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⑫ # EUROPEAN PATENT APPLICATION

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(54) **Deactivation of catalyst in solution process for polymerization of alpha-olefins.**

(57) The present invention relates to a solution polymerization process for the preparation of high molecular weight polymers of α-olefins selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and C_3–C_{12} α-olefins. The process comprises feeding monomer, coordination catalyst and inert hydrocarbon solvent to a reactor, polymerizing the monomer at a temperature in the range of, in particular, 105–320 °C and a pressure of less than 24 MPa and deactivating the catalyst in the solution so obtained by admixing therewith a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent. The hydrocarbon solvent is then separated from the resultant solution and a composition comprising high molecular weight polymer is recovered. Any catalyst residues remain with the polymer. In a preferred embodiment the catalyst contains vanadium. A particular salt is the salt of a C_8 aliphatic acid, especially calcium 2-ethyl hexanoate.

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DEACTIVATION OF CATALYST IN SOLUTION PROCESS FOR POLYMERIZATION OF ALPHA-OLEFINS

The present invention relates to a process for the polymerization of α-olefins and especially to the deactivation of the coordination catalyst used in a solution process for the polymerization of α-olefins. In particular the present invention relates to such deactivation wherein the coordination catalyst contains vanadium.

Polymers of ethylene, for example, homopolymers of ethylene and copolymers of ethylene and higher α-olefins, are used in large volumes for a wide variety of end uses, for example, in the form of film, fibres, moulded or thermoformed articles, pipe, coatings and the like.

Processes for the preparation of homopolymers of ethylene and copolymers of ethylene and higher α-olefins are known. Such processes include processes in which the monomers are polymerized in the presence of a coordination catalyst, for example, a catalyst comprising a compound of a transition metal belonging to Groups IVB-VIB of the Periodic Table and an organometallic compound of a metal belonging to Groups I-IIIA of the Periodic Table.

A particularly preferred process for the polymerization of α-olefins is the high temperature or "solution" polymerization process, an example of which is described in Canadian Patent 660 869 of A.W. Anderson, E.L. Fallwell and J.M. Bruce, which issued 1963 April 9. In a solution process the process parameters are selected in such a way that both the monomer and polymer are soluble in the reaction medium. Under such conditions accurate control over the degree of polymerization, and hence the molecular weight of the polymer obtained, may be achieved, for example, by control of the reaction temperature.

The polymerization reaction in a solution polymerization process is normally terminated by addition of a so-called "deactivator", for example, a fatty acid or an alcohol. The fatty acid is admixed with hydrocarbon solvent, normally the solvent of the polymerization process, and fed into the polymerization mixture, usually shortly after that mixture passes from the reactor. The polymerization mixture that has been treated with deactivator contains catalyst residues which may be removed by contacting the mixture with an adsorbent, for example, alumina. Such a deactivation and catalyst removal process is described in Canadian Patent 732 279 of B.B. Baker, K.M. Brauner and A.N. Oemler, which issued 1966 April 12.

A method for the deactivation of a coordination catalyst in a high pressure solvent-free process for the polymerization of α-olefins is disclosed in U.S. 4 105 609 of J-P. Machon, B. Levresse and P. Gloriod, issued 1978 August 8. The method involves injecting into the polymerization reaction mixture an alkali or alkaline earth metal salt of a carboxylic acid e.g. sodium stearate, calcium stearate or sodium benzoate.

It has now been found that the catalyst in a solution polymerization process may be deactivated by contacting the polymerization mixture with a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in the hydrocarbon solvent used in the polymerization process.

Accordingly the present invention provides a solution polymerization process for the preparation of high molecular weight polymers of α-olefins selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and $C_3 - C_{12}$ α-olefins, said process comprising feeding monomer selected from the group consisting of ethylene and mixtures of ethylene and at least one C_3-C_{12} α-olefin, a coordination catalyst and inert hydrocarbon solvent to a reactor, polymerizing said monomer under solution polymerization conditions at a temperature of up to 320°C and a pressure of less than 25 MPa, deactivating the catalyst in the solution so obtained by admixing therewith a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent, separating the hydrocarbon solvent and other volatile matter from the resultant solution and recovering a composition comprising said high molecular weight polymer.

