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(54) Titre : METHODE D'AMELIORATION DE LA STABILITE THERMIQUE OXYDATIVE DE POLYMERES D'ETHYLENE
(54) Title: METHOD OF IMPROVING THE OXIDATIVE THERMAL STABILITY OF ETHYLENE POLYMERS

(57) **Abrégé/Abstract:**

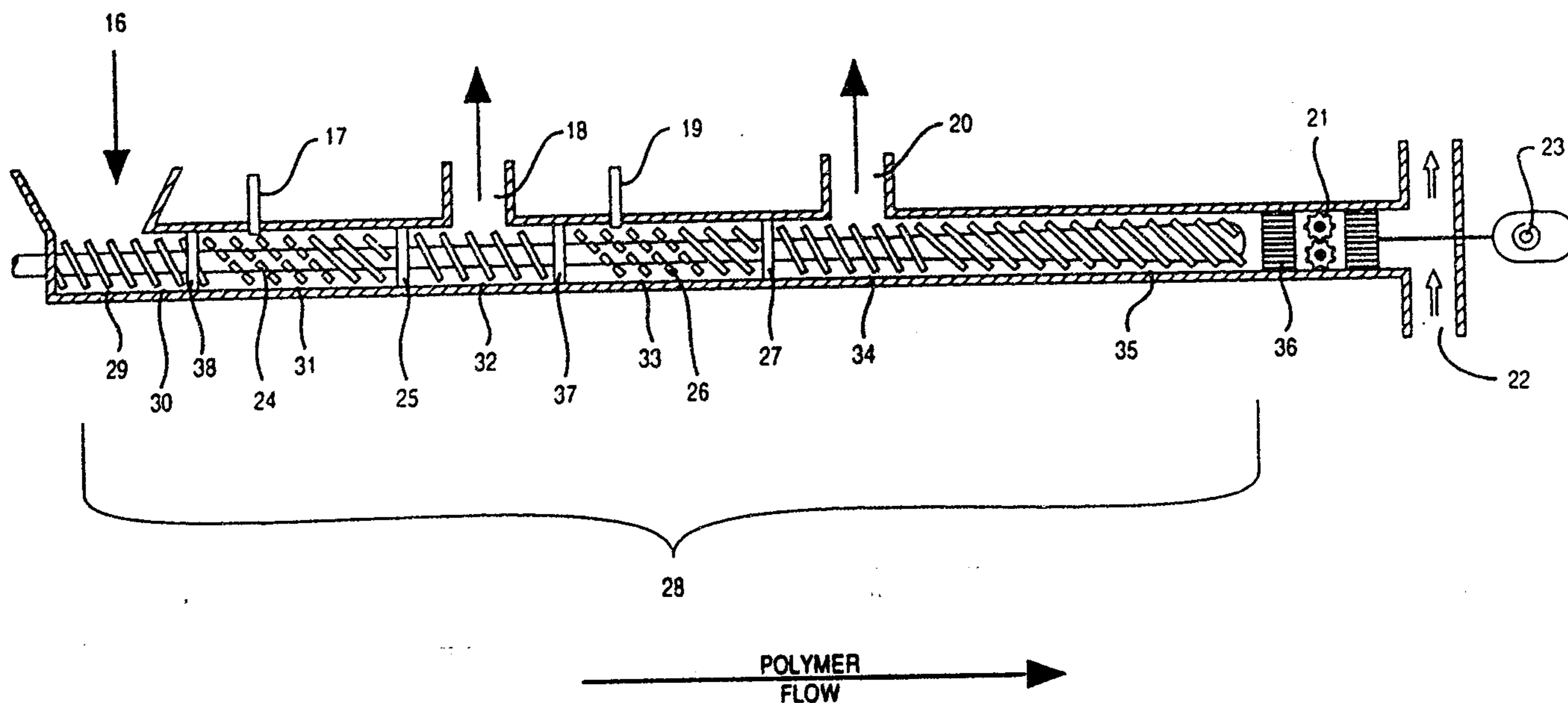
A method of improving the oxidative thermal stability of ethylene polymers is disclosed. The method comprises removing residual unreacted monomer(s), solvent and thermally unstable species from the polymer using a stripping agent and subsequent devolatilization. The resulting polymer is characterized by having an oxidative exotherm of not more than 50 percent of the original polymer, as measured by differential scanning calorimetry, as well as improved taste and odor properties.



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<p>(21) International Application Number: PCT/US92/01720 (22) International Filing Date: 4 March 1992 (04.03.92) (30) Priority data: 663,995 4 March 1991 (04.03.91) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: HUGHES, Morgan, M. ; 708 Milton, Angleton, TX 77515 (US). ROWLAND, Michael, E. ; 402 Daffodil, Lake Jackson, TX 77566 (US). STRAIT, Chad, A. ; 211 Basswood, Lake Jackson, TX 77566 (US). (74) Agent: KRUPP, Stephen, P.; The Dow Chemical Company, Patent Department, Building B-1211, Freeport, TX 77541-3257 (US).</p>		<p style="text-align: center; font-size: 1.5em; font-weight: bold;">2081105</p> <p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: METHOD OF IMPROVING THE OXIDATIVE THERMAL STABILITY OF ETHYLENE POLYMERS



(57) Abstract

A method of improving the oxidative thermal stability of ethylene polymers is disclosed. The method comprises removing residual unreacted monomer(s), solvent and thermally unstable species from the polymer using a stripping agent and subsequent devolatilization. The resulting polymer is characterized by having an oxidative exotherm of not more than 50 percent of the original polymer, as measured by differential scanning calorimetry, as well as improved taste and odor properties.

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METHOD OF IMPROVING THE OXIDATIVE THERMAL STABILITY OF
ETHYLENE POLYMERS

5 This invention relates to a method of improving the taste and odor properties and the oxidative thermal stability of thermoplastic homopolymers and/or interpolymers of ethylene and at least one comonomer in the presence of oxygen. The method comprises removing residual unreacted monomer(s), solvent and thermally unstable species. The resultant polymer is more oxidatively thermally stable and has an oxidative exotherm of not more than about 50 percent of the oxidative exotherm of the first polymer, as measured by differential scanning calorimetry. This method of improving oxidative thermal stability is especially effective for ethylene/acrylic acid interpolymers.

