

26 MAR 2005

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International publication date
11 April 2002 (11.04.2002)

PCT

(10) International publication number
WO 02/28950 A2

(51) International patent classification⁷: C08K 5/32

(21) International application number: PCT/FR01/03010

(22) International filing date: 28 September 2001 (28.09.2001)

(25) Language of filing: French

(26) Language of publication: French

(30) Data relating to the priority:
00/12,581 3 October 2000 (03.10.2000) FR

(71) Applicant (for all designated States except US): ATOFINA
[FR/FR]; 4/8, cours Michelet, F-92800 Puteaux (FR).

(72) Inventors; and

(75) Inventors/Applicants (US only): DEBAUD, Fabien [FR/FR];
50, avenue du Point du Jour, F-69005 Lyon (FR).
DEFRANCISCI, Alfredo [FR/FR]; 43, cours Franklin
Roosevelt, F-69006 Lyon (FR). GUERRET, Olivier [FR/FR];
26, allée des Chênes, F-69280 Marcy l'Etoile (FR).
KERVENNAL, Jacques [FR/FR]; 134, rue E.-Locard,
F-69005 Lyon (FR).

(74) Representative: DANG, Doris; Atofina, Département
Propriété Industrielle, Cours Michelet - La Défense 10,
F-92091 Paris la Défense Cedex (FR).

(81) Designated states (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, LR, LS, LT, LU, LV, MA,
MD, MG, MK, MN, MW, MX, MZ, 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.

(84) Designated states (regional): ARIPO Patent (GH, GM,
KE, LS, MW, MZ, 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, TR), OAPI
Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

- of inventorship (Rule 4.17(iv)) for the following
designation US.

Published:

- Without the International Search Report and to be
republished once the report has been received.

For an explanation of the two-letter codes and the other
abbreviations, reference is made to the explanations
("Guidance Notes on Codes and Abbreviations") at the
beginning of each regular edition of the PCT Gazette.

As printed

WO 02/28950 A2

(54) Title: SCORCH-DELAYING COMPOSITION

(54) Titre : COMPOSITION RETARDANT LE GRILLAGE

(57) Abstract: The invention concerns a scorch-delaying composition. More particularly, the invention concerns a composition comprising a nitroxide (N) containing at least an unsaturation. The invention also concerns a crosslinking method in the presence of a nitroxide (N).

(57) Abrégé : La présente invention concerne une composition retardant le grillage. Plus particulièrement, elle a pour objet une composition comprenant un nitroxyde (N) renfermant au moins une insaturation. L'invention concerne également un procédé de réticulation en présence d'un nitroxyde (N).

SCORCH-DELAYING COMPOSITION

The present invention relates to the prevention of scorching before crosslinking of a thermoplastic and/or elastomeric composition with
5 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
10 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
15 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
20 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
25 overcome this drawback. Thus, it has been proposed to use an initiator with a halflife 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 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 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.

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.

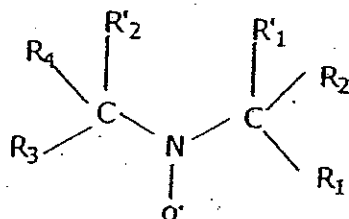
However, the use of the additives of the prior art cited above to increase the scorch-resistance time has a harmful effect on the curing time and/or on the final crosslinking density. It leads to a reduction in the production efficiency and/or properties of the final product.

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 family

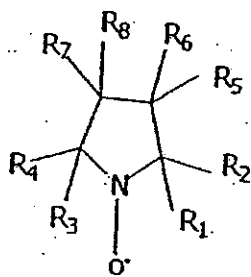
of specific nitroxides as additive.

In a first aspect of the present invention, there is provided scorch-retardant crosslinking composition comprising a nitroxide (N) containing at least one unsaturation and a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds, and mixtures thereof.

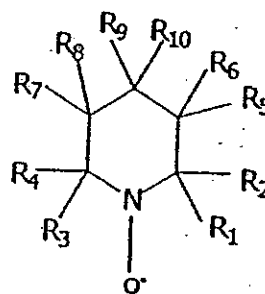
In a second aspect of the present invention there is provided a composition as defined in the first aspect, characterised in that, the nitroxide (N) is represented by formulae (I) to (III):



(I)



(II)



(III)

3a

in which at least one of the substituents R'₁,
R'₂, R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉ and R₁₀ contains at
10 least one unsaturation which is reactive towards free-
radical addition; the remaining substituents, 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
15 hydrocarbon-based group such as an alkyl radical, a

substituted or unsubstituted aromatic group, a cyano group -CN, an amide group -CONRR_a, an ester group -COOR, an alkoxy group -OR, a phosphonate group -PO(OR)(OR_a), a hydroxyl group -OH or an acid group such as -COOH or
5 -PO(OH)₂ or SO₃H. R and R_a, which may be identical or different, may represent a hydrogen atom, a linear, branched or cyclic alkyl group containing a number of carbons ranging from 1 to 20, or an optionally substituted phenyl group.