In a preferred embodiment of the process of the present invention the carboxylic acid is a C_8 carboxylic acid.

In another embodiment the alkaline earth metal is calcium.

In a further embodiment the coordination catalyst contains vanadium.

The present invention is directed to a solution polymerization process for the preparation of high molecular weight polymers of α-olefins. In particular the polymers of α-olefins are homopolymers of ethylene and copolymers of ethylene and higher α-olefins, especially such higher α-olefins having 3 to 12 carbon atoms i.e. $C_3 - C_{12}$ α-olefins, including bicyclic α-olefins, examples of which are 1-butene, 1-hexene,1-octene and bicyclo-(2,2,1)-2-heptene. In addition cyclic endomethylenic dienes and other non-conjugated dienes may be fed to the process with the ethylene or mixtures of ethylene and C_3- C_{12} α-olefin, as is described in Canadian Patent 980 498 of C. T. Elston, which issued 1975 December 23.

In the solution polymerization process of the present invention α-olefin monomer, a coordination catalyst and inert hydrocarbon solvent are fed to a reactor. Coordination catalysts for solution polymerization processes are known, for example those described in the aforementioned Canadian Patent 660 869 and in Canadian patent application No. 301 862 of A.N. Mollison and V.G. Zboril, filed 1978 April 25. The α-olefin monomer may be solely ethylene or a mixture of ethylene and one or more of the higher α-olefins.

Solution polymerization processes may be operated at temperatures of up to 320°C, in particular in the range of 105-320°C and especially in the range 105-310°C. The pressures used in the process of the present invention are those known for solution polymerization processes viz less than 25 MPa and especially in the range of about 4-25 MPa. The pressure and temperature are controlled so that both the unreacted monomers and the polymer formed remain in solution.

The hydrocarbon solvent used in the polymerization process is a hydrocarbon solvent that is inert with respect to the coordination catalyst. Such solvents are known and include hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha. The solvent used in the polymerization process is preferably also used in the preparation of the coordination catalyst. The hydrocarbon solvent is the major component of the polymerization mixture fed to the reactor, usually comprising at least 80% of the reaction mixture. In the process the α-olefin is dissolved in the solvent.

The mixture that exits from the polymerization reactor comprises polymer, unreacted monomer, coordination catalyst some of which remains in an active state, and hydrocarbon solvent. A deactivator is added to the mixture to terminate the polymerization process. In the process of the present invention the deactivator is a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent. In particular the hydrocarbon solvent used for the deactivator is the same as the solvent used in the polymerization process. If a different solvent is used, it must be compatible with the solvent used in the polymerization process, not cause precipitation of any component of the polymerization mixture and not cause adverse effects on the solvent recovery system associated with the polymerization process.

The salt of the deactivator solution must be dissolved in the solvent in order to obtain intimate contact between the deactivator and any remaining active catalyst and to obtain uniform dispersion of the deactivator and catalyst residues i.e. the form of the catalyst after deactivation, throughout the polymer, thereby facilitating the production of polymer of uniform properties.

In the salt of the deactivator solution, the metal is an alkaline earth metal or zinc, especially magnesium or calcium. The remainder of the salt is derived from an aliphatic carboxylic acid, especially such an acid having 6 to 20 carbon atoms. In a preferred embodiment the acid has 8 to 12 carbon atoms. The acid is preferably a branched chain aliphatic acid although straight chain aliphatic acids and cycloaliphatic acids may be used. Moreover the acids may be saturated or unsaturated acids. However the acid must be such that the salt thereof that is used in the process of the present invention is soluble in the hydrocarbon solvent used therein. In preferred embodiments the salt is calcium 2-ethyl hexanoate, calcium naphthenate, calcium tallate or the like.