15 Volatile components can be removed from thermoplastic polymers in a variety of ways. One traditional method is extrusion devolatilization using vacuum equipped extruders. The use of vacuum alone, however, is generally insufficient to remove residual monomer and other volatiles from the molten polymer to sufficiently improve the oxidative thermal stability of the polymer. Residual monomer and volatiles also contribute to odor deficiencies in the polymers, a fact

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which is particularly important when the polymers are used in food storage applications.

5 US-A-4,094,942 (Nakai et al.) discloses a method for removing unreacted monomer from an ethylene polymer during pelletization by injecting water or steam into the nose portion of the mixing section of an extruder, intermixing the polymer with the water or steam and removing the unreacted monomer and water or steam using vacuum of 500 mm Hg absolute or less. Nakai
10 et al. teach that products thus produced have increased commercial value with respect to odor, but does not teach or suggest how to improve the taste performance or thermal stability of the polymer.

15 Thermal stability of such polymers is important because they are thermally processed at elevated temperatures where they are subject to accelerated degradation and/or cross-linking, especially in the presence of oxygen. Oxidative thermal degradation of ethylene polymers can cause gel formation and loss of
20 physical properties in the processed polymers (e.g., poorer extrusion performance (such as neck-in and lower line speeds in extrusion coating) and reduced optical properties (such as haze and gloss or even color)), in addition to poor taste and odor properties from the
25 oxidative by-products formed during processing.

30 Anti-oxidants (e.g., organic phosphites and hindered phenols) have been added to various polymers, including polyethylene, to improve their thermal stability. However, anti-oxidants can have deleterious side effects, e.g., color formation, and they can also create food contact problems in themselves, thus negating the benefits.

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The taste and odor performance and the oxidative thermal stability of thermoplastic polymers continue to be areas of commercial need.

A method of improving the taste and odor
5 properties and the oxidative thermal stability of
thermoplastic ethylene polymers has now been discovered.
The novel method is characterized by removing residual
unreacted monomer or monomers, solvent and thermally
unstable species from a first ethylene polymer, thereby
10 forming a second more oxidatively thermally stable ethylene
polymer having an oxidative exotherm of not more than 50
percent of the oxidative exotherm of the first polymer, as
measured by differential scanning calorimetry.

The novel method is particularly useful in
15 improving the taste and odor properties and the oxidative
thermal stability of ethylene/acrylic acid interpolymers
which are widely used in the food packaging industry in
single or multilayer laminate film structures for food
wraps, beverage containers or condiment pouches.

20 In one aspect, the invention provides a method of
improving the taste and odor properties and the oxidative
thermal stability of a first thermoplastic ethylene polymer,
comprising removing residual unreacted monomer or monomers,
solvent and thermally unstable species from the first
25 polymer, thereby forming a second more oxidatively thermally
stable ethylene polymer having an oxidative exotherm of not
more than about 50 percent of the oxidative exotherm of the
first polymer, as measured by differential scanning
calorimetry, the method comprising: (a) feeding the first
30 polymer into a devolatilization extrusion system having at
least two vacuum zones and at least one barrel, the at least
one barrel having: i. a first vacuum zone, ii. at least one

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stripping agent injection port, iii. at least one confined mixing zone, and iv. a second vacuum zone, wherein the at least one confined mixing zone is situated immediately downstream of the at least one stripping agent injection port, the second vacuum zone is situated downstream of the first vacuum zone, and the first vacuum zone is designed to operate partially-filled with the first polymer; (b) conveying the first polymer through the extrusion system; (c) applying vacuum to the first vacuum zone; (d) concurrently injecting at least about 0.1 percent by weight based on total first polymer feed of at least one inert stripping agent to at least one stripping agent injection port; (e) mixing the first polymer and the inert stripping agent in the at least one confined mixing zone; (f) applying vacuum to the second vacuum zone; and (g) recovering the extruded second polymer.

Figure 1 schematically shows an extrusion system comprising two single screws operated in series which can be used to improve the oxidative thermal stability of ethylene polymers.

Figure 2 schematically shows a twin screw extrusion system which can be used to improve the oxidative thermal stability of ethylene polymers.

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Figure 1 schematically shows the cross-section of an extrusion system comprising two single screws useful for improving the oxidative thermal stability of ethylene polymers, as disclosed in Comparative Examples 1-3 and Example 4 below. In Figure 1, the polymer is fed into the feed section (1) of a first extruder system (13) and is melted and conveyed into zone 1 by a screw. The temperature of the entire extruder system is controlled by a hot oil system (not shown). Ethylene (as a stripping agent) is injected into zone 2 through a port (2). The melt temperature of the first extruder is monitored by means of a thermocouple (3). A transfer line (4) is used to transfer the polymer/ethylene mixture to a second extruder system (12). Preferably, the screw in the first extruder operates at slower revolutions per minute (rpm) than the screw in the second extruder such that the feed to the second extruder is less than that required to fill the screw channels (i.e., the second extruder is "starve fed"). A first injection port (5) is used to inject an additional stripping agent into the polymer melt stream in the second extruder and the polymer/ethylene/additional stripping agent mixture is conveyed into a mixing zone (10). The polymer/ethylene/additional stripping agent mixture is temporarily confined and controlled within the mixing area by a melt seal (11) and the compression side (up-stream side) of the screw. The polymer/ethylene/additional stripping agent mixture flows past the melt seal (11) and into the first vacuum port area (6). Vacuum is applied to the first vacuum port (6) and the unreacted monomer(s), residual solvent and residual thermally unstable species are partially devolatilized. The polymer then enters a second

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compression zone and an effective melt seal is formed. A second injection port (7) is utilized to inject a second stripping agent into the polymer melt stream, immediately followed by a mixing zone (14), and a melt seal (15). The polymer/additional stripping agent mixture is temporarily confined between the melt seal and the compression side (up-stream side) of the screw to ensure adequate mixing. A second vacuum port (8) is used to remove additional unreacted monomer(s), residual solvent and residual thermally unstable species, thus forming a polymer with greater oxidative thermal stability. A melt thermocouple (9) monitors the temperature of the exiting melt stream.