10 The substituents containing at least one unsaturation may each in particular represent a linear, branched or cyclic unsaturated hydrocarbon-based group or an acrylate, methacrylate, acrylamide or methacrylamide group. When several unsaturations are present on
15 the same group, these may be conjugated, such as, for example, in a butadienyl group, or unconjugated.

When the abovementioned formulae also comprise at least one substituent containing at least one unsaturation, a hydroxyl group and/or an acid
20 group, the hydroxyl group and/or the acid group is preferably represented by R₅, R₆, R₇, R₈, R₉ and R₁₀.

A subject of the present invention is also a scorch-retardant crosslinking composition (C) comprising a nitroxide (N) and a free-radical initiator
25 chosen from the group consisting of organic peroxides and azo compounds, and mixtures thereof.

Another subject of the invention is a crosslinkable composition (A) comprising a

thermoplastic polymer and/or elastomeric polymer which may be crosslinked by means of a peroxide or an azo compound, a nitroxide (N) and a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds, and mixtures thereof.

In a third aspect of the present invention there is provided a process for crosslinking a crosslinkable composition comprising a thermoplastic polymer and/or an elastomeric polymer which may be crosslinked by means of a peroxide or an azo compound, characterised in that the said polymer is mixed with a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds, an mixtures thereof, in the presence of a nitroxide (N) as defined above.

An embodiment may relate to a process according to the third aspect characterized in that the conversion of the crosslinkable composition (A) into moulded or extruded articles is carried out during or after crosslinking.

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

The moulded or extruded articles may be electrical cables or wires obtained from a crosslinkable composition (A).

According to the present invention, a nitroxide (N) of formula (III) is preferably used, in which:

- R_1 , R_2 , R_3 and R_4 , which may be identical or different, represent a methyl, ethyl, propyl, isopropyl, butyl, sec-butyl or tert-butyl radical,

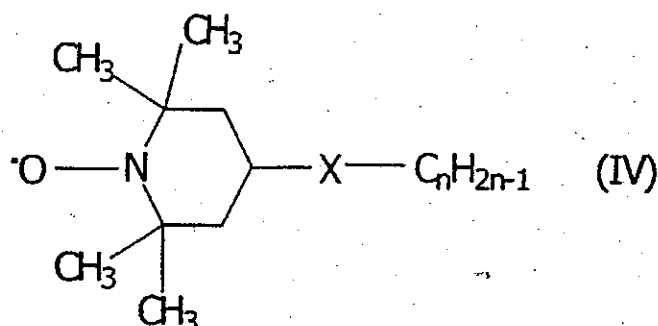
- R_5 , R_6 , R_7 , R_8 and R_9 each represent a hydrogen atom, and

- R_{10} represents a linear, branched or cyclic unsaturated hydrocarbon-based group or an acrylate, acrylamide, methacrylate or methacrylamide group.

Mention may be made, for example, of:

- 2,2,6,6-tetraethyl-4-piperidyloxy acrylate
- 2,2,6,6-tetraethyl-4-piperidyloxy methacrylate.

It is preferred to use, in particular, a
 5 nitroxide (N) containing an unsaturation, represented by formula (IV):



in which X represents a divalent group
 $-OC(O)-$, $-NR_bC(O)-$ or $-P(O)(OR_b)O-$ with R_b having the
 10 same meaning as R and n is an integer which may range from 2 to 20 and preferably from 2 to 10. The position of the unsaturation on the group C_nH_{2n-1} is irrelevant, but unsaturations located either in position 1 relative to X or in the terminal position are preferred.

15 Mention may be made, for example, of:

- 2,2,6,6-tetramethyl-4-piperidyloxy acrylate
- 2,2,6,6-tetramethyl-4-piperidyloxy methacrylate

20 amide

- 2,2,6,6-tetramethyl-4-piperidyloxyacryl-
- amide.
- 2,2,6,6-tetramethyl-4-piperidyloxymethacryl-
- amide.

