

DESCRIPTION

Title: Use of at least one perester to initiate polymerization or copolymerization of ethylene under high pressure

5 The present invention concerns the use of at least one organic peroxide selected from the group consisting of peresters, as defined hereinafter, for the radical polymerization or copolymerization of ethylene under high pressure.

10 The invention also pertains to a process for preparing polyethylene, especially low-density polyethylenes (LDPEs), or an ethylene copolymer, especially copolymers of ethylene and vinyl acetate (EVA), (meth)acrylic ethylene copolymers, copolymers based on ethylene and at least one alpha- or alpha,omega-olefin, copolymers based on ethylene and carbon monoxide, and copolymers based on ethylene and unsaturated cyclic anhydride comonomers, comprising a step of radical polymerization or copolymerization of ethylene under high pressure in the presence of at least one peroxide selected from the group consisting of peresters, as defined hereinafter.

15 The present invention also relates to a composition comprising at least one olefinic monomer and at least one peroxide chosen from the group consisting of peresters, as defined below.

20 Low-density polyethylenes (also called LDPEs) and ethylene copolymers are generally prepared in an autoclave or tubular reactor under high pressure, by continuous introduction of ethylene, one or more optional comonomers and one or more initiators, such as organic peroxides, which are usually diluted in an organic solvent. The pressure inside the reactor is generally between 500 and 5000 bar, whereas the temperature at initiation of the reaction varies usually from 80°C to 250°C. The maximum reaction temperature is typically between 120°C and 350°C. The polymerization initiators may be injected into one or more reaction zones of the reactor.

25 The search for gains in production, and consequently for cost rationalization, while retaining high reliability of the process carried out, is a constant preoccupation for producers of polyethylene and ethylene copolymers. In particular, it is important to develop a process which allows the manufacture of polyethylene or of ethylene

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copolymers that is of high productivity, accompanied by appropriate rationalization of the production costs, while retaining high reliability.

These searches for improvement in the implementation of this type of process are even more important given the commercial interest in polyethylenes and ethylene copolymers, since these polymers can be used in diverse fields of application, owing to their compatibility with many other polymers or resins.

Thus low-density polyethylenes are commonly used in the manufacture of films within the sector of packaging or flexible bottles.

Moreover, ethylene copolymers can be used in the manufacture of cables, of hotmelt adhesive compositions, of multilayer packaging films or of masterbatches. They may also be used as an impact modifier in the production of polymers such as polyamides and polyesters for the electronic and automotive sectors.

The organic peroxides conventionally used may be compounds capable of initiating a radical polymerization or copolymerization reaction of ethylene under high pressure across a range of elevated temperatures, called high temperatures. These organic peroxides are especially tert-butyl peroxy-3,5,5-trimethylhexanoate, sold under the trade name Luperox® 270, tert-butyl peracetate, sold under the trade name Luperox® 7, or tert-butyl perbenzoate, sold under the trade name Luperox® P.

The replacement, owing to suspicion of producing benzene in LDPE, of the high temperature initiator tert-butyl perbenzoate (sold under the name Luperox® P, and with the CAS number 614-45-9) by the non-aromatic initiator tert-butyl peroxy-3,5,5-trimethylhexanoate (Luperox® 270, CAS 13122-18-4) has for many years suffered from its mediocre radical efficacy, which is manifested in a specific consumption that may exceed 30% in certain initiator cocktails. Non-aromatic initiators that can decompose within the operating temperature range of Luperox® P have been proposed, such as Luperox® 220, Luperox® 520 and Luperox® 7, with the respective drawbacks of possibly generating methyl tert-butyl ether (MTBE), which is toxic in the LDPE process; of limiting the presence of di-tert-alkyl peroxide, which is liable to initiate polymerization outside the reactor; or of drawbacks with handling (odor and classification as toxic by inhalation) and with risk of corrosion of the plants.

There is therefore a need to find a non-aromatic peroxide which does not exhibit these drawbacks and which is significantly greater in efficacy than tert-butyl peroxy-3,5,5-trimethylhexanoate.

5 In the implementation of a process for preparing polyethylene or an ethylene copolymer, it is conventional practice to inject an organic peroxide or a collective of organic peroxides (commonly referred to as a cocktail of organic peroxides) into one or more reaction zones of a reactor in order to bring about the radical polymerization or copolymerization of ethylene under high pressure. In particular, it is known practice to inject a collective of organic peroxides which are capable of initiating the radical
10 polymerization or copolymerization reaction of ethylene within different temperature ranges, for example in a temperature range of from 160°C to 240°C and in a temperature range of from 240°C to 280°C, into two or more reaction zones of a reactor. This type of system of peroxidic initiators including one initiator more reactive than the others has the advantage of covering a wide range of initiation temperatures for the ethylene
15 polymerization or copolymerization reaction.

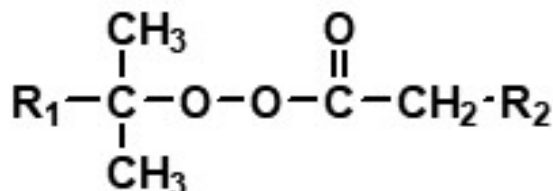
One of the objectives of the present invention, therefore, is to propose a compound or an association of compounds that is capable of initiating the radical polymerization or copolymerization reaction of ethylene under high pressure in a reliable way while reducing the amount of initiator(s) consumed during the reaction relative to the
20 organic peroxides conventionally used in the prior art.

In other words, there is a genuine need for effective replacement of some or all of the organic peroxides conventionally used in the radical polymerization or copolymerization of ethylene under high pressure by a system containing one or more initiators that is easy to store, handle and/or transport, and which is capable of reducing
25 the specific consumption of initiator(s) employed in the radical polymerization or copolymerization reaction.

