

PATENT SPECIFICATION

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(19)



(54) IMPROVED PROCESS FOR ETHYLENE POLYMERISATION

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, a corporation organized 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:—

This invention relates to an improved process for producing ethylene homopolymers and copolymers by high pressure polymerisation.

It is well known that high molecular weight ethylene polymers with good properties can be obtained by polymerising ethylene, or a monomer mixture comprising a major proportion of ethylene, under a pressure of at least 500 kg/cm², generally from 1,000 to 3,000 kg/cm², and at a reaction temperature of from 30° to 500°C, generally from 50° to 300°C, using as catalyst oxygen or a compound which readily generates free radicals.

Two types of reactors are used for performing this polymerisation 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 type of reactor gives polymers with characteristic properties.

When a stirred autoclave reactor is used for the industrial scale polymerisation of ethylene, or of a monomer mixture comprising a major proportion of ethylene, the polymer yield per single pass of monomer through the reactor (i.e. the percentage by weight of the polymer being formed per unit weight of the reactant gas fed to the reactor) is governed by the heat balance in the reactor, though also depending on the reaction temperature and the type and amount of the catalyst used. The

fairly large amount of heat evolved during the polymerisation of ethylene is usually removed by utilizing the difference between the feed temperature and the reaction temperature, and by external cooling of the reactor. However, the polymer yield is usually limited to 10—20% by weight in an autoclave reactor.

The invention makes it possible to improve the monomer conversion in autoclave reactors, and to produce ethylene polymers with a different molecular weight distribution and better properties than the polymers obtained by conventional autoclave reactor processes.

The invention provides a process for producing an ethylene polymer by polymerising ethylene, or a mixture of ethylene with one or more other monomers copolymerisable therewith, in a series of at least two autoclave reactors connected in cascade, in which the reaction mixture withdrawn from each but the last reactor is cooled to a temperature which is above 120°C but is at least 20°C lower than the reaction temperature in the reactor from which it has been withdrawn, and is then fed to the next reactor in the series without removal of the polymerisate.

Apparatus which may be used in the process of the invention for polymerising ethylene comprises a series of at least two autoclave reactors connected in cascade, each reactor having an inlet, internal stirring means and an outlet provided with a pressure reduction valve, the inlet of the first reactor being connected to a gas compressor, and the outlet of each but the last reactor being connected to the inlet of the next reactor in the series *via* a heat exchanger.

In accordance with the process of the invention, compressed cold ethylene, or a cold mixture of ethylene with one or more other monomers copolymerisable therewith, is fed from a gas compressor to the first in a series of stirred autoclave reactors. A catalyst is added to the reactor, and the monomer is allowed to react until a given conversion is reached, while utilizing to the full extent the increase in sensible heat of the cold gas. The

resulting reaction mixture, comprising the polymerisate and unreacted monomer, is fed to the second autoclave reactor in the series, to continue the polymerisation and increase the monomer conversion. The piping connecting the first and second reactors is provided with a heat exchanger for cooling the reaction mixture withdrawn from the first reactor, in order to increase the conversion in the second reactor. If desired, the reaction mixture can similarly be fed from the second reactor to a third reactor *via* a heat exchanger, and so on with succeeding reactors, in order further to increase the conversion. A reducing valve provided at the outlet of each reactor permits control of the reaction pressure and temperature in that reactor.

The intermediate cooling of the reaction mixture between adjacent reactors in the series is important, and the temperature of the mixture must be lowered by at least 20°C below that in the preceding reactor. The greater the temperature drop in excess of 20°C, the higher will be the conversion in the succeeding autoclave reactor. However, the reaction mixture should not be cooled to a temperature below 120°C, otherwise there is a risk of blocking the pipes or of pressure loss due to precipitated polymerisate. This risk might necessitate the separation of the polymerisate from the unreacted monomer between adjacent reactors, which would complicate the process and destroy the advantage of simplicity possessed by the present invention.

