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LINEAR LOW DENSITY ETHYLENE INTERPOLYMERS FOR INJECTION MOLDING

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(57) Certain ethylene interpolymers known as linear low density polyethylenes (LLDPE) having critical ranges of properties are used in injection moldings.

CLAIM

1. A process for preparing linear low density polyethylene (LLDPE) ~~wherein LLDPE~~ articles having wall thicknesses in the range of 0.15 to 1.5 mm are made by injection-molding of molten LLDPE polymer ^{characterized in that} ~~wherein~~ the LLDPE has the following combination of properties:

(i) a sufficient amount of at least one copolymerized C5-C12 alpha-olefin to produce a density in the range of 0.91 to 0.945 gm/cc;

(ii) a melt flow rate in the range of 60 to 200 gms./10 minutes as determined by ASTM D-1238, and

(iii) an I₁₀/I₂ ratio of from 7.2 to 18, as determined by ASTM D-238.

11. An injection-molded article prepared by the process of Claim 1.

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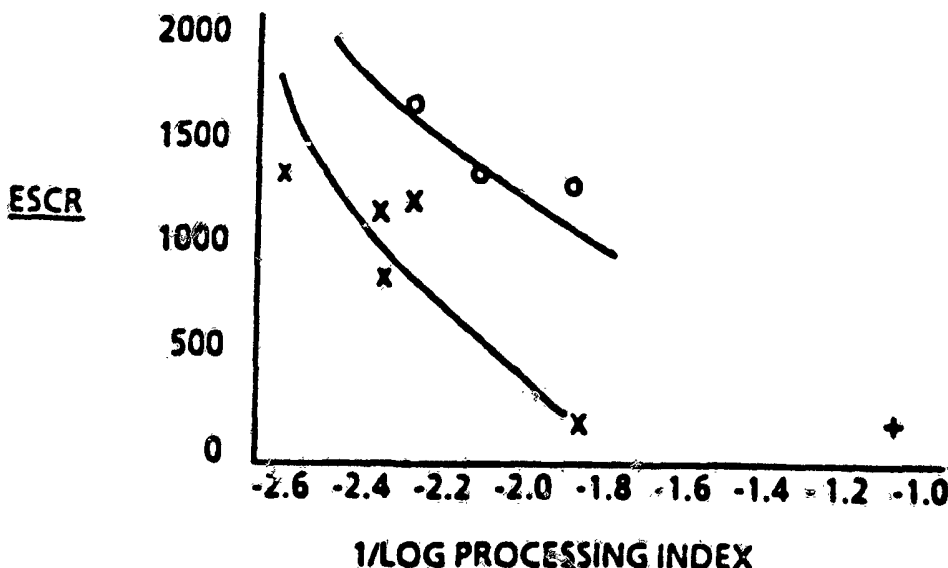
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<p>(21) International Application Number: PCT/US89/02083 (22) International Filing Date: 12 May 1989 (12.05.89) (30) Priority data: 193,433 12 May 1988 (12.05.88) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: TREYBIG, Duane, S. ; 226 Banyan Drive, Lake Jackson, TX 77566 (US). HARRIS, Wendy, D. ; 600 Pecan Estates, Angleton, TX 77515 (US). THOMAS, Christopher, J. ; 142 Daffodil, Lake Jackson, TX 77566 (US). (74) Agent: MACLEOD, Roderick, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).</p>		<p>(81) Designated States: AU, JP, KR. Published <i>With international search report.</i></p> <div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <p>This document contains the amendments made under Section 49 and is correct for printing.</p> </div>

(54) Title: LINEAR LOW DENSITY ETHYLENE INTERPOLYMERS FOR INJECTION MOLDING



(57) Abstract

Improved injection-molded LLDPE articles, especially those having a wall thickness in the range of 0.15 mm to as much as 1.5 mm, are prepared using an LLDPE containing a sufficient amount of at least one C₅-C₁₂ 1-alkene copolymerized with the ethylene to provide a density in the range of 0.91 to 0.945 g/cc, a melt flow rate in the range of 60 to 200 g/10 minutes, and an I₁₀/I₂ ratio of 7.2 to about 18. Articles such as lids and containers are prepared having improved properties such as environmental stress crack resistance.

LINEAR LOW DENSITY ETHYLENE INTERPOLYMERS
FOR INJECTION MOLDING

5 Certain ethylene interpolymers known as linear low density polyethylenes (LLDPE) having critical ranges of properties are used in injection moldings.

