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(54) Title: SOLUTION PROCESS FOR THE OLEFINS POLYMERIZATION

(57) Abstract: A process for the polymerization of one or more olefins under solution polymerization conditions to produce a polymeric solution, said process comprising contacting the produced polymeric solution with one or more antioxidant compounds before or concurrently with subjecting the polymeric solution to a devolatilization step to separate the polymer from the unreacted monomers.



TITLE: "Solution process for the olefins polymerization"

The present invention relates to a process comprising the polymerization of α -olefins in a solution phase. In particular, it relates to α -olefin solution polymerization wherein the obtained polymeric solution is subjected to devolatilization in order to remove the unreacted monomers from the polyolefin.

It is known that when the polymerization of one or more olefins is carried out in a solution phase, a solution of a polyolefin in the reaction medium is withdrawn from the polymerization reactor. The reaction medium comprises the liquid monomers and optionally, depending on the α -olefin to be polymerized, an inert hydrocarbon solvent, which can be used to favor the solubility of the obtained polymer in the liquid medium. Highly viscous polymeric solutions are discharged from the polymerization reactor, the viscosity being generally comprised between 1000 and 100000 centiPois.

Butene-1 (co)polymers are well known and are preferably produced by means of solution polymerization of butene-1 in the presence of coordination catalysts, which are generally referred to as Ziegler-Natta catalysts. Butene-1 (co)polymers are mainly used in the manufacture of molded products such as pipes, packaging films, adhesives. The solution polymerization is generally carried out in liquid butene-1 at conditions under which a solution of polybutene-1 in butene-1 is discharged from the polymerization reactor. The polymerization reaction may be performed in one or more continuously stirred tank reactors or static mixer reactors (SMR).

The bulk polymerization of butene-1, i.e. without the use of any inert hydrocarbon solvent, is feasible since polybutene-1 dissolves in butene-1 at relatively low temperatures. Furthermore, the two components of the solution perfectly mix together at the optimum working temperatures of a Ziegler-Natta or a single-site catalyst system. In order to obtain the best performance of the polymerization catalyst together with a complete miscibility of monomer and polymer, the polymerization temperature in step a) is generally kept at a value comprised in the range of from 65 to 85°C, while the pressure is generally comprised between 8 and 40 bar.

The solution polymerization of olefins necessarily requires the successive separation of the obtained polyolefin from the unreacted monomers. The monomer recovery is generally carried out in a separation step wherein high temperatures, of about 150-250°C, are required. Before such a separation step, a deactivation of the catalyst residues is therefore necessary in order to avoid an undesired modification of the properties of the final polymer due to a further uncontrolled polymerization of the monomers and/or a thermal degradation of the polymer.

The patent application WO 04/000895 describes the liquid-phase polymerization of butene-1 to produce a solution of polybutene-1 in butene-1, the polymerization being carried out in one or more stirred tank reactors. The polymeric solution is discharged from the polymerization reactor and is conveyed to a deactivation step of the catalyst residues, which is preferably carried out in a deactivation apparatus equipped with a sequence of mixing stages. A catalyst deactivator is mixed to the polymer solution, the catalyst deactivator being an organic compound having at least a hydroxy group, a boiling point higher than 150°C, and a ratio between the molecular weight (MW) and the number of hydroxy groups (n_{OH}) comprised between 20 and 100. The catalyst deactivator is preferably selected from propylen glycol, dipropylen glycol, glycerol, diethylen glycol, butandiol.

Also the description of WO 05/058979 relates to the catalyst deactivation of a polymeric solution obtained by a liquid-phase polymerization of butene-1. This application faces the problems correlated with the high viscosity of the polymer solution to be deactivated and consequent difficulty in pursuing a homogeneous mixing of the catalyst deactivator with the highly viscous polymer solution. The problem is solved by using a catalyst deactivator with a high viscosity, in particular an aqueous mixture with a dynamic viscosity at 30°C higher than 50 cP (centiPoise) and comprising one or more organic compounds having at least a hydroxy or epoxy group. Preferably, said aqueous mixture comprises one or more alkyldiethanolamines of formula $R-N(CH_2CH_2OH)_2$, wherein R is an alkyl radical $C_{12}-C_{18}$.

The patent application WO 04/000891 describes a method for removing the unreacted butene-1 from a solution of polybutene in butene-1 coming from a solution polymerization reactor. The polymeric solution is first subjected to heating and mixing conditions, so as to form a two-phase mixture consisting of a polybutene melt and supercritical gaseous butene-1, then said two-phase mixture is transferred to a sequence of two devolatilization chambers operated at a decreasing pressure. In particular, both the volatilizers are operated at a high temperature, in the order of 200-220°C, and the second volatilizer is operated under vacuum. According to the working examples of this application, an antioxidant compound (Irganox® 1010) is added to the polymer melt discharged from the second volatilizer and is fed into a static mixer used to perform the polymer extrusion.

The Applicant has performed further experimental work on the devolatilization method described in WO 04/000891 and has observed that, notwithstanding the deactivation of the catalyst residues upstream the devolatilization chambers, the final polymer pellets may show values of melt index (MI), polydispersity index (PI) and molecular weight distribution (MWD) substantially different from the values measured at the outlet of the polymerization

reactor: as a consequence, the mechanical properties of the obtained polyolefin differ considerably from the targeted properties.

The above drawback is probably due to the severe operative conditions maintained inside the two volatilization chambers (temperatures of 200-220°C with a residence time of 3-4 hours), which may cause phenomena of thermal degradation of the polymeric chains. Above all, the second devolatilization chamber is operated under vacuum conditions (10-50 mbar), so that it is very difficult to maintain this volatilization chamber completely sealed: air infiltrations from outside may bring little amounts of oxygen in contact with the polymeric chains, with consequent breakage of the chains and modification of the values of melt index, PI and MWD of the polyolefin.

It is therefore felt the need to improve the process described in WO 04/000891, so as to solve the above technical problem, which is caused by the severe operative conditions adopted when subjecting a polyolefin solution to devolatilization.

The Applicant has now found that the use of antioxidant compounds downstream the solution polymerization of α -olefins allows to maintain substantially unaltered the physical properties of the obtained polyolefin when subjected to a melt devolatilization technique.

It is therefore an object of the present invention a process for the polymerization of one or more olefins under solution polymerization conditions to produce a polymeric solution, said process comprising contacting the produced polymeric solution with one or more antioxidant compounds before or concurrently while subjecting the polymeric solution to a devolatilization step to separate the polymer from the unreacted monomers.

According to the invention the above devolatilization step may be carried out in a sequence of a first and a second devolatilization chamber. In this case, the polymeric solution is preferably contacted with one or more antioxidant compounds inside the first devolatilization chamber.

The polymeric solution coming from the reactor is generally subjected to a deactivation step, wherein the polymeric solution is contacted with a catalyst deactivator, said deactivation step taking place before contacting the polymeric solution with the one or more antioxidant compounds.

