously that such a combination makes it possible to maintain an increase in the scorch time while at the same time giving a
20 higher crosslinking density and a lower crosslinking time.

Table 1

	Additive(s)	Maximum torque at 180°C (M _H) (N.m)	Scorch time at 145°C (Ts5) (min/s)	Crosslinking time at 180°C (T ₉₀) (min/s)
Example 1	TEMPO	1.21	19:00	7:10
Example 2	-	1.95	8:40	6:50
Example 3	TEMPO + DIPB	2.88	19:10	6:02
Example 4	-	5.94	2:50	5:21
Example 5	OH-TEMPO	5.14	16:19	5:39
Example 6	MBM	6.61	1:43	3:54
Example 7	OH-TEMPO + MBM	6.45	14:38	4:46

Example 4: (not in accordance with the invention)

5 318 g of compound EPDM DIN 7863 (containing 100 g of ethylene-propylene-diene terpolymer and 218 g of fillers) were conditioned in a Banbury-type mixer with a volume of 350 cm³ at 50°C for 5 minutes at a speed of 50 revolutions/min. 8 g of Luperox F40ED (40%
10 di(tert-butylperoxyisopropyl)benzene and 60% inert fillers) were added and mixed with the compound for 5 minutes at 50°C at a speed of 50 revolutions/min.

Example 5: (not in accordance with the invention)

15 Example 4 is repeated but with the addition

not only of Luperox F40ED but also of 0.677 g of
4-hydroxy-2,2,6,6-tetramethylpiperidyloxy (OH-TEMPO).

Example 6: (not in accordance with the
invention)

5 Example 5 is repeated but adding, instead of
the OH-TEMPO, 0.5 g of N,N'-m-phenylenedimaleide
(N,N'-m-phenylenebismaleimide or MBM).

Example 7:

10 Example 5 is repeated but with the addition
not only of Luperox F40ED and OH-TEMPO but also of
0.5 g of MBM.

CLAIMS

1. Scorch-retardant composition comprising
a nitroxide and at least one promoter chosen from the
group (P) consisting of compounds containing at least
5 one double bond.

2. Composition according to Claim 1,
characterized in that the nitroxide is used in weight
proportions ranging from 1:0.2 to 1:5 relative to the
10 amount of promoter present.

3. Composition according to Claim 1,
characterized in that it also comprises a free-radical
initiator chosen from the group consisting of organic
peroxides and azo compounds, and mixtures thereof.

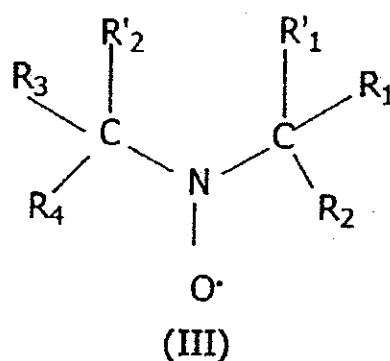
15 4. Composition according to Claim 3,
characterized in that the free-radical initiator is
used in weight proportions of from 1:0.02 to 1:1
relative to the amount of nitroxide present.

5. Composition according to Claim 3 or 4,
20 characterized in that the free-radical initiator is
used in weight proportions of from 1:0.02 to 1:1
relative to the amount of promoter used.

6. Composition according to any one of
Claims 3 to 5, characterized in that it also comprises
25 a thermoplastic polymer and/or an elastomeric polymer
which may be crosslinked by means of a peroxide or an
azo compound.

7. Composition according to Claim 6, characterized in that the free-radical initiator represents between 0.2 and 5 parts and preferably between 0.5 and 3 parts per 100 parts by weight of 5 polymer.

8. Composition according to any one of Claims 1 to 7, characterized in that the nitroxide is represented by:

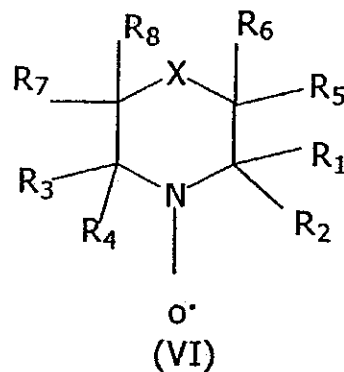
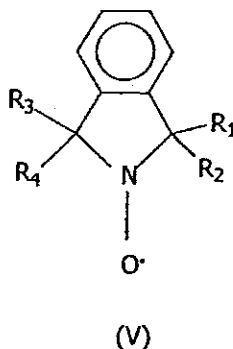
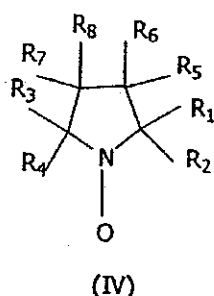


10

in which R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , which may be identical or different, represent a hydrogen atom, a halogen atom such as fluorine, chlorine, bromine or 15 iodine, a linear, branched or cyclic, saturated or unsaturated hydrocarbon-based group such as an alkyl or phenyl radical, a polymer chain which may be, for example, a polyalkyl (meth)acrylate chain, for instance polymethyl methacrylate, a polydiene, polyolefin or 20 polystyrene chain, a functionalized group such as a cyano -CN group, an ester -COOR group, an amide -CON(R)₂

group, an alkoxy -OR group or a phosphonate -PO(OR)₂ group in which R represents a hydrocarbon-based chain containing from 1 to 9 carbon atoms.

