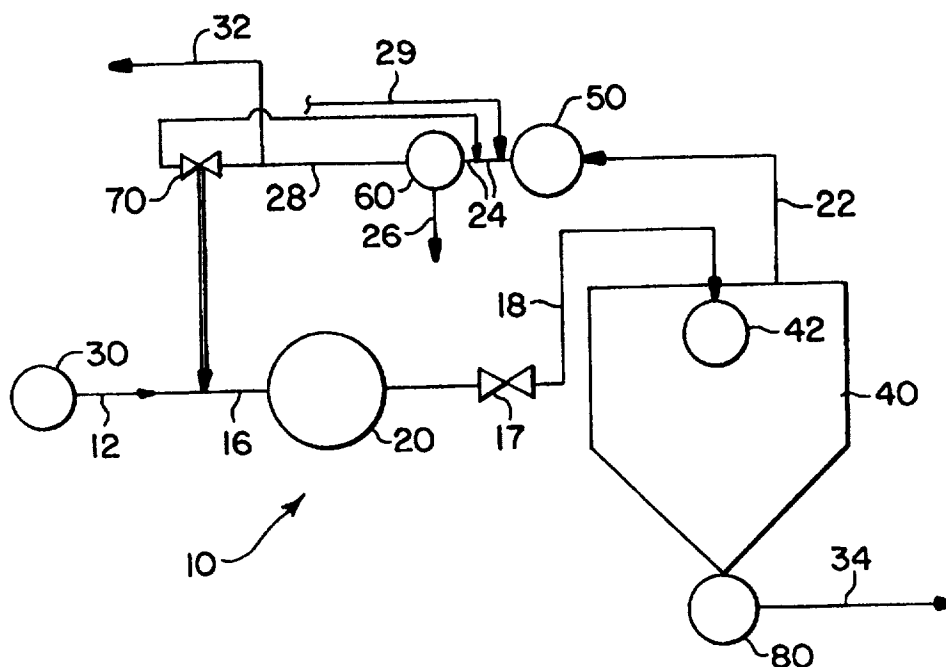




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(60) Parent Application or Grant (63) Related by Continuation US 08/685,314 (CIP) Filed on 23 July 1996 (23.07.96)			
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(54) Title: POLYMER DEVOLATILIZATION



(57) Abstract

A process has been invented for removing contaminants (including solvent) from a flowing polymer, the process, in one aspect, including dissolving a sparingly soluble stripping agent into a flowing polymer, the sparingly soluble stripping agent stripping contaminants from the flowing polymer creating a mixture of contaminants and sparingly soluble stripping agent, which flows out from the flowing polymer, and separating the mixture from the polymer. In one aspect, recyclable sparingly soluble stripping agent is recovered and re-used.

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POLYMER DEVOLATILIZATION

This invention is directed to polymer devolatilization and, in certain aspects, to the use of a sparingly soluble stripping agent to significantly reduce the level of volatile contaminants in a flowing polymer.

10

Ideally solution polymerization would result in one hundred percent complete polymerization of monomer. In actual practice complete polymerization is never achieved and the resulting polymer has a variety of volatile contaminants, including unreacted monomer, solvent, and oligomers. Typically such contaminants are volatile relative to the polymer which is nonvolatile.

15

Residual monomer and other volatile contaminants in a product polymer may have an undesirable effect on polymer quality.

20

There has long been a need for improved methods for more efficient and effective polymer devolatilization. There has long been a need for such a method which avoids problems associated with the use of water as a stripping agent. There has long been a need for such a process which achieves very low volatile levels in a relatively short time, and with relatively small power requirements.