According to a preferred embodiment the solution process of the invention comprises:

- (a) polymerizing said one or more α -olefins in a solution phase in the presence of a polymerization catalyst to produce a polymeric solution;
- (b) conveying the polymeric solution to a deactivation tank, where a catalyst deactivator is mixed with the polymeric solution;

(c) separating the produced polyolefin from the unreacted monomers by means of a devolatilization step comprising a first and a second devolatilization chamber; the process being characterized in that one or more antioxidant compounds are added to said polymeric solution upstream the devolatilization step (c) or alternatively inside the first devolatilization chamber of step (c).

The process of the invention is aimed to neutralize the detrimental effects due to the presence of oxygen inside the volatilization chambers of the above defined step c).

According to a first embodiment one or more antioxidant compounds are added to the polyolefin directly inside the first volatilization chamber of step c). As known to those skilled in the art, a volatilization chamber is operated in such a way that the polymer settles downwards as a "polymer melt", while the monomers and optional polymerization solvents flow upward to the top of the volatilization chamber. With the term "polymer melt" is meant an olefin polymer in the molten state: in spite of its very high viscosity (of about 20×10^6 cP), said polymer melt is still able to be pumped by means of a gear pump. In particular, the polymer melt collects in the lower portion of the volatilizer, while the unreacted monomers are released from the upper surface of the polymer melt, so that a high turbulence regime is established inside the polymer melt. This high turbulence contributes to mix homogeneously the antioxidant compounds with the polyolefin, so as to favor an intimate contact of the antioxidant compound with the polyolefin.

According to a second embodiment of the present invention one or more antioxidant compounds are added to the polymeric solution upstream the devolatilization step (c).

In both the first and second embodiment of the invention, the positive effect of the invention is the consequent reaction of these antioxidant compounds with the oxygen, which penetrates inside the volatilization chambers of step c): said reaction brings to the formation of by-products, which differently from oxygen, do not interfere with the polymer chains of the produced polyolefin and do not modify their physical properties.

According to a preferred embodiment of the invention, the antioxidant compounds are added to the polymer solution downstream the deactivation step (b) and upstream the devolatilization step (c).

The antioxidant compounds preferably used in the solution polymerization of the invention are selected from the group of sterically hindered phenols, phosphites, thioesters.

The suitable compounds belonging to the class of sterically hindered phenols are:

- tetrakis(methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate) methane, sold under the trademark IRGANOX® 1010;
- octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate (IRGANOX® 1076);
- 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl) benzene (IRGANOX® 1030);
- 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)isocyanurate (IRGANOX® 3114);
- 2,6-bis(α -methylbenzyl)-4-methylphenol (Naugard® 431);
- 1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (CYANOX® 1790);
- 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol) (CYANOX® 425)
- 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) (CYANOX® 2246)

The suitable compounds belonging to the class of phosphites are:

- tris (2,4-di-*t*-butyl phenyl) phosphite (Irgafos 168)
- bis (2,4-ditertbutylphenol) pentaerythritol diphosphite (Ultranox® 626)
- tris(nonylphenyl) phosphite (Alkanox TNPP);
- 2,4,6-tri-*t*-butylphenyl-2-butyl-2-ethyl-1,3 propane-diolphosphite (ULTRANOX® 641);
- bis (2,4-dicumylphenyl) pentaerythritol diphosphite (Doverphos® S-9228)

The suitable compounds belonging to the class of thioesters are:

- dialkyl ester of thiodipropionic acid (Irganox® PS 802);
- didodecyl-3,3'-thiodipropionate (Irganox® PS 800).

Particularly preferred antioxidant compounds used in the present invention are IRGANOX® 1010 and IRGANOX® 1076.

The above compounds are generally added to the polymer at a temperature such that the antioxidant compound is in a liquid state. For most of these compounds the suitable feeding temperature is from 50°C to 100°C, preferably from 60°C to 90°C.

The suitable amount of antioxidant compounds ranges from 300 to 2000 ppm by weight, preferably from 500 to 1200 ppm, with respect to the polyolefin produced in the polymerization step a).

As regards the polymerization step a) one or more α -olefins of formula $\text{CH}_2=\text{CHR}$, where R is hydrogen or a hydrocarbon radical C_{1-8} , are subjected to polymerization in a solution phase. The polymerization reaction may be performed in one or more continuously stirred tank reactors or static mixer reactors (SMR). A solution of a polyolefin in the reaction medium is obtained from the polymerization reactor. The reaction medium comprises the liquid monomers and optionally, depending on the α -olefin to be polymerized, an inert hydrocarbon solvent, which

can be used to favor the solubility of the obtained polymer in the liquid medium. The catalyst system used in the polymerization step may be a Ziegler-Natta catalyst system and/or a single-site catalyst system comprising an alumoxane compound as the cocatalyst.

The alpha-olefin to be polymerized in step a) is preferably butene-1 or propylene. When butene-1 is to be polymerized, the bulk polymerization in the liquid monomer is the preferred one, without using any inert hydrocarbon solvent. The bulk polymerization is feasible since polybutene-1 dissolves in butene-1 at relatively low temperatures. Furthermore, the two components of the solution perfectly mix together at the optimum working temperatures of a Ziegler-Natta or a single-site catalyst system. In order to obtain the best performance of the polymerization catalyst together with a complete miscibility of butene-1 and polybutene-1, the polymerization temperature in step a) is generally kept at a value comprised in the range of from 65 to 85°C, while the pressure is generally comprised between 8 and 40 bar. The residence time of the liquid inside the reactor is generally comprised between 30 minutes and 4 hours, preferably between 2 and 3 hours.

When propylene is to be polymerized, step (a) is carried out in liquid monomer, preferably together with a polymerization solvent selected from a paraffinic, isoparaffinic, naphtenic, or aromatic hydrocarbon solvent, which has the function to foster the solubility of the obtained polypropylene in the polymerization medium. Suitable polymerization solvents are, for example, toluene, cyclohexane, hexane, heptane, octane, nonane, isooctane, ethylbenzene, isopentane and IsoparTM, which is a C₈-C₁₀ hydrocarbon mixture. Depending on the selected solvent and catalyst system, the polymerization of propylene is generally operated at a high temperature, generally in a range from 80 to 180°C, preferably from 90 to 130°, at a high pressure, generally in a range from 20 to 80 bar, preferably from 25 to 60 bar. The residence time of the liquid inside the reactor is generally comprised between 10 minutes and 90 minutes, preferably between 20 minutes and 60 minutes.

A highly viscous polymeric solution is discharged from the polymerization reactor of step a): the viscosity of the polymeric solution is generally comprised between 1000 and 100000 centiPois.

The obtained polymeric solution is transferred to step b) of present invention aimed to deactivate the catalyst components contained in the polymer solution. The catalyst deactivation can be performed in one or more mixing tanks placed in series or, alternatively, in a single deactivation apparatus equipped with a sequence of more mixing stages. In the case of polymerization carried out in the presence of a Ziegler-Natta catalyst, any of the deactivating compounds known in the art can be employed. Suitable deactivating compounds

are water or organic compounds with a boiling point higher than 150°C and at least a hydroxy group. Examples of preferred deactivating compounds are water, propylenglycol, dipropylenglycol, glycerol; more preferably water is used as the deactivator.

