

PATENT SPECIFICATION

(11)

1 535 568

- (21) Application No. 7682/76 (22) Filed 26 Feb. 1976 (19)
(31) Convention Application No. 7506436 (32) Filed 28 Feb. 1975 in
(33) France (FR)
(44) Complete Specification Published 13 Dec. 1978
(51) INT. CL.² C08F 10/02 6/02
(52) Index at Acceptance
C3P HX



(54) PROCESS FOR THE PREPARATION OF AN ETHYLENE POLYMER

(71) We, SOCIETE CHIMIQUE DES CHARBONNAGES, A French Body Corporate of Tour Aurore-Cedex 5-, 92080 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 The present invention relates to the preparation of polyethylene by the high pressure, high temperature process using a catalyst of the ZIEGLER type. 5

10 The conventional processes for the polymerisation and copolymerisation of ethylene under high pressures and at high temperatures are carried out at pressures above 500 bars and at temperatures above about 160°C, using known catalysts. On leaving the high pressure reactor (in which the polymerisation has been carried out) the pressure of the reaction mixture is let down in at least one separator in which the working conditions are chosen so as to separate the ethylene (and, where relevant, the other monomers) in one or more stages from the polymer which has formed in the reactor. In particular, the pressure in this first separator is below 500 bars. 10

15 If catalysts of the ZIEGLER type, which are active over a wide range of temperatures and pressures, are used in the polymerisation reactor, the working conditions (temperature, pressure and residence time) in the said separator(s) may be such that the polymerisation (or copolymerisation) of the monomer (or monomers) can continue and give rise to undesirable products (for example low molecular weight products, waxes and the like), the formation of which it is desirable to avoid. The present invention provides a process for avoiding such disadvantages. 15

20 It has already been disclosed, in connection with the use of catalysts of the ZIEGLER type for the low pressure and low temperature polymerisation of alpha-olefins, to add various reactants (alcohols, epoxides, alkali metal hydroxides and the like), to the reaction mixture in order to eliminate the organo-aluminium compound of the polymer by causing it to react with the additive to produce a reaction product soluble in a solvent (alcohol, water and the like). In the present invention on the other hand, the reactant, which is of a different chemical nature from the additives cited above, deactivates the two constituents of the catalyst so that its reaction products with them remain in the polymer. 20

30 Accordingly, the present invention provides an improved process for the continuous polymerisation and copolymerisation of ethylene, which process comprises polymerising or copolymerising ethylene under a pressure above 500 bars and at temperatures above 160°C in the presence of a catalyst comprising a transition metal compound (as hereinafter defined) and an organo-metallic compound of aluminium, e.g. an aluminium alkyl said polymerisation or copolymerisation being stopped by injecting into the reaction mixture at least one zinc, alkali metal or alkaline earth metal (as hereinafter defined) salt of a carboxylic acid which is either in the pure molten state or in suspension or in solution in a hydrocarbon in an amount sufficient to bring about the deactivation of the catalyst, the said salt being so chosen that its reaction products with the constituents of the catalyst remain in the recovered polymer. This process aims to avoid the secondary reactions which might develop in the separator(s) and the products obtained as a result of the reaction between the metal salt and the constituents of the catalyst remain in the finished polymer (i.e. the polymer recovered from the reaction system after monomer separation). 30

40 A "transition metal compound" is defined herein as a compound of an element occurring in any of Groups IIIa to VIII of the Periodic Table shown in Cotton and Wilkinson's 45

"Advanced Inorganic Chemistry", 3rd edition, excluding elements occurring in the Lanthanide and Actinide series. Alkaline earth metals in the context of this Specification are beryllium, magnesium, calcium, strontium and barium.