25

The present invention discloses processes for removing volatile contaminants from a flowing polymer. In one aspect the process includes making a flowing polymer-solvent solution and then dissolving therein a sparingly soluble stripping agent ("SSSA") (for example, but not limited to, an agent such as nitrogen, ethylene, methane, hydrogen, or carbon dioxide; and, preferably an agent with certain solubility level, for example with a weight fraction Henry's constant of more than 500 ATM (51 MPa)). The solubility of a gas in a polymer at pressure P is conveniently expressed by the weight-fraction Henry's constant

30

$$H^{(P)} = \lim_{w_1 \rightarrow 0} (f_1 / w_1)$$

35

where subscripts 1 and 2 represent solute and polymer, respectively; f stands for fugacity; and w is the weight fraction in the polymer phase at the process temperature. Stripping creates a mixture of SSSA, solvent, and volatile contaminants stripped from the flowing polymer-solvent solution by the SSSA. Then the mixture is separated from the flowing polymer. Preferably the combined polymer, solvent and SSSA are single phase. In certain aspects the

5 polymer is polystyrene, styrene copolymers, ethylene styrene interpolymers, low density polyethylene (LDPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), or ethylene alpha-olefin interpolymers.

In one aspect, the SSSA is dissolved into the flowing polymer stream under sufficient controlled pressure; for instance, 250 pounds per square inch gauge (psig (1.7 MPa)) or
10 greater and, in certain aspects, 500 psig (3.4 MPa) or greater, and, for instance, up to 4500 psig (31 MPa).

In one aspect, polymer is foamed under controlled vacuum conditions to facilitate separation from the mixture of SSSA and contaminants; for example, but not limited to 5 to 25 mm mercury (0.7 to 3.3 kPa). Foaming may be accomplished with any known effective
15 foaming device such as a flashing heat exchanger.

Further treatment of the mixture of SSSA and contaminants results in an amount of recyclable SSSA. For example, the mixture is cooled and compressed and then contaminants are condensed to recover reusable SSSA which is reinjected into contaminated flowing polymer. Thus, problems associated with remixing of contaminated SSSA with polymer are
20 avoided.

In certain preferred processes according to the present invention, the level of volatile contaminants in an amount of polymer is reduced to at most one hundred parts per million by weight and, in certain aspects, to at most fifty parts per million by weight, and, in other embodiments, to at most eight parts per million by weight. In certain preferred processes,
25 such contaminant levels are achieved in a relatively short time; in one aspect in at most about fifteen minutes residence time in a mixer; or in sufficient time to dissolve the SSSA and polymer. In certain aspects the solution is effected in seven minutes or less.

In certain preferred processes according to the present invention, the SSSA is broken into relatively small droplets (for example droplets with a largest dimension equal to or less
30 than one millimeter, preferably equal to or less than 0.4 mm, more preferably equal to or less than 0.1 mm) to facilitate dissolution in the polymer. Also, it is possible to use relatively smaller amounts of SSSA (as compared to processes using water) to achieve similar or better polymer contaminant levels, due, in part, to solution of SSSA in the polymer.

In one aspect, a process according to the present invention is a "falling strand" or
35 "falling foam" operation requiring no moving parts in a devolatilizer vessel, producing a significant reduction in power requirements as compared to certain stripping extruders and requiring reduced capital outlay. Since water is not used, no additional clean-up is required to

5 strip residual organic contaminants from water. In one aspect, SSSA and contaminated polymer are preflushed (within the vessel and/or immediately prior to the vessel) producing a two-phase mixture which is introduced into a devolatilizer vessel.

In one aspect of processes according to the present invention, SSSA's are employed for the dual purpose of increasing polymer surface area (promoting maximum mass transfer) and of reducing partial pressure of residual volatiles to maximize thermodynamic driving
10 force for the separation of volatiles from the polymer.

The present invention, in certain aspects, is directed to the production of a variety of polymers, including but not limited to thermoplastic polymer compositions containing polystyrene, polyethylene, acrylic plastic resins, epoxy resins, polypropylene, and,
15 polyolefins. In certain aspects useful stripping agents include, but are not limited to nitrogen, ethylene, methane, carbon dioxide, hydrogen, and hydrocarbons having one or two carbon atoms, and mixtures of two or more of these.

