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PATENT SPECIFICATION

(11) 1 490 892

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- (21) Application No. 12995/75 (22) Filed 27 March 1975
(31) Convention Application No. 49/036431
(32) Filed 29 March 1974 in
(33) Japan (JA)
(44) Complete Specification published 2 Nov. 1977
(51) INT CL² C08F 10/02 2/02
(52) Index at acceptance
C3P 7D1A D11 P1E3 P1E6 P5 P6A P6B



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(54) PROCESS FOR PRODUCING ETHYLENE POLYMERS IN A TUBULAR REACTOR

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organised and existing under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, 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 continuous process for producing polyethylene or a copolymer of ethylene with a copolymerizable monomer.

Specifications such as those of Japanese Patent Publication Nos. 3,026/65, 3,027/65, 13,068/65, 20,917/70, and 18,642/72 and U.S. Patent No. 1,852,501 describe high pressure processes for producing polyethylene in a tubular reactor. In each of these processes pulsed flow is employed to give efficient polymerization. Flow pulses are generated by so called flow pulse generating equipment, and help to prevent clogging within the reactor by the polyethylene produced and to reduce the incidence of abnormal reactions, as well as preventing any undue increase in the pressure drop in the reactor. Generally, the flow pulses are induced by sudden and momentary decrease of the pressure at programmed intervals.

In effect, the pulsed flow polymerization proceeds continuously, but there are certain serious disadvantages with this type of process. Firstly, each sudden change in the polymerization pressure leads to a variation in the reaction temperature, which in turn makes it difficult to control the temperature properly. Secondly, and as a consequence of the variations in polymerization pressure and reaction temperature, there are undesirable fluctuations in the quality of the polymerize product. Thirdly, the sudden and repeated changes in the pressure place heavy demands on the reactor and associated equipment, and isolated instances of material fatigue may occur. Finally, the investment and main-

tenance costs with this type of plant are high.

Previous attempts have been made to provide a process for polymerizing ethylene in a tubular reactor which do not require pulsed flow. For example, the specification of Dutch Patent Application No. 7,201,394 proposes the use of a tubular reactor which comprises two polymerization sections in series. The two sections have different diameters in order to give satisfactory discharge of the reactor contents, but it will be appreciated that considerable reconstruction of a conventional reactor is necessary. Moreover, even when the reconstruction has been effected it has been found difficult to achieve satisfactory operation. The difficulty mainly stems from the lack of attention which has been paid to the properties of the reaction mixture.

We have carried out extensive research to find a method for producing polyethylene in a tubular reactor where polymerization might proceed without the need for pulsed flow. We have studied in detail the various factors which effect the behavior of the polymerization reaction mixture. From our studies we have found that factors such as the flow characteristics of the reaction mixture, the dimensions of the reactor, the polymerization pressure, the polymerization temperature and the concentration as well as the mean molecular weight of the product polymer are all interrelated. We have been able to identify those factors which are particularly important for successful operation of a steady state process.

Accordingly, we now provide a process for producing polyethylene or a copolymer of ethylene with a copolymerizable monomer, which process comprises polymerizing ethylene or copolymerizing ethylene and a monomer copolymerizable therewith in the presence of an initiator in a tubular reactor without imposing flow pulses; the temperature and pressure at any point

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in the entire reaction zone being kept within the range expressed by the formula

$$\gamma = P_0 + 2T_0 \geq 1850$$

provided that

$$4000 \geq P_0 \geq 1000 \text{ and } 400 \geq T_0 \geq 150$$

wherein P_0 represents pressure (kg/cm²), T_0 represents temperature (°C), and γ represents the non-pulsation factor;

the flow rate of the fluid in said tubular reactor being from 8 to 30 m/sec;

the monomer conversion being 35% or less; and

the melt index of the resulting polymer being 0.1 or more.

With this process it is now possible to dispense with pulse flow. Provided that the temperature and pressure at any point in the entire reaction zone satisfy the formula given above, and provided that the other conditions such as flow rate, conversion and melt index are complied with, we have found that the reaction mixture has the flow characteristics which render pulsation unnecessary.

