

PATENT SPECIFICATION

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(54) PROCESS FOR THE HIGH PRESSURE PRODUCTION OF POLYETHYLENE

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, a corporation organized under the laws of Japan, 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:—

The present invention relates to a process for polymerizing monomer comprising ethylene in first and second autoclave reaction zones arranged in series.

The process provided by the invention can be used for polymerizing ethylene by the high pressure process to give ethylene homopolymers, and also for polymerizing ethylene with other comonomers to give ethylene copolymers.

Polyethylene is produced industrially by various processes, and polyethylenes having different properties are available commercially. These distinct types of polyethylene are usually classified by the density of the polymer into so-called low, medium, and high-density polyethylene. Of these, low-density polyethylene has a density within the range of 0.900 to 0.935 g/cm³ and is widely used as a film and in packaging. For these purposes it is necessary that the low-density polyethylene has excellent optical properties, the appropriate stiffness and good processability.

In Patent Specification No. 1,208,120 there is disclosed a process for producing low-density polyethylene by polymerizing ethylene at high pressure in first and second reaction zones at different temperatures, using a two-zone autoclave reactor. In this process ethylene is polymerized in the first reaction zone at a lower reaction temperature than that in the second reaction zone in order to produce low-density polyethylene having the desirable properties mentioned above. In performing this process, it is usual to keep the reaction temperature in the first reaction zone at a temperature as low as 130°C to 200°C.

The initiators used in the known two

reaction zone process thus have to be those which are active (i.e. have a high decomposition rate) at the low temperatures employed in the first reaction zone.

In any high pressure polymerization of ethylene using an autoclave reactor, the initiator used will have its own optimum temperature at which it will exhibit maximum efficiency as an initiator (as measured by the number of moles of ethylene polymerized by 1 mole of initiator).

Now, we have found that, when the polymerization temperature is less than the optimum one, and irrespective of the type of initiator, initiator efficiency μ is approximately represented by the following equation:

$$\mu \exp \theta = \frac{1}{RT} (2E_p - E_t)$$

wherein R is the gas constant (1.987 cal/mole.K), T is the reaction temperature (°K), E_p is the activation energy of the polymerization reaction (cal/mole), E_t is the activation energy of the termination reaction (cal/mole) and θ is the mean residence time of ethylene in the reactor (sec).

When the polymerization temperature is less than the optimum one for the initiator, the initiator efficiency therefore increases with increase in polymerization temperature in accordance with the theoretical curve derived from this equation. When the reaction temperature exceeds the optimum one, it has been found that the efficiency then decreases again.

With the known two reaction zone process the efficiency μ will necessarily be low because of the relatively low reaction temperature employed in the first reaction zone. This result obtains even if an initiator is used whose activity reaches a maximum at the temperatures employed. That this might be so can be seen from the above equation, wherein μ is proportional to the exponential of T^{-1} .

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Since the initiator efficiency is low, the relative amount of initiator required is large. As a consequence the conventional two-reaction zone process for producing polyethylene has the drawback that uneconomical amounts of initiator are necessary.

According to the present invention there is provided a process for polymerizing monomer comprising ethylene in first and second autoclave reaction zones arranged in series, which process comprises feeding 75% or more of the monomer to the first zone through two or more feed inlets, feeding the rest of the monomer, if any, to the second zone, polymerizing monomer in the first zone in the presence of an initiator fed in through two or more feed inlets, transferring the resulting reaction mixture from the first to the second zone, and promoting further polymerization in the second zone in the presence of an initiator at a temperature higher than that in the first zone, the volume ratio of the first: second zones being 1.5:1 to 6:1 and the arrangement of the feed inlets being such as to give a substantially uniform reaction temperature in the first reaction zone.

When this process is used for producing low-density polyethylene, an increase in initiator efficiency is possible. While not wishing to be bound by any theory, this increase can be rationalised on the basis that, from the above equation, the initiator efficiency is proportional to the mean residence time of the ethylene gas in the reaction zone. That is to say, the use of a larger first reaction zone permits a decrease in the amount of initiator required for producing polyethylene. By feeding 75% or more of ethylene to the first reaction zone and at the same time providing the zone with two or more feed inlets for each of the ethylene and the initiator, it is now possible to obtain a polyethylene having excellent optical properties and processability using a two-reaction zone process.