More particularly, one of the objectives of the present invention is to provide a system containing one or more initiators for the radical polymerization or copolymerization of ethylene under high pressure so as to enhance the productivity and
30 the rationalization of the production costs of a process for preparing polyethylene or an ethylene-based copolymer.

A subject of the present invention especially is the use of at least one organic peroxide, alone or in combination with one or more distinct additional organic peroxide(s), selected from the group consisting of the peresters of formula (I) below:

[Chem 1]



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in which formula (I):

R₁ represents a linear or branched, nonaromatic, C₁-C₁₀ alkyl group, and

R₂ represents a linear C₁-C₁₆ alkyl group,

10 for the radical polymerization or copolymerization of ethylene under high pressure.

The organic peroxide according to the invention is used in particular, alone or in combination with one or more distinct additional organic peroxides, for initiating the polymerization or copolymerization of ethylene by a radical route under high pressure.

15 In other words, the invention proposes using a peroxidic initiator system composed of one or more organic peroxides in which at least one organic peroxide is selected from the group consisting of the peresters of formula (I) for the radical polymerization or copolymerization of ethylene under high pressure, especially for initiating the radical polymerization or copolymerization of ethylene under high pressure.

20 An advantage of the organic peroxide as defined above, alone or in combination with one or more distinct additional organic peroxides, is the effective initiation of the radical polymerization or copolymerization of ethylene under high pressure so as to produce polyethylene or an ethylene-based copolymer.

25 Thus the use of the organic peroxide according to the invention enables effective replacement of some or all of the organic peroxides conventionally used in the prior art for the radical polymerization or copolymerization of ethylene under high pressure.

Moreover, the organic peroxide according to the invention also has the advantage of having a self-accelerating exothermic decomposition temperature of greater than 50°C, which allows it to be stored, transported and handled at room temperature.

Moreover, the peroxidic initiator system according to the invention enables a reduction in the specific consumption of initiator(s) for a given injection zone, whether the consumption of the organic peroxide, as defined above, when it is used alone, or the overall consumption of the mixture of organic peroxides containing the organic peroxide as defined above and the additional organic peroxide(s).

More generally, the specific consumption of the organic peroxide according to the invention, when it is used alone, and the overall specific consumption of a combination of organic peroxides based on the organic peroxide according to the invention and one or more additional organic peroxides are reduced during the radical polymerization or copolymerization of ethylene under high pressure, relative to the organic peroxides used in the prior art.

Consequently, the organic peroxide according to the invention or the system containing an organic peroxide of this kind has an economic advantage associated with the limitation to the costs of producing polyethylene or ethylene-based copolymer(s), and an environmental advantage linked to the limitation to risks of producing volatile organic compounds resulting from the breakdown of the organic peroxide(s) employed.

In the sense of the present invention, “specific consumption of initiator(s)” refers to the amount in kilograms of initiator that is needed to produce one metric ton of polymer (resin). The specific consumption of initiator(s) may also be expressed in grams of initiator(s) per kilogram of polymer obtained.

Moreover, the peroxidic initiator system according to the invention is able to span a wide range of initiation temperatures for the radical polymerization or copolymerization of ethylene.

The invention also concerns a process for preparing polyethylene or an ethylene copolymer, comprising a step of radical polymerization or copolymerization of ethylene under high pressure in the presence of at least one organic peroxide selected from the group consisting of the peresters of formula (I), alone or in combination with one or more distinct additional organic peroxides.

The present invention also relates to a composition comprising:

- (i) at least one olefinic monomer,
- (ii) at least one perester of formula (I) as defined above, and
- (iii) optionally at least one additional organic peroxide distinct from the peroxide (ii).

The composition enables a reduction in the specific consumption of initiator(s) relative to the organic peroxides conventionally used in the preparation of polyethylene or of ethylene copolymer(s).

The composition according to the invention allows the polymerization to result in polyethylene or an ethylene-based copolymer.

The composition according to the invention is therefore polymerizable or able to polymerize.

In the sense of the present invention, “high pressure” means a pressure of greater than 50 MPa. Preferably, the pressure varies from 500 bar (50 MPa) to 3000 bar (300 MPa), preferentially from 1200 bar (120 MPa) to 3000 bar (300 MPa).

Other features and advantages of the invention will emerge more clearly on reading the description and the examples that follow.

In the following text, and unless otherwise indicated, the limits of a range of values are included in this range.

The expression “at least one” is equivalent to the expression “one or more”.

Organic peroxide

As indicated above, the invention pertains to the use of one or more peresters corresponding to the formula (I) described above for the radical polymerization or copolymerization of ethylene under high pressure.

The term “nonaromatic” is understood to mean, within the meaning of the present invention, that R_1 does not comprise an aromatic ring.

In other words, R_1 represents an aliphatic C_1 - C_{10} alkyl group.

Preferably, in the formula (I), R₁ represents a linear or branched, nonaromatic, C₁-C₆, more preferentially still C₁-C₅, better still C₁-C₄, more preferentially still C₁-C₃, alkyl group.

5 Advantageously, in the formula (I), R₁ represents a linear C₁-C₆, more preferentially still C₁-C₅, better still C₁-C₄, more preferentially still C₁-C₃, more preferentially C₁-C₂, alkyl group, and more preferentially is a -CH₃ group.

Advantageously, in the formula (I), R₂ represents a linear C₂-C₁₆ alkyl group.

10 Preferably, in the formula (I), R₂ represents a linear C₂-C₁₁, more preferentially C₃-C₁₁, more preferentially still C₅-C₁₀, more preferentially still C₅-C₆ and more preferentially C₆ alkyl group.