It is, therefore, an object of at least certain preferred embodiments of the present invention to provide:

20 New, useful, unique, efficient, nonobvious methods for devolatilizing a polymer with a sparingly soluble stripping agent;

Such a method in which SSSA separated from a treated polymer is recycled to treat additional polymer;

Such a method in which polymer volatile contaminant levels are reduced to fifty parts
25 per million or less, and preferably to twenty-five parts per million or less, and most preferably to eight parts per million or less;

Such a method in which at least 99 percent of the contaminants, including solvent and SSSA, are removed from the polymer - solvent solution;

Such a method that avoids the problems associated with the use of water as a stripping
30 agent;

Such methods in which a relatively small amount of stripping agent is needed;

Such a method in which the SSSA both increases surface area of flowing polymer and reduces partial pressure of solvent to facilitate decontamination; and

Such a method in which low levels of polymer volatile contaminants are achieved
35 without significant polymer degradation, with low shear heating, low work input into the polymer, and in a relatively short time, for instance, fifteen minutes or less.

5 Certain embodiments of this invention are not limited to any particular individual feature disclosed here, but include combinations of them distinguished from the prior art in their structures and functions. Features of the invention have been broadly described so that the detailed descriptions that follow may be better understood, and in order that the contributions of this invention to the arts may be better appreciated. There are, of course,
10 additional aspects of the invention described below and which may be included in the subject matter of the claims to this invention. Those skilled in the art who have the benefit of this invention, its teachings, and suggestions will appreciate that the conceptions of this disclosure may be used as a creative basis for designing other structures, methods and systems for carrying out and practicing the present invention. The claims of this invention are to be read
15 to include any legally equivalent devices or methods which do not depart from the spirit and scope of the present invention.

A more particular description of embodiments of the invention briefly summarized above may be had by references to the embodiments which are shown in the drawings which form a part of this specification. These drawings illustrate certain preferred embodiments and
20 are not to be used to improperly limit the scope of the invention which may have other equally effective or legally equivalent embodiments.

Fig. 1 is a schematic illustration of a system for practicing a method according to the present invention.

Fig. 1 shows a system 10 useful in a method according to the present invention for
25 producing a product polymer (for instance, polystyrene or polyethylene, such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), or high density polyethylene (HDPE)). Polymer under pressure (for example 1500 psig (10.3 MPa)) flows in a line 12 to contact in a line 16 a sparingly soluble stripping agent ("SSSA") flowing in a line 14. A resulting mixture of polymer and SSSA flows in a line 16 into and is sheared in a mixer 20
30 (which may be a commercially available mechanical mixer or static mixer) to produce bubbles of SSSA in the mixture, with such bubbles preferably having a largest dimension equal to or less than 1 mm. A number of high pressure injection valves may be used at the junction of the lines 12 and 14 to more evenly distribute SSSA radially into the polymer.

A pressure source 30 (for instance, a pump) and a control valve 17 control the
35 pressure (for instance, to pressures between 1500 and 500 psig (10.3 and 3.4 MPa)) so that, preferably, between about 0.05 to about 0.5 weight percent of the SSSA is forced into solution in the flowing polymer. Preferably the residence time of the polymer between the

5 point at which it is mixed with the SSSA and the control valve 17 is between one minute and thirty minutes. Initially the control valve 17 is opened and the polymer mixed with SSSA flows through line 18 into a vessel 40 through a distributor 42. Vessel 40 is preferably operated at a pressure less than 50 mm Hg absolute (6.7 kPa) which is maintained by a vacuum system or by a valve in the line 22. A vacuum system 50 with a compressor 60
10 removes vapor containing SSSA and volatiles from the vessel 40 through a line 22. The removed vapor is introduced through a line 24 to the compressor 60. Volatile contaminants condensed in the compressor 60 through a line 26. Compressed SSSA formed by compression in the compressor is forwarded from the compressor via flow line 28 and the majority of the SSSA may be recycled back into the flowing polymer via the lines 28 and 14.
15 Injection pressure is controlled by a two-way valve 70 in line 14. This may feed back to the suction of the compressor.