In practising the present invention, an autoclave reactor having a substantially or nearly cylindrical form can be used. The ratio of length to diameter of such a reactor is typically 2:1 to 20:1, preferably 5:1 to 15:1. Polymerization is effected in first and second reaction zones which are kept at different temperatures from each other, using an initiator. The initiator may be the same or different for the two zones.

Processes can be conducted in accordance with the invention in a single autoclave reactor having first and second reaction zones partitioned by a baffle (partition plate) or other partition means. Alternative processes in accordance with the invention are conducted in two autoclave reactors connected in series and each providing one of the two reaction zones. In conducting these latter processes, a pressure control valve may be mounted on

the line connecting the first reactor with the second.

The volume ratio of the first:second zone is preferably from 2:1 to 5:1.

When the volume ratio is less than 1.5:1, the mean residence time in the first zone is not such that improvement in initiator efficiency can be obtained.

The larger the volume ratio is, the better is the initiator efficiency. However, particularly when polymerizing ethylene, practical considerations put an upper limit on the volume ratio.

In the polymerization of ethylene, a polymerization heat of about 800 cal/g is generated and this heat is preferably used for heating the reactants being fed into the reaction zones. In this way it is possible to arrange for the polymerization of the ethylene to proceed as a so-called "autothermal" reaction, wherein the polymerization heat generated is substantially equal to the amount of heat required for heating the incoming reactants to the required reaction temperature.

We have found that with too large a volume ratio the mean residence time in the second zone usually becomes too short for autothermal operation to be possible. Sufficient heat of polymerization is not generated in the second zone to heat the incoming reactants (reaction mixture from the first zone together with 25% or less of the ethylene).

The upper limit of the volume ratio cannot be determined unconditionally, because it depends chiefly upon the reaction temperature of the second reaction zone, the type of initiator, the volume of the reaction zones and the feed rate of monomer. But, by considering the feed rates of ethylene and the volumes of the autoclave reactors which are currently employed in the production of polyethylene, we set the upper limit in the volume ratio at 6:1.

In practising the present invention, the initiator and the monomer can be fed to the reaction zones using the same or different inlets.

The positions of the inlets at which the initiator and the monomer are fed to the first reaction zone can be arranged in many combinations. In order to obtain from ethylene polyethylene having the desired optical properties and processabilities, the positions of the inlets should be arranged so as to make the distribution of reaction temperature in the first reaction zone as uniform as possible. Such arrangements can easily be determined by those skilled in the art. If desired an automatic control system can be used for so feeding the initiator that positions in the zones keep the desired temperatures.

In order to obtain satisfactory products we have found it necessary to feed both the monomer and the initiator through two or

agents include paraffins e.g. ethane, propane, butane, pentane, hexane, heptane; α -olefins e.g. propylene, but-1-ene, hex-1-ene, 3-methylpent-1-ene; aldehydes e.g. formaldehyde, acetaldehyde, propionaldehyde; ketones e.g. acetone, methyl ethyl ketone, diethyl ketone, cyclohexanone; aromatic hydrocarbons e.g. benzene, toluene, xylene; and mixtures thereof.

The process of this invention can be applied not only to the production of ethylene homopolymers, but also to the production of copolymers of ethylene with other comonomers, for example, ethylene-vinyl acetate, ethylene-methyl acrylate, ethylene-ethyl acrylate, and ethylene-styrene copolymers.

The present invention will be described further by way of example and comparison with reference to the accompanying drawings, in which:

Figures 4, 5 and 6 are schematic diagrams of three forms of apparatus for performing comparative processes.

The apparatus shown in Figure 1 comprises a single autoclave reactor 1 partitioned by a baffle 6 into a first reaction zone 3 and a second reaction zone 4. Disposed within the reactor is a paddle blade agitator 5 whose shaft also carries the baffle 6. The design of the baffle 6 is such as to allow the reaction products from the first zone 3 to be transferred to the second zone 4. Two monomer feed inlets 7 and 8 are provided for the first zone 3 as well as two initiator feed inlets 9 and 10. The second reaction zone 4 has a single initiator feed inlet 11, but no monomer inlet.