Advantageously, in the formula (I):

- R₁ represents a linear C₁-C₃, more preferentially C₁-C₂, alkyl group, and more preferentially is a CH₃ group, and
 - R₂ represents a linear C₂-C₁₁, more preferentially C₃-C₁₁, more preferentially still C₅-C₁₀, more preferentially still C₅-C₆ and more preferentially C₆ alkyl group.
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The perester or peresters according to the invention is or are preferentially selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-amyl peroxy-n-heptanoate, tert-hexyl peroxy-n-heptanoates, tert-heptyl peroxy-n-heptanoates, tert-octyl peroxy-n-heptanoates, tert-butyl peroxy-n-octanoate, tert-amyl peroxy-n-octanoate, tert-hexyl peroxy-n-octanoates, tert-heptyl peroxy-n-octanoates, tert-octyl peroxy-n-octanoates and mixtures thereof.

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Preferably, the perester or peresters is or are selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-amyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate, tert-amyl peroxy-n-octanoate and mixtures thereof; more preferentially, the perester or peresters according to the invention is or are selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate and mixtures thereof, and more preferentially is a tert-butyl peroxy-n-octanoate.

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The peresters according to the invention are obtained especially from the reaction between tert-alkyl hydroperoxides and acid halides, more particularly acid chlorides, especially in the presence of one or more alkaline agents.

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Preferably, the peresters according to the invention are obtained especially from the reaction between tert-butyl or tert-amyl hydroperoxides and acid halides, preferably acid chlorides, more particularly n-heptanoyl or n-octanoyl chlorides.

5 Preferably, the perester or peresters according to the invention has or have a half-life temperature at 1 hour, denoted HLT 1h, of greater than or equal to 110°C.

The “half-life temperature at 1 hour” is the temperature at which half of the peroxide has decomposed in 1 hour. In other words, it is the temperature at which a loss of half of the active oxygen content of the peroxide occurs after 1 hour.

10 The half-life temperature at 1 hour, denoted HLT 1h, of the peresters according to the invention is preferably measured in an isododecane solution.

Preferably, the peresters according to the invention have a half-life temperature at 1 hour, denoted HLT 1h, of less than or equal to 130°C.

Preferably, the peresters according to the invention have a half-life temperature at 1 hour of between 110°C to 130°C, more preferably of between 115°C to 125°C.

15 The peresters according to the invention may additionally exhibit a self-accelerating decomposition temperature (SADT) of greater than or equal to 50°C, preferably greater than or equal to 60°C.

20 The term “self-accelerating decomposition temperature” (SADT) is understood to mean the lowest temperature at which an uncontrolled reaction, that is to say a self-accelerating decomposition, takes place in its packaging. Preferably, this self-accelerating decomposition is measured in a 25 kg HDPE packaging. In other words, the self-accelerating decomposition temperature represents the temperature at which the chemical process bringing about the uncontrolled decomposition, possibly accompanied by self-combustion and explosion phenomena, begins. The self-accelerating decomposition
25 temperature is, for example, measured according to the standard UN H.3 of the United Nations Manual of Tests and Criteria, 7th, revised edition of 2019.

Advantageously, the peresters according to the invention exhibit a half-life temperature at 1 hour (HLT 1h) of greater than or equal to 115°C and a self-accelerating decomposition temperature (SADT) of greater than or equal to 50°C, preferably greater
30 than or equal to 60°C.

Preferably, the peresters according to the invention correspond to the formula (I) in which R₂ represents a linear C₂-C₇, in particular C₅ or C₆, alkyl group and exhibit a half-life temperature at 1 hour (HLT 1h) ranging from 115°C to 125°C.

5 Advantageously again, the perester or peresters according to the invention results or result from biobased starting materials.

The term “biobased” is understood to mean, within the meaning of the present invention, that the perester or peresters results or result from compounds of plant and/or animal origin, preferably plant origin.

10 The perester or peresters according to the invention can comprise a content of biobased carbon, that is to say carbon of plant and/or animal origin, especially of plant origin, of at least 20% by weight, preferably of at least 50% by weight, more preferentially 100% by weight, relative to the total weight of the carbons present in the perester compound.

15 Advantageously, the perester or peresters according to the invention can comprise a content of carbon resulting from renewable starting materials of greater than or equal to 50% by weight, preferably ranging from 55% to 70% by weight, more preferably ranging from 60% to 65% by weight, relative to the total weight of the carbons present in the perester compound.

20 The content of ¹⁴C is substantially constant from the extraction of the renewable starting materials up to the manufacture of the copolymer according to the invention and even up to the end of life of the object manufactured from said copolymer.

 Consequently, the presence of ¹⁴C in a material, whatever the amount thereof, gives an indication as to the origin of its constituent molecules, namely that they originate
25 from renewable starting materials and not from fossil materials.

The amount of ¹⁴C in a material may be determined by one of the methods described in the standard ASTM D6866-06 (Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis).

This standard comprises three methods of measurement of the organic carbon resulting from renewable starting materials, which is denoted “biobased carbon”. The proportions indicated for the perester of the invention are preferably measured according to the mass spectrometry method or the liquid scintillation spectrometry method described in this standard, and very preferentially by mass spectrometry.

These measurement methods evaluate the ratio of the $^{14}\text{C}/^{12}\text{C}$ isotopes in the sample and compare it with a ratio of the $^{14}\text{C}/^{12}\text{C}$ isotopes in a material of biological origin giving the 100% standard, in order to measure the percentage of organic carbon in the sample.

Preferably, the perester or peresters according to the invention is or are liquid at room temperature, that is to say at a temperature ranging from 21°C to 30°C.

Peroxidic initiator system

As indicated above, the present invention proposes the use of a peroxidic initiator system, namely a system containing at least one organic peroxide, as defined above, alone or in combination with one or more distinct additional organic peroxides.

The peroxidic initiator system may be either the organic peroxide as defined above, used alone, or a combination of the organic peroxide and one or more distinct additional organic peroxides as defined hereinafter.

With the peroxidic initiator system it is possible to initiate the radical polymerization or copolymerization of ethylene under high pressure.

In the sense of the present invention, “combination” means that the at least one organic peroxide, as defined above, is in a mixture with one or more distinct additional organic peroxides in a single formulation, or that said at least one organic peroxide and the additional organic peroxide or peroxides are in distinct formulations.

