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(72) Inventors MINORU MORIKAWA, RYUICHI SONODA
and KIYOSHI MATSUYAMA

(54) PROCESS FOR THE HIGH-PRESSURE POLYMERIZATION OF ETHYLENE

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a Japanese body corporate, 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:—

This invention relates to a process for producing ethylene homopolymers and copolymers by high-pressure polymerization.

The high-pressure polymerization of ethylene is generally performed at a reaction pressure of from 500 to 4,000 kg/cm² and a reaction temperature of from 150° to 300°C, in the presence of oxygen or a peroxide as catalyst. At the end of the polymerization, the pressure on the reaction mixture is reduced to 50–600 kg/cm², whereupon the mixture separates out into the polymerizate and unreacted gaseous monomer.

Two types of reactor are used for performing this polymerization process on an industrial scale: namely, the autoclave reactor and the tubular reactor. The autoclave reactor is of a generally cylindrical shape with a relatively large diameter, the ratio of its height to diameter usually being from 5:1 to 20:1, and is normally provided with stirring means. The tubular reactor is also of generally cylindrical shape but with a relatively small diameter, the ratio of its length to diameter usually being from 300:1 to 40,000:1.

Each of these two types of reactor has its own advantages and disadvantages. For example, the autoclave reactor requires no pre-heating of the ethylene feed, but the molecular weight distribution of the polymer formed is relatively narrow. On the other hand, the tubular reactor can produce a polymer with a relatively broad molecular weight distribution, but it is not suitable for copolymerization reactions and it needs pre-heating of the ethylene feed. This essential

preheating can engender the accumulation of a high molecular weight polymer, or sometimes of a cross-linked polymer, on the walls of the reactor tube in the preheating zone or the high temperature zone, which is liable to cause blocking of the tube or a reduction in the heat-transfer coefficient. Contamination with high molecular weight polymer and cross-linked polymer can spoil the optical properties of products made from the polymer, for example by the formation of "fisheyes" (insufficiently fused globular masses resembling a small lens) in film made from the polymer.

In both types of reactor, the conversion per pass (i.e. the yield of polymer expressed as a percentage of the monomer feed) is normally limited to around 10–20% by weight. In order to optimize the ethylene conversion, the heat evolved during the polymerization must be removed from the reaction system. In an autoclave reactor, the heat of polymerization is removed chiefly by utilizing the difference between the feed temperature and the reaction temperature. On the other hand, in a tubular reactor, it is not possible fully to utilize this temperature difference for removing the heat of polymerization, because at least some of the gaseous monomer feed must be preheated in order to initiate the reaction. In tubular reactors the heat of polymerization has been removed by externally cooling the reactor tube, by introducing a portion of the ethylene feed cold to a high temperature zone in the reactor (Japanese Patent Publication No. 18,984/63), or by feeding in the catalyst at two or more positions in the reactor tube (Japanese Patent Publication No. 4,686/63).

Surprisingly, it has now been discovered that the advantages of the two types of reactor can be combined while their disadvantages are compensated, by performing the high-pressure polymerization of ethylene successively in an autoclave reactor and a tubular reactor, without removing the

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polymer from the reaction mixture in the interim. In particular, it has been found that this can give a higher monomer conversion than is attainable with either type of reactor on its own, and that it makes possible the production of ethylene polymers with a broader molecular weight distribution. Contrary to expectations, no difficulties arise; and the process can be used for producing ethylene copolymers as well as homopolymers.

Accordingly, the invention provides a process for producing an ethylene polymer, which comprises: feeding compressor ethylene, or a compressed monomer mixture comprising ethylene and one or more other monomers copolymerizable therewith, into an autoclave reactor, polymerizing the ethylene or monomer mixture in the autoclave reactor, in the presence of a catalyst; transferring the reaction mixture from the autoclave reactor to a tubular reactor, *via* a heat exchanger, where the reaction mixture is cooled; and continuing the polymerization in the tubular reactor, in the presence of a further quantity of catalyst.

Apparatus for carrying out the process of the invention suitably includes a high-pressure gas compressor connected to the inlet of the autoclave reactor, the outlet of which is connected *via* a heat exchanger to one end of the tubular reactor, the other end of the tubular reactor being provided with a pressure-regulating valve.