Product polymer is removed from the vessel 40 by a pump 80 and flows out in a flow line 34.

20 When the product polymer is LLDPE and the SSSA is preferably nitrogen, and the amount of nitrogen is preferably less than or equal to 0.5 weight percent so that foaming of the majority of the polymer-SSSA mixture occurs in the distributor 42. SSSA contaminants (and a small amount of SSSA) exit through a line 32. Fresh SSSA (preferably oxygen-free) may be added as needed in a line 29.

Table I presents data from the production of LLDPE using nitrogen as the SSSA. In
25 Table One, "Melt Temp °C" is the temperature of the polymer flowing in line 12, Fig. 1. "Feed Solvent Conc (ppm)" is the level, in parts per million by weight, of undesirable volatile contaminants (for example but not limited to a mixture of C₈ and C₉ alkanes) in the line 12. "Product Solvent Conc (ppm)" is the level of all volatile contaminants in the line 34. "Injection Point Pressure psig (MPa)" is the pressure in line 16 at the mixture point. "Control
30 Point Pressure psig (MPa)" is the pressure in psig (MPa) immediately in front of the valve 17. "N₂ stripping Level wt percent" is the weight percent of nitrogen in line 16. "Vessel Pressure mm Hg absolute (kPa)" is pressure in mm of Hg absolute (kPa). Table I indicates that 99 percent or more of the volatile contaminants (including solvent) are removed from the flowing polymer-agent solution.

TABLE I

	Melt Temp C°	Feed Solvent Conc (ppm by weight)	Product Solvent Conc (ppm by weight)	Injection Point Pressure Psig (MPa)	Control Point Pressure Psig (MPa)	N ₂ Stripping Level Wt percent in polymer	Vessel Pressure mm Hg Absolute (kPa)
1.	225° C	1100	11	1629 (11.23)	767 (5.29)	0.5 percent	11.2 mm (1.49)
2.	225° C	1100	32	1587 (10.94)	753 (5.19)	0.5 percent	28.2 mm (3.76)
3.	225° C	1100	32	1561 (10.76)	740 (5.10)	0.75 percent	30.1 mm (4.01)
4.	225° C	1100	8	1547 (10.67)	738 (5.09)	1.0 percent	10.8 mm (1.44)
5.	225° C	1100	32	905 (6.24)	473 (3.26)	0.75 percent	20.7 mm (2.76)
6.	225° C	1100	29	635 (4.38)	293 (2.02)	0.5 percent	10.7 mm (1.43)
7.	225° C	1100	67	673 (4.64)	308 (2.12)	0.5 percent	27.1 mm (3.61)
8.	225° C	1100	64	625 (4.31)	285 (1.97)	1.0 percent	30.6 mm (4.08)
9.	225° C	1100	25	596 (4.11)	270 (1.86)	1.0 percent	10.9 mm (1.45)
10.	225° C	1100	41	1605 (11.07)	721 (4.97)	0.3 percent	15.8 mm (2.11)
11.	225° C	1100	83	1520 (10.48)	699 (4.82)	0.2 percent	37.4 mm (4.99)

5 In conclusion, therefore, it is seen that the present invention and the embodiments disclosed herein and those covered by the appended claims are well adapted to carry out the objectives and obtain the ends set forth. Certain changes can be made in the subject matter without departing from the spirit and the scope of this invention. It is realized that changes are possible within the scope of this invention and it is further intended that each element or
10 step recited in any of the following claims is to be understood as referring to all equivalent elements or steps.