The transition metal compound which can be used as a constituent of the polymerisation catalyst is generally a titanium derivative and more particularly titanium trichloride which can optionally contain co-crystallised aluminium chloride. The alkyl aluminium which can be used as the other constituent of the catalyst is preferably a trialkyl-aluminium, a dialkyl-aluminium monohalide, or a pentalkylsiloxalane. Furthermore, the catalysts of the type described in French Patent No. 2,027,788, and consisting of an activated solid obtained by reacting a halogen derivative of a transition metal (for example $TiCl_4$) with a compound of the formula $X_{m-n}M(OR)_n$ in which X represents a monovalent inorganic radical, M represents a metal occurring in any of Groups Ia, IIa, IIb, IIIb, and VIIa of the Periodic Table, R is a monovalent organic radical, m denotes the valency of M and n is an integer such that $1 \leq n \leq m$, and an organo-metallic compound of the aluminium-alkyl type are catalysts of the Ziegler type which can be used in the invention. As usual in this art, the proportions of the catalyst constituents are preferably such that the atomic ratio $\frac{M}{Al}$ is between 1 and 10.

The process of the invention is applicable to the polymerisation of ethylene and to the copolymerisation of ethylene with other monomers which are copolymerisable with ethylene in the presence of catalysts of this type; these comonomers include, for example, alpha-olefins such as propylene and 1-butene.

The ethylene polymerisation or copolymerisation reaction can be carried out in a stirred autoclave reactor or in a tubular reactor or in a series of reactors of either the autoclave type or the tubular type. Preferably in all cases, the working conditions are such that the reaction medium is homogeneous, i.e. the polymer is soluble in the reaction mixture. In this polymerisation reaction it is of course possible to use known processes for regulating the molecular weight of the polymers (e.g. injection of suitable transfer agents) or for improving the properties of the resulting products (e.g. injection of antioxidants or similar additives into the polymerisation reactor or at the outlet from the latter).

The polymerisation or copolymerisation reaction of the invention is carried out continuously. Therefore the metal salt(s) must be injected into the reaction mixture at the point in the installation where it is considered that the polymerisation or copolymerisation reaction must be stopped. This point in the installation may be located at or near to the outlet from the reactor or at or near the inlet of one of the monomer/polymer separators in which the reaction mixture leaving the reactor is collected. In general, it is preferred that the material should be injected as close as possible to the point where the polymer leaves the polymerisation reactor, e.g. the reactor outlet valve.

The amount of metal salt injected must be sufficient to ensure deactivation of the catalyst. This deactivation is effected by destruction of at least one of the constituents of the catalyst, namely the transition metal derivative and the alkyl-aluminium. However, it is preferable to use sufficient metal salt for both of the constituents of the catalyst to react with the said salt. According to the invention, the amount of salt used is preferably such that the atomic ratio of the metal in the said salt to the aluminium and titanium or other transition metal in the catalyst is between 0.4 and 8.

Among the alkali and alkaline earth metal salts of the carboxylic acids which can be used in the invention, the alkali and alkaline earth metal salts of saturated fatty acids and of aromatic acids are preferred, for example, sodium stearate, potassium stearate, calcium stearate, magnesium stearate, sodium benzoate and potassium benzoate. Sodium naphthenate and potassium naphthenate may also be employed. All these salts can be injected either in the pure (molten) state or in suspension or in solution in a hydrocarbon.

The main industrial advantages of the process of the invention are the following:

Secondary reactions which might develop in the separator(s) and lead to the formation of undesirable polymeric products (for example greases or waxes) are avoided. The formation of 1-butene by dimerisation of ethylene is also avoided.

Easier control of the composition of the gases, and consequently of the polymerisation reaction itself, is possible when the gases are recycled.

The chlorine which may be present in the catalyst and which is liberated in uncontrolled destruction of the catalyst, is neutralised.

Examples 2 to 8, 12 to 16, 18 and 20 which follow illustrate the invention. Examples 1, 9 to 11, 17 and 19 are comparative. The deactivator is added in the form of a hydrocarbon emulsion.

EXAMPLES 1 to 8

These Examples are carried out on a high pressure (1,500 bars) ethylene polymerisation line comprising a reactor of the stirred autoclave type, the volume of which is 5 litres, and two separators in series, the first of which operates at a pressure of 250 bars and the second at a pressure of 15 bars; the reaction temperature is of the order of 260°C, and the mean

temperature in the separators is 260 to 270°C; the average residence time of the ethylene in the reactor is 50 seconds; the catalyst used consists of violet titanium trichloride (in the form of a co-crystallised product of the formula $TiCl_3 \cdot \frac{1}{3} AlCl_3$) and of tributyl-aluminium, the atomic ratio Al/Ti being between 1 and 5; about 1% of hydrogen, acting as a transfer agent, was injected into the reactor.