In other words, “combination” means that the at least one organic peroxide as defined above and the additional organic peroxide or peroxides belong to a single overall system of initiators which is capable of performing the polymerization or copolymerization of ethylene by a radical route under high pressure.

This means that the at least one organic peroxide as defined above and the distinct additional organic peroxide or peroxides participate overall in the polymerization or copolymerization of ethylene by a radical route under high pressure, depending on the temperature at which they initiate the reaction, and that they are not necessarily formulated in the same composition.

Thus, for example, the organic peroxide as defined above may be injected at one point of a reactor, while the additional organic peroxide or peroxides may be injected at another point of the reactor.

According to one embodiment, the organic peroxide as defined above is in a mixture with one or more distinct additional organic peroxide(s), i.e. they are formulated in the same composition. In this case, the combination corresponds to a mixture of the at least one organic peroxide according to the invention and one or more additional organic peroxide(s).

Distinct additional organic peroxide(s)

According to one embodiment, the at least one organic peroxide according to the invention is used in combination with one or more distinct additional organic peroxides, so as to cover a more extended temperature range for initiation of the radical polymerization or copolymerization of ethylene under high pressure than the range obtained with the organic peroxide according to the invention when used alone.

The term “distinct additional organic peroxide” means that the one or more additional organic peroxides is or are structurally distinct from the organic peroxide according to the invention selected from the group of peresters as defined above.

The additional organic peroxide or peroxides is or are selected preferably from the group consisting of organic peroxides capable of initiating the radical polymerization or copolymerization of ethylene under high pressure within a temperature range of from 110°C to 320°C.

Thus the peroxidic initiator system may comprise one or more organic peroxides, as defined above, and one or more additional organic peroxides selected from the group consisting of:

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- organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as low temperatures, ranging up to less than 160°C (i.e. strictly lower than 160°C), preferably selected from the group consisting of: di(2-ethylhexyl) peroxydicarbonate, tert-butyl peroxyneodecanoate, cumyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate, di-sec-butyl peroxydicarbonate, dibutyl peroxydicarbonate, and di-n-butyl peroxydiacyl, more preferentially selected from the group consisting of di(2-ethylhexyl) peroxydicarbonate and tert-butyl peroxyneodecanoate;
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- organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as medium temperatures, ranging from 160°C to less than 240°C (i.e. strictly lower than 240°C), preferably selected from the group consisting of: tert-butyl peroxy-2-ethylhexanoate,

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tert-amyl peroxy-2-ethylhexanoate and tert-amyl peroxyisobutyrate;
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- organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as high temperatures, ranging from 240°C to less than 280°C, preferably selected from the group consisting of: tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-amyl peroxy-3,5,5-trimethylhexanoate, tert-butyl peroxybenzoate, tert-amyl peroxybenzoate, tert-butyl peroxyacetate, and 2,2-di(tert-butylperoxy)butane, more preferentially selected from the group consisting of tert-butyl peroxy-3,5,5-trimethylhexanoate and tert-butyl peroxybenzoate;

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- organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as very high temperatures, from 280°C, preferably from 280°C to 320°C, preferably selected from the group consisting of: di-tert-butyl peroxide, di-tert-amyl peroxide and 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane.

In other words, in accordance with this embodiment, the peroxidic initiator system covers a range of temperatures for initiation of the reaction of ethylene by a radical route under high pressure, of from 110°C to 320°C.

Preferably, the one or more additional peroxides is or are selected from the group consisting of:

- peroxides having a half-life temperature at 1 h which is lower than the half-life temperature at 1 h of the perester as defined above, or, in the case of two or more peresters as defined above, of the perester having the lowest half-life temperature at 1 h among the peresters; and
- peroxides having a half-life temperature at 1 h which is higher than the half-life temperature at 1 h of the perester as defined above, or, in the case of more than one perester as defined above, of the perester having the highest half-life temperature at 1 h and atmospheric pressure among the peresters; and
- mixtures thereof.

The peroxidic initiator system preferably comprises:

- a perester of formula (I) selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-amyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate, tert-amyl peroxy-n-octanoate and mixtures thereof; more preferentially, the perester or peresters according to the invention is or are selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate and mixtures thereof, and more preferentially a tert-butyl peroxy-n-octanoate,
- tert-butyl peroxy-2-ethylhexanoate (such as Luperox® 26), and
- tert-butyl perpivalate (such as Luperox® 11).

The reason is that such a system of initiators leads to good results in terms of gain in the overall specific consumption of the initiators engaged in the radical reaction of ethylene.

In accordance with this embodiment, the additional organic peroxide or peroxides is or are different from the peresters described above.

The initiator system is preferably formulated in the same composition.

More preferentially, the peroxidic initiator system is a composition comprising:

- 5 - a perester of formula (I) selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-amyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate, tert-amyl peroxy-n-octanoate and mixtures thereof; more preferentially, the perester or peresters according to the invention is or are selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate and mixtures thereof, and more preferentially a tert-butyl peroxy-n-octanoate.
- 10 - tert-butyl peroxy-2-ethylhexanoate (Luperox® 26), and
- tert-butyl perpivalate (Luperox® 11).

Solvent

15 The organic peroxide according to the invention and the additional organic peroxide or peroxides may be diluted in a solvent or a mixture of solvents. The solvent or solvents may be selected from the group consisting of C₆-C₂₀ alkanes and C₄-C₁₂ alpha-olefins. The solvent or solvents is or are preferably selected from the group consisting of C₆-C₂₀, especially C₈-C₁₄, preferably C₁₂ alkanes. Preferably, when said solvent or mixture of solvents is present, the ratio of organic peroxide (or said system of peroxidic initiators) to the solvent(s) is at least 1:1; preferably at least 3:2, more preferentially 7:3.