Figure 2 schematically shows the cross-section of one screw of a co-rotating twin screw extrusion system useful for improving the oxidative thermal stability of ethylene polymers, as disclosed in Comparative Examples 5-7 and Example 8. In Figure 2, the polymer is fed into the feed section (16) of a twin screw extruder system (28) and is melted and conveyed into zone 1 by two intermeshing screws. The temperature of each extruder zone is controlled by a temperature controller and resistance heaters (not shown). The temperature of the extruder is monitored by means of a series of thermocouples (29-36). Preferably, the feed to the extruder is controlled such that it is less than that required to fill the screw channels of the devolatilization zone (i.e., the vacuum zone of the extruder is partially filled). A first injection port (17) is used to inject a first stripping agent into the polymer melt stream and the polymer/stripping agent mixture is homogenized in a mixing zone (24). The mixed polymer/stripping agent mixture is temporarily confined and controlled within the mixing area by two melt seals

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(38, 25). The polymer/stripping agent mixture flows past the melt seal (25) and into the first vacuum port area (18). Vacuum is applied to the first vacuum port (18) and the unreacted monomer(s), residual solvent and residual thermally unstable species are partially devolatilized. A second melt seal (37) separates the first vacuum zone from a second stripping agent injection port (19). The second injection port (19) is utilized to inject a second stripping agent into the polymer melt stream, immediately followed by a mixing zone (33), and a melt seal (27). The mixed polymer/stripping agent mixture is temporarily confined and controlled within the mixing area by two melt seals (37, 27). The polymer/stripping agent mixture flows past the melt seal (27) and into the second vacuum port area (20). The second vacuum port (20) is used to remove additional unreacted monomer(s), residual solvent and residual thermally unstable species, thus forming the more oxidatively thermally stable polymer. A motor (not shown) drives a gear pump (21) which pumps the thermally stable polymer into a pelletizer (23) which chops the more thermally stable polymer into pellets. A liquid stream (22) cools and solidifies the polymer into pellets. The cooling liquid stream conveys the chopped/pelletized polymer to a separation point (not shown) where the liquid is separated from the polymer pellets and, optionally, is recycled back through the process.

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Detailed Description of the Invention

The thermoplastic ethylene polymers used in this invention can be homopolymers or interpolymers of ethylene with at least one comonomer, such as alpha-olefins or substituted alpha-olefins.

5 Homopolymers of ethylene for use in the present invention include homopolymers of ethylene made using a high pressure, free radical generating process and are generally known as low density polyethylene. Low
10 density polyethylene (LDPE), also known as High Pressure Polyethylene and historically as ICI-type polyethylene, is a branched ethylene homopolymer made using free radical polymerization techniques under high pressures. The ethylene is randomly polymerized into the polymer
15 chains and forms numerous branch points. The density of LDPE is dictated by the degree and length of branches and is typically in the range of 0.91-0.925 grams per cubic centimeter (g/cm^3). The molecular weight of the LDPE is indicated by melt index (MI) as measured using
20 ASTM D-1238 (E) ($190^\circ\text{C}/2.16$ kilograms). The MI range for LDPE for use in the present invention can be from 0.01 to 1000 grams/10 minutes, preferably 0.1 to 100.

25 Linear polyethylene is another type of polyethylene useful in practicing the present invention. Manufacture of linear polyethylene is disclosed, e.g., in US-A-4,076,698 and involves coordination catalysts of the "Ziegler" type or "Phillips" type and includes
30 variations of the Ziegler type, such as the Natta type. These catalysts may be used at very high pressures, but may also (and generally are) used at very low or intermediate pressures. The products made by these coordination catalysts are generally known as "linear" polymers because of the substantial absence of branched

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chains of polymerized monomer units pendant from the main polymer "backbone." Two types of linear polyethylene are also suitable for use in the present invention: linear high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

5 Linear high density polyethylene has a density from 0.941 to 0.965 g/cm³ while linear low density polyethylene typically has a density from 0.880 g/cm³ to 0.940 g/cm³. The density of the linear polyethylene is
10 lowered by polymerizing ethylene with minor amounts of alpha, beta-ethylenically unsaturated alkenes (i.e., alpha-olefins) having from 3 to 20 carbons per alkene molecule, preferably 4 to 8 (e.g., 1-butene, 4-methyl 1-pentene, 1-hexene) and most preferably 8 carbons per
15 alkene molecule (i.e., 1-octene). The amount of the alkene comonomer is generally sufficient to cause the density of the linear low density polymer to be substantially in the same density range as LDPE, due to the alkyl side chains on the polymer molecule, yet the
20 polymer remains in the "linear" classification. These polymers retain much of the strength, crystallinity, and toughness normally found in HDPE homopolymers of ethylene, but the higher alkene comonomers impart high
25 "cling" and "block" characteristics to extrusion or cast films and the high "slip" characteristic inherently found in HDPE is diminished.

The use of coordination-type catalysts for polymerizing ethylene into homopolymers, either in
30 solution or slurry type polymerization, or copolymerizing ethylene with higher alkenes to make copolymers having densities above 0.94 g/cm³ as defined in ASTM D-1248 (i.e., HDPE polymers) and/or for copolymerizing ethylene with higher alkenes to make copolymers having densities in the range of LDPE and

medium density polyethylene (i.e., LLDPE copolymers) is disclosed variously in, e.g., US-A-2,699,457; US-A-2,862,917; US-A-2,905,645; US-A-2,846,425; US-A-3,058,963 and US-A-4,076,698. Thus, the density of the linear polyethylene useful in the present invention is from 0.88 g/cm³ to 0.965 g/cm³.

The molecular weight of the linear polyethylene is indicated and measured by melt index according to ASTM D-1238, Condition (E) (i.e., 190°C/2.16 kilograms). The melt index of the linear polyethylene useful in the present invention can be from 0.001 grams/10 minutes (g/10 min) to 1000 g/10 min, preferably from 0.01 g/10 min to 100 g/10 min.