Temperature probes T_1 to T_4 are arranged within the reactor 1. The relative disposition along the reactor length of these probes, and of the baffle 6 and inlets 7 to 11, is as indicated in Figure 1. By arranging the inlets 7 to 11 in this way it is possible, when performing a process in accordance with the present invention, to maintain the reaction temperatures in each of the two zones at desired values. Although not specifically shown in the drawing, a pressure reducing valve is mounted at the bottom of the autoclave reactor 1 and forms an outlet to the second reaction zone 4.

The apparatus shown in Figure 2 is very similar to that in Figure 1, and it is only necessary to draw attention to the difference between them. In this second form of apparatus for performing processes embodying the present invention, the volume ratio of the first to the second reaction zones has been increased by moving the position of the baffle 6.

Whereas the forms of apparatus shown in 130

Figures 1 and 2 are based on a single autoclave reactor 1, that shown in Figure 3 is based on two separate autoclave reactors 1, 2 connected in series. The first reactor 1 constitutes a first reaction zone 3, and the second reactor 2 constitutes a second reaction zone 4. Each of the two reactors 1, 2 has a paddle blade agitator 5, and as before feed inlets 7 to 11 are provided for feeding monomer and initiator to the two zones. However in this instance the second autoclave 2 is fed with monomer by an extension from the feed inlet 7 of the first autoclave 3. Temperature probes are disposed within the two zones in much the same way as with the two previous forms of apparatus.

In using one of the forms of apparatus shown in Figures 1 to 3 to perform a process in accordance with the present invention, compressed monomer is fed to the first reaction zone 3 through the feed inlets 7 and 8. Initiator is fed to the first zone through the feed inlets 9 and 10 at a rate sufficient to maintain the temperature in the zone at the desired reaction temperature. The resulting reaction mixture passes to the second reaction zone 4 and further polymerization occurs. Initiator is fed to the second zone 4 through the feed inlet 11 at the rate required to maintain the desired reaction temperature. In the case of using the apparatus shown in Figure 3, up to 25% of the monomer is fed directly to the second autoclave reactor 2 without first passing through the first autoclave reactor 1. The polymeric product issues from the pressure reducing valve of the second reaction zone 4.

Figures 4 to 6 of the accompanying drawing illustrate comparative forms of apparatus. Each of these comparative forms differs in at least one respect from apparatus required for carrying out a process in accordance with the present invention. Thus, the forms shown in Figures 4 and 5 have only one initiator feed inlet 9 for the first reaction zone and the forms shown in Figures 4 and 6 have first and second reaction zones of equal volume

rather than of the volume ratio required by the present invention. That these differences are critical can be seen from the following examples.

By way of example, the forms of apparatus shown in Figures 1, 2 and 3 were used for performing processes embodying the invention. The monomer employed was ethylene, and the precise conditions employed are shown in the following Table. In each instance the product, comprising polyethylene and unreacted ethylene, was fed into a conventional separator and the polyethylene thereby separated. The unreacted ethylene was compressed and recycled to the monomer feed inlets 7,8.

For comparison, ethylene was polymerized in the forms of apparatus shown in Figures 4, 5 and 6. As will be understood from the Table, the conditions employed in comparative Examples 1 and 3 are a modification of Example 1, and those in comparative Examples 2 and 4 are a modification of those in Examples 2 and 4, respectively. Comparative Example 5 is an example illustrating that the present invention may not provide polyethylene of good optical properties when the reaction pressure is unduly high.

In each of the examples and comparative examples the physical properties of the polyethylenes obtained were determined. The density was measured according to ASTM D-1505, the melt index according to ASTM D-1238, the hazes according to ASTM D-1003 and the gloss according ASTM D-523 and D-2103. "Draw-down", the ability to form thin films, was determined by measurement of the minimum film thickness attainable when the polymer is formed into film at 160°C. It is to be noted that the smaller the value of haze and the larger the value of gloss, the more superior are the optical properties of the product. Additionally, the smaller the thickness of the film at 160°C, the more superior are the draw-down characteristics.