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Use

As indicated above, the organic peroxide according to the invention is used, alone or in combination with one or more additional organic peroxides, for preparing polyethylene or an ethylene copolymer, preferably polyethylene.

25 The organic peroxide according to the invention is preferably used, alone or in combination with one or more additional organic peroxides, for the radical polymerization of ethylene under high pressure.

Method

The present invention also concerns a process for preparing polyethylene or an ethylene copolymer, comprising a step of radical polymerization or copolymerization of ethylene under high pressure in the presence of at least one organic peroxide selected from the group consisting of the peresters of formula (I), as described above, alone or in
5 combination with one or more distinct additional organic peroxides as defined above.

The organic peroxide according to the invention, alone or in combination with the additional organic peroxide or peroxides, is or are generally present in a quantity by mass of from 20 to 1000 ppm, relative to the quantity by mass of ethylene.

Moreover, the organic peroxide according to the invention and the additional
10 organic peroxide or peroxides are preferably diluted in a solvent or a mixture of solvents. The solvent or solvents may be selected from the group consisting of C₆-C₂₀ alkanes and C₄-C₁₂ alpha-olefins. The solvent or solvents is or are preferably selected from the group consisting of C₆-C₂₀, especially C₈-C₁₄, preferably C₁₂ alkanes.

The polymerization or copolymerization by a radical route may be performed in
15 an autoclave or tubular reactor.

The reaction temperature is generally between 120°C and 350°C.

As explained above, the radical polymerization or copolymerization of ethylene is initiated at a temperature which may be from 160°C to 250°C, preferably from 160°C to 190°C.

20 The radical polymerization or copolymerization of ethylene proceeds at a pressure of 500 bar (50 MPa) to 3000 bar (300 MPa) and preferably of 1200 bar (120 MPa) to 3000 bar (300 MPa).

The organic peroxide according to the invention, alone or in combination with one or more additional organic peroxides, may be injected at one point or at two or more
25 points of a reactor. The peroxidic initiator system according to the invention may therefore be injected once or a number of times into a reactor.

When the peroxidic initiator system according to the invention is injected at two or more points of a reactor, the reactor is referred to as a multizone reactor, preferably a multizone autoclave reactor or a multizone tubular reactor.

More particularly, in the case of a combination injected at two or more points of the reactor, it will be possible to use the organic peroxide according to the invention in increasing concentrations in the various formulations. In this way, the organic peroxide according to the invention may be formulated in a plurality of formulations based on additional organic peroxide(s) as defined above, at different concentrations, so as to optimize the conversion of ethylene in the reactor. These various formulations may be injected into two or more points of a reactor.

Moreover, in the case of injection at two or more points of the reactor of an organic peroxide combination as described above (i.e., multiple injection), the organic peroxide according to the invention may be injected at one point of the reactor and the additional organic peroxide or peroxides as described above may be injected at one or other points of the reactor. In this case, the organic peroxide according to the invention and the additional organic peroxide or peroxides as described above are not formulated in the same composition, but belong to the same peroxidic initiator system, so as to ensure the entirety of the polymerization or copolymerization of the ethylene.

When a tubular reactor is used, the mixture of ethylene and optional comonomer(s) is preferably introduced at the top of the tubular reactor. The organic peroxide according to the invention or the combination of organic peroxides may be injected by means of a high-pressure pump at the top of the reactor, after the location at which the mixture of ethylene and the one or more comonomers is introduced.

The mixture of ethylene and the optional comonomer(s) may be injected at at least one other point of the reactor, and this injection is in turn followed by another injection of the organic peroxide according to the invention or of a combination of organic peroxides as defined above, this being then referred to as a multipoint injection technique. When the multipoint injection technique is used, the combination is preferably injected in such a way that the weight ratio of the combination injected at the reactor inlet to the entirety of the combination injected is between 10% and 90%.

Other processes for high-pressure tubular polymerization or copolymerization which can be used are for example those described in US2006/0149004 A1 or in US2007/0032614 A1.

It is also possible to use an autoclave reactor for implementing the high-pressure radical polymerization or copolymerization of ethylene and the optional comonomers. An

autoclave reactor generally consists of a cylindrical reactor into which a stirrer is placed. The reactor can be separated into several zones connected to one another in series.

The process according to the invention is preferably implemented in an autoclave reactor, especially in a multizone reactor.

5 Advantageously, the residence time in the reactor is between 30 and 120 seconds.

The organic peroxide according to the invention, alone or in combination with one or more additional organic peroxides, is also injected into this first reaction zone when the reaction zone reaches a temperature of between 150°C and 200°C

10 In the course of the reaction, the temperature may be between 150°C and 320°C, since the reaction is exothermic. If the reactor is a multizone reactor, the stream of ethylene and of optional comonomers which have not reacted and also the polymer formed then pass through the subsequent reaction zones.

15 In each reaction zone, ethylene, optional comonomers and initiators can be injected, at an initiation temperature of between 160°C and 190°C. The temperature of the zones after initiation is between 150°C and 320°C.

20 The ethylene copolymer is preferentially selected from the group consisting of copolymers of ethylene and acrylate(s), ethylene-vinyl acetate (EVA) copolymers, copolymers based on ethylene and one or more alpha- or alpha,omega-olefin monomers, copolymers based on ethylene and carbon monoxides, and copolymers based on ethylene and unsaturated cyclic anhydride comonomers.

The copolymer of ethylene and acrylate comprises at least one unit obtained from ethylene and at least one unit obtained from an acrylate.

25 The acrylate is especially selected from the group consisting of alkyl (meth)acrylates, more particularly C₁-C₃₀ alkyl (meth)acrylates, and arylalkyl (meth)acrylates, alkanol (meth)acrylates, such as hydroxyethyl (meth)acrylate, and (meth)acrylates containing an epoxy group.

The alkyl and arylalkyl groups may be linear or branched and may contain from 1 to 30 carbon atoms, preferably from 1 to 24 carbon atoms.

