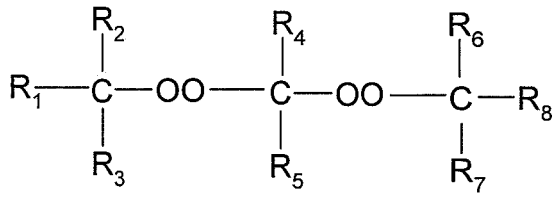
Finally, document EP 2673307 is known, filed in the name of the applicant, in which it has been shown that certain organic peroxides of the diperketal type made it possible to increase the productivity of the process to values greater than 3000 g/g for a particular initiation temperature range of between 150 and 200°C.This document illustrates, through the examples therein, the particular benefit of 2,2-di(tert-amylperoxy)butane (diluted to 50% in isododecane, known in the commercial form under the name Luperox® 520M50) as high-productivity initiator for LDPE (low-density polyethylene).

The abovementioned peroxide initiator is satisfactory since it improves productivity and the search for gains in productivity is a major goal for polyethylene resin producers.

Nonetheless, it is desirable to propose an even greater improvement in productivity.

Summary

Unlike what could have been expected by those skilled in the art, the applicant has surprisingly discovered that the use of a pair of diperketal organic peroxides of formula



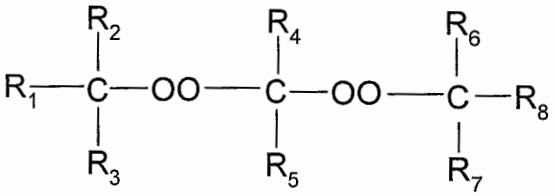
(I)

the groups R essentially consisting of C1-C6 alkyl groups, these two peroxides having a one minute half-life temperature of between 150°C and 185°C, made it possible to reduce the specific consumption (mass of polymer produced per gram of peroxides injected) in terms of peroxide used, in the initiation temperature range of 140°C-200°C.

The possibility emerges therefrom of obtaining productivities greater than or equal to 3000 g/g for an initiation temperature range of between 140°C and 200°C conventionally used for this type of process, and to increase the productivity at a high reaction temperature (polymerization temperature) of between 200°C and 290°C for a better thermal initiation progression, that is to say a better productivity with peroxides making it possible to reach very high temperatures (T_{max} = maximum temperature reached by the polymerization exotherm) typically 295-305°C, such as with di-tert-butyl peroxide.

In an aspect, there is provided a process for manufacturing polyethylene or an ethylene copolymer, comprising a step of radical polymerization or copolymerization of ethylene in the presence:

- of a first peroxide polymerization initiator chosen from the diperketal peroxide compounds of formula:

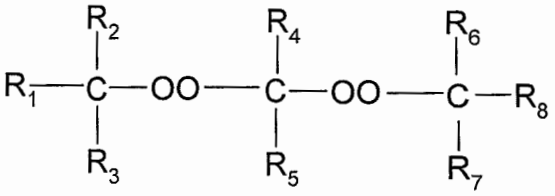


(I)

in which the R_1, R_2, R_3, R_6, R_7 and R_8 groups consist of substituted or unsubstituted, linear, branched or cyclic C1-C10 alkyl groups,

- of a second initiator, other than said first initiator, also consisting of a diperketal peroxide of formula (I).

In particular, the present disclosure relates to a process for manufacturing polyethylene or an ethylene copolymer by continuous introduction of ethylene and optional comonomer(s) into an autoclave or tubular reactor, comprising a step of radical polymerization or copolymerization of the ethylene at an initiation temperature ranging from 140°C to 200°C, at a pressure ranging from 1200 to 3000 bar, in the presence of a first peroxide polymerization initiator chosen from diperketal peroxides of formula



(I)

in which the R_1, R_2, R_3, R_6, R_7 and R_8 groups consist of C1-C6 alkyl groups,

characterized in that a second initiator, also consisting of a diperketal peroxide of formula (I), is present during the abovementioned step, the first and second peroxides, forming a mixture of peroxides, having a one minute half-life temperature of between 150°C and 185°C as measured in n-dodecane at a

concentration of 0.1 mol per liter (mol.l^{-1}) by means of a differential scanning calorimetry (DSC) curve.

The half-life temperature may be simply determined from DSC data which serve to characterize the thermal stability of the peroxides in question. Said one minute half-life temperature is measured in n-dodecane at a concentration of 0.1 mol per liter (mol.l^{-1}) by means of a differential scanning calorimetry (DSC) curve.