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-radical initiators used as crosslinking agents, dialkyl peroxides and diperoxyketals 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(cyanopentanoic acid) and 2,2'-azobismethylbutyronitrile.

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

The thermoplastic and/or elastomeric polymers taken into consideration in the present invention may be defined as natural or synthetic polymers which have
10 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, pages 26-32, and in *Rubber and Plastic News*, "Organic
15 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
Plastics Encyclopedia* 89, pages 63-67 and 74-75. By way
20 of example, mention may be made of linear low density polyethylene, low density polyethylene, high density polyethylene, chlorinated polyethylene, ethylene-propylene-diene terpolymers (EPDM), ethylene-vinyl acetate copolymers, ethylene-propylene copolymers,
25 silicone rubber, chlorosulphonated polyethylene, fluoroelastomers, natural rubber (NR), polyisoprene (IR), polybutadiene (BR), acrylonitrile-butadiene copolymers (NBR) or styrene-butadiene copolymers (SBR).

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

The weight ratio of the free-radical
5 initiator to the nitroxide (N) in the crosslinking composition (C) and in the crosslinkable composition (A) is preferably between 1 and 50 and advantageously between 2 and 10.

In the crosslinkable composition (A), the
10 free-radical initiator preferably represents between 0.2% and 5% by weight of the amount of polymer and advantageously between 0.5% and 3% by weight.

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

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

20 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 and of nitroxide
25 such that the initiator/polymer and nitroxide/polymer weight ratios are close to those of composition (A).

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
5 abbreviations are used:

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

10 This value determines the crosslinking
density.

T_{90} : curing time, the time required to reach
90% of the maximum torque at a given
temperature.

15 T_{S5} : 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
20 (Alpha Technologies, oscillation arc: 3°, oscillation
frequency: 100 cycles/min).

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

25 The scorch time was measured at 145°C using a
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) and 3 g of 2,2,6,6-tetramethylpiperidyloxy (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 invention):

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

Example 3:

The process is performed as described in Example 1, except that the 3 g of 2,2,6,6-tetramethylpiperidyloxy are replaced with 4.4 g of NT1 (2,2,6,6-tetramethyl-4-piperidyloxy methacrylate) so as to carry out a comparison for an equivalent concentration of nitroxide function.

The comparison of the results with those obtained in the preceding examples shows unambiguously that this nitroxide makes it possible to increase the scorch time while at the same time increasing the crosslinking density.

	Additive	Maximum torque at 180°C (M _H) (N.m)	Scorch time at 145°C (T _{s5}) (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	NT1	2.42	14:10	6:20
Example 4	-	5.94	2:50	5:21
Example 5	OH-TEMPO	5.14	16:19	5:39
Example 6	NT1	6.14	15:47	4:12

Table 1

Example 4 (not in accordance with the invention)

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% 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.

26 MAR 2005

13

Example 5 (not in accordance with the invention)

Example 4 is repeated but with the addition not only of the Luperox F40ED but also of 0.677 g of
5. 4-hydroxy-2,2,6,6-tetramethylpiperidyloxy (OH-TEMPO).

Example 6:

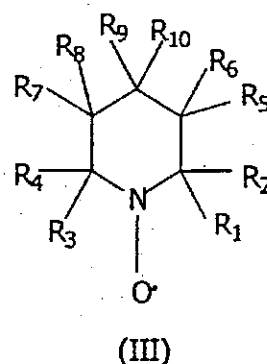
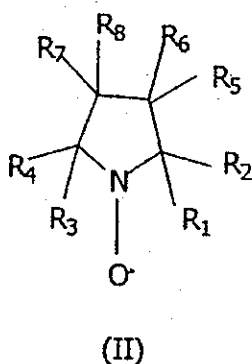
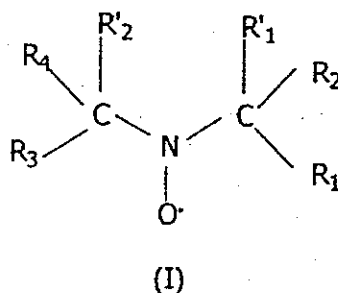
Example 5 is repeated but adding, instead of the OH-TEMPO, 0.931 g of NT1.