The polymerisation of ethylene in two or more autoclave reactors connected in series has previously been described in United Kingdom Patent Specifications No. 762,592 and No. 765,501. The first of these describes a process in which a hard-grade polyethylene and a soft-grade polyethylene are produced and mixed: this is quite different from the process of the present invention, in which the reaction mixture is cooled between consecutive reactors in the series, thereby increasing the monomer conversion. Specification No. 765,501 describes a process in which the reaction mixture is cooled between consecutive reactors in the series, and again heated after addition of a catalyst, to continue the reaction and increase conversion of ethylene. However, before being fed to the next reactor, the cooled reaction mixture passes through a separator wherein the polymerisate is removed. This necessity for a separation step between consecutive reactors introduces undesirable complications in the apparatus and its operation. In contradistinction in the present invention the cooling between successive reactors is controlled so that the temperature does not fall below 120°C, which makes it possible to dispense with the separation of the polymerisate between reactors, and simplifies the apparatus and its operation. This simplification is of great significance in the industrial process.

The reaction pressure and temperature used in each autoclave reactor in the process of the invention can be chosen over a wide range. The reaction pressure can be regulated freely by means of the reducing valve provided at the outlet of each reactor, with the proviso that the maximum reaction pressure possible in each reactor is less than that in the immediately preceding reactor, due to the pressure loss in the interconnecting pipes. The reaction pressure is generally from 500 to 4,000 kg/cm², preferably from 1,000 to 3,000 kg/cm². The reaction temperature, which can be controlled in each reactor independently of the other reactors, is generally from 140° to 300°C.

Conventional ethylene polymerisation catalysts can be used in the process of the invention, including oxygen, organic peroxide and azo catalysts, for example dialkyl peroxides such as di-*t*-butyl peroxide and diethyl peroxide, tertalkyl percarboxylates such as *t*-butyl benzoate 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, benzoyl peroxide and dioctanoyl peroxide, dicarboxylates such as diisopropyl peroxydicarbonate, organic peracids such as succinic acid peroxides, oximes such as acetone oxime, azines such as benzylidene azine, and azo compounds such as azobis(isobutyronitrile), 2,2'-azobis(methylisobutyrate) and 2,2'-azobis(isobutylamide). One or more such catalysts may be used. In general, from 5 to 3,000 parts by weight of catalyst are used for the first reactor, and from 5 to 2,000 parts by weight of catalyst for each succeeding reactor, per 1,000,000 parts by weight of monomer.

Not only ethylene homopolymers but also ethylene copolymers can be produced by means of the invention. Monomers which can be copolymerised with the ethylene include vinyl esters such as vinyl acetate, vinyl formate and vinyl butyrate, acrylates and methacrylates such as methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate, acrylamides and methacrylamides such as methyl acrylamide, ethyl acrylamide, methyl methacrylamide and ethyl methacrylamide, 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.

By selecting the reaction conditions in the process of the invention, it is possible to obtain an easily processible polymer with a molecular weight distribution different from that of polymers obtained by the conventional autoclave processes. Furthermore, polymers produced by the process of the invention can be used to make moulded products, such as sheet and film, which have optical properties markedly superior to those of products made

from polymers produced by the conventional processes.

The invention is illustrated by the following Examples, in conjunction with the accompanying drawing, which is a simplified flow diagram for the process described therein. In the drawing, (1) is a superhigh pressure gas compressor, (2) and (3) are autoclave reactors, (4) is a heat exchanger, and (5) and (6) are outlet valves. In the Examples, parts are by weight unless otherwise stated.

Example 1.

4000 litres per hour of ethylene were compressed by means of the superhigh pressure gas compressor (1) to a pressure of 1,500 kg/cm² and cooled to 30°C. by passing through a cooler. Ninety percent of the cooled ethylene was fed to the autoclave reactor (2), which had a capacity of 250 litres, and the remaining 10% to the autoclave reactor (3), of the same capacity as autoclave (2). One ten-thousandth part of di-t-butyl peroxide catalyst was added to the first reactor (2) per part of ethylene fed to this reactor, and polymerisation was allowed to proceed at 250°C. In the first reactor, about 15% of the ethylene was converted into polyethylene. After having been cooled to 170°C. in the heat exchanger (4), the reaction mixture was fed to the second autoclave reactor (3), to which was added 1/30,000 part of fresh di-t-butyl peroxide catalyst, and the polymerisation was continued therein at 260°C. The reaction pressure was adjusted to 1,200 kg/cm² by means of outlet valves (5) and (6). The reaction mixture was withdrawn from the reactor (3) and the pressure on it was released in a separator, whereupon the mixture separated into the polymerisate and unreacted ethylene, which latter was recycled for reuse. The overall conversion attained by this process was about 25%, whilst the conversion was only 17% when a single autoclave reactor was used.