15

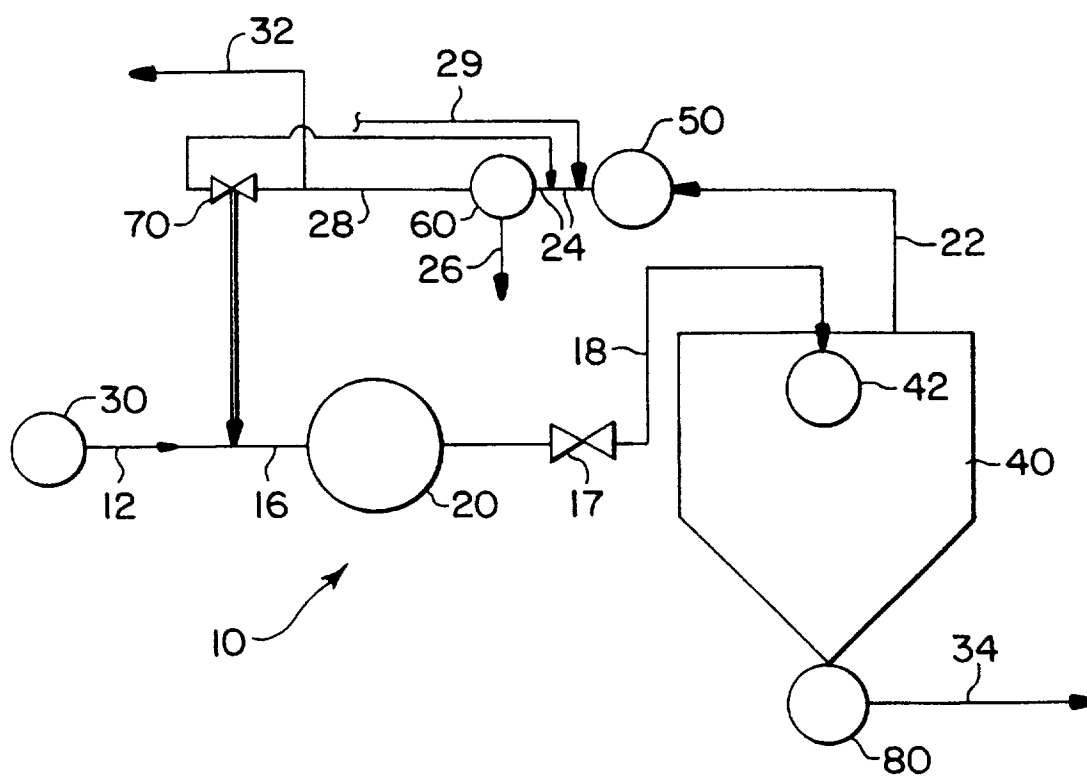
- 5 1. A process for removing contaminants from a flowing polymer, the process characterized by:
- making a flowing polymer-solvent solution,
- dissolving a sparingly soluble stripping agent into the flowing polymer-solvent solution,
- 10 stripping contaminants from the flowing polymer-solvent solution with the sparingly soluble stripping agent, creating a mixture of contaminants including solvent and sparingly soluble stripping agent, the mixture flowing out of the flowing polymer producing a product polymer, and
- separating the mixture from the product polymer.
- 15 2. The process of claim 1 further characterized by:
- separating recyclable sparingly soluble stripping agent from the mixture, and
- recycling the recyclable sparingly soluble stripping agent for dissolution into flowing polymer.
- 20 3. The process of claim 1 or claim 2 further characterized by foaming the polymer-solvent solution with sparingly soluble stripping agent therein to facilitate separation of the sparingly soluble stripping agent and other contaminants.
- 25 4. The process of any of claims 1-3 conducted in a falling foam devolatilizer system in a devolatilizer vessel without moving parts therein.
5. The process of claim 4 further characterized by preflashing the polymer solvent solution prior to introducing it into the devolatilizer vessel.
- 30 6. The process of any of the preceding claims wherein the contaminants including solvent are reduced in the polymer to a level of at most 50 parts per million by weight.
7. The process of any of the preceding claims wherein initial solvent concentration is at least 1000 parts per million by weight and the process produces a product polymer
- 35 with a solvent concentration of at most 50 parts per million by weight.