In performing a process in accordance with the present invention it is necessary to maintain the pulsation factor γ throughout the entire reaction zone. This consideration applies not only to the inlet region of the reactor, but also to the outlet region where the pressure is often lower. Similarly it also applies to the cooling region where the temperature is often appreciably lower than in other regions. Heretofore, the temperature and pressure of polymerization processes have usually only been determined where they are at a maximum. With the present process, it is necessary to ensure that the appropriate values are maintained throughout the reactor. Preferably γ is kept within the range 1850—2000.

The rate of flow of the reaction fluid through the reactor is an important factor, since it determines the thickness of the boundary layer for flow and heat transfer, and thereby the pressure drop and resistance to heat transfer. With a high flow rate there is decreased resistance to heat transfer, which in turn means that there is increased removal of heat through the reactor wall and thus increased monomer conversion. Moreover a high flow rate favours dispersions of the initiator and thus helps to prevent abnormal or side reactions. However we have found that a flow rate of 30 m per sec represents a practical upper limit to the flow rate. With a greater flow rate the pressure drop along the reactor becomes too high and particularly towards the end of the reactor it becomes difficult to maintain the desired pressure. This difficulty is critical because it is not possible to raise the temperature beyond that

at which decomposition begins to occur. Adjustment of the pressure by use of an exit valve is only an effective solution within a narrow pressure range, since limits are imposed by economical and constructional constraints.

A flow rate of 8m per sec represents a practical lower limit to the flow rate. If a lower rate is employed, there is too great a build up of polymer on the reactor wall and additionally the initiator is not dispersed in a satisfactory manner.

Processes in accordance with the present invention thus employ a flow rate of from 8 to 30 m per sec. It will be understood that by the term "flow rate" we means the volume of flow per unit time per unit cross-sectional area of the reactor.

From the aforesaid formula it will be seen that the reaction pressure should be in the range from 1000 to 4000 kg per cm² throughout the entire reaction zone. We prefer a reaction pressure of from 1200 to 3500 kg per cm². It will also be seen that the temperature throughout the entire reaction zone should be from 150° to 400°C. We prefer a temperature of from 160° to 350°C.

The pressure and temperature can be controlled by use of conventional techniques. For example, when the pressure is at a desired value but the temperature is too low, the temperature can be raised by increasing the rate of feed of initiator or by decreasing the amount of external cooling of the reactor. When the temperature is at a desired value the pressure can be adjusted as desired by operating an exit valve of the reactor. By the use of these and other techniques the man skilled in the art can easily ensure that the polymerization conditions throughout the reactor are in accordance with the preceding formula. In this way he can operate the reactor continuously and without the need for pulse flow.

Conventional initiators can be used in polymerization processes embodying the present invention. Suitable initiators include organic peroxides such as di-tert-butyl peroxide, tert-butyl peroxybenzoate, lauroyl peroxide, acetyl peroxide and tert-butyl hydroperoxide; oxygen; azo compounds such as azobisisobutyronitrile; and dicarbonates.

Operation without pulse flow requires that the monomer conversion be 35% or less. With higher conversion the concentration of polymer in monomer becomes high and the reaction mixture becomes too viscous. The extent of monomer conversion, which is preferably from 15 to 30%, can be controlled by regulating the conditions within the reactor. The most important factors which determine the rate of conversion are the reaction temperature and the rate of cooling along the reactor.

The melt index of the product polymer also greatly effects the viscosity of the reaction mixture, and for satisfactory operation without pulsation it has to be over 0.1 or more (when measured in accordance with the testing method of JIS K 6760). We prefer that the melt index of the polymer produce is kept within the range 0.1 to 50.

The melt index can be adjusted in the known manner by the addition of a chain transfer agent to the reaction mixture. Suitable chain transfer agents include those conventionally used in the production of polyethylene e.g. hydrogen, methane, ethane, propane, propylene, n-butane, isobutane, butene-1, isobutene, butene-2, and appropriate mixtures of these agents.

The process provided by the present invention can be used not only for the production of polyethylene, but also for production of copolymers of ethylene with other copolymerizable monomers. Suitable comonomers include one or more of vinyl compounds such as vinyl acetate or vinyl chloride, methyl or ethyl acrylate, methyl or ethyl methacrylate, acrylamide and vinyl ethers.

In performing processes which embody the invention we prefer to use a tubular reactor which has an inner diameter of $\frac{3}{4}$ " or more and an L/D (length to diameter ratio) of 10,000 or more, preferably 10,000 to 100,000.

The present invention will now be illustrated and compared in the following examples and comparative examples.