TABLE

		Example 1
Schematic diagram of reactor		Fig. 1
Volume ratio	$\frac{\text{first reaction zone}}{\text{second reaction zone}}$	2
Feed rate of ethylene (kg/hr)	via inlet 7 via inlet 8	44 44
Mean residence time (sec)	$\frac{\text{first reaction zone}}{\text{second reaction zone}}$	49/23
Chain transfer agent	Type Concentration (mole %)	ethane 1.1
Reaction pressure (kg/cm ²)		1200
Reaction temperature (°C)	first reaction zone T ₂	170
	first reaction zone T ₃	170
	second reaction zone T ₄	260
Radical initiator	first reaction zone (via inlets 9, 10) amount fed (g/hr)	3,5,5-trimethyl hexanoyl peroxide 28
	second reaction zone (via line 11) amount fed (g/hr)	di-tert-butyl peroxide 2.2
Production rate of polyethylene (kg/hr)		15.1
Properties	Density (g/cm ³)	0.923
	Melt index (g/10 min)	1.5
	Optical properties	3.3
	Haze (%)	120
	Gloss (%)	14
	Processability	
	Draw-down property (μ)	

TABLE (Cont'd)

Example 2	Comparative example 1	Comparative example 2	Comparative example 3
Fig. 2	Fig. 4	Fig. 5	Fig. 6
4	1	4	1
44 44	44 44	44 44	44 44
59/14	36/34	59/14	36/34
ethane 4.2	ethane 0.7	ethane 2.8	ethane 0.8
1200	1200	1200	1200
170	170	170	170
170			170
260	260	260	260
3,5,5-trimethyl hexanoyl peroxide a 20	THMPO 36	THMPO 24	THMPO 34
di-tert-butyl peroxide b 3.0	DBP 1.3	DBP 2.8	DBP 1.4
15.2	15.1	15.1	15.1
0.923	0.923	0.923	0.923
1.5	1.5	1.5	1.5
2.9	5.6	5.2	5.0
130	100	100	100
13	22	20	20

a) abbreviated to THMPO

b) abbreviated to DBP

TABLE (Cont'd)

Example 3	Example 4	Comparative example 4	Example 5	Comparative example 5
Fig. 1	Fig. 2	Fig. 4	Fig. 3	Fig. 1
2	4	1	4	2
44	44	44	40	44
44	44	44	44	44
51/24	61/14	38/34	74/17	54/26
propane 4.0	ethane 4.5	ethane 2.7	propylene 1.1	propane 6.9
1350	1400	1400	1200	1800
165	170	170	170	170
165	170		170	170
240	265	265	260	260
octanoyl peroxide ^c	OPO	OPO	TMPO	TMPO
20	14	24	17	10
tert- butyl peroxy- benzoate 2.0	DBP	DBP	DBP	DBP
	1.8	0.6	2.5	0.8
11.3	15.5	15.4	15.7	15.3
0.926 2	0.923 0.3	0.923 0.3	0.922 2	0.927 1.5
3.1	3.6	6.3	3.5	6.8
140	110	90	120	85
13	20	32	14	17

^c) abbreviated to OPO

It can be seen from the foregoing Table that the present invention provides a process which enables low-density polyethylene to be produced with improved optical properties and processabilities. The products obtained by the processes of Examples 1 to 5 have lower haze, higher gloss, and better draw-down than the products of the comparative examples.

In order to demonstrate that there is a practical limit to the reaction zone volume ratio, a reactor similar to that shown in Figures 1 and 2 was employed, but with a volume ratio (first:second reaction zone) of 7:1. Ethylene containing three mole % of propylene was compressed to a reaction pressure of 1100 kg per cm² and fed to the first reaction zone at a rate of 44 kg/hr. 3,5,5-trimethylhexanoyl peroxide was fed to the first reaction zone at a rate of 18 g/hr and the ethylene polymerized at 170°C. The resultant reaction mixture was transferred into the second reaction zone and further polymerization attempted by feeding di-tert-butyl peroxide. However autothermal operation of the process proved impossible in that the reaction mixture could not reach the required reaction temperature of 260°C.