Ethylene can also be interpolymerized with substituted alpha-olefins by known techniques. The substituted alpha-olefins are a known class of polymerizable monomers that include, for example, ethylenically unsaturated carboxylic acids, esters and anhydrides (e.g., acrylic acid, methacrylic acid, maleic acid, maleic anhydride, methyl methacrylate, butyl acrylate), vinyl esters of alkanolic acids (e.g., vinyl acetate) and vinyl alcohol.

Interpolymers of ethylene and at least one ethylenically unsaturated carboxylic acid are particularly useful in the present invention. The term "interpolymer" means that ethylene is copolymerized with at least one comonomer. Thus the term "interpolymer" can indicate a copolymer, a terpolymer and so forth. Such interpolymers can be made by any of the known techniques. For example, US-A-4,599,392 (McKinney et al.) and US-A-4,248,990 (Pieski et al.) disclose processes for manufacturing random and non-random

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interpolymers, respectively, of ethylene/acrylic acid and ethylene/methacrylic acid. The amount of unsaturated carboxylic acid can vary from 0 (i.e., LDPE) to as high as 40 percent, dependent on the carboxylic acid used in the interpolymerization.

5 Ethylene/unsaturated carboxylic acid(s) interpolymers made by use of telogenic modifiers, as disclosed in US-A-4,988,781, are also suitable for practicing the present invention. The molecular weight of the
10 ethylene/unsaturated carboxylic acid interpolymers is indicated by melt index and is also measured by ASTM D-1238. Condition E (i.e., 190°C/2.16 kilograms). The melt index of the ethylene/unsaturated carboxylic acid interpolymers can be from 0.1 g/10 min to 3000 g/10 min.
15 preferably from 1 g/10 min to 300 g/10 min.

Ionomers of various interpolymers (e.g., metal ionomers of ethylene/acrylic acid or
20 ethylene/methacrylic acid interpolymers) are also within the scope of this invention. US-A-3,404,134 (Rees), for example, discloses a process for cross-linking polymers thereby creating ionomers which are useful in the present invention. In one embodiment of the present
25 invention, aqueous solutions of metal hydroxides (e.g., sodium hydroxide or potassium hydroxide), nitrogenous bases (e.g., ammonium hydroxide), or water-soluble strong base organic amines (e.g., mono-, di- and tri-
30 methyl amines) can be added to a devolatilizing extruder in a first injection zone and mixed with ethylene/unsaturated carboxylic acid(s) interpolymers to effectively function as both a stripping agent and neutralizing/ionizing agent. The water is subsequently stripped under vacuum thus removing residual unreacted

monomer or monomers. solvent and thermally unstable species forming a more thermally stable ionomer.

5 Additives can be included in the interpolymers useful in practicing the present invention. but are preferably added after forming the more thermally stable polymer. These additives include pigments (e.g., titanium dioxide), wetting agents, fillers, slip and anti-block compounds. Anti-oxidants can also be included in the interpolymers, but they need not be present for the present invention to be effectively used.

15 Solvents (or diluents) can be and generally are used in both the high pressure process (e.g., LDPE) or the low pressure process (e.g., LLDPE) to make the ethylene polymers. Some of the typical solvents used during interpolymerization include: paraffinic hydrocarbons such as pentane, hexane, heptane, 20 cyclohexane, branched alkanes, alkenes, and alkynes (plus their various isomeric forms); or aromatic hydrocarbons such as benzene, toluene, chloro-substituted aromatic hydrocarbons such as dichlorobenzene; or polar solvents such as alcohols, 25 etners, ketones and esters; or various naphtha distillates such as those sold under the trademark ISOPAR by EXXON. These solvents are difficult to remove from the interpolymer, even after pelletization. Residual monomer (e.g., ethylene and/or acrylic acid) 30 can also be retained in the interpolymer. Thermally unstable species (e.g., free radical species) can react with oxygen and cause taste problems. Thermally unstable species, as defined herein, are compounds which thermally degrade in the presence of oxygen at elevated temperatures (i.e., at polymer melt processing

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temperatures). These semi-volatile components can cause taste and/or odor problems in fabricated parts made from the interpolymers, depending on the application, and surprisingly, can also cause the interpolymers to have less oxidative thermal stability.

5

Removal of the residual unreacted monomer or monomers, solvent and thermally unstable species to form the oxidatively thermally stable interpolymers of the present invention can be accomplished by any conventional means.

10

Batch operation includes such pieces of equipment as a Banbury mixer, or a roll mill. In batch operation, a specific amount of polymer and stripping agent(s) is placed into the equipment. The polymer is then melted and fluxed or mixed for a pre-designated amount of time. The equipment is vented periodically to allow for devolatilization. The sample is then removed for processing into pellets or other forms for final usage. Steam can be added during this processing to aid in devolatilization.

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Continuous devolatilization can be performed on a single or twin screw extruder as shown in the examples. Other continuous devolatilization equipment includes Bolling Mixtrumat™ continuous process or Farrel Discpack™ and other types of continuous extrusion equipment which can be fitted with vacuum ports/adapters. Many of these systems can be fitted with a mixing section prior to devolatilization to improve the contact of the stripping agent and the interpolymers. The devolatilization occurs by producing

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a thin melt which is continuously regenerating a new surface that is exposed to a vacuum.

A particularly effective embodiment for forming more oxidatively thermally stable ethylene polymers of the present invention comprises the consecutive steps of:

(a) feeding a first ethylene polymer to an extruder comprising an optional stripping agent injection zone, an optional confined mixing zone, at least a first partially filled vacuum zone, at least a first stripping agent injection zone, at least one first confined mixing zone, at least a second partially filled vacuum zone;

(b) melting the first ethylene polymer;

(c) applying vacuum to the first partially filled vacuum zone;

(d) cocurrently injecting at least 0.1 percent by weight, based on total ethylene polymer feed, of at least one stripping agent to the first stripping agent injection zone;

(e) mixing the stripping agent with the first ethylene polymer in the first confined mixing zone;

(f) applying vacuum to the second partially filled vacuum zone; and

(g) recovering the second more oxidatively thermally stable ethylene polymer.