The deactivated polymer solution is discharged from the deactivation tank and is transferred by means of a volumetric pump to the successive separation step c), where unreacted monomers and the polymerization solvents, if present, are recovered and re-circulated to the polymerization reactor of step a).

The polymeric solution discharged from the deactivation tank of step b) is transferred by means of a volumetric pump, preferably a screw pump, to the separation step c). The melt devolatilization technique of step c) requires the heating of the polymer solution at high values of temperature. Therefore, the polymeric solution is first pressurized by means of said screw pump to a pressure ranging from 40 to 100 bar, and then it is heated in one or more heat exchangers to raise its temperature to values comprised between 150 and 300°C, this value of temperature being bound to the volatility of the specific monomers and solvents to be recovered. One or more multi-tube heat exchangers, optionally containing static mixing elements inside each tube can be used to this purpose, as described in the Patent Application WO 04/000891 in the name of the same Applicant.

Preferably, the antioxidant compounds of the invention are added to the polymer solution along the line connecting the above screw pump to said first volatilization chamber of step c). Preferably, a sequence of a first and a second volatizer operating at a decreasing pressure is used in step c). The first volatizer is operated at a pressure higher than the atmospheric pressure and the second one is operated under vacuum: by this technique a polymer melt substantially free of monomers and polymerization solvents is obtained at the outlet of the second volatizer.

The present invention will be, thereafter, described in more details with reference to the enclosed Figs. 1-2, which are illustrative and non-limitative of the scope of the invention and refer in particular to a solution process for polymerizing butene-1 as the main monomer.

Fig 1 shows a first embodiment of the process of the invention, where the antioxidant compounds are added to the polyolefin in correspondence of the first volatilization chamber of step c).

Fig 2 shows a second embodiment of the process of the invention, where the antioxidant compounds are added to the polyolefin along the line connecting the catalyst deactivation tank to the first volatilization chamber.

According to the process set-up shown in Figure 1 the solution polymerization of step a) of

the invention is performed in a continuously stirred tank reactor 1. A transition metal compound, optionally supported on a carrier, an aluminum alkyl compound and optionally an electron donor compound are first pre-contacted in one or more pre-contacting pots (not shown) and then fed to the continuously stirred tank reactor 1 via line 2.

A liquid stream containing liquid butene-1, and optionally olefin comonomers, is introduced into the polymerization reactor 1 via line 3. The olefin monomers coming from the monomer recovery section are recycled to the reactor 1 via line 4.

A highly viscous solution of a polybutene-1 in butene-1 is discharged via line 5 from the reactor 1. Part of the polymeric solution is continuously recycled to the reactor 1 by a pump 6, which conveys the polymeric solution into a heat exchanger 7 and then, after suitable cooling, is recycled to the polymerization reactor 1 via line 8.

The remaining part of polymeric solution discharged from the reactor 1 is conveyed to a deactivation tank 9, where is contacted with a catalyst deactivator, such as water, fed in a suitable amount to the tank 9 via line 10. After the catalyst deactivation, the solution of polybutene-1 in butene-1 is pressurized in order to contrast the head loss along the successive heating stage. The polymer solution is pressurized and transferred by means of a screw pump 11 to a sequence of two multitube heat exchangers 12, 13, where the polymer solution is heated at the high temperatures required to perform the devolatilization step c).

The polymeric solution is pumped by the screw pump 11 to the inlet of a first heat exchanger 12. The heat exchanger 12 is a multi-tube heat exchanger with static mixing elements inserted inside each tube: the heating fluid is preferably steam. By means of heat exchanger 12 the temperature of the polymeric solution is slowly increased without substantially to evaporate the liquid monomer with the purpose of decreasing considerably the viscosity of the polymer solution.

The solution of polybutene-1 in butene-1 exits the heat exchanger 12 and enters a second heat exchanger 13, which is a multi-tube heat exchanger using a diathermic oil as the heating fluid. During the passage along the tubes of the heat exchanger 13 the polymer solution is heated in such a way that at the outlet of the heat exchanger 13 a two-phase mixture is obtained consisting substantially of: (1) polybutene melt containing entrapped butene-1 and (2) supercritical gaseous butene-1.

The two-phase mixture coming from the heat exchanger 13 is then passed to the devolatilization step c) of present invention, carried out in a sequence of two volatilizers operating at decreasing pressures.

The polymeric stream exiting from the heat exchanger 13 is introduced via line 14 at the top

of a first volatilizer 15, which is operated at a temperature of 170-220°C and a pressure from 2 to 12 bar.

In said first volatilizer 15 the evaporated monomers are separated from the polymeric components: a polymer melt settles downwards at the bottom part of the volatilizer 15, while the evaporated monomers are realized away from the polymer, flowing upward as a gaseous stream. The gas phase exiting the top of the volatilizer 15 is transferred via line 16 to the monomer recovery section of the polymerization plant. The monomer recovery section comprises one or more distillation columns to separate the heavy components from the light components, a drying unit, and recycle lines of liquid monomers to the polymerization reactor.

According to the embodiment of Fig. 1 one or more antioxidant compounds in a liquid form are fed via line 17A to the top of the first volatilizer 15 and fall on the surface of the polymer melt which occupies the bottom portion of the volatilizer 15. Due to high turbulence existing inside the volatilizer, said antioxidant compounds are intimately mixed with the polymer melt. A polymer melt additivated with the antioxidant compounds of the present invention is withdrawn from the bottom of the first volatilizer 15 by means of a gear pump 18 and transferred via line 19 into a heat exchanger 20, which adjusts the temperature of the polymer melt at the values requested in the second volatilizer. The polymer melt exiting the heat exchanger 20 is introduced via line 21 at the top of a second volatilizer 22, which is operated at a temperature of 170-220°C and a pressure from 5 to 100 mbar. Said pressure values are maintained by means of the vacuum pump 23.

In the second volatilizer 22 the residual monomers are realized away from the polymer melt, which settles downwards at the bottom of the volatilizer 22. The unreacted monomers flow upward along the volatilizer 22: this gaseous stream collects at the top of the volatilizer 22 and is withdrawn by vacuum pump 23 and transferred via line 16 to the monomer recovery section.

A polymer melt, further purified from the unreacted monomers is withdrawn by means of a gear pump 24 from the bottom of the second volatilizer 22 and transferred via line 25 into a static mixer 26 to be subjected to extrusion. The static mixer 26 has the function of mixing the polymer melt with suitable additives, such as nucleating agents, pigments, etc. A side-arm extruder (not shown) can be used for melting and mixing each other the additives used for the polyolefin compounding. The compounded butene-1 (co)polymer exiting the static mixer 26 is then passed via line 27 to an underwater pelletizer 28, where it is cut into pellets by the action of rotating knife blades: the pellets are then cooled by means of cooling water.