The unreacted ethylene which is separated from the polymer in any of the separators is recycled into the installation.

Except in Comparative Example 1, the metal salt (i.e. the agent for destroying the catalyst) is injected into the reactor just before the extrusion valve. The results obtained are shown in Table I below. In this Table, the following items have been shown in the various columns:

The number of the experiment;
the name of the salt injected;
the hourly feed rate (in g/hour) of the salt (destroying agent);
the hourly production (in kg/hour) of polymer;
the density of the polyethylene expressed in g/cm³, this being measured at 20°C, on products which have been reheated for 1 hour at 150°C, and been cooled at a speed of 50°C/hour;
the melt index (M.I.) measured in accordance with standard specification ASTM 1238-62 at a temperature of 190°C, and with a load of 2.16 kg;
the polydispersity index which is the ratio $\frac{M_w}{M_n}$ of the weight average molecular weight to the number average molecular weight as defined in "Polythene", Renfrew & Morgan (1957), p. 90;
the content of catalyst residues, namely Al, Ti and alkali metal or alkaline earth metal (M) expressed in ppm;
the percentage of l-butene recycled;
the percentage of ethyl branches; this percentage expressed in moles and determined by infra-red spectroscopy - constituting an approximate measure of the degree of copolymerisation of the l-butene.

Each experiment is characterised by a sample taken after two hours' running (A) and after four hours' running (B); this procedure makes it possible to check that none of the destroying agent or of the products produced in the reaction between the destroying agent and the ZIEGLER initiator has been recycled (and that there are no major variations in the content of catalyst residues).

For each of experiments 1 to 8, a particular feed rate of the titanium constituent of the catalyst, and two ratios Al/Ti of the constituents of the said catalyst, one of these ratios being 1 and the other being 5, were used; Table I bis below shows the amounts of salts used in each experiment, these amounts being expressed as the ratio of the number of atoms of the metal of the said salt to the number of atoms of aluminium and titanium in the catalyst.

TABLE I

Injection of the destroying agent under high pressure, with use of medium pressure and low pressure separator

Example	Destroying agent	Hourly feed rate of the destroying agent (g/hour)	Hourly production of polymer (kg/hour)	Density	M.I.	Mw/Mn	Catalyst residues			% of 1-butene recycled	% of C ₂ H ₅ groups (mol)
							Ti	Al	M		
1	—	—	28.4	0.960	4.3	8.5	14	25	—	2.5	0.5
				0.959	5.2	9.0	13	24	—	3.0	0.6
2	Calcium stearate	15	28.0	0.965	3.8	4.1	12	22	30	1.5	0.3
				0.965	3.5	4.1	13	22	29	1.6	0.3
3	Calcium stearate	10	28.4	0.964	3.8	4.3	13	24	22	1.7	0.3
				0.963	4.0	4.2	12	23	20	1.8	0.4
4	Magnesium stearate	15	28.0	0.963	4.0	6.5	14	27	28	2.0	0.35
				0.963	4.1	6.5	14	26	27	2.0	0.4

19

TABLE I (Continued)

5	A	Zinc stearate	15	27.3	0.962	5.1	7.3	13	25	—	2.1	0.45
	B				0.961	4.9	7.2	14	26	—	2.0	0.5
6	A	Sodium stearate	15	27.6	0.965	4.2	4.5	12	24	30	1.4	0.3
	B				0.966	4.0	4.6	12	25	28	1.5	0.25
7	A	Sodium naphthoate	5	28.1	0.963	4.5	4.0	14	24	26	1.7	0.35
	B				0.962	4.5	4.2	13	23	28	1.9	0.40
8	A	Sodium benzoate	5	28.0	0.962	5.0	4.0	15	28	23	1.8	0.4
	B				0.962	4.8	3.9	15	27	25	1.8	0.4