9. Composition according to Claim 8,
5 characterized in that R'₁ and R'₂ may be linked together to form a ring to give:

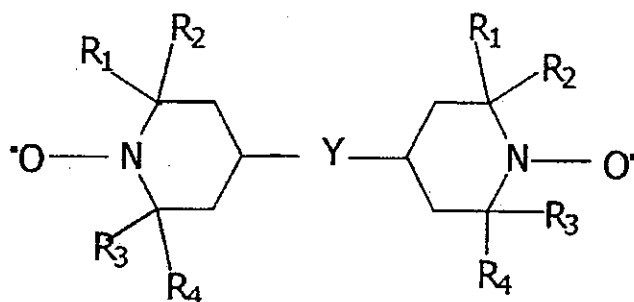


- 10 in which R₅, R₆, R₇ and R₈, which may be identical or different, may be chosen from the same family of groups as that envisaged for R₁, R₂, R₃ and R₄ and, furthermore, may represent a hydroxyl -OH group, an acid group such as -COOH or -PO(OH)₂ or -SO₃H.
- 15 Furthermore, X in formula (VI) represents a divalent group chosen from methylene, -CH₂-, -C(OR)(OR')-, carbonyl -C(O)-, oxy -O- and -CHZ- with Z representing a monovalent residue chosen from cyano: -CN, amino: -NRR', alkoxy: -OR, iminoyl -N=CRR',
- 20 carboxylate: -OC(O)-R and amide: -NHR-C(O)R' groups, in which R and R', which may be identical or different, represent a hydrogen atom, a linear or branched alkyl

group containing a number of carbon atoms ranging from 1 to 10, or a benzyl or phenyl group.

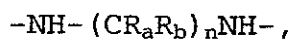
10. Composition according to Claim 9, characterized in that X in formula (VI) is phosphonate
5 -OP(O)R''R''' with R'' and R''' having the same meaning as Z.

11. Composition according to any one of Claims 1 to 7, characterized in that the nitroxide is represented by the general formula (VII):



(VII)

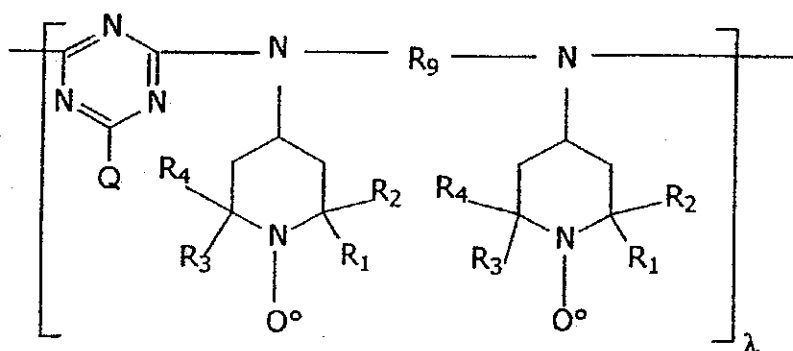
in which R₁, R₂, R₃ and R₄, which may be identical or different, have the same meaning as those
15 used for formulae (III) to (VI) and Y represents a divalent group chosen from:



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

atoms ranging from 1 to 10 and n represents an integer ranging from 0 to 20.

12. Composition according to any one of Claims 1 to 7, characterized in that the nitroxide is represented by the general formula (VIII):

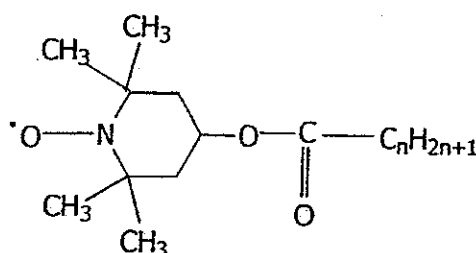


(VIII)

in which R_1 , R_2 , R_3 and R_4 , which may be identical or different, have the same meaning as those in the above formulae (III) to (VII), λ is an integer between 1 and 20, R_9 represents an alkylene group containing a number of carbon atoms ranging from 2 to 12 which may be interrupted with an $-O-$ or $-NR_{10}-$ with R_{10} denoting a hydrogen atom, an alkyl group containing a number of carbon atoms of between 1 and 12, or a cycloalkyl group, and Q represents a radical $-OR_{11}$, $-NHR_{12}$ or $-NR_{12}R_{13}$ in which R_{11} represents a linear or branched alkyl radical containing 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-tetrapiperidyl residue, R_{12} and R_{13} have the same meaning as R_{11} and may moreover also form, together and
 5 with the nitrogen atom which bears them, a 5-, 6- or 7-membered heterocyclic radical which may also contain an oxygen.