The alkyl and arylalkyl groups may also contain ether or thioether functions.

The alkyl (meth)acrylates are preferably selected from the group consisting of methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, n-heptyl acrylate, n-octyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, n-heptyl methacrylate, n-octyl methacrylate, and mixtures thereof.

The (meth)acrylates containing an epoxy group are preferably selected from the group consisting of glycidyl methacrylate, glycidyl acrylate and mixtures thereof.

The acrylate is advantageously selected from the group consisting of alkyl (meth)acrylates, more particularly C₁-C₃₀ alkyl (meth)acrylates, and more particularly still C₁-C₂₄ alkyl (meth)acrylates.

The acrylate is selected more advantageously from the group consisting of methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, or mixtures thereof, especially butyl acrylate.

The aim of the process according to the invention is preferably to prepare low-density polyethylene (LDPE) or a copolymer of ethylene and vinyl acetate (EVA).

The aim of the process according to the invention more preferably still is to prepare polyethylene, preferably low-density polyethylene (LDPE).

The invention also relates to the ethylene polymer or copolymer obtained by the process above.

Composition

The present invention also relates to a composition comprising:

- (i) at least one olefinic monomer,
- (ii) at least one peroxide selected from the group consisting of the peresters of formula (I), as described above, and
- (iii) optionally at least one additional organic peroxide, distinct from the peroxide (ii), as described above.

The composition may further comprise one or more comonomers amenable to copolymerization with ethylene by a radical route under high pressure.

5 The comonomers are preferably selected from the group consisting of esters of unsaturated carboxylic acids (or salts thereof), anhydrides of carboxylic acids, vinyl esters, such as vinyl acetate or vinyl pivalate, alpha-olefins such as propene, 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene, unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid and fumaric acid, derivatives of (meth)acrylic acids such as (meth)acrylonitrile and (meth)acrylamide, vinyl ethers such as vinyl methyl ether and vinyl phenyl ether, and vinyl aromatic compounds such as styrene and alpha-methylstyrene, or mixtures thereof.

10 The comonomers or comonomers are more preferably selected from esters of unsaturated carboxylic acids (or salts thereof), vinyl esters, and mixtures thereof.

The esters of unsaturated carboxylic acids are preferably selected from the group consisting of alkyl (meth)acrylates, more particularly C₁-C₂₄ alkyl (meth)acrylates, and (meth)acrylates containing an epoxy group.

15 The alkyl (meth)acrylates are preferably selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, n-heptyl acrylate, n-octyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, n-heptyl methacrylate and n-octyl methacrylate.

20 The comonomer or comonomers are more preferably selected from the group consisting of vinyl ethers, especially vinyl acetate.

The composition according to the invention enables access to a polyethylene or an ethylene-based copolymer.

25 “At least one olefinic monomer” means that the composition comprises at least ethylene monomers, and optionally other comonomers as defined above.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

EXAMPLES

Example 1

Preparation of tert-butyl peroxy-n-heptanoate

74 g of a tert-butyl hydroperoxide solution (70%) are mixed with 116 g of a potassium hydroxide solution (30%) at a temperature of 5-10°C in a glass reactor equipped with a jacket, with a condenser and with a stirring system. 70 g of n-heptanoyl chloride (99.7%) are then added to this solution in a controlled manner so as to maintain the temperature between 5°C and 10°C. After 45 min of reaction at 5-10°C, the temperature is raised to 20-25°C over 15 min. After reaction, the two phases are left to separate by settling. The organic phase is washed with a sodium hydroxide solution (10%), then with a sodium metabisulfite solution (10%) and then with water. 67 g of a tert-butyl peroxy-n-heptanoate solution are recovered.

Preparation of tert-butyl peroxy-n-octanoate

41 g of a tert-butyl hydroperoxide solution (70%) are mixed with 62 g of a potassium hydroxide solution (30%) at a temperature of 5-10°C in a glass reactor equipped with a jacket, with a condenser and with a stirring system. 39 g of n-octanoyl chloride (99.7%) are then added to this solution in a controlled manner so as to maintain the temperature between 5°C and 15°C. The mixture is then left to react at 5°C for 100 min. After reaction, the two phases are left to separate by settling. The organic phase is washed with a sodium hydroxide solution (10%), then with a sodium metabisulfite solution (10%) and then with water. 43 g of a tert-butyl peroxy-n-octanoate solution are recovered.

Organic peroxides tested

In the example that follows, a radical polymerization of ethylene under high pressure was carried out, on the one hand with tert-butyl peroxy-3,5,5-trimethylhexanoate (Luperox® 270), called the reference peroxide, and on the other hand with tert-butyl peroxy-n-heptanoate, called peroxide (1), and with tert-butyl peroxy-n-octanoate, called peroxide (2).

In this comparative example, the reference peroxide was replaced weight for weight by peroxide (1) or by peroxide (2).

Experimental protocol

In a 435 ml high-pressure stirred batch reactor of autoclave type, the ethylene is injected until a pressure of 1800 bar is reached, i.e. approximately 207 g. Stirring is at 1000 rpm

(revolutions per minute). The initial temperature was established at the reactor wall temperature at 170°C by means of heater rods placed in the walls of the reactor.

The organic peroxides (peroxide (1), peroxide (2) and reference peroxide) are respectively diluted in heptane before being injected into the reactor.

5 A transfer agent, propionaldehyde, is also used in order to limit the molecular masses and the fouling of the reactor.

10 Thus each organic peroxide (peroxide (1), peroxide (2) and reference peroxide) is diluted in heptane and the propionaldehyde upstream of the reactor and at low temperature, so as not to initiate the reaction prior to entry into the reactor. Each mixture is then injected into the reactor using a high-pressure pump. The polymerization is triggered as soon as the peroxide is injected at an initial temperature of 170°C.