The stripping agents useful in the present invention are preferably inert with respect to the interpolymerization process. When forming oxidatively thermally stable ionomers from interpolymers of ethylene and at least one unsaturated carboxylic acid, however, the stripping agent should react with the unsaturated carboxylic acid. The stripping agent(s) should also

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have a vapor pressure sufficient to either be a gas or form gas bubbles at the devolatilizing operating conditions (i.e., when the interpolymer is molten). Preferably, the stripping agent(s) is a light hydrocarbon (e.g., ethylene, propylene or isobutane).
5 water, steam, alcohol, carbon dioxide and/or nitrogen. Super critical fluids (e.g., super critical carbon dioxide) are also useful as stripping agents for use in the present invention. Aqueous solutions of alkali
10 metal hydroxides (e.g., sodium hydroxide), nitrogenous bases (e.g., ammonium hydroxide), water-soluble organic strong base organic amines (e.g., mono-, di- and tri-methyl amines) are particularly effective when
15 simulataneously devolatilizing ethylene/unsaturated carboxylic acid interpolymers while forming the corresponding ionomer. Mixtures of stripping agents are also useful in the present invention. The stripping agent should be used in amounts effective to remove
20 enough residual unreacted monomer(s), solvent and stripping agent(s) such that the oxidative exotherm of the interpolymer or ionomer is reduced by at least 50 percent.

25 The devolatilization of the interpolymers is preferably performed using a single or twin screw system with water injection as described in US-A-4,094,942, with the added feature of using a screw which has a
30 surface renewal ratio of at least about two pounds per square meter or less, preferably about one pound per square meter or less. When creating a more thermally stable interpolymer made using a high pressure process (e.g., LDPE or ethylene/acrylic acid interpolymers) and the devolatilizing screw is installed in-line with the process (i.e., before the pelletization step), the

extruder(s) vacuum devolatilization zone(s) should be partially-filled (i.e., the flow of the interpolymer is restricted such that the channels of the screw are partially filled; this can be accomplished, e.g., using a device which controls/restricts flow, such as a slide valve or a gear pump). The extruder comprises an optional stripping agent injection zone, an optional confined mixing zone, at least a first partially filled vacuum zone, at least a first stripping agent injection zone, at least one first confined mixing zone, and at least a second partially filled vacuum zone. Preferably, a vacuum of 100 mm Hg absolute or less is applied to the first vacuum zone, at least one inert stripping agent is cocurrently injected at a concentration of at least 0.1 percent by weight based on total interpolymer feed to the first stripping agent zone, and a vacuum of 100 mm Hg absolute or less is applied to the second vacuum zone. The stripping agent should form small gas bubbles when in the vacuum zone to effectively strip the interpolymer of volatiles thereby forming the more oxidatively thermally stable interpolymer.

The screw channels of the vacuum zone should be partially filled with the stripping agent/polymer mix, creating frequent polymer surface renewal (i.e., a relatively low specific surface renewal ratio, measured in pounds of polymer per square meter of surface) which is exposed to the vacuum. Partially filling each vacuum zone of the extruder such that each vacuum zone has a specific surface renewal ratio of two pounds per square meter or less, preferably one pound per square meter or less, is especially effective when used in a devolatilizing extruder vacuum zone.

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Partially filling the channels can be controlled in different ways, including modifying the geometry of the vacuum zone. This can be accomplished by increasing flight depth, and/or by simultaneously increasing flight pitch while increasing the number of flight starts (i.e., using a multi-start screw design in the region of vacuum).

The stripping agent/polymer mix should be confined to adequately mix the stripping agent with the polymer. Confinement of the stripping agent/polymer mix can be accomplished using various means, such as by using melt seals (i.e., blisters) on single or twin screw extruder systems, reverse flights on a twin screw extruder system, by incorporating high pressure compression zones along the screw, or by using axial, radial, and/or trans-axial throttle valves on single or twin screw extruder systems.

To be effective in the present invention, the devolatilization method used should remove enough residual unreacted monomer(s), solvent, thermally unstable species and stripping agent(s) from the polymer such that the oxidative exotherm of the interpolymer is reduced by at least 50 percent.

The more oxidatively thermally stable polymers produced by the present invention are useful in a variety of thermal forming processes, including molding techniques (e.g., injection molding, rotomolding and blow molding), film forming techniques (e.g., cast, blown and extrusion coating) and fiber forming techniques. The oxidatively thermally stable polymers and/or ionomers have particular utility when they are used as at least one layer of a multilayered film

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structure having an inner layer and an outer layer, e.g., a food package. The ionomers have particular utility when they are used in skin packaging.

Comparative Examples 1-3 and Example 4

5 An ethylene/acrylic acid interpolymer having a melt index of 10 grams/10 minutes and about 10 percent by weight of interpolymer of acrylic acid was made according to the technique described in US-A-4,599,392. This interpolymer was pelletized for later use in a stripping
10 experiment.

The stripping experiment was performed by feeding ethylene/acrylic acid interpolymer pellets into a first 90 mm single screw extruder having a length/diameter (L/D) ratio of 25 and a stripping agent injection port at a rate
15 of 350 pounds/hour (160 kg/hour). This screw was operated according to the conditions outlined in Table 1:

TABLE 1

Extrusion Conditions for the First Screw

Extruder Zone 1 (°C)	220
Extruder Zone 2 (°C)	220
Transfer Line (°C)	220
Melt Temp. (°C)	210
Extruder rpm	95
Ethylene injection (weight percent, based on polymer fed)	0.2

20 The molten ethylene/acrylic acid interpolymer was conveyed to a second 90 mm single screw extruder

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having L/D of 40, two stripping agent injection ports and two vacuum ports operated according to the conditions described in Table 2:

TABLE 2
Extrusion Conditions for the Second Screw

5	Extruder Zone 1 (°C)	220
	Extruder Zone 2 (°C)	220
	Water Injection Zone 1 (weight percent)	0.5
10	Melt Temp. (°C)	220
	Water Injection Zone 2 (weight percent)	0.5
	Extruder rpm	130
15	Vacuum Zone 1 (mm Hg)	45 (60 mbars)
	Vacuum Zone 2 (mm Hg)	30 (40 mbars)

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The screws were operating at differing speeds in order that the devolatilizing screw was only partially filled. The second screw was equipped with two injection ports and two vacuum ports along its length, as shown in Figure 1. Each injection section of the screw itself was equipped with two melt seals (i.e., a "blister" or restrictor ring) to confine the mixing zone. The melt seals confine the stripping agent to the area of the mixing zone to ensure that the stripping agent and the interpolymer were well mixed prior to devolatilization.