Comparative Example 1

A mixture of 100 parts by weight of ethylene and 0.00015 part by weight of oxygen, which had been compressed in known manner to 2,000 kg/cm² and heated at 170°C, was introduced into the first reaction zone (L/D=10.6×10³) of a tubular reactor (L/D=1.5×10⁴). The flow rate in the first reaction zone was 8 m/sec.

After the reaction mixture had attained a maximum temperature of 260°C, the reactor was cooled externally with Dowtherm (Registered Trade Mark) at 140°C to cool the reaction fluid to 230°C. The reaction mixture was then introduced into the second reaction zone (L/D=4.4×10³) and fed with 0.0005 part by weight of tert-butyl peroxide for 100 parts by weight of ethylene feed. After the reaction fluid had attained a maximum temperature of 260°C, the reactor was cooled to cool the reaction fluid at the outlet of the reactor to 210°C. The polymerization was carried out without imposing flow pulses. The pressure in the reactor at the beginning of polymerization was 1,300 kg/cm². The difference between the pressures at the inlet and outlet of the reactor increased at a rate of 300 kg/cm²/hr and steady operation of the reactor was

difficult to attain. Ethane was used as chain transfer agent. The melt index of the polymer obtained was 2.0, and ethylene conversion was 10%. The non-pulsation factor at the exit of the reactor was 1720, that is, $\gamma < 1850$.

Example 1

In a manner similar to that in Comparative Example 1, a mixture of ethylene and oxygen was introduced into the first reaction zone of a reactor. After the reaction mixture had attained the maximum temperature of 300°C, it was cooled to 260°C and introduced into the second reaction zone. tert-Butyl peroxide was fed to the second zone to increase the reaction temperature to 300°C. Thereafter the reaction mixture was cooled so as to reach the exit at 240°C and a pressure of 1400 kg/cm². The polymerization was carried out under steady state conditions without imposing flow pulses and no increase in pressure difference was noticed between the inlet and outlet. All of the non-pulsation factors measured at various spots in the reactor satisfied the inequality $\gamma \geq 1880$.

After about ten hours of continuous and steady running, no increase in the pressure difference was observed. The ethylene conversion was 14%. The polymer obtained had a melt index of 2.0, and a density of 0.92, and was of uniform quality.

Comparative Example 2

A mixture of 100 parts by weight of ethylene and 0.00084 part by weight of tert-butyl peroxybenzoate, which had been compressed in a usual way to 2,000 kg/cm² and heated at 170°C, was introduced at a flow rate of 8 m/sec into the first reaction zone (L/D=5.6×10³) of a tubular reactor (L/D=1.5×10⁴). Ethane was used as a chain transfer reagent. After the reaction mixture had attained the maximum temperature of 250°C, it was cooled to 220°C and introduced into the second reaction zone (L/D=4.4×10³). To the reaction mixture, was further fed 0.0005 part by weight of tert-butyl peroxybenzoate to increase the temperature to 250°C, and then it was cooled to 220°C. The mixture was introduced into the third reaction zone where it was fed again with 0.0005 part by weight of the same initiator. After the reaction mixture had attained the maximum temperature of 250°C, it was cooled to 220°C. The pressure at the exit of the reactor was 1,350 kg/cm² at the beginning of the polymerization. The polymerization was carried out without pulsation. The pressure at the exit decreased at a rate of 250 kg/cm²/hr, increasing the pressure difference between the inlet and the exit thus increasing more and more, and it was impossible to carry out the polymerization under steady state conditions. Ethylene conversion was 12%. The polymer formed had

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a melt index of 7.0. The non-pulsation factor (γ) was 1790.

Example 2

In the same manner as in Comparative Example 2, ethylene with di-tert-butyl peroxide as initiator were introduced into the first reaction zone. After the maximum reaction temperature of 300°C was attained, the reaction mixture was cooled to 260°C. Thereafter the reaction mixture was introduced successively into the second and the third reaction zones where it was further fed with di-tert-butyl peroxide in the same amount as in Comparative Example 2. After the temperature had risen to 300°C, the reaction mixture was cooled to 260°C. The pressure at the exit of the reactor became 1,450 kg/cm². Polymerization was carried out without imposing flow pulses and no increase in the pressure difference between the inlet and outlet of the reactor was observed, indicating steady progress of the polymerization. Ethylene conversion was 23%. The polymer formed had a melt index of 7.0. The non-pulsation factors throughout the entire reaction zone satisfied the inequality $\gamma \geq 1970$.