Optionally, a pressure-regulating valve can also be fitted between the outlet of the autoclave reactor and the heat-exchanger.

During the first stage of the polymerization, performed in the autoclave reactor, the reaction temperature can be controlled by utilizing a cold monomer feed; while in the second stage, performed in the tubular reactor, the temperature can be controlled by external cooling. The deterioration in product quality due to contamination with molecular weight polymer or cross-linked polymer formed in the preheating zone or high temperature zone of a conventional tubular reactor is avoided by means of the present invention. Previously, gel formation in tubular reactors has been avoided by the addition of a *p*-*t*-alkylphenol aldehyde (as described in United States Patent Patent No. 3,157,627) or of butene; but, by operating in accordance with the present invention, it is possible to avoid gel formation without the use of such additives.

The invention will be further described with reference to the accompanying drawing, which is a flow diagram of an embodiment thereof. In the drawing, (1) represents a high-pressure gas compressor, (2) an autoclave reactor, (3) and (6) pressure-regulating

valves, (4) a heat exchanger, (5) a tubular reactor, and (A) a catalyst inlet.

The gaseous polymerization feed stock is compressed in the high-pressure gas compressor (1) and fed into the autoclave reactor (2). A catalyst is added, and the monomer is polymerized in the conventional manner. The polymerization mixture, normally containing 10–20% by weight of ethylene polymer, flows from the autoclave reactor (2) to the heat exchanger, in which it is cooled (4) *via* the pressure-regulating valve (3), which can be used to reduce its pressure if desired. The mixture is then fed into the tubular reactor (5) to continue the polymerization, with the addition of fresh catalyst at (A). If desired, two or more tubular reactors connected in series can be used at this point. The pressure in the tubular reactor can be regulated by means of valve (6).

One or more of the conventional ethylene polymerization catalysts can be used in the process of the invention, including oxygen, organic peroxide catalysts and azo compound catalysts. Examples of specific catalysts are dialkyl peroxides such as di-*t*-butyl peroxide and diethyl peroxide, tertiary alkyl percarboxylates such as *t*-butyl perbenzoate and *t*-butyl peracetate, ketone peroxides such as methyl ethyl ketone peroxide, alkyl hydroperoxides such as *t*-butyl hydroperoxide, acyl peroxides such as acetyl peroxide and benzoyl peroxide, dicarbonates such as diisopropyl peroxydicarbonate, organic acid peroxides such as succinic acid peroxide, oximes such as acetoneoxime, azines such as benzylidene azine, and azo compounds such as azobis(isobutyronitrile), 2,2'-azobis(methylisobutyrate) and 2,2'-azobis(isobutylamide). In general, from 5 to 3,000 parts by weight of catalyst are used per 1,000,000 parts by weight of ethylene or monomer mixture in the feed.

The catalyst can be introduced into the tubular reactor at one or more points along the reactor tube.

It is desirable to operate the process of the invention so that the linear velocity of the fluid reaction mixture in the heat exchanger and tubular reactor is from 5 to 35 metres per second.

The reaction pressure used in the process of the invention is generally from 1,000 to 4,000 kg/cm², preferably from 1,200 to 3,000 kg/cm². The reaction pressures in the autoclave reactor and the tubular reactor are normally controlled simultaneously but, if desired, they can be controlled independently of each other by means of regulating valves at the outlet of each reactor. It is also possible to produce a pulsed flow of the fluid reaction mixture, as described in Japanese Patent Publication No. 693/61, by independently controlling the pressures in

the autoclave reactor and the tubular reactor and providing an intermittent delivery valve at the exit of the tubular reactor. Such a pulsed flow method helps to prevent blocking of the tubular reactor by polymer. Pulsed flow of the reaction mixture can be used in the tubular reactor alone, so as not to adversely affect the temperature control in the autoclave reactor.

The polymerization temperature used in the process of the invention is normally from 120° to 350°C, preferably from 150° to 300°C. The reaction temperature can be controlled independently in the autoclave reactor and the tubular reactor, so that each can be operated under optimum temperature conditions.

The cumulative monomer conversion in the autoclave reactor and tubular reactor is normally at least 20% by weight; and, by judicious selection of the reaction conditions, the conversion can easily reach 25–35% by weight. As well as improving the conversion, the molecular weight and molecular weight distribution of the polymer can be controlled by varying the reaction conditions: this allows the production of polymers with a more widely varying range of characteristic properties than is possible by the conventional polymerization processes.