The interpolymer was extruded through the system described above, with varying degrees of stripping and devolatilization. Table 3 describes these differences:

Table 3

Example	Interpolymer processing description
1*	Base interpolymer without further processing
2*	Extruded interpolymer without stripping or vacuum
3*	Extruded interpolymer with vacuum only
4	Extruded interpolymer with ethylene injection, dual water stripping injection and dual vacuum zones

*Comparison example only, not an example of the invention.

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Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was used to determine the thermal activity of resin samples in the presence of oxygen. For each sample, a known amount of resin (approximately 5 milligram) was placed in a very small glass ampule. The bottom of the glass ampule was cooled with liquid nitrogen and the top of the ampule was sealed. The sealed ampule containing the resin sample was placed in the DSC sample chamber at room temperature. The DSC sample and reference chambers were then heated at a constant rate of 10°C per minute to a final temperature of 300°C. The thermal activity of the sample resin was continuously monitored versus the reference. The reference was an empty glass ampule. The thermal activity (i.e., exotherm) of the resin sample up to 300°C was calculated in terms of joules per gram.

Solvent Analysis

Residual solvent concentrations in the resin samples were determined using multiple headspace gas chromatography. For each sample, a known amount of resin (approximately 0.5 gram) was placed in a septum sealed vial. The sample vial was then placed on an automated headspace analyzer connected to a gas chromatograph. The sample vial was then analyzed using a quantitative multiple headspace extraction procedure. The concentration of the residual solvent in the sample vial was determined from the quantitative analysis of known solvent standards analyzed under identical multiple headspace extraction conditions.

Residual Comonomer Analysis

Residual comonomer concentration in the resin samples was determined using a solvent extraction procedure followed by high performance liquid chromatography (HPLC) analysis. For each sample, a
5 known amount of resin (approximately 0.5 grams) was placed in container along with 75 ml of a xylene/butanol (at a 3:1 ratio) extraction solvent. The container was sealed and heated for 4 hours at 160°F (71°C). The
10 container was allowed to cool and the extraction solvent was analyzed using HPLC. In the case of acrylic acid, the concentration of residual acrylic acid in the sample was determined from the quantitative analysis of known
15 acrylic acid standards.

Table 4 summarizes the melt index, total volatiles content and oxidative exotherm data of the interpolymer after treatment according to the trials
20 outlined in Table 3. For Comparative Examples 1-3 and Example 4, the maximum oxidative exotherm was reduced by 73 percent over that of the the original polymer (Comparative Example 1*) and occurred at about 240°C. Ethylene was not detected in any of the samples, either
25 prior to or after extrusion. The residual comonomer for this experiment was acrylic acid.

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Table 4

Example	Melt Index (gms/10 min)	Total Volatiles (ppm)	Oxidative Exotherm (Joules/gm)	Percent Oxidative Exotherm Reduction
1*	11.2	950	27	NA
2*	10.8	490	19	29.6
3*	11.1	293	21	22.2
4	10.9	45	10	73

*Comparison example only, not an example of the invention.
NA = Not Applicable.

Table 5 lists the components of the total volatiles for the four interpolymers tested after the interpolymer sample was strand chopped and sealed for later analysis:

15

Table 5

Example	Residual Monomer and Solvent Level (ppm)		
	Total	Unreacted monomer	Solvent
1*	950	320	630
2*	ND	ND	490
3*	293	113	180
4	45	35	10

20

25

*Comparison example only,
not an example of the invention.
ND = Not determined.

Comparative Examples 5-7 and Example 8

30

An ethylene/acrylic acid interpolymer having a melt index of 10 grams/10 minutes and 9.7 percent by weight of interpolymer of acrylic acid was made according to the technique described in US-A-4,599,392. This interpolymer was pelletized for later use in the following stripping experiment.

The ethylene/acrylic acid interpolymer pellets were gravity fed into a co-rotating 90 mm twin screw extruder having L/D of 33, two stripping agent injection ports and two vacuum ports at a rate of 2000 pounds/hour (908 kg/hour). This twin screw system was operated according to the conditions outlined in Table 6:

Table 6
Extrusion Conditions

10	Thermocouple 29 (°C)	112
	Thermocouple 30 (°C)	240
	Thermocouple 31 (°C)	200
	Thermocouple 32 (°C)	200
	Thermocouple 33 (°C)	200
15	Thermocouple 34 (°C)	200
	Thermocouple 35 (°C)	200
	Melt Temp/Thermocouple 36 (°C)	210
	Extruder rpm	300
20	Water Injection Zone 1 (weight percent)	0.5
	Water Injection Zone 2 (weight percent)	0.5
	Vacuum 1 (mm Hg)	56 (75 mbars)
25	Vacuum 2 (mm Hg)	38 (50 mbars)

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The twin screw was equipped with two injection ports and two vacuum ports along its length, as shown in Figure 2. The first injection section of the screw itself was equipped with two melt seals (i.e., blisters) to confine the mixing zone. The second injection section has a melt seal up-stream of the vacuum port to prevent the stripping agent from premature devolatilization. The melt seals confine the stripping agent to the area of the mixing zone to ensure that the stripping agent and the interpolymer were well mixed prior to devolatilization.

The interpolymer was extruded through the system described above using a weigh belt feeder (not shown in Figure 2) to ensure that the extruder was partially filled. Table 7 describes processing differences for the extruded resins:

Table 7

Inter-polymer	Resin processing description
5*	Base resin without further processing
6*	Extruded resin without stripping or vacuum
7*	Extruded resin with vacuum only
8	Extruded resin with dual water stripping injection and dual vacuum zones

*Comparison example only, not an example of the invention.

Table 8 summarizes the melt index, total volatiles content and oxidative exotherm data of the interpolymers after treatment according to the trials outlined in Table 7.

Table 8

Example	Melt Index (gms/10 min)	Total Volatiles (ppm)	Exotherm (Joules/gm)	Percent Oxidative Exotherm Reduction
5*	10.3	950	27	NA
6*	10.2	520	27	0
7*	10	440	16	40.7
8	9.8	200	8	70.3

*Comparison example only, not an example of the invention.
NA = Not Applicable.