10 Until the invention described and claimed herein, it had been believed that the injection molding of numerous different olefinic polymers required the use of polymers having a narrow molecular weight distribution (in contrast to a broad molecular weight distribution) in order to obtain the best molded article. In contrast to the foregoing, it has now been
15 surprisingly discovered that certain types of molded article are best prepared from certain types of olefinic polymers having a broad molecular weight distribution rather than a narrow molecular weight distribution.

20 Interpolymers prepared by copolymerizing ethylene with a minor amount of at least one alkene in the range of C₃-C₁₂, especially in the range of C₅-C₉, using a metal or coordination catalyst, such as those of
25 the Ziegler-type, the Natta-type, or the Phillips-type,

have become known as "linear low density polyethylene" (LLDPE); the "polyethylene" portion of the expression is actually an "interpolymer of ethylene", which is a particular form of a "copolymer of ethylene". The LLDPE copolymers in this disclosure are significantly different from the branched-chain low density polyethylene (LDPE) polymers and the linear high density polyethylene (HDPE) homopolymers which are also well known in the art.

10

Various patents disclose catalysts and processes which produce LLDPE polymers with various amounts of ethylene/1-alkenes having various properties. Also disclosed are various reasons for attempting to achieve certain combinations of polymer properties for various end-uses.

15

Prior art representative of the widely-held belief that narrow molecular distribution is describable for injection molding olefinic polymers includes the following four publications.

20

U.S. Patent 4,076,698 (Anderson et al) discloses the process of making linear low density ethylene/1-alkene copolymers using metal coordination catalysts, and demonstrates that the properties are different from the branched low density ethylene homopolymers made in a high pressure reactor using a free radical catalyst. It is also disclosed that the amount and size of the 1-alkene used in making the copolymer gives densities in the "low" range as opposed to the "high" densities obtained using metal coordination catalyst in making linear ethylene homopolymers. Anderson et al disclose that a polymer with a narrow molecular weight distribution (MWD) is

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necessary for the best environmental stress crack
resistance. See, e.g. Anderson et al col. 11, lines 65-
69 which discloses that stress crack resistance is
improved by synthesizing a polymer with a narrow
5 molecular weight distribution.

J. H. Herman et al in Polymer Engineering
Science page 341, October, 1966 disclosed that narrowing
the MWD at constant melt index improves the stress crack
10 resistance of polymers.

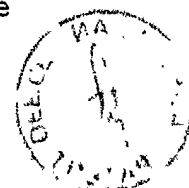
U.S. Patents 4,192,935 and 4,294,794 disclose
interpolymer compositions having a density in the range
of 0.940-0.960 gm/cc, a melt index in the range of 100
15 to 200 grams/10 minutes and a ratio of weight-average
molecular weight to number-average molecular weight of
less than 5 for use in injection molding thin-wall
containers; this represents a narrow molecular weight
distribution.

20

In marked contrast to the prior art, we have
now found that improvements in the injection molding of
articles (such as lids, containers, bottles, and the
like, especially lids) from LLDPE are obtained by
25 employing LLDPE which has properties and features within
the following critical ranges:

amount of C₅-C₁₂ 1-alkene(s) in the
interpolymer sufficient to produce the desired density,
said amount generally being in the range of 1 percent to
30 15 percent, as measured by carbon-13 nuclear magnetic
resonance (N.M.R.), depending on the length of the 1-
alkene molecular chain;

Density in the range of 0.91 to 0.945 g/cc;
35 Melt flow rate (MFR) (also known as melt index
(MI) when referring to ethylene homopolymers) in the



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range of 60 to 200 g/10 min. as measured in accordance with ASTM D-1238, Condition 190/2.16;

Ratio of I_{10}/I_2 of 7.2 to 18.

5 Accordingly, a first broad aspect of the invention is a process for preparing linear low density polyethylene (LLDPE) ~~wherein LLDPE~~ articles having wall thicknesses in the range of 0.15 to 1.5 mm are made by injection-molding of molten LLDPE polymer ^{characterized in that} ~~wherein~~ the

10 LLDPE has the following combination of properties:

(i) a sufficient amount of at least one copolymerized C5-C12 alpha-olefin to produce a density in the range of 0.91 to 0.945 gm/cc;

15 (ii) a melt flow rate in the range of 60 to 200 gms./10 minutes as determined by ASTM D-1238, and

(iii) an I_{10}/I_2