The process of the invention is applicable not only to the homopolymerization of ethylene, but also to its copolymerization with other monomers, for example vinyl esters such as vinyl acetate, vinyl formate and vinyl butyrate, acrylic and methacrylic esters such as methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate, acrylamides and methacrylamides amide, methyl methacrylamide and ethyl such as methyl acrylamide, ethyl acrylamide, vinyl ethers such as methyl vinyl ether and t-butyl vinyl ether, vinyl ketones such as methyl vinyl ketone, dicarboxylates such as diethyl fumarate and diethyl maleate, acid anhydrides such as maleic anhydride, and styrene.

The invention is illustrated by the following Examples, in which all parts are by weight unless otherwise stated.

EXAMPLE 1

One million parts per hour of ethylene compressed to 2,000 kg/cm², were passed through a cooler and fed at 40°C into an autoclave reactor. As the same time, 6 parts per hour of di-t-butyl peroxide were introduced into the autoclave reactor, to initiate polymerization at a reaction temperature of 250°C. In the autoclave reactor, 170,000 parts per hour of ethylene were converted into polyethylene.

The pressure on the reaction mixture was reduced to 1,500 kg/cm² by means of a valve, and the mixture was passed through

a heat exchanger where it was cooled to 200°C. The mixture was then fed into a tubular reactor, to continue the reaction, while being admixed with 75 parts of a mixture of di-t-butyl peroxide and t-butyl perbenzoate as catalyst for the ethylene feed. The reaction temperature rose to a maximum of 270°C. In the tubular reactor, 80,000 parts per hour of ethylene were polymerized. The reaction mixture from the tubular reactor was discharged into a separator and the pressure on it was released, whereupon the polymer separated out from the unreacted ethylene, which latter was recycled for reuse.

The process yielded 250,000 parts per hour of polyethylene having a specific gravity of 0.918–0.922 and a melt index of 2–4 (both measured in accordance with JIS K 6760–1960).

The yield in the single autoclave reactor was 170,000 parts per hour. Thus, by connecting the autoclave reactor to the tubular reactor, the conversion was increased to 250,000 parts per hour.

The polymer obtained had excellent probability and was free from fisheyes and other gel-forming substances.

EXAMPLE 2

One million parts per hour of ethylene, compressed to 2,500 kg/cm², were passed through a cooler and fed at 40°C into an autoclave reactor. At the same time, 4 parts per hour of di-t-butyl peroxide were introduced into the reactor, as catalyst, to initiate polymerization at a reaction temperature of 250°C. In the autoclave reactor, 170,000 parts per hour of ethylene were converted into polyethylene.

The reaction mixture was cooled to 200°C by passage through a heat exchanger and fed into a first tubular reactor, to continue the reaction, while being admixed with 50 parts of a mixture of di-t-butyl peroxide and t-butyl perbenzoate as catalyst for the ethylene feed. The reaction temperature rose to 270°C, and 80,000 parts per hour of ethylene were polymerized in this tubular reactor.

The reaction mixture was cooled to 200°C and fed to a second tubular reactor, to continue the reaction, while being admixed with 40 parts of a mixture of di-t-butyl peroxide and t-butyl perbenzoate as catalyst.

The maximum reaction temperature reached 255°C, and 60,000 parts per hour of ethylene were polymerized in this tubular reactor. The reaction mixture from the second tubular reactor was discharged into a separator and the pressure on it was released, whereupon the polymer separated out from the unreacted ethylene gas, which latter was recycled for reuse.

The process yielded 310,000 parts per

hour of polyethylene having a density of 0.92—0.924 and a melt index of 1—4. The yield was raised from 170,000 parts per hour in the autoclave reactor alone to 310,000 parts per hour by connecting the autoclave reactor to the two tubular reactors in series.

The polymer obtained had excellent processibility and was free from fisheyes and other gel-forming substances.

WHAT WE CLAIM IS:—

1. A process for producing an ethylene polymer, which comprises: feeding compressed ethylene, or a compressed monomer mixture comprising ethylene and one or more other monomers copolymerizable therewith, into an autoclave reactor; polymerizing the ethylene or monomer mixture in the autoclave reactor, in the presence of a catalyst; transferring the reaction mixture from the autoclave reactor to a tubular reactor *via* a heat exchanger, where the reaction mixture is cooled; and continuing the polymerization in the tubular reactor, in the presence of a further quantity of catalyst.