- 5 8. The process of any of the preceding claims wherein the sparingly soluble stripping agent is an agent with a Henry's Constant of more than 500 atmospheres (51MPa).
9. The process of any of the preceding claims wherein the polymer is selected from the group consisting of polystyrene, ethylene styrene interpolymers, and polyethylene and the sparingly soluble stripping agent is selected from the group consisting of nitrogen, ethylene, methane, and hydrogen.
- 10 10. The process of claim 9 wherein the polymer is polyethylene and the process is conducted at a temperature between 150 and 300 degrees C, and wherein the stripping of contaminants occurs in at most 15 minutes.
- 15 11. The process of claim 3 conducted under a vacuum ranging between 5 and 25 mm Hg (0.7 and 3.3 kPa).
- 20 12. The process of any of the preceding claims wherein the sparingly soluble stripping agent is bubbled, producing bubbles with a largest dimension equal to or less than 1 millimeter, to facilitate dissolution in the flowing polymer.
13. The process of claim 4 or claim 5 wherein the flowing polymer-solvent solution having a residence time between a point of polymer-solvent contact and introduction into the devolatilizer vessel of at most thirty minutes.
- 25 14. The process of claim 4, 5, or 13 wherein the devolatilizer vessel operates at less than 500 mm Hg absolute (67 kPa).
- 30 15. A process for removing contaminants from a flowing polymer, the process comprising making a flowing polymer-solvent solution, dissolving a sparingly soluble stripping agent into the flowing polymer-solvent solution, stripping contaminants from the flowing polymer-solvent solution with the sparingly soluble stripping agent, creating a mixture of contaminants including solvent and sparingly soluble stripping agent, the mixture flowing out of the flowing polymer
- 35

- 5 producing a product polymer, and
 separating the mixture from the product polymer,
 wherein initial solvent concentration is at least 1000 parts per million by
weight and the process produces a product polymer with a solvent concentration of at
most 50 parts per million by weight,
- 10 separating recyclable sparingly soluble stripping agent from the mixture, and
 recycling the recyclable sparingly soluble stripping agent for dissolution into
flowing polymer,
 wherein the sparingly soluble stripping agent is an agent with a weight fraction
Henry's Constant of more than 500 atmospheres (51 MPa),
- 15 wherein the sparingly soluble stripping agent is bubbled, producing bubbles
with a largest dimension equal to or less than 1 millimeter, to facilitate dissolution in
the flowing polymer, and
 wherein the polymer is selected from the group consisting of polystyrene,
ethylene styrene interpolymers, and polyethylene; and the sparingly soluble stripping
agent is selected from the group consisting of nitrogen, ethylene, methane, and
20 hydrogen.

1 / 1

FIG. 1



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 97/12288

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 583 082 A (NOVACOR CHEM INT) 16 February 1994 see abstract; claims; figure; examples see page 2, line 29 - line 35 see page 2, line 52 - page 4, line 46 ---	1,3-7, 9-14
X	EP 0 584 926 A (NOVACOR CHEM INT) 2 March 1994 see abstract; claims; examples; tables ---	1,3-7
X	US 3 987 235 A (FUJIMOTO SUMIO) 19 October 1976 see abstract; claim 1; tables see column 2, line 9 - line 62 ---	1,3
A	US 4 501 885 A (SHERK FRED T ET AL) 26 February 1985 see abstract; figure ---	1



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Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Intern .ial Application No

PCT/US 97/12288

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 798 314 A (NOVA CHEMICALS INTERNATIONAL S) 1 October 1997 see abstract; claims; examples; table 1 see page 2, line 46 - page 4, line 36 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12288

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EP 0798314 A	01-10-97	NONE	