Fig 2 shows a second and alternative embodiment of the process of the invention, always referring to a solution polymerization of butene-1, as represented in Fig 1. The only difference in the process set-up of Fig 2 is due to the fact that the antioxidant compounds are added to the polyolefin solution via feed line 17B, which merges on the line connecting the catalyst deactivation tank 9 to the first volatilization chamber 15.

The olefin monomers polymerized by the process of the invention have formula $\text{CH}_2=\text{CHR}$, where R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms. The process of the invention is particularly suitable to be exploited in the production of homopolymers and copolymers based on ethylene, propylene and 1-butene, especially when the obtained polyolefin is characterized by bimodality, so as to be successfully employed in the production of pipes.

The solution polymerization of olefins herewith described is not restricted to the use of any particular family of polymerization catalysts. The invention is useful in any exothermic polymerization reaction employing any catalyst, whether it is supported or unsupported, and regardless of whether it is in pre-polymerized form.

The polymerization reaction can be carried out in the presence of highly active catalytic systems, such as Ziegler-Natta catalysts, single site catalysts, chromium-based catalysts.

A Ziegler-Natta catalyst system comprises the catalysts obtained by the reaction of a transition metal compound of groups 4 to 10 of the Periodic Table of Elements (new notation) with an organometallic compound of group 1, 2, or 13 of the Periodic Table of element.

In particular, the transition metal compound can be selected among compounds of Ti, V, Zr, Cr, and Hf. Preferred compounds are those of formula $\text{Ti}(\text{OR})_n\text{X}_{y-n}$ in which n is comprised between 0 and y; y is the valence of titanium; X is halogen and R is a hydrocarbon group having 1-10 carbon atoms or a COR group. Among them, particularly preferred are titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates. Preferred specific titanium compounds are TiCl_3 , TiCl_4 , $\text{Ti}(\text{OBu})_4$, $\text{Ti}(\text{OBu})\text{Cl}_3$, $\text{Ti}(\text{OBu})_2\text{Cl}_2$, $\text{Ti}(\text{OBu})_3\text{Cl}$.

Preferred organometallic compounds are the organo-Al compounds and in particular Al-alkyl compounds. The alkyl-Al compound is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$ optionally in mixture with said trialkyl aluminum compounds.

Particularly suitable high yield ZN catalysts are those wherein the titanium compound is supported on magnesium halide in active form which is preferably MgCl_2 in active form.

Particularly for the preparation crystalline polymers of CH_2CHR olefins, where R is a C1-C10 hydrocarbon group, internal electron donor compounds can be supported on the MgCl_2 . Typically, they can be selected among esters, ethers, amines, and ketones. In particular, the use of compounds belonging to 1,3-diethers, cyclic ethers, phthalates, benzoates, acetates and succinates is preferred.

It is also possible to use, besides the electron-donor present in the solid catalytic component, an external electron-donor (ED) added to the aluminium alkyl co-catalyst component or to the polymerization reactor. These external electron donors can be selected among alcohols, glycols, esters, ketones, amines, amides, nitriles, alkoxysilanes and ethers. The electron donor compounds (ED) can be used alone or in mixture with each other. Preferably the ED compound is selected among aliphatic ethers, esters and alkoxysilanes. Preferred ethers are the C2-C20 aliphatic ethers and in particular the cyclic ethers preferably having 3-5 carbon atoms, such as tetrahydrofuran (THF), dioxane.

Preferred esters are the alkyl esters of C1-C20 aliphatic carboxylic acids and in particular C1-C8 alkyl esters of aliphatic mono carboxylic acids such as ethylacetate, methyl formiate, ethylformiate, methylacetate, propylacetate, i-propylacetate, n-butylacetate, i-butylacetate.

The preferred alkoxysilanes are of formula $\text{R}_a^1\text{R}_b^2\text{Si}(\text{OR}^3)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1 , R^2 , and R^3 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^1 and R^2 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R^3 is a C₁-C₁₀ alkyl group, in particular methyl.

Other useful catalysts are those based on chromium compounds, such as chromium oxide on silica, also known as Phillips catalysts.

Other suitable catalysts are single site catalysts, for instance metallocene-based catalyst systems which comprise:

at least a transition metal compound containing at least one π bond;

at least an alumoxane or a compound able to form an alkylmetallocene cation; and

optionally an organo-aluminum compound.

A preferred class of metal compounds containing at least one π bond are metallocene compounds belonging to the following formula (I):



wherein M is a transition metal belonging to group 4, 5 or to the lanthanide or actinide groups of the Periodic Table of the Elements; preferably M is zirconium, titanium or hafnium;

the substituents X, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R^6 , OR^6 , $OCOR^6$, SR^6 , NR^6_2 and PR^6_2 , wherein R^6 is a hydrocarbon radical containing from 1 to 40 carbon atoms; preferably, the substituents X are selected from the group consisting of -Cl, -Br, -Me, -Et, -n-Bu, -sec-Bu, -Ph, -Bz, $-CH_2SiMe_3$, -OEt, -OPr, -OBu, -OBz and -NMe₂;

p is an integer equal to the oxidation state of the metal M minus 2;

n is 0 or 1; when n is 0 the bridge L is not present;

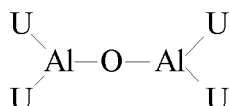
L is a divalent hydrocarbon moiety containing from 1 to 40 carbon atoms, optionally containing up to 5 silicon atoms, bridging Cp and A, preferably L is a divalent group $(ZR^7_2)_n$; Z being C, Si, and the R^7 groups, equal to or different from each other, being hydrogen or a hydrocarbon radical containing from 1 to 40 carbon atoms;

more preferably L is selected from $Si(CH_3)_2$, $SiPh_2$, $SiPhMe$, $SiMe(SiMe_3)$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$;

Cp is a substituted or unsubstituted cyclopentadienyl group, optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings;

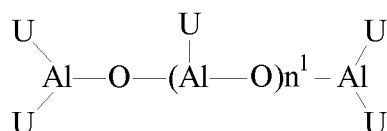
A has the same meaning of Cp or it is a NR^7 , -O, S, moiety wherein R^7 is a hydrocarbon radical containing from 1 to 40 carbon atoms;

Alumoxanes used as component b) are considered to be linear, branched or cyclic compounds containing at least one group of the type:

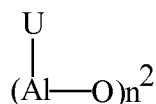


wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n^1 is 0 or an integer of from 1 to 40 and where the U substituents, same or different, are hydrogen atoms, halogen atoms, C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number; or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n^2 is an integer from 2 to 40 and the U substituents are defined as above.

The following examples have to be considered representative and non-limiting of the scope of the invention.