TABLE I (bis)

Experiment	Feed rate of the catalyst (milliatoms of Ti/hour)	Amount of destroying agent used	
		Al/Ti = 1	Al/Ti = 5
1	8.6	0	0
2	7.6	3.3	1.1
3	7.7	2.13	0.71
4	8.2	3.1	1.03
5	8	3	1
6	6.9	3.54	1.18
7	8.2	1.56	0.52
8	8.8	2	0.67

EXAMPLES 9 to 16

In these Examples, which were carried out in an apparatus similar to that described in the Examples above, the circuits for recycling the ethylene coming from the medium pressure (250 bars) separator are not used, and are shut off. Accordingly, only the circuits for recycling the ethylene from the low pressure separator (at 8 bars) are used.

The working conditions are as follows:

Reactor pressure: 1,500 bars.

Stirred autoclave reactor, 1 zone : volume 1.4 l.

Average residence time : 35 seconds.

Average molar percentage of hydrogen : 1 to 2%.

Catalyst system : $\text{TiCl}_3 \cdot 3 \text{AlCl}_3 - \text{AlBu}_3$.

The temperature of the separator was different in each experiment.

Except in Comparative Examples 9 to 11, the metal salt (destroying agent) is injected into the reactor just before the extrusion valve.

The results obtained are shown in Table II below. In this Table, the various columns give the following items:

Number of the experiment;

name of the injected salt (destroying agent);

hourly feed rate (g/hour) of the injected salt;

hourly production (in kg/hour) of polymer;

temperature of the reactor ($^{\circ}\text{C}.$);

temperature of the separator ($^{\circ}\text{C}.$);

density of the polyethylene (in g/cm^3) measured as above;

melt index (M.I.) of the polyethylene, measured as above;

percentage of 1-butene recycled;

content of catalyst residues in the polyethylene: Al, Ti and M (alkali metal or alkaline earth metal) expressed in ppm.

For experiments 12 to 16 Table II bis gives the feed rate of the titanium constituent of the catalyst (in milliatoms of titanium per hour) and the amounts of destroying agent used for two ratios Al/Ti, one of these ratios being 1 and the other being 5.

TABLE II

Injection of the destroying agent under high pressure without use of the medium pressure separator

Example	Destroying agent	Hourly feed rate of the destroying agent (g/hour)	Hourly production of polymer (kg/hour)	Reactor temperature (°C)	Separator temperature (°C)	Density	M.I.	% of butene butene recycled	Content of residues Ri Al M
9	—	—	10.3	240	220	0.967	1.5	1.5	11 20 —
					270	0.966	2.0	1.7	11 18 —
10	—	—	11.0	260	220	0.963	3.1	2.0	13 26 —
					270	0.963	3.0	2.2	12 25 —
11	—	—	11.8	280	220	0.959	6.3	3.5	17 31 —
					270	0.958	6	4.0	18 30 —
12	Calcium stearate	5	10.5	240	220	0.966	2	1.3	10 20 32
					270	0.966	2.3	1.3	11 19 34

21

22

TABLE II (Continued)

13	Calcium stearate	10	11.7	280	220	0.960	5.5	3.0	18	30	55
					270	0.960	5.5	3.1	18	28	56
14	Sodium	5	11.0	260	220	0.964	4.1	1.5	12	26	33
					270	0.963	4	1.7	12	24	31
15	Sodium benzoate	5	11.0	260	220	0.963	3	1.8	13	22	65
					270	0.963	3	1.9	12	24	67
16	Sodium benzoate	5	11.8	280	220	0.960	7	3.0	18	29	65
					270	0.959	7.5	3.3	16	27	63

(23)

TABLE II (bis)

Experiment	Feed rate of the catalyst (milliatoms of Ti/hour)	Amount of destroying agent used	
		Al/Ti = 1	Al/Ti = 5
12	2.4	3.42	1.14
13	4.4	3.75	1.25
14	2.75	3	1
15	3	5.85	1.95
16	4	3.96	1.32