In the process of the present invention the deactivated polymerization mixture is fed to a separator, which may be a multistage separator, to separate unreacted monomer, hydrocarbon solvent and any other volatile matter from the polymer. In contrast to the usual practice in a solution process, no steps are taken to remove catalyst residues and/or deactivator from the polymer using adsorbents or other techniques. In the present invention the deactivator remains with the polymer. After separation from solvent and unreacted monomer, the polymer may be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives may be added to the polymer, especially immediately prior to the formation of the pellets or other comminuted shapes.

The polymer obtained according to the process of the present invention may be used in a wide variety of end-uses, as is known for homopolymers of ethylene and copolymers of ethylene and higher α-olefins.

The use of the deactivation process of the present invention may result in a reduction in corrosion of those parts of the apparatus of the process that are located down-stream from the introduction of deactivator. The use of the deactivation process of the present invention may also result in the production of polymer of improved colour, especially when the coordination catalyst used in the process contains vanadium.

The present invention is illustrated by the following examples.

Example I

A polymerization catalyst was prepared by in-line mixing a solution containing 0.36 mmol/l of titanium tetra-chloride and 1.44 mmol/l of vanadium oxytrichloride in cyclohexane with a 3.6 mmol/l solution of isoprenyl aluminum in cyclohexane. The catalyst was fed to a continuous 70 ml stirred polymerization reactor. A solution containing about 3% ethylene in cyclohexane was also fed to the reactor. The ethylene was polymerized in the reactor which was operated under solution polymerization conditions. The ratio of aluminum to the sum of titanium and vanadium, on an atomic basis, in the catalyst was adjusted so as to achieve the optimum conversion of ethylene to polymer; that ratio was in the range 1.4 - 2.0. The reactor was operated at a temperature of 200°C, a pressure of 7.5 MPa, a space velocity of 0.36 min^{-1}, a conversion of ethylene to polymer of greater than 80%, a combined concentration of titanium and vanadium, atomic basis, of 0.3 - 0.4 mmol/l and a concentration of aluminum, atomic basis, of 0.5 - 0.8 mmole/l.

A deactivator was continuously added to the reaction mixture shortly after it passed from the reactor. The pressure of the deactivated reaction mixture was then reduced to 110 kPa by means of a needle valve made of stainless steel. The polymer slurry thus obtained was cooled to ambient temperature and subjected to a Waring* blender for about 30 seconds. The polymer, including deactivator, was separated from the solvent by filtration, dried at room temperature in the dark and pressed at about 190°C into plaques measuring about 2 mm in thickness.

The colour of the plaques was rated visually on a scale of 0-5, the former representing colourless. The hue of the colour was also noted.

The results obtained for three different deactivators were as follows:

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* denotes trade mark

Run No.	Deactivator		Polymer Colour	
	Type	Amount*	Rating	Hue
1	Acetylacetone in 2-butanol	55/50 000	5	green
2	Capric acid in 2-butanol	55/50 000	4	brown, aging to green
3	Calcium 2-ethyl hexanoate	38	2	beige

*g of deactivator per g of combined amount of titanium and vanadium (as metals).

Example II

A number of polymers were prepared using the procedure of Run 1 of Example I. After about 150 hours of operation of the continuous reactor, the pressure-reducing needle valve was corroded to such an extent that the valve malfunctioned. When examined under a microscope extensive corrosion was noted, especially on the seat of the valve.

Example III

A number of polymers were prepared using the procedure of Run 3 of Example I. After operating the polymerization unit for about 2000 hours, an inspection showed no significant corrosion of the pressure-reducing needle valve.

Example IV

A thick-walled glass tube measuring approximately 14 cm in length and 2.5 cm in diameter was charged, under an atmosphere of nitrogen, with separate solutions of titanium tetrachloride, vanadium oxytrichloride and isoprenyl aluminum, each in decalin solvent, so that the tube contained 0.006 mmol of titanium tetrachloride, 0.024 mmol of vanadium oxytrichloride and 0.053 mmol of isoprenyl aluminum. In addition 0.026 mmoles of each of acetylacetone and of pelargonic acid, in decalin solvent, were charged to the tube. Additional decalin was added to bring the total volume in the tube to 10 ml. The tube was then sealed under vacuum. The sealed tube was immersed in a silicone oil bath at 300°C for 15 minutes, briefly inspected visually, and heated at 300°C for a further 15 minutes. The contents of the tube, on cooling, were bright yellow in colour; a small amount of a light coloured precipitate was also present. After exposure to air for several days the contents of the tube had turned a green colour and a precipitate of green solids had formed.