As compared with conventionally produced polyethylene, the polymer thus obtained had little odour and had improved processibility, as indicated on extrusion by a decrease in the working pressure at the extrusion die and a decrease in the power consumption for extrusion. Moulded articles, sheet and film formed from the polymer had better transparency, impact strength, tear strength and drawdown than comparable articles formed from conventionally produced polyethylene.

Example 2.

4000 litres per hour of ethylene were compressed to a pressure of 2,500 kg/cm² and

cooled to 30°C. by passing through a cooler. Seventy-five percent of the cooled ethylene was introduced into the autoclave reactor (2), which had a capacity of 250 litres, and the remaining 25% into the autoclave reactor (3), of the same capacity as autoclave (2). One two-thousandth part of dioctanoyl peroxide catalyst was added to the first reactor (2) per part of the ethylene introduced into this reactor, and polymerisation was allowed to proceed at 190°C. The reaction pressure was adjusted to 2,400 kg/cm² by means of the outlet valve (5). After having been cooled in the heat exchanger (4) to 140°C., the reaction mixture was introduced into the second autoclave reactor (3), to which was added 1/30,000 part of fresh di-t-butyl peroxide catalyst, and the polymerisation was continued therein at 250°C. The reaction pressure was adjusted to 1,200 kg/cm² by means of the outlet valve (6). The reaction mixture was withdrawn from the reactor (3) and the pressure on it was released in a separator, whereupon the mixture separated into the polymerisate and unreacted ethylene, which latter was recycled for reuse. The overall conversion attained by this process was about 20%.

For comparative purposes, ethylene was polymerised in an apparatus comprising a single autoclave reactor. Ethylene was compressed to a pressure of 2,500 kg/cm², cooled to 30°C. by passing through a cooler, and allowed to polymerise at 190°C. after the addition of 1/1,500 part of dioctanoyl peroxide catalyst per part of ethylene which had been fed. The reaction pressure was adjusted to 2,400 kg/cm² by means of the outlet valve. The reaction mixture was withdrawn and the pressure on it was released in a separator, whereupon the mixture separated into the polymerisate and unreacted ethylene, which latter was recycled for reuse. The overall conversion attained by this process was 13.5%.

Characteristic properties of the polyethylene obtained by the process of this invention were compared with those of the polyethylene obtained by using the single autoclave reactor. The results obtained are shown in the following Table. The melt index and density were measured by the methods of JIS K 6760—1966. Optical properties were measured on a film, 0.03 mm thick and 180 mm wide, prepared by extrusion at a resin temperature of 160°C., by the method of JIS K 6714—1961 for haze and of ASTM D 523—53T for gloss. The drawdown was evaluated by determining the minimum thickness of film obtainable by stable extrusion for 10 minutes.

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TABLE

	Polymer of the invention	Comparative polymer
Melt index, g/10 min.	2.0	2.0
Density, g/cc	0.924	0.924
Optical properties:		
Haze, %	5.6	7.6
Gloss, %	107	78
Processibility:		
Drawdown, μ	12	20
Pressure at extrusion die, kg/cm ²	232	263

As is evident from the Table, the polyethylene obtained by the process of this invention had superior processibility and optical properties, as compared with the polyethylene obtained by the single autoclave reactor process.

WHAT WE CLAIM IS:—

1. A process for producing an ethylene polymer by polymerising ethylene, or a mixture of ethylene with one or more other monomers copolymerisable therewith, in a series of at least two autoclave reactors connected in cascade, in which the reaction mixture withdrawn from each but the last reactor is cooled to a temperature which is above 120°C but is at least 20°C lower than the reaction temperature in the reactor from which it has been withdrawn, and is then fed to the next reactor in the series without removal of the polymerisate.
2. A process according to Claim 1, in which the cooling of the reaction mixture is effected by passage through a heat exchanger.
3. A process according to Claim 1 or Claim

2, in which the polymerisation reaction is performed at a temperature of from 140°C to 300°C.

4. A process according to any preceding Claim, in which the polymerisation reaction is performed at a pressure of from 500 to 4,000 kg/cm².

5. A process according to any preceding Claim, in which ethylene is copolymerised with vinyl acetate, methyl methacrylate or styrene.

6. A process according to Claim 1, substantially as herein described in either of the Examples.

7. Ethylene homopolymers and copolymers when produced by the process of any preceding Claim.

8. Moulded articles produced from a polymer according to Claim 7.

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