EXAMPLES 17 to 20

Experiments were carried out as in Examples 9 to 16 while modifying the catalyst used. In experiments 17 and 18, a catalyst system composed of TiCl_3 (in the form of $\text{TiCl}_3 \cdot \text{AlCl}_3$) and of pentalkylsiloxalane ($\text{Me}_2\text{EtSiOAlEt}_2$) was used, with a catalyst feed rate corresponding to 2.7 milliatoms of titanium per hour and a ratio Ti/Al of 1 or 5. In experiments 19 to 20, a catalyst system composed of TiCl_4 supported on $\text{Mg}(\text{OEt})_2$ and activated with tributyl aluminium was used. Before activation the solid catalyst had the following weight composition: Ti = 8.2%, Mg : 28.4%, Cl : 62.3%. The catalyst feed rate is 2.2 milliatoms of titanium per hour and the ratio Al/Ti is 1 or 5. The results obtained are reported in Table III which has the same columns as those given in Table II.

TABLE III

Example	Destroying agent	Hourly feed rate of the destroying agent (g/hour)	Production polymer, (kg/hour)	Temperature (°C)	Screen temperature (°C)	Density	M.I.	% of butene butene recycled	Content of residues		
									Ri	Al	M
17	—	—	10.5	260	220	0.964	3	1.5	12	20	—
18	Calcium stearate	5	10.7	260	220	0.964	3.5	1.3	12	22	34
19	—	—	10.5	260	220	0.960	1	3.0	11	20	—
20	Calcium stearate	5	10.5	260	220	0.961	1	2.4	10	20	30

WHAT WE CLAIM IS:-

1. Continuous process for the polymerisation and copolymerisation of ethylene which process comprises polymerising or copolymerising under a pressure above 500 bars and at temperatures above 160°C in the presence of a catalyst comprising a transition metal compound (as hereinbefore defined) and an organometallic compound of aluminium, said polymerisation or copolymerisation being stopped by injecting into the reaction mixture at least one zinc, alkali metal or alkaline earth metal (as hereinbefore defined) salt of a carboxylic acid which is either in the pure molten state or in suspension or in solution in a hydrocarbon in an amount sufficient to bring about the deactivation of the catalyst the said salt being so chosen that its reaction products with the constituents of the catalyst remain in the recovered polymer.
 2. Process according to claim 1, in which the said alkali or alkaline earth metal salt is a salt of a saturated fatty acid or a salt of an aromatic acid.
 3. Process according to claim 1 or 2, in which the said salt is injected into the reactor at or near the point where the polymer leaves the polymerisation reactor.
 4. Process according to claim 1 or 2, in which the said salt is injected at or near the inlet of one of the monomer/polymer separators in which the reaction mixture is collected after leaving the reactor.
 5. Process according to any one of the proceeding claims in which the transition metal compound of the catalyst is a titanium derivative.
 6. Process according to claim 5, in which the said salt is used in an amount such that the atomic ratio of the metal in the said salt to the aluminium and titanium in the catalyst is between 0.4 and 8.
 7. Process according to any of claims 1 to 4, in which the transition metal in the catalyst is other than titanium, and the said salt is used in an amount such that the atomic ratio of the metal in said salt to the aluminium and transition metal in the catalyst is between 0.4 and 8.
 8. Process according to claim 1, substantially as hereinbefore described in any one of Examples 2 to 8, 12 to 16, 18 or 20.
 9. An ethylene polymer or copolymer whenever obtained by the process of any one of claims 1 to 6 or 8.
 10. An ethylene polymer or copolymer whenever obtained by the process of claim 7.
- J. A. KEMP & CO.
Chartered Patent Agents
14 South Square
Gray's Inn London WC1R 5EU.



ERRATA

SPECIFICATION NO 1535568

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are Pierre Gloriod, Bernard Levresse and Jean-Pierre Machon all citizens of France of rue Sagnol — 62 Bully-les Mines Pavillon Le Toupin no. 5 76170 Lillebonne and 366 rue Benoitte Vincent 62 — Bethune, France.

Bas 53556/1

*

14