2. A process according to claim 1, in which the linear velocity of the reaction mixture in the tubular reactor is from 5 to 35 metres per second.

3. A process according to claim 1 or claim 2, in which the polymerization is performed under a pressure of from 1,000 to 4,000 kg/cm².

4. A process according to claim 3, in which the polymerization is performed under a pressure of from 1,200 to 3,000 kg/cm².

5. A process according to any preceding claim, in which the polymerization is

performed at a temperature of from 120°C to 350°C.

6. A process according to claim 5, in which the polymerization is performed at a temperature of from 150°C to 300°C.

7. A process according to any preceding claim, in which ethylene is copolymerized with vinyl acetate, vinyl formate, vinyl butyrate, methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, acrylamide, methacrylamide, methyl vinyl ether, *t*-butyl vinyl ether, methyl vinyl ketone, maleic anhydride, or styrene.

8. A process according to any preceding claim, in which the catalyst comprises oxygen, di-*t*-butyl peroxide, diethyl peroxide, *t*-butyl perbenzoate, *t*-butyl peracetate, methyl ethyl ketone peroxide, *t*-butyl hydroperoxide, acetyl peroxide, benzoyl peroxide, di-isopropyl peroxydicarbonate, succinic acid peroxide, acetone oxime, benzylidene azine, azobis(isobutyronitrile), 2,2'-azobis-methylisobutyrate), or 2,2'-azobis(isobutylamide).

9. A process according to any preceding claim, in which catalyst is introduced at one or more points along the tubular reactor.

10. A process according to claim 1, substantially as herein described in any of the Examples.

11. A process according to claim 1, substantially as herein described with reference to the accompanying drawing.

12. Ethylene polymers when produced by a process according to any preceding claim.

MARKS & CLERK,
Chartered Patent Agents,
57—60 Lincoln's Inn Fields,
London WC2A 3LS.
Agents for the Applicants.

hour of polyethylene having a density of 0.92—0.924 and a melt index of 1—4. The yield was raised from 170,000 parts per hour in the autoclave reactor alone to 310,000 parts per hour by connecting the autoclave reactor to the two tubular reactors in series.

The polymer obtained had excellent processibility and was free from fisheyes and other gel-forming substances.

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2. A process according to claim 1, in which the linear velocity of the reaction mixture in the tubular reactor is from 5 to 35 metres per second.
3. A process according to claim 1 or claim 2, in which the polymerization is performed under a pressure of from 1,000 to 4,000 kg/cm².
4. A process according to claim 3, in which the polymerization is performed under a pressure of from 1,200 to 3,000 kg/cm².
5. A process according to any preceding claim, in which the polymerization is

performed at a temperature of from 120°C to 350°C.

6. A process according to claim 5, in which the polymerization is performed at a temperature of from 150°C to 300°C.

7. A process according to any preceding claim, in which ethylene is copolymerized with vinyl acetate, vinyl formate, vinyl butyrate, methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, acrylamide, methacrylamide, methyl vinyl ether, t-butyl vinyl ether, methyl vinyl ketone, maleic anhydride, or styrene.

8. A process according to any preceding claim, in which the catalyst comprises oxygen, di-t-butyl peroxide, diethyl peroxide, t-butyl perbenzoate, t-butyl peracetate, methyl ethyl ketone peroxide, t-butyl hydroperoxide, acetyl peroxide, benzoyl peroxide, di-isopropyl peroxydicarbonate, succinic acid peroxide, acetone oxime, benzylidene azine, azobis(isobutyronitrile), 2,2'-azobis-methylisobutyrate), or 2,2'-azobis(isobutylamide).

9. A process according to any preceding claim, in which catalyst is introduced at one or more points along the tubular reactor.

10. A process according to claim 1, substantially as herein described in any of the Examples.

11. A process according to claim 1, substantially as herein described with reference to the accompanying drawing.

12. Ethylene polymers when produced by a process according to any preceding claim.

MARKS & CLERK,
Chartered Patent Agents,
57—60 Lincoln's Inn Fields,
London WC2A 3LS.
Agents for the Applicants.

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