WHAT WE CLAIM IS:—

1. A continuous process for producing polyethylene or a copolymer of ethylene with a copolymerizable monomer, comprising polymerizing ethylene or copolymerizing ethylene and a monomer copolymerizable with ethylene in the presence of an initiator in a tubular reactor without imposing flow pulses:

the temperature and pressure at any point in the entire reaction zone being kept within the range expressed by the formula

$$\gamma = P_0 + 2T_0 \geq 1850$$

provided that

$$4000 \geq P_0 \geq 1000 \text{ and } 400 \geq T_0 \geq 150,$$

wherein P_0 represents pressure (kg/cm²), T_0 represents temperature (°C), and γ represents the non-pulsation factor;

the flow rate of the fluid in said tubular reactor being from 8 to 30 m/sec;

the monomer conversion being 35% or less; and

the melt index of the resulting polymer being 0.1 or more.

2. A process according to claim 1 in which the pressure P_0 is kept in the range 1200—3500 kg/cm².

3. A process according to claim 1 or claim 2 in which the temperature T_0 is kept within the range 160—350°C.

4. A process according to any of claims 1 to 3 in which the monomer conversion is kept within the range 15 to 30%.

5. A process according to any of claims 1 to 4 in which the melt index of the polymer produced is kept within the range 0.1 to 50.

6. A process according to any of claims 1 to 5 in which γ is kept within the range 1850—2000.

7. A process according to any of claims 1 to 6, wherein inner diameter of the tubular reactor is 3/4 inch or more and L/D (length to inner diameter ratio) is 10,000 or more.

8. A process according to any of claims 1 to 7, wherein the monomer copolymerizable with ethylene is vinyl acetate, vinyl chloride, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylamide or a vinyl ether.

9. A process according to any of claims 1 to 8, wherein the initiator is di-tert-butyl peroxide, tert-butyl peroxybenzoate, lauroyl peroxide, acetyl peroxide, tert-butyl hydroperoxide, oxygen, azobisisobutyronitrile, or a dicarbonate.

10. A process according to any of claims 1 to 9 substantially as herein described.

11. A process for the polymerization of ethylene substantially as described in Example 1 or Example 2.

12. A polymer or copolymer of ethylene when prepared by a process according to any of claims 1 to 11.

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WHAT WE CLAIM IS:—

1. A continuous process for producing polyethylene or a copolymer of ethylene with a copolymerizable monomer, comprising polymerizing ethylene or copolymerizing ethylene and a monomer copolymerizable with ethylene in the presence of an initiator in a tubular reactor without imposing flow pulses:

the temperature and pressure at any point in the entire reaction zone being kept within the range expressed by the formula

$$\gamma = P_g + 2T_g \geq 1850$$

provided that

$$4000 \geq P_g \geq 1000 \text{ and } 400 \geq T_g \geq 150,$$

- wherein P_g represents pressure (kg/cm²), T_g represents temperature (°C), and γ represents the non-pulsation factor;

the flow rate of the fluid in said tubular reactor being from 8 to 30 m/sec; the monomer conversion being 35% or less; and the melt index of the resulting polymer being 0.1 or more.

2. A process according to claim 1 in which the pressure P_g is kept in the range 1200—3500 kg/cm².

3. A process according to claim 1 or claim 2 in which the temperature T_g is kept within the range 160—350°C.

4. A process according to any of claims 1 to 3 in which the monomer conversion is kept within the range 15 to 30%.

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6. A process according to any of claims 1 to 5 in which γ is kept within the range 1850—2000.

7. A process according to any of claims 1 to 6, wherein inner diameter of the tubular reactor is 3/4 inch or more and L/D (length to inner diameter ratio) is 10,000 or more.

8. A process according to any of claims 1 to 7, wherein the monomer copolymerizable with ethylene is vinyl acetate, vinyl chloride, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylamide or a vinyl ether.

9. A process according to any of claims 1 to 8, wherein the initiator is di-tert-butyl peroxide, tert-butyl peroxybenzoate, lauroyl peroxide, acetyl peroxide, tert-butyl hydroperoxide, oxygen, azobisisobutyronitrile, or a dicarbonate.

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