EXAMPLES

Characterization

Melt Index E (MIE): ASTM-D 1238 method E

Polydispersity index (P.I.): this property is strictly connected with the molecular weight distribution of the polymer under examination. In particular it is inversely proportional to the creep resistance of the polymer in the molten state. Said resistance, called modulus separation at low modulus value, i.e. 500 Pa, was determined at a temperature of 200°C by using a parallel plates rheometer model RMS-800 marketed by RHEOMETRICS (USA), operating at an oscillation frequency which increases from 0.1 rad/s to 100 rad/s.

From the modulus separation value the PI is derivable by means of the equation:

$P.I. = 54.6 * (\text{modulus separation})^{-1.76}$, where the modulus separation is defined as:

$\text{Modulus separation} = (\text{frequency at } G'=500\text{Pa})/(\text{frequency at } G''=500\text{Pa})$

where G' is the storage modulus and G'' is the low modulus value.

Preparation of the solid catalyst component

Into a 500 ml four-necked round flask, purged with nitrogen, 225 ml of TiCl_4 were introduced at 0°C. While stirring, 6.8 g of microspheroidal $\text{MgCl}_2 \cdot 2.7\text{C}_2\text{H}_5\text{OH}$ (prepared as described in Ex. 2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000) were added. The flask was heated to 40°C and 4.4 mmoles of diisobutylphthalate were thereupon added. The temperature was raised to 100°C and maintained for two hours, then stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

200 ml of fresh TiCl_4 were added, the mixture was reacted at 120°C for one hour, then the supernatant liquid was siphoned off and the solid obtained was washed six times with anhydrous hexane (6 x 100 ml) at 60°C and then dried under vacuum. The catalyst component contained 2.8 wt% of Ti and 12.3 wt% of phthalate.

Example 1

Polymerization - step a)

The liquid-phase polymerization of butene-1 is performed in two continuously stirred tank reactors (CSTR) placed in series in the presence of a Ziegler-Natta polymerization catalyst comprising:

- a solid catalyst component based on a Titanium compound, prepared as above indicated;
- triisobutylaluminum (TIBA) as a catalyst activator;
- thexyltrimethoxysilane as a donor compound for the stereoregularity control.

The catalyst is fed exclusively to the first reactor of the two CSTR type reactors in series.

Liquid butene-1 together with H₂ as a molecular weight regulator is continuously fed to the polymerization reactors. The polymerization conditions in the first and second reactors are reported in Table A, as well as the feeding ratio H₂/C₄H₈.

TABLE A

Polymerization conditions	-1 st Reactor	2 nd Reactor
Temperature (°C)	71.5	75
Pressure (bar)	20	20
Residence Time (min)	103	67
Polymer concentration (% weight)	25	25
H ₂ (ppm mol)	160	2050

26 t/h of a solution of polybutene in butene-1 with a polymer concentration of 25% by weight is discharged from the second polymerization reactor. A sample of polymeric solution is taken away at the outlet of the second reactor in order to evaluate the Melt Flow Index (MIE) and Polydispersity index (PI) of the obtained polybutene-1: MIE=0.35 and PI=7.0 were measured.

Deactivation – step b)

The PB-1 solution is transferred to a deactivation apparatus for the killing of the catalyst residues: 2.0 kg/h of H₂O, as the catalyst deactivator, is continuously fed to the top of the deactivation apparatus together with 26 t/h of polymeric solution.

Separation and monomer recovery – step c)

Once deactivated, the polymeric solution is successively pressurized by means of a screw pump and is then subjected to heating in a sequence of two multi-tube heat exchangers. The first heat exchanger is provided with mixing rods inside each tube and uses steam at a temperature of 135°C as the heating fluid. The second heat exchanger uses a diathermic oil (MARLOTHERM N) at 260°C as the heating fluid.

At the outlet of the second heat exchanger a mixture of polybutene-1 melt and gaseous

butene-1 is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated a temperature of 210°C and a pressure of 7 bar. The polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous butene-1 flows upward.

According to the embodiment shown in Fig. 1 of present description antioxidant compounds are introduced into the first volatilizer. In particular, a mixture of IRGANOX® 1010 (70% wt) and IRGANOX® 1076 (30% wt) is fed to the bottom part of the first volatilizer. Said mixture is fed at a temperature of 75°C and a flow rate of 3.25 kg/h (corresponding to 500 ppm weight referred to the polymer).

The PB-1 melt is therefore discharged from the bottom of the first volatilizer and is introduced into a heat exchanger in order to raise its temperature up to the value requested into the second devolatilization chamber.

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. At the outlet of the second volatilizer the content of butene-1 in the polybutene-1 melt is measured obtaining a value of only 40 ppm weight.

The polybutene- 1 melt is compounded in an extruder and finally, the compounded polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets.

The values of MIE and PI of the obtained PB-1 pellets are reported in Table C, where MIE^(A) and PI^(A) refer to the polymer at the outlet of the polymerization step a), while MIE^(B) and PI^(B) refer to the polymer pellets. It may be observed that the process of the invention ensures a limited and negligible MIE shift and PI shift.

Example 2

The same solution of PB-1 in butene-1 obtained by the polymerization conditions of Example 1 is subjected to catalyst deactivation as described in Example 1.

Once deactivated, the polymeric solution is pressurized by means of a screw pump before to be subjected to heating in two multi-tube heat exchangers.

According to the embodiment shown in Fig. 2 of present description, antioxidant compounds are fed to the polymer solution along the line connecting the deactivation tank to the first volatilization chamber. In particular, a mixture of IRGANOX® 1010 (70% wt) and IRGANOX® 1076 (30% wt) is fed to the polymer solution downstream the screw pump and upstream the first heat exchanger. Said mixture is fed at a temperature of 75°C and a flow rate of 3.25 kg/h (500 ppm wt referred to the polymer).

The temperature at the outlet of the second heat exchanger is 210°C and a mixture of polybutene-1 melt and gaseous butene-1 is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated a temperature of 210°C and a pressure of 7 bar. The

polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous butene-1 flows upward.

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. At the outlet of the second volatilizer the content of butene-1 in the polybutene-1 melt is measured obtaining a value of only 40 ppm weight.

The polybutene-1 melt is compounded in an extruder and finally, the compounded polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets.

The values of MIE and PI of the obtained PB-1 pellets are reported in Table C. It may be observed that the process of the invention ensures a limited and negligible MIE shift and PI shift.

Example 3 (comparative)

The same solution of PB-1 in butene-1 obtained by the polymerization conditions of Example 1 is subjected to catalyst deactivation as described in Example 1.

Once deactivated, the polymeric solution is pressurized by means of a screw pump before to be subjected to heating in the same multi-tube heat exchangers of example 1.

The temperature at the outlet of the second heat exchanger is 210°C and a mixture of polybutene-1 melt and gaseous butene-1 is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated at a temperature of 210°C and a pressure of 7 bar. The polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous butene-1 flows upward.

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. At the outlet of the second volatilizer the polybutene-1 melt is sent to an extruder, where it is additivated with a mixture of IRGANOX® 1010 (70% wt) and IRGANOX® 1076 (30% wt). Said mixture is fed at a flow rate of 3.25 kg/h.