Example V

The procedure of Example IV was repeated except that the acetylacetone and pelargonic acid were replaced with 0.415 mmoles of pelargonic acid.

After heating at 300°C for 30 minutes, the contents of the tube were, on cooling, faintly straw yellow in colour. After exposure to air for about one week, a heavy bright green precipitate had formed.

Example VI

The procedure of Example IV was repeated except that the acetylacetone and pelargonic acid were replaced with 0.418 mmoles of calcium 2-ethyl hexanoate.

After heating at 300°C for 30 minutes, the contents of the tube were, on cooling, faintly straw yellow in colour with a darker "gummy" residue at the base of the tube. After exposure to air for several weeks no colour change was apparent.

Examples IV-VI indicate that the use of a catalyst deactivator of the present invention viz. calcium 2-ethyl hexanoate, is less susceptible to colour formation with the catalyst system used than the use of acetylacetone and/or pelargonic acid deactivators.

CLAIMS :

1. A solution polymerization process for the preparation of high molecular weight polymers of α-olefins selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and C_3 - C_{12} α-olefins, said process comprising feeding monomer selected from the group consisting of ethylene and mixtures of ethylene and at least one C_3 - C_{12} α-olefin, a coordination catalyst and inert hydrocarbon solvent to a reactor, polymerizing said monomer under solution polymerization conditions at a temperature of up to 320°C and a pressure of less than 25 MPa, deactivating the catalyst in the solution so obtained by admixing therewith a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent, separating the hydrocarbon solvent and other volatile matter from the resultant solution and recovering a composition comprising said high molecular weight polymer.

2. A solution polymerization process for the preparation of high molecular weight polymers of α-olefins selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and C_3 - C_{12} α-olefins, said process comprising feeding monomer selected from the group consisting of ethylene and mixtures of ethylene and at least one C_3 - C_{12} α-olefin, a coordination catalyst and inert hydrocarbon solvent to a reactor, said catalyst containing vanadium, polymerizing said monomer under solution polymerizing conditions at a temperature of up to 320°C and a pressure of

less than 25 MPa, deactivating the catalyst in the solution so obtained by admixing therewith a solution of a salt of an alkaline earth metal or zinc and an aliphatic monocarboxylic acid dissolved in hydrocarbon solvent, separating the hydrocarbon solvent and other volatile matter from the resultant solution and recovering a composition comprising said high molecular weight polymer.

3. The process of Claim 1 or Claim 2 in which the aliphatic monocarboxylic acid has 6 to 20 carbon atoms.

4. The process of Claim 1 or Claim 2, in which the aliphatic monocarboxylic acid has 8 to 12 carbon atoms.

5. The process of any one of Claims 1 to 4, in which the salt is a calcium salt.

6. The process of any one of Claims 1 to 5 in which the aliphatic monocarboxylic acid is a C_8 aliphatic acid.

7. The process of Claim 5 in which the salt is calcium 2-ethyl hexanoate.

8. The process of any one of Claims 1 to 7 in which the hydrocarbon solvent of the salt solution is the same as that fed to the reactor.

9. The process of any one of Claims 1 to 8 in which the temperature is in the range of 105 - 320°C.

European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 81 30 4965

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	US-A-4 105 609 (J.P.MACHON) *Claims 1,5,9* -----	1-9	G 08 F 10/00 C 08 F 6/02
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 08 F 6/02 C 08 F 6/06 C 08 F 6/08 C 08 F 6/10 C 08 F 6/12

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-05-1982	PERMENTIER W.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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