The thermokinetic curve of the decomposition recorded using this technique makes it possible to obtain the kinetic parameters relating to the thermal decomposition of unstable substances according to a decomposition equation of Arrhenius type.

In the case of a treatment according to kinetics of order n, the three parameters k_0 (pre-exponential factor), E_a (activation energy) and n (order of the decomposition reaction) are linked and optimized so as to minimize differences between the model and the experimental curve.

The half-life temperature T is the temperature at which, after the time t, the amount of thermally unstable matter remaining is equal to half of the initial amount.

It should be noted that in the remainder of this text the expression "one minute half-life temperature" is always understood in the context of a measurement carried out in n-dodecane at a concentration of 0.1 mol per liter (mol.l^{-1}).

The expression “C1-C10 alkyl group”, preferably “C1-C6 alkyl group” means that this is a substituted or unsubstituted, linear, branched or cyclic alkane-derived group comprising at least one (1) carbon atom and up to ten (10), preferably up to six (6) carbon atoms. For unbranched structures, this conventionally refers, for example, to methyl, ethyl, n-propyl, n-butyl, n-pentyl or n-hexyl groups.

According to one embodiment, the disclosure is moreover particularly improved when the one minute half-life temperature is between 160°C and 170°C as measured in n-dodecane at a concentration of 0.1 mol per liter (mol.l^{-1}).

Thus, generally, organic peroxides having an ester function, like Luperox® 230, are not *a priori* retained within the context of the present disclosure, not because of the lack of "booster" effect but because of their damaging release of CO_2.

The applicant also discovered a very significant improvement to the disclosure when the two organic peroxides used differ structurally from one another by a single carbon, at the two central groups R_4 or R_5. This is presented below with the pair 2,2-(di-tert-amylperoxy)butane (Luperox® 520M50) and 2,2-(di-tert-amylperoxy)propane (in all the examples below, diluted to 50% by weight in isododecane), but this efficiency relationship was confirmed in the laboratory with other diperketal organic peroxide pairs.

This particularly advantageous structural relationship between the two diperketals is established when the group R_4 or R_5 of the first initiator differs from the corresponding group, R_4 or R_5 respectively, of the second initiator, by a single carbon.

It will be noted that this small difference in molecular structure made it impossible to predict the markedly superior conversion efficiency (ability of the peroxide to initiate a certain number of polymer chains by monomer initiation reaction).

Other characteristics or embodiments of the disclosure are presented below:

- preferably, the groups R_4 and R_5 are substituted or unsubstituted, linear, branched or cyclic C1-C10 alkyl groups, preferably substituted or unsubstituted, linear, branched or cyclic C1-C6 alkyl groups.
- preferably, at least 1, preferably at least 2, preferably at least 3, preferably at least 4, preferably at least 5, preferably at least 6 of the groups R_2 to R_7 are substituted or unsubstituted, linear, branched or cyclic C1-C6 alkyl groups.
- preferably, at least 1, preferably at least 2, preferably at least 3, preferably at least 4, preferably at least 5, preferably at least 6 of the groups R_2 to R_7 are linear.
- preferably, at least 1, preferably at least 2, preferably at least 3, preferably at least 4, preferably at least 5, preferably at least 6 of the groups R_2 to R_7 are unsubstituted.
- preferably, at least 1, preferably at least 2, preferably at least 3, preferably at least 4, preferably at least 5, preferably at least 6 of the groups R_2 to R_7 are linear and unsubstituted.

- advantageously, the groups R_2, R_3, R_6 and R_7 of the two abovementioned initiators each consist of a methyl group.

- preferably, the group R_4 consists of a methyl group.

- preferably, the groups R_2, R_3, R_4, R_6 and R_7 each consist of a methyl group.

- according to a preferred embodiment, the groups R_1 and R_8 of the two abovementioned initiators each consist of a C2-C5, preferably C2-C4, alkyl group.

- according to another advantageous embodiment, the group R_5 of the two abovementioned initiators represents a C1-C2 alkyl group.

- according to a preferred solution afforded by the disclosure, the first polymerization initiator is 2,2-di(tert-amylperoxy)butane.

- similarly, according to a preferred solution afforded by the dislcosure, the second polymerization initiator is 2,2-di(tert-amylperoxy)propane.

- preferably, said first polymerization initiator is 2,2-di(tert-amylperoxy)butane and said second polymerization initiator is 2,2-di(tert-amylperoxy)propane.