Finally, the compounded polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets. The values of MIE and PI of the obtained PB-1 pellets are reported in Table C.

It may be observed that the final pellets show a considerable MIE shift and PI shift.

Example 4

Polymerization - step a)

The liquid-phase polymerization of butene-1 and ethylene is performed in two continuously stirred tank reactors (CSTR) placed in series in the presence of the same Ziegler-Natta catalyst of Example 1.

The catalyst is fed exclusively to the first reactor of the two CSTR type reactors in series. H₂ is used as a molecular weight regulator.

The polymerization conditions in the first and second reactor are reported in Table B, as well as the feeding ratios ethylene/butene-1 and hydrogen/butene-1.

TABLE B

Polymerization conditions	-1 st Reactor	2 nd Reactor
Temperature (°C)	75	75
Pressure (bar)	24	24
Residence Time (min)	102	102
Polymer concentration (% wt)	21.5	21.5
C ₂ H ₄ (% wt)	3.5	3.5
H ₂ (ppm mol)	1450	1450

A solution of random copolymer dissolved in butene-1 is continuously withdrawn from the second reactor at a flow rate of 26 t/h. The polymer concentration is of 21.5% by weight.

A sample of polymeric solution is taken away at the outlet of the second reactor in order to evaluate the Melt Flow Index (MIE) and Polydispersity index (PI) of the obtained random copolymer. The values are shown in table C.

Deactivation – step b)

The polyolefin solution is transferred to the deactivation apparatus for the killing of the catalyst residues: an amount of 2.0 kg/h of H₂O is continuously fed to the top of the deactivation apparatus.

Separation and monomer recovery – step c)

Once deactivated, the polymeric solution is successively pressurized by means of a screw pump and is then subjected to heating in the sequence of two multi-tube heat exchangers. The temperature at the outlet of the second heat exchanger is 210°C and a mixture of polyolefin melt and gaseous monomers is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated at a temperature of 210°C and a pressure of 7 bar. The polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous monomers flow upward. A mixture of IRGANOX® 1010 (50% wt) and IRGANOX® 1076 (50% wt) is introduced into the first volatilizer according to the first embodiment of present invention (shown in FIG 1). Said mixture is fed at T=75°C and a flow rate of 4.47 kg/h (800 ppm wt referred to the polymer).

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. At the outlet of the second volatilizer the content of butene-1 in the polybutene-1 melt is measured obtaining a value of only 60 ppm weight.

The polybutene- 1 melt is compounded in an extruder and finally, the compounded

polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets.

The values of MIE and PI of the obtained PB-1 pellets are reported in Table C.

Example 5

The same solution of butene-1 random copolymer obtained by Example 4 is subjected to catalyst deactivation according to same modality described in Example 4.

Once deactivated, the polyolefin solution is pressurized by means of the screw pump before to be subjected to heating in two multi-tube heat exchangers.

According to the second embodiment of present invention (shown in FIG 2), a mixture of IRGANOX® 1010 (50% wt) and IRGANOX® 1076 (50% wt) is fed to the polymer solution downstream the screw pump and upstream the first heat exchanger. Said mixture is fed at $T=75^{\circ}\text{C}$ and a flow rate of 4.47 kg/h (800 ppm wt referred to the polymer).

The temperature at the outlet of the second heat exchanger is 210°C and a mixture of polyolefin melt and gaseous butene-1 is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated at a temperature of 210°C and a pressure of 7 bar. The polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous butene-1 flows upward.

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. The polybutene-1 melt is compounded in an extruder and finally, the compounded polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets.

The values of MIE and PI of the obtained PB-1 pellets are reported in Table C.

Example 6 (comparative)

The same solution of butene-1 random copolymer obtained by Example 4 is subjected to catalyst deactivation according to same modality described in Example 4.

Once deactivated, the polymeric solution is pressurized by means of a screw pump before to be subjected to heating in the same multi-tube heat exchangers of previous examples.

At the outlet of the second heat exchanger a mixture of polybutene-1 melt and gaseous butene-1 is obtained. Said mixture is fed to the inlet of a first devolatilization chamber, operated at a temperature of 210°C and a pressure of 7 bar. The polybutene-1 melt settles by gravity to the bottom of the chamber, while the gaseous butene-1 flows upward.

The PB-1 melt is therefore discharged from the bottom of the first volatilizer and is introduced into a heat exchanger in order to raise its temperature up to the value requested into the second devolatilization chamber.

The second devolatilization chamber is operated under vacuum at 210°C and 25 mbar. At the outlet of the second volatilizer the polybutene-1 melt is sent to an extruder, where it is

additivated with a mixture of IRGANOX® 1010 (50% wt) and IRGANOX® 1076 (50% wt). Said mixture is fed at $T=165^{\circ}\text{C}$ and a flow rate of 4.47 kg/h.

Finally, the compounded polybutene-1 melt is conveyed to an underwater pelletizer to be cut into pellets.

The values of MIE and PI of the obtained PB-1 pellets are reported in Table C. It may be observed that the final pellets show a considerable MIE shift and PI shift.

TABLE C

	Antioxidant compound	Amount (ppm wt)	MIE ^(A)	MIE ^(B)	PI ^(A)	PI ^(B)
Ex. 1	IRGANOX 1010/1076	500	0.35	0.37	7.0	7.0
Ex. 2	IRGANOX 1010/1076	500	0.35	0.37	7.0	7.0
Ex. 3 (comp)	IRGANOX 1010/1076	500	0.35	0.45	7.0	6.0
Ex. 4	IRGANOX 1010/1076	800	2.8	3.0	4.5	4.5
Ex. 5	IRGANOX 1010/1076	800	2.8	3.0	4.5	4.5
Ex. 6 (comp)	IRGANOX 1010/1076	800	2.8	3.6	4.5	4.0

MIE^(A) measured downstream the polymerization step

PI^(A) measured downstream the polymerization step

MIE^(B) measured downstream pelletization

PI^(B) measured downstream pelletization

CLAIMS

1. A process for the polymerization of one or more olefins under solution polymerization conditions to produce a polymeric solution, said process comprising contacting the produced polymeric solution with one or more antioxidant compounds before or concurrently while subjecting the polymeric solution to a devolatilization step to separate the polymer from the unreacted monomers.
2. The process according to claim 1, wherein said devolatilization step is carried out in a sequence of a first and a second devolatilization chambers.
3. The process according to claim 2, wherein the polymeric solution is contacted with the one or more antioxidant compounds inside the first devolatilization chamber.
4. The process according to any of claims 1 to 3 comprising subjecting the polymeric solution to a deactivation step, wherein the polymeric solution is contacted with a catalyst deactivator, said deactivation step taking place before contacting the polymeric solution with the one or more antioxidant compounds.
5. The process according to any of claims 1 to 4 comprising:
 - (a) polymerizing said one or more α -olefins in a solution phase in the presence of a polymerization catalyst to produce a polymeric solution;
 - (b) conveying the polymeric solution to a deactivation tank, where a catalyst deactivator is mixed with the polymeric solution;
 - (c) separating the produced polyolefin from the unreacted monomers by means of a devolatilization step comprising a first and a second devolatilization chamber;the process being characterized in that one or more antioxidant compounds are added to said polymeric solution upstream the devolatilization step (c) or alternatively inside the first devolatilization chamber of step (c).
6. The process according to claim 5, wherein in step c) said first devolatilization chamber is operated at a pressure higher than the atmospheric pressure, while the second devolatilization chamber is operated under vacuum.
7. The process according to claim 5, wherein the polymer solution is discharged from said deactivation tank and is transferred by means of a screw pump to the separation step c).
8. The process according to claim 7, wherein said antioxidant compounds are added to the polymer along the line connecting said screw pump to said first volatilization chamber of step c).