15 During the radical polymerization reaction, the thermal evolution curve, which follows the introduction of each peroxide into the reactor and corresponds to the exotherm of polymerization of ethylene, is ascertained. The exothermic curve corresponds to the kinetics of the radical reaction.

The exothermic curve passes through a temperature maximum, referred to as the maximum temperature attained and recorded as Tmax.

Determinations are made of Tmax and also the rate at which this Tmax is attained for a given level of addition.

20 The reaction proceeds until the final temperature returns to the same level of value as the initial temperature.

The reactor is then depressurized and the resin is recovered for measurement of the specific consumption of organic peroxide.

Results

25 Attainment of Tmax

Under the operating conditions referred to above (initial temperature = 170°C and pressure = 1800 bar), the Tmax values observed for the three organic peroxides, tert-butyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate and tert-butyl peroxy-3,5,5-trimethylhexanoate (Luperox® 270), and for a respective concentration in ppm by weight

relative to the ethylene monomer of 14.3, 14.3 and 16.3 ppm by relative weight, are attained respectively in: 13.8 s, 14.0 s and 13.2 s.

Specific consumption

5 The specific consumption of the organic peroxides is also measured for two radical polymerizations using the same levels of addition and enabling the attainment of the maximum temperature T_{max} , for each of said organic peroxides, of 231°C, still with an initial temperature of 170°C.

[Table 1]

Overall specific consumption of organic peroxides				
Organic peroxides	Tmax in °C	Peroxides injected (total in ppm by weight of peroxides)	Specific consumption in g pure peroxide/kg LDPE	Gain in specific consumption %
Luperox®270	231	16.3	0.300	36
tert-butyl peroxy- n-heptanoate	231	14.3	0.190	
tert-butyl peroxy- n-octanoate	231	14.3	0.180	40

5 According to this example, it is found that the production of LDPE in the case where a single initiator is used allows a gain in specific consumption of the order of 36% in organic peroxide with peroxide (1) and of the order of 40% in organic peroxide with peroxide (2) relative to the reference peroxide (Luperox® 270).

Example 2

Organic peroxides tested

10 In the example which follows, a radical polymerization of ethylene under high pressure was carried out, with three organic peroxide collectives containing respectively one peroxide of the medium range of operational temperatures (peroxide (1) or peroxide (2) or reference peroxide from example 1) combined with a more reactive organic peroxide and another less reactive organic peroxide, as defined above.

15 The three radical polymerizations of ethylene under high pressure were therefore carried out with the following peroxidic initiator systems:

- ternary collective 1: tert-butyl peroxy-pivalate (Luperox® 11), tert-butyl peroxy-2-ethylhexanoate (Luperox® 26) and tert-butyl peroxy-3,5,5-trimethylhexanoate (Luperox® 270),

- ternary collective 2: tert-butyl peroxy-pivalate (Luperox® 11), tert-butyl peroxy-2-ethylhexanoate (Luperox® 26) and tert-butyl peroxy-n-heptanoate,

- ternary collective 3: tert-butyl peroxy-pivalate (Luperox® 11), tert-butyl peroxy-2-ethylhexanoate (Luperox® 26) and tert-butyl peroxy-n-octanoate.

The mass ratio of the three peroxides (Luperox®11M75/Luperox®26/Luperox®270, Luperox®11M75/Luperox®26/tert-butyl peroxy-n-heptanoate, and Luperox®11M75/Luperox®26/tert-butyl peroxy-n-octanoate) was 2:1:1.

Only Luperox® 11 was used in a diluted commercial form for safety reasons, at 75% in the phlegmatizer isododecane, in the commercial presentation of Luperox® 11M75, the other peroxides being available in undiluted form. The mass ratio of the Luperox®11/Luperox®26/Luperox®270 system therefore expresses a weight ratio between undiluted peroxidic active substances of 1.5:1:1 respectively, corresponding to the 2:1:1 by weight mixture of Lup11M75/Lup26/Lup270.

Experimental protocol

The two radical polymerizations were carried out in the same batch reactor as that of example 1.

However, the initial temperature of the ethylene charge at 1800 bar was established at the lower initial temperature of 145°C, by virtue of the ternary cocktail, in which the most reactive organic peroxide dictates operation at a lower initial temperature than in example 1.

As in example 1, the ternary collectives were tested at the same overall level of addition in terms of organic peroxides in a first phase, in order to judge the kinetics (examination of the rise ramp in the reaction exotherm and T_{max} attained as a function of time).

Specific consumption

The specific consumption of the overall amounts of peroxides involved in the two ternary collectives was measured, at three maximum temperatures Tmax, specifically of 232°C, 240°C and 245°C, with an initial temperature of 145°C for each of the collectives.

5

[Table 2]

Overall specific consumption of organic peroxides				
Cocktail of peroxides	Tmax in °C	Sum of peroxides injected (ppm by weight of peroxides)	Specific consumption in g peroxides/kg LDPE	Gain in specific consumption of peroxides %
Luperox®11M75/ Luperox®26/ Luperox®270	232	53.4	0.655	/
Luperox®11M75/ Luperox®26/ tert-butyl peroxy-n-heptanoate	232	50.3	0.589	10
Luperox®11M75/ Luperox® 26/ tert-butyl peroxy-n-octanoate	232	36.0	0.411	37
Luperox®11M75/ Luperox®26/	240	74.5	0.803	/

Luperox®270				
Luperox®11M75/ Luperox®26/ tert-butyl peroxy-n- heptanoate	240	51.1	0.515	36
Luperox®11M75/ Luperox®26/ tert- butyl peroxy-n- octanoate	240	43.3	0.496	38

Luperox®11M75/ Luperox®26/ Luperox®270	245	86.6	0.883	/
Luperox®11M75/ Luperox®26/ tert-butyl peroxy-n- heptanoate	245	71.0	0.710	19
Luperox®11M75/ Luperox®26/ tert- butyl peroxy-n- octanoate	245	49.7	0.554	37

According to this example, it is found that the production of LDPE benefits from a gain in specific consumption of the overall cocktail of 10% to 38% in peroxides with tert-butyl peroxy-n-heptanoate or tert-butyl peroxy-n-octanoate relative to Luperox® 270.