- advantageously, the mixture/the proportion of the two diperketal peroxides/initiators has a share of the second initiator of between 2 and 50 mol% (all of the two perketal peroxides representing 100% of the mixture), preferably between 10 and 40 mol%, even more preferentially between 15 and 35 mol%.

- preferably, the total proportion of said first and second initiators is between 1 and 10 000 ppm, preferably between 10 and 1000 ppm, even more preferentially between 50 and 150 ppm by weight relative to the weight of final polyethylene or ethylene copolymer.

Said first and second initiators may be added to the reaction mixture together or separately.

Said first and second initiators are preferably added together, and they preferably form a mixture of peroxides.

The polymerization or copolymerization may also be carried out in the presence of at least one additional peroxide initiator. Preferably, said at least one additional peroxide initiator is not a compound of formula (I).

In particular, said at least one additional peroxide initiator is not a diperketal according to the definition of the independent claim of the present patent application.

This additional peroxide initiator may be selected from the group consisting of: tert-butyl peroxyneodecanoate, tert-butyl peroxypivalate, tert-amyl peroxypivalate, bis(3,5,5-trimethylhexanoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-amyl peroxy-3,5,5 trimethylhexanoate, tert-butyl peroxybenzoate, tert-butyl peroxyacetate, di-tert-butyl peroxide and di-tert-amyl peroxide.

The polymerization or copolymerization may be carried out in the presence of at least one additive, preferably selected from the group consisting of: antioxidants; UV protection agents; processing agents, having the function of improving the final appearance when it is used, such as fatty amides, stearic acid and the salts thereof, ethylenebis(stearamide) or fluoro polymers; antifogging agents; antiblocking agents, such as silica or talc; fillers, such as calcium carbonate, and nanofillers, such as, for example, clays; coupling agents, such as silanes; crosslinking agents, such as peroxides; antistatic agents; nucleating agents; pigments; dyes; plasticizers; fluidizers and flame-retardant additives, such as aluminum hydroxide or magnesium hydroxide.

These additives are generally used in contents of between 10 ppm and 100 000 ppm by weight relative to the weight of the final polyethylene or ethylene copolymer. In particular, the plasticizers, the fluidizers and the flame-retardant additives can reach amounts well above 10 000 ppm.

Aside from the improved productivity results, the process according to the disclosure moreover has a large number of advantages, a non-exhaustive list of which is given below:

- ease of processing by simply adding the pair of peroxides, which can be introduced in a single formulation to the formulation/dilution of initiators;
- the organic peroxides used within the context of the disclosure are peroxides of the same family (diperketals) and therefore have the same advantage of lower CO_2 production (inert gas which is detrimental to ethylene conversion by replacement effect), and a higher conversion than with peresters;
- a lower specific consumption of the first diperketal peroxide used (the main one), which is not compromised by the addition of the second diperketal

peroxide (optionally designated by the term "booster"); rather, the addition of the second diperketal peroxide makes it possible to reduce the amounts of the two peroxides used, by approximately 5 to 10% (compared to the use of just the first diperketal peroxide);

- a compatibility with existing high-pressure polymerization technologies, in other words no adaptation of the current autoclave or tubular process or equipment is necessary to carry out the process according to the disclosure.

Detailed description of the invention

The polymerization or copolymerization is carried out at a pressure ranging from 500 to 3500 bar, preferably from 500 to 3000 bar, preferably from 1200 to 3000 bar, even more preferentially from 1200 to 2600 bar.

High-pressure polymerization is generally carried out in an autoclave or tubular reactor. The reaction temperature is generally between 100°C and 330°C, preferably between 120°C and 300°C, and even more preferentially between 140°C and 200°C.

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 initiator or the mixture of initiators is preferably injected by means of a high-pressure pump at the top of the reactor, after the location at which the mixture of ethylene and optional comonomer(s) is introduced.

The mixture of ethylene and optional comonomer(s) may be injected at at least one other point of the reactor, and this injection may in turn be followed by another injection of initiator or of a mixture of initiators; reference is then made to the multipoint injection technique. When the multipoint injection technique is used, the mixture is preferentially injected such that the weight ratio of the mixture injected at the reactor inlet to the whole mixture injected is between 10 and 90%.

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

It is also possible to use an autoclave reactor to carry out the high-pressure radical polymerization.

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. Advantageously, the residence time in the reactor is between 30 and 120 seconds. Preferentially, the length/diameter ratio