9. The process according to claim 1, wherein said antioxidant compounds are fed in an amount from 300 to 2000 ppm by weight with respect to the polyolefin produced in said polymerization step a).
10. The process according to claim 1, wherein said antioxidant compounds are added to the polymer in a liquid state at a feeding temperature ranging from 50°C to 100°C.
11. The process according to claim 1, wherein said antioxidant compounds are selected from the group of sterically hindered phenols, phosphites, thioesters.
12. The process according to claim 11, wherein said sterically hindered phenols are selected from:
 - tetrakis(methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate) methane,
 - octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate,
 - 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl) benzene
 - 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate;
 - 2,6-bis(α -methylbenzyl)-4-methylphenol;
 - 1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;
 - 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol);
 - 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol);
13. The process according to claim 11, wherein said phosphites are selected from:
 - tris (2,4-di-*t*-butyl phenyl) phosphate;
 - bis (2,4-di-*tert*-butylphenol) pentaerythritol diphosphite;
 - tris(nonylphenyl) phosphite;
 - 2,4,6-tri-*t*-butylphenyl-2-butyl-2-ethyl-1,3propane-diolphosphite;
 - bis (2,4-dicumylphenyl) pentaerythritol diphosphite.
14. The process according to claim 11, wherein said thioesters are dialkyl ester of thiodipropionic acid and didodecyl-3,3'-thiodipropionate.