Table 9 lists the components of the total volatiles for the four interpolymers tested:

Table 9

Example	Volatiles (ppm)		
	Total	Unreacted monomer	Solvent
5*	950	320	630
6*	ND	ND	520
7*	440	180	260
8	200	100	100

*Comparison example only, not an example of the invention. ND = Not Determined

The resultant interpolymers from trials 5*, 6*, 7* and 8 were each extrusion coated onto paper roll stock at a thickness of 1 mil (.025 mm) on a Black

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Clawson Extrusion Coater and monitored for performance. The Extrusion Coater had a 30:1 L/D ratio, a 3.5 inch (8.9 cm) diameter screw and a 30 inch coathanger die. The processing temperature was 550°F(288°C) and the screw speed was 85 revolutions per minute (RPM). The chill roll was operated at 440 feet (134 m) per minute for the neck-in determinations. To determine maximum line speed, the chill roll speed was increased until the web began to nip on each side of the die. Data for these tests appears in Table 10:

Table 10

Interpolymer from example number	Neck-in (inches)	Maximum Line Speed (feet/min)	
		Side 1	Side 2
5*	1.875 (4.76 cm)	1000 (305 m/min)	1200 (366 m/min)
6*	1.625 (4.13 cm)	900 (274 m/min)	900 (274 m/min)
7*	1.875 (4.76 cm)	1000 (305 m/min)	1000 (305 m/min)
8	1.875 (4.76 cm)	1100 (335 m/min)	1250 (381 m/min)

*Comparison example only, not an example of the invention.

These data show that more oxidatively thermally stable interpolymers processed according to the present invention exhibit equivalent if not superior neck-in and line-speed performance to that of the base interpolymer.

Film Fabrication Procedure for Taste and Odor Evaluations

5 Cast films were prepared from Example 5* and from Example 8. The cast films were prepared on a small cast film unit. The extruder had a 1.5 inch (3.8 cm) diameter screw and a 20:1 L/D. The cast film unit was equipped with a 12 inch (30 cm) slot die. The films were fabricated at a temperature of 550°F (288°C). The fabrication conditions used result in one mil (0.025 mm) cast films.

10

Odor Evaluation Procedure

15 For each sample, 10 grams of cast film were placed in 16 ounce (473 ml) glass containers. These containers were sealed and placed in an oven at 60°C for 16 hours. The samples were removed and allowed to cool. The headspace odor in the samples was then compared using a group of test panelists. The panelists were asked to choose the sample which was preferred (i.e. preference) and the results recorded.

20

Taste Evaluation Procedure

25 For each sample, 20 grams of cast film were placed in a glass container with 800 milliliters of drinking water. The containers were then sealed and placed in an oven set at 60°C for 16 hours. The samples were then removed and allowed to cool. The water from each sample was divided into aliquots and tasted by the test panelists. The panelists were asked to choose the sample which was preferred (i.e. preference) and the results recorded.

30

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Taste and Odor Results

The taste and odor results from the evaluation of the cast films are summarized in Tables 11 and 12, respectively.

5

Table 11
Taste Results

Cast Film	Number of Panelists	Percent Preference
10 Example 5* (Control Sample)	6	27
Example 8 (Vacuum Devolatilized Sample)	16	73

Total number of panelists = 22

15

Table 12
Odor Results

Cast Film	Number of Panelists	Percent Preference
20 Example 5* (Control Sample)	6	30
25 Example 8 (Vacuum Devolatilized Sample)	14	70

Total number of panelists = 20

30

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CLAIMS:

1. A method of improving the taste and odor properties and the oxidative thermal stability of a first thermoplastic ethylene polymer, comprising removing residual
5 unreacted monomer or monomers, solvent and thermally unstable species from the first polymer, thereby forming a second more oxidatively thermally stable ethylene polymer having an oxidative exotherm of not more than about 50 percent of the oxidative exotherm of the first polymer, as
10 measured by differential scanning calorimetry, the method comprising:

(a) feeding the first polymer into a devolatilization extrusion system having at least two vacuum zones and at least one barrel, the at least one barrel having:

- 15 i. a first vacuum zone,
ii. at least one stripping agent injection port,
iii. at least one confined mixing zone, and
iv. a second vacuum zone,

wherein the at least one confined mixing zone is
20 situated immediately downstream of the at least one stripping agent injection port, the second vacuum zone is situated downstream of the first vacuum zone, and the first vacuum zone is designed to operate partially-filled with the first polymer;

25 (b) conveying the first polymer through the extrusion system;

(c) applying vacuum to the first vacuum zone;

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(d) concurrently injecting at least about 0.1 percent by weight based on total first polymer feed of at least one inert stripping agent to at least one stripping agent injection port;

5 (e) mixing the first polymer and the inert stripping agent in the at least one confined mixing zone;

(f) applying vacuum to the second vacuum zone; and

(g) recovering the extruded second polymer.

2. The method of claim 1, wherein step (a)
10 immediately follows an interpolymerization reaction of ethylene with at least one other comonomer.

3. The method of claim 1, wherein step (a) immediately follows an interpolymerization reaction of ethylene with an unsaturated carboxylic acid.

15 4. The method of claim 1, 2 or 3, wherein each vacuum zone of the extruder has a specific surface renewal ratio of about two pounds per square meter or less.

5. The method of any one of claims 1 to 4, wherein the extruder has a specific surface renewal ratio of about
20 one pound per square meter or less.

6. The method of any one of claims 1 to 5, wherein the stripping agent is a C₂-C₁₈ hydrocarbon, methane, water, aqueous solutions of metal hydroxides, steam, alcohol, carbon dioxide, nitrogen or a mixture thereof.

25 7. The method of any one of claims 1 to 5, wherein the stripping agent is selected from the group consisting of aqueous solutions of metal hydroxides, nitrogenous bases and water-soluble, strong base organic amines.