26 MAR 2005

PCT/FR01/03010

CLAIMS

1. Scorch-retardant crosslinking composition comprising a nitroxide (N) containing at least one unsaturation and a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds, and mixtures thereof.
2. Composition according to Claim 1, characterized in that the nitroxide (N) is represented by formulae (I) to (III):

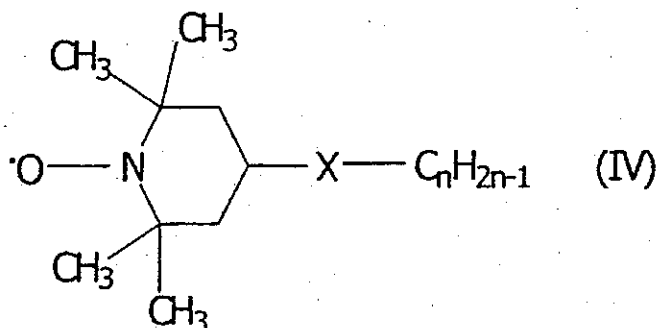


in which at least one of the substituents R'1, R'2, R1, R2, R3, R4, R5, R6, R7, R8, R9 and R10 contains at least one unsaturation which is reactive towards free-radical addition; the remaining substituents, which may

be identical or different, represent a hydrogen atom, a halogen atom such as fluorine, chlorine, bromine or iodine, a linear, branched or cyclic, saturated hydrocarbon-based group such as an alkyl radical, a substituted or unsubstituted aromatic group, a cyano group -CN, an amide group -CONRR_a, an ester group -COOR, an alkoxy group -OR, a phosphonate group -PO(OR)(OR_a), a hydroxyl group -OH or an acid group such as -COOH or -PO(OH)₂ or SO₃H; R and R_a, which may be identical or different, may represent a hydrogen atom, a linear, branched or cyclic alkyl group containing a number of carbons ranging from 1 to 20, or an optionally substituted phenyl group.

3. Composition according to Claim 2, characterized in that the substituents containing at least one unsaturation may each represent a linear, branched or cyclic unsaturated hydrocarbon-based group or an acrylate, methacrylate, acrylamide or methacrylamide group.

4. Composition according to Claim 1 or 2, characterized in that the nitroxide (N) is represented by formula (IV):



26 MAR 2005

16

in which X represents a divalent group
-OC(O)-, -NR_bC(O)- or -P(O)(OR_b)O- with R_b having the
same meaning as R and n is an integer which may range
from 2 to 20 and preferably from 2 to 10.

5 5. Composition according to Claim 4,
characterized in that the nitroxide (N) is:

- 2,2,6,6-tetramethyl-4-piperidyloxy acrylate
- 2,2,6,6-tetramethyl-4-piperidyloxy
methacrylate
- 10 - 2,2,6,6-tetramethyl-4-piperidyloxyacryl-
amide or
- 2,2,6,6-tetramethyl-4-piperidyloxymethacryl-
amide.

15 6. Composition according to one of the
preceding claims, characterized in that the free-
radical initiator is dicumyl peroxide or
α,α'-di[(t-butylperoxy)isopropyl]benzene.

20 7. Composition according to one of the
preceding claims, characterized in that it comprises a
thermoplastic polymer and/or an elastomeric polymer.

25 8. Composition according to Claim 7,
characterized in that the polymer is chosen from low
density polyethylene, high density polyethylene,
chlorinated polyethylene, ethylene-propylene-butadiene
terpolymers, ethylene-vinyl acetate copolymers,
ethylene-propylene copolymers, silicone rubber,
chlorosulphonated polyethylene, fluoroelastomers,

ethylene-methyl (meth)acrylate copolymers and ethylene-glycidyl methacrylate copolymers.

9. Composition according to any one of the preceding claims, characterized in that the weight
5 ratio of the free-radical initiator to the nitroxide (N) is between 1 and 50 and preferably between 2 and 10.

10. Composition according to any one of Claims 7 to 9, characterized in that the free-radical
10 initiator represents between 0.2% and 5% by weight of the amount of polymer and preferably between 0.5% and 3% by weight.

11. Process for crosslinking a crosslinkable composition comprising a thermoplastic polymer and/or
15 an elastomeric polymer which may be crosslinked by means of a peroxide or an azo compound, characterized in that the said polymer is mixed with a free-radical initiator chosen from the group consisting of organic peroxides and azo compounds, and mixtures thereof, in
20 the presence of a nitroxide (N) according to one of Claims 1 to 5.

12. Process according to Claim 11, characterized in that the conversion of the crosslinkable composition (A) into moulded or extruded
25 articles is carried out during or after crosslinking.

13. Moulded or extruded articles which may be obtained according to Claim 12.