Example 3

Organic peroxides tested

In the example that follows, a radical polymerization of ethylene under high pressure was carried out, on the one hand with tert-butyl peroxy-2-ethylhexanoate (Luperox® 26), called peroxide (3), and on the other hand with tert-butyl peroxy-n-octanoate, called peroxide (2).

In this comparative example, peroxide (3) was replaced weight for weight by peroxide (2) in order to see the difference between the branched isomer and the linear isomer.

Experimental protocol

The two radical polymerizations were carried out under the same conditions as for example 1.

Specific consumption

The specific consumption of the organic peroxides is also measured for two radical polymerizations using the same levels of addition and enabling the attainment of the maximum temperature Tmax, for each of said organic peroxides, of 231°C, still with an initial temperature of 170°C.

[Table 3]

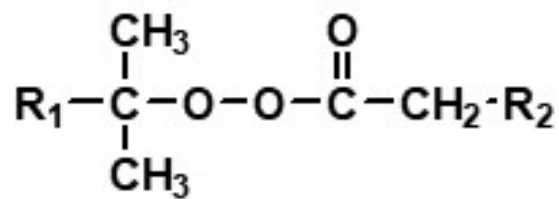
Overall specific consumption of organic peroxides				
Organic peroxides	Tmax in °C	Peroxides injected (total in ppm by weight of peroxides)	Specific consumption in g pure peroxide/kg LDPE	Gain in specific consumption %
Luperox® 26	231	15.6	1.662	/
tert-butyl peroxy- n-octanoate	231	15.4	0.220	86

According to this example, it is found that the production of LDPE when using a single initiator allows a gain in specific consumption of the order of 86% in terms of organic peroxide with peroxide (2), the linear isomer, relative to peroxide (3) (Luperox® 26), the branched isomer.

CLAIMS

1. The use of at least one organic peroxide, alone or in combination with one or more distinct additional organic peroxides, selected from the group consisting of the peresters of formula (I) below:

[Chem 1]



in which formula (I):

- R₁ represents a linear or branched, non-aromatic, C₁-C₁₀ alkyl group, and
- R₂ represents a linear- C₁-C₁₆ alkyl group,

for the radical polymerization or copolymerization of ethylene under high pressure.

2. The use as claimed in claim 1, characterized in that, in the formula (I), R₁ represents a linear C₁-C₆, preferably C₁-C₅, more preferentially C₁-C₄, more preferentially still C₁-C₃, more preferentially C₁-C₂ alkyl group, and more preferentially is a -CH₃ group.
3. The use as claimed in claim 1 or 2, characterized in that, in the formula (I), R₂ represents a linear C₂-C₁₁, more preferentially C₃-C₁₁, more preferentially still C₅-C₁₀, more preferentially C₅-C₆ and more preferentially C₆ alkyl group.
4. The use as claimed in any one of the preceding claims, characterized in that the perester or peresters is or are selected from the group consisting of tert-butyl peroxy-

5 n-heptanoate, tert-amyl peroxy-n-heptanoate, tert-hexyl peroxy-n-heptanoates, tert-heptyl peroxy-n-heptanoates, tert-octyl peroxy-n-heptanoates, tert-butyl peroxy-n-octanoate, tert-amyl peroxy-n-octanoate, tert-hexyl peroxy-n-octanoates, tert-heptyl peroxy-n-octanoates, tert-octyl peroxy-n-octanoates, and mixtures thereof, preferably at least one perester selected from the group consisting of tert-butyl peroxy-n-heptanoate, tert-butyl peroxy-n-octanoate and mixtures thereof, and more preferentially is a tert-butyl peroxy-n-octanoate.

10 5. The use as claimed in any one of the preceding claims, characterized in that the perester or peresters has or have a half-life temperature at 1 hour (HLT 1h) of greater than or equal to 110°C.

15 6. The use as claimed in any one of the preceding claims, characterized in that the perester or peresters has or have a self-accelerating decomposition temperature (SADT) of greater than or equal to 50°C, preferably greater than or equal to 60°C.

7. The use as claimed in any one of the preceding claims, characterized in that the additional peroxide or peroxides is or are selected from the group consisting of:

20 - organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as low temperatures, ranging up to less than 160°C, preferably selected from the group consisting of: di(2-ethylhexyl) peroxydicarbonate, tert-butyl peroxyneodecanoate, cumyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate, di-sec-butyl peroxydicarbonate, dibutyl peroxydicarbonate, and di-n-butyl peroxydiacyl, more preferentially selected from the group consisting of di(2-ethylhexyl) peroxydicarbonate and tert-butyl peroxyneodecanoate;

25 - organic peroxides capable of initiating the radical reaction of ethylene under high pressure in a temperature range known as medium temperatures, ranging from 160°C to less than 240°C, preferably selected from the group consisting

30

11. The process as claimed in claim 9 or 10, characterized in that the ethylene copolymer is selected from the group consisting of copolymers of ethylene and acrylate(s), copolymers based on ethylene and at least one alpha- or alpha,omega-olefin, copolymers based on ethylene and carbon monoxides, and copolymers based on ethylene and unsaturated cyclic anhydride comonomers.
12. The process as claimed in claim 9 or 10, characterized in that the polymer for preparation is polyethylene, preferably low-density polyethylene.
13. A composition comprising:
- (i) at least one olefinic monomer,
 - (ii) at least one peroxide selected from the group consisting of peresters as defined in any one of claims 1 to 6, and
 - (iii) optionally at least one additional peroxide, distinct from the peroxide (ii),
- as defined in any one of claims 1 and 7.