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8. The method of any one of claims 1 to 5, wherein the stripping agent is an aqueous solution of sodium hydroxide, thereby forming a more oxidatively thermally stable ionomer.
- 5 9. The method of any one of claims 1 to 8, wherein the first polymer is molten when entering the first vacuum zone.
10. The method of any one of claims 1 to 9, wherein a gear pump is located at the downstream end of the extruder
10 barrel to maintain a constant feed pressure out of the extruder.
11. The method of any one of claims 1 to 10, wherein the diameter of the root of a screw of the extrusion system increases at the end of the barrel to increase pressure on
15 the polymer.
12. The method of any one of claims 1 to 11, wherein the first polymer is low density polyethylene.
13. The method of any one of claims 1 to 12, wherein the first polymer is linear polyethylene.
- 20 14. The method of claim 13, wherein the linear polyethylene is ultra low density polyethylene.
15. The method of any one of claims 1 to 11, wherein the first polymer is an interpolymer of ethylene and acrylic or methacrylic acid.
- 25 16. The method of claim 15, wherein the first polymer is an interpolymer of ethylene and acrylic acid.
17. The method of claim 15, wherein the first polymer is an interpolymer of ethylene and methacrylic acid.

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18. The method of claim 1, wherein step (a) immediately follows a homopolymerization reaction of ethylene.
19. The ionomer produced by the method of claim 8.
- 5 20. The ethylene/unsaturated carboxylic acid interpolymer produced by the method of claim 3.
21. The ethylene/acrylic acid interpolymer produced by the method of claim 16.
22. The ethylene/methacrylic acid interpolymer
10 produced by the method of claim 17.
23. A multilayered film structure having an inner layer and an outer layer, at least one layer of which comprises the interpolymer of claim 20.
24. A multilayered film structure having an inner
15 layer and an outer layer, at least one layer of which comprises the interpolymer of claim 21.
25. A multilayered film structure having an inner layer and an outer layer, at least one layer of which comprises the interpolymer of claim 22.
- 20 26. The multilayered film structure of claim 23, 24 or 25, wherein the structure is used in food products wraps, beverage containers or condiment pouches.
27. An ethylene polymer produced by the method of any one of claims 1 to 7, 9 to 14 and 18.

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28. A multilayered film structure having an inner layer and an outer layer, at least one layer of which comprises the ethylene polymer of claim 27.

29. Use of a multilayered film structure of claim 28,
5 for food product wraps, beverage containers or condiment pouches.

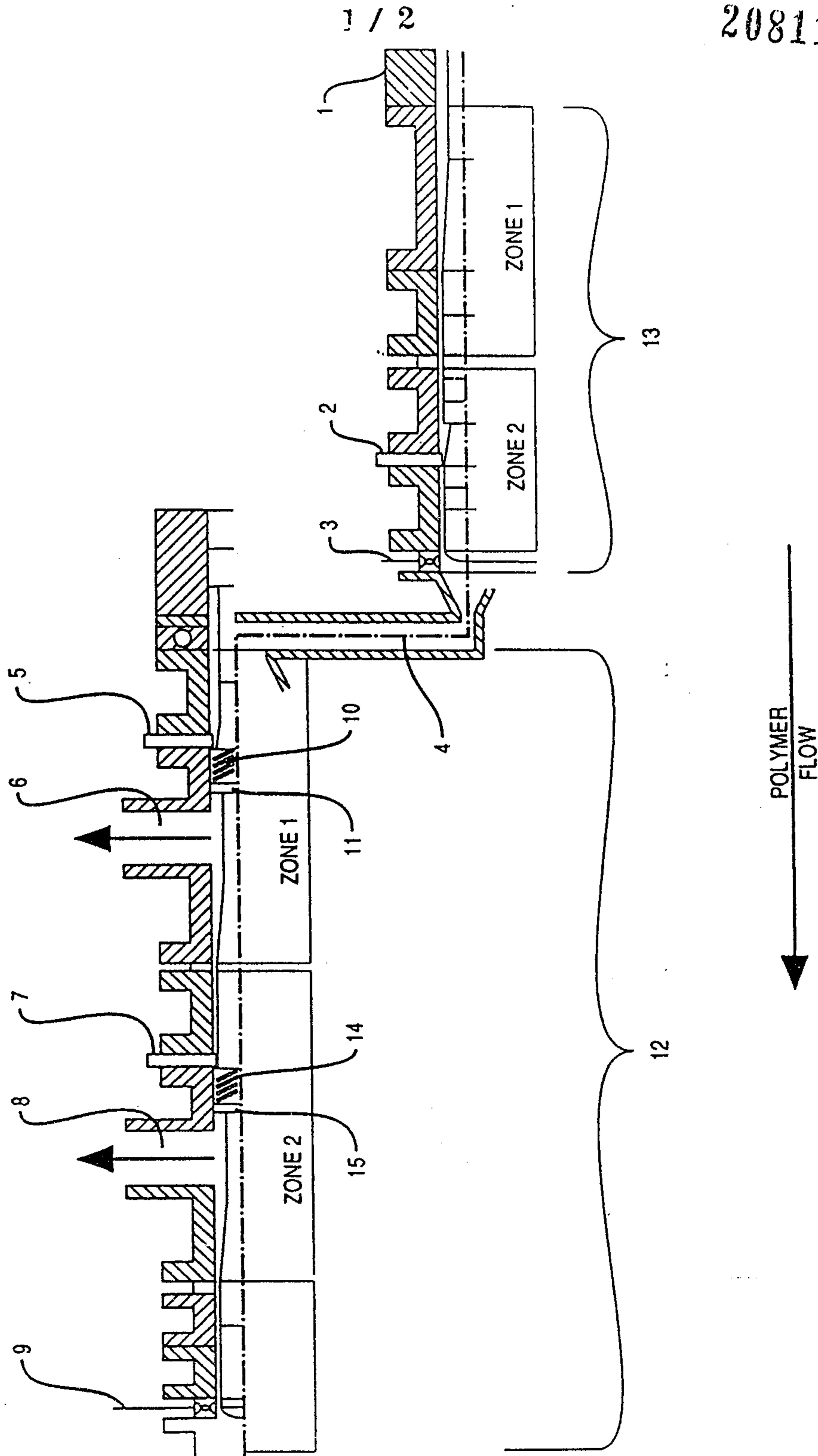
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FIG. 1



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FIG. 2