13. Composition according to any one of Claims 1 to 7, characterized in that the nitroxide is
 10 chosen from those represented by the following formula:

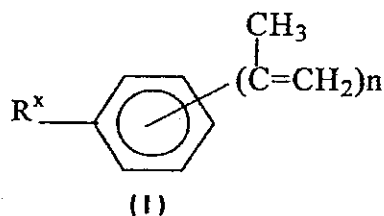


with n possibly ranging from 1 to 20.

15 14. Composition according to any one of Claims 1 to 7, characterized in that the nitroxide is 2,2,6,6-tetramethyl-1-piperidyloxy, generally sold under the name TEMPO, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidyloxy, sold under the name 4-hydroxy TEMPO,
 20 4-methoxy-2,2,6,6-tetramethyl-1-piperidyloxy, commonly known as 4-methoxy TEMPO, 4-oxo-2,2,6,6-tetramethyl-1-piperidyloxy, commonly known as 4-oxo TEMPO, 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, sold under the brand name PROXYL, bis(1-oxy-2,2,6,6-tetramethyl-

4-piperidyl) sebacate, sold under the brand name
 CXA 5415 by the company Ciba Specialty Chemical,
 2,2,6,6-tetramethyl-4-hydroxy-1-piperidyloxy
 monophosphonate and 3-carboxy-2,2,5,5-tetramethyl-
 5 pyrrolidinyloxy (commonly known as 3-carboxy Proxyl).

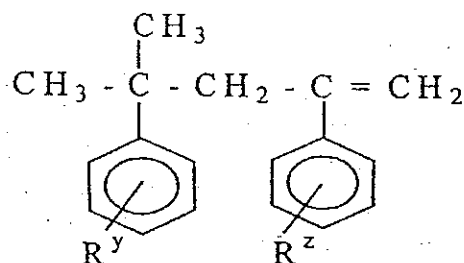
15. Composition according to any one of
 Claims 1 to 14, characterized in that the promoter is
 chosen from trans-stilbene, divinylbenzene,
 trans,trans-2,6-dimethyl-2,4,6-octatriene,
 10 dicyclopentadiene, 3,7-dimethyl-1,3,6-octatriene
 (OCIMENE), the compounds represented by the general
 formula (I):



15

in which R^x represents a hydrogen atom or an
 alkyl group of 1 to 9 carbon atoms and n is an integer
 between 1 and 3,

- and the compounds represented by the
 20 general formula (II):



(II)

in which R^y and R^z , which may be identical or different, represent an alkyl group of 1 to 4 carbon atoms.

16. Composition according to Claim 15, characterized in that the promoter is α -methylstyrene, ortho-, meta- and para-diisopropenylbenzene, 1,2,4-triisopropenylbenzene, 1,3,5-triisopropenylbenzene, 3-isopropyl-ortho-diisopropenylbenzene, 4-isopropyl-ortho-diisopropenylbenzene, 4-isopropyl-m-diisopropenylbenzene, 5-isopropyl-m-diisopropenylbenzene, 2-isopropyl-p-diisopropenylbenzene, 2,4-bis(3-isopropylphenyl)-4-methyl-1-pentene, 2,4-bis(4-isopropylphenyl)-4-methyl-1-pentene, 2-(3-isopropylphenyl)-4-(4-isopropylphenyl)-4-methyl-1-pentene, 2-(4-isopropylphenyl)-4-(3-isopropylphenyl)-4-methyl-1-pentene, 2,4-bis(3-methylphenyl)-4-methyl-1-pentene and 2,4-bis(4-methylphenyl)-4-methyl-1-pentene.

17. Composition according to any one of claims 1 to 14, characterised in that the promoter is

chosen from methyl methacrylate, lauryl methacrylate, allyl methacrylate, trimethylolpropane triacrylate, triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), triallyl phosphate, tetraallyloxyethane,
5 diallyldiglycol carbonate, triallyl trimellitate, triallyl citrate, diallyl adipate, diallyl terephthalate, diallyl oxalate, diallyl fumarate, ethylene glycol dimethacrylate and 2-hydroxyethyl methacrylate.

10 18. Composition according to any one of Claims 3 to 17, characterized in that the free-radical initiator is dicumyl peroxide and α,α' -di[(t-butylperoxy)isopropyl]benzene.

15 19. Composition according to any one of Claims 6 to 18, characterized in that the polymer is chosen from linear low density polyethylene, low density polyethylene, high density polyethylene, chlorinated polyethylene, ethylene/propylene/butadiene terpolymers, ethylene/vinyl acetate copolymers,
20 ethylene/propylene copolymers, silicone rubber, chlorosulphonated polyethylene, fluoroelastomers, ethylene/methyl (meth)acrylate copolymers and ethylene/glycidyl methacrylate copolymers.

25 20. Crosslinking process comprising a thermoplastic and/or elastomeric polymer, in which the said polymer is mixed in the presence of a free-radical

initiator, a nitroxide and a promoter chosen from the group (P).

21. Process according to Claim 20,
characterized in that the conversion into moulded or
5 extruded articles is carried out during or after
crosslinking.

22. Moulded or extruded articles which may
be obtained according to Claim 21.