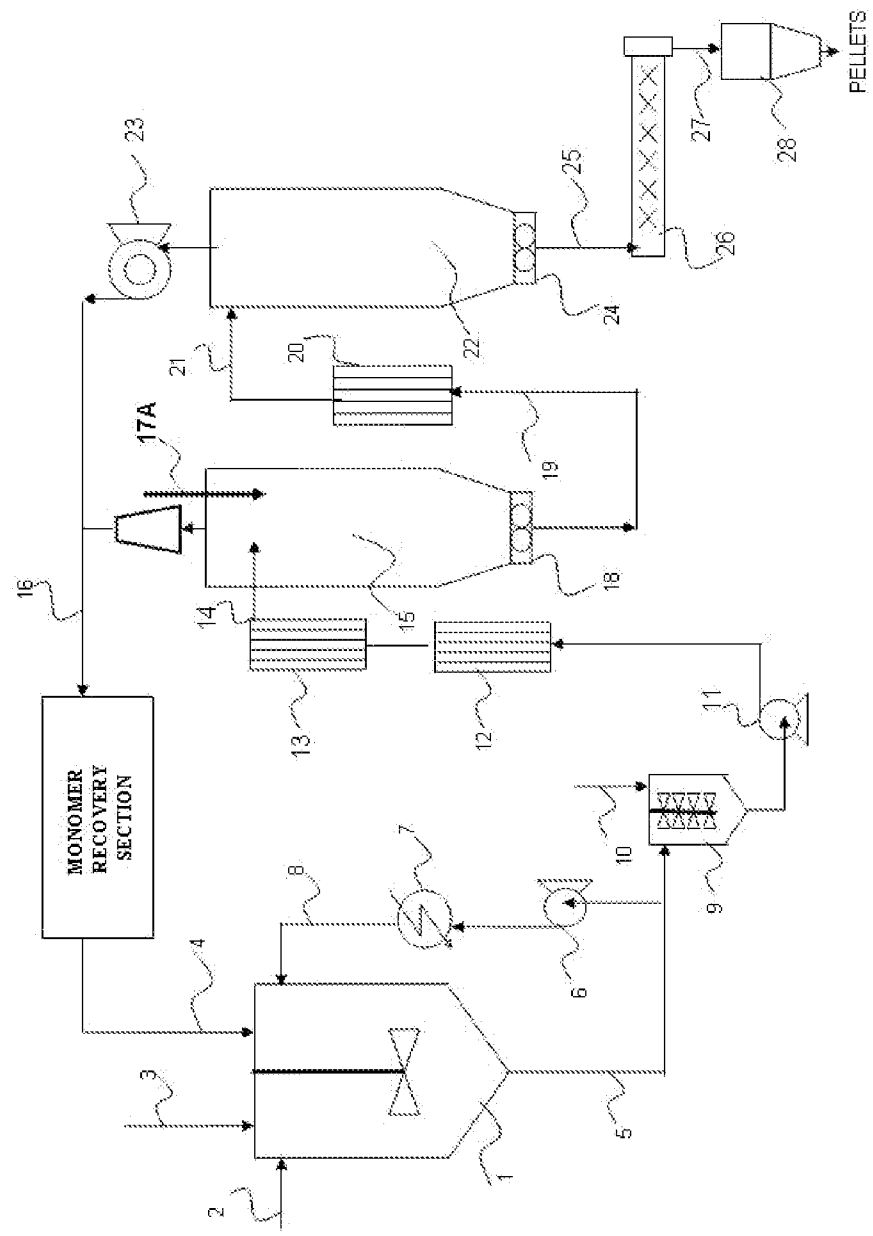


FIG 1

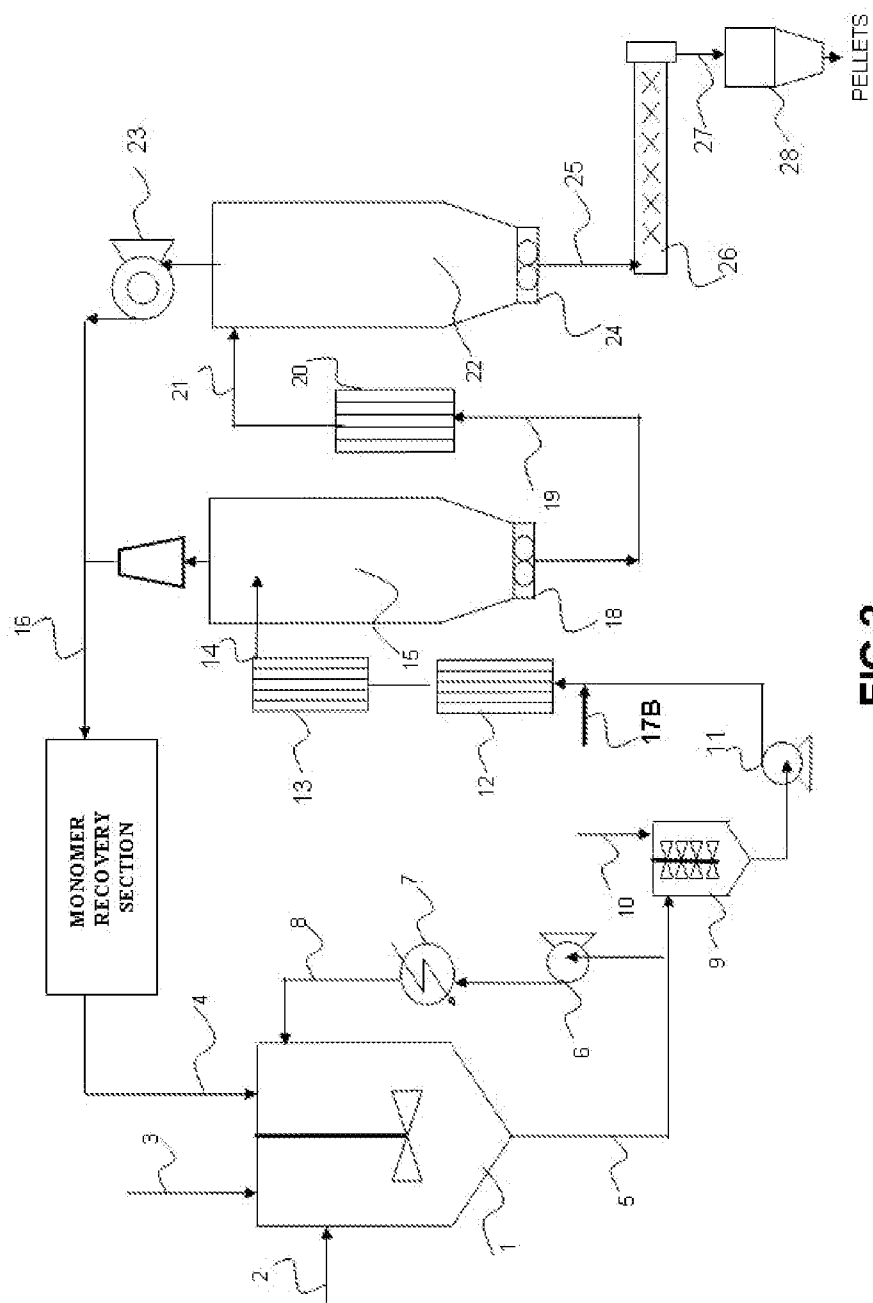


FIG 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/064976

A. CLASSIFICATION OF SUBJECT MATTER INV. C08F6/00 C08F6/02 C08F10/00 C08K5/00 C08K5/13 C08K5/38 C08K5/526 C08F10/04 ADD. C08F2/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08F C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EP0-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/149274 A2 (DOW GLOBAL TECHNOLOGIES INC [US]; VANSPEYBROECK RONY S L [BE]) 27 December 2007 (2007-12-27) page 1, line 5 - line 17 page 2, line 3 - line 10 page 8, line 22 - page 9, line 17 examples; page 11, line 26 - page 12, line 33 ----- -/--	1-6,8-12
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 8 February 2010		Date of mailing of the international search report 12/02/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gold, Josef

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/064976

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 604 958 A2 (UNION CARBIDE CHEM PLASTIC [US]) 6 July 1994 (1994-07-06) page 1, line 1 - line 20 page 1, line 40 - page 2, line 2 page 2, line 54 - line 55 page 4, line 5 - line 24 page 6, lines 16,24,26,35,38 page 6, line 45 - line 47 examples; page 8, line 4 - line 6; claims 1-3	1-6,8-14
X	WO 01/13381 A1 (DOW CHEMICAL CO [US]; BETSO STEPHEN R [DE]; GUEST MARTIN J [US]; REMEN) 22 February 2001 (2001-02-22) page 1, line 26 - line 31 page 17, line 25 page 25, line 16 - line 21 page 26, line 1 - line 19	1-2,4,7, 11-12
X	WO 2006/101926 A2 (DOW GLOBAL TECHNOLOGIES INC [US]; HUGHES MORGAN MARK [US]; CHEUNG YUNW) 28 September 2006 (2006-09-28) paragraph [0151]; example 7a	1,7,9, 11-12
X	US 6 160 060 A (HOLLIDAY ROBERT E [US] ET AL) 12 December 2000 (2000-12-12) column 4, line 41 - line 45; figure 3 column 5, line 47 - line 52 column 7, line 48 - line 63 column 8, line 37 - line 60 examples 1,2	1-6,8-12
X	WO 2007/094866 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; CHANG ANDY C [US]) 23 August 2007 (2007-08-23) page 41, line 9 - line 31	1-6,8-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/064976

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2007149274	A2	27-12-2007	AR 061556 A1	03-09-2008
			AU 2007261565 A1	27-12-2007
			CA 2656927 A1	27-12-2007
			CN 101495520 A	29-07-2009
			EP 2035467 A2	18-03-2009
			JP 2009541529 T	26-11-2009
			KR 20090031574 A	26-03-2009
			US 2009209719 A1	20-08-2009
EP 0604958	A2	06-07-1994	BR 9305240 A	05-07-1994
			CA 2112448 A1	29-06-1994
			CN 1092078 A	14-09-1994
			JP 2694600 B2	24-12-1997
			JP 6234808 A	23-08-1994
			MX 9400147 A1	29-07-1994
			US 5324798 A	28-06-1994
			ZA 9309703 A	29-08-1994
WO 0113381	A1	22-02-2001	AU 6400700 A	13-03-2001
			AU 6526000 A	13-03-2001
			CA 2381499 A1	22-02-2001
			CA 2381760 A1	22-02-2001
			EP 1210716 A1	05-06-2002
			EP 1228515 A1	07-08-2002
			JP 2003507848 T	25-02-2003
			JP 2003507849 T	25-02-2003
			WO 0113380 A1	22-02-2001
			US 6524702 B1	25-02-2003
WO 2006101926	A2	28-09-2006	CA 2601245 A1	28-09-2006
			EP 1861441 A2	05-12-2007
			JP 2008540695 T	20-11-2008
US 6160060	A	12-12-2000	BR 9912715 A	02-05-2001
			CN 1323317 A	21-11-2001
			EP 1144460 A1	17-10-2001
			JP 2003509518 T	11-03-2003
			WO 0008062 A1	17-02-2000
WO 2007094866	A1	23-08-2007	AT 444335 T	15-10-2009
			CN 101370869 A	18-02-2009
			EP 1966302 A1	10-09-2008
			JP 2009521581 T	04-06-2009
			KR 20080090434 A	08-10-2008
			US 2008319130 A1	25-12-2008