This last comparative example demonstrates the practical limitations which are put upon the upper limit for the volume ratio of the reaction zones. Only by using a volume ratio which is at most 6:1 it is possible for the higher reaction temperature in the second zone to compensate for the decrease in initiator efficiency occasioned by the short mean residence time. If an increase in initiator efficiency was all that was required it would be possible to use a conventional two-zone reactor and feed most of the monomer direct to the second reaction zone. However most of the polymerization would then occur in the second reaction zone (and thus at the higher temperature), and it would not be possible to obtain a polyethylene with the desired optical properties and processability.

WHAT WE CLAIM IS:—

1. A process for polymerizing monomer comprising ethylene in first and second autoclave reaction zones arranged in series, which process comprises feeding 75% or more of the monomer to the first zone through two or more feed inlets, feeding the rest of the monomer, if any, to the second zone, polymerizing monomer in the first zone in the presence of an initiator fed in through two or more feed inlets, transferring the resulting reaction mixture from the first to the second

zone, and promoting further polymerization in the second zone in the presence of an initiator at a temperature higher than that in the first zone, the volume ratio of the first:second zones being 1.5:1 to 6:1 and the arrangement of the feed inlets being such as to give a substantially uniform reaction temperature in the first reaction zone.

2. A process according to Claim 1, wherein all the monomer is fed to the first reaction zone.

3. A process according to Claim 1 or 2, wherein the monomer and the initiator are each fed into the first zone through two feed inlets.

4. A process according to any one of Claims 1, 2 or 3 wherein the first and second reaction zones are provided by a single autoclave reactor which is internally partitioned.

5. A process according to any one of Claims 1, 2 or 3, wherein the first and second reaction zones are provided by two separate autoclave reactors connected in series by piping.

6. A process according to any one preceding Claim, wherein different initiators are used in the first and second zones.

7. A process according to any one preceding Claim, wherein the volume ratio of the first:second zone is from 2:1 to 5:1.

8. A process according to any one preceding claim wherein the monomer consists of ethylene.

9. A process according to Claim 8, wherein the temperature in the first reaction zone is 130° to 200°C, that in the second reaction zone is 220° to 280°C, and the reaction pressure is 1,000 to 1,800 kg/cm².

10. A process according to any one preceding Claim which operates autothermally.

11. A process according to Claim 1 substantially as hereinbefore described.

12. A process for polymerizing ethylene in first and second autoclave reaction zones arranged in series, the process being substantially as described in any one of Examples 1 to 5 herein.

13. Polymerized monomer comprising ethylene when obtained by a process according to any one preceding claim.

14. Polyethylene when obtained by a process according to any one preceding claim.

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zone, and promoting further polymerization in the second zone in the presence of an initiator at a temperature higher than that in the first zone, the volume ratio of the first:second zones being 1.5:1 to 6:1 and the arrangement of the feed inlets being such as to give a substantially uniform reaction temperature in the first reaction zone.

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3. A process according to Claim 1 or 2, wherein the monomer and the initiator are each fed into the first zone through two feed inlets.

4. A process according to any one of Claims 1, 2 or 3 wherein the first and second reaction zones are provided by a single autoclave reactor which is internally partitioned.

5. A process according to any one of Claims 1, 2 or 3, wherein the first and second reaction zones are provided by two separate autoclave reactors connected in series by piping.

6. A process according to any one preceding Claim, wherein different initiators are used in the first and second zones.

7. A process according to any one preceding Claim, wherein the volume ratio of the first:second zone is from 2:1 to 5:1.

8. A process according to any one preceding claim wherein the monomer consists of ethylene.

9. A process according to Claim 8, wherein the temperature in the first reaction zone is 130° to 200°C, that in the second reaction zone is 220° to 280°C, and the reaction pressure is 1,000 to 1,800 kg/cm².

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12. A process for polymerizing ethylene in first and second autoclave reaction zones arranged in series, the process being substantially as described in any one of Examples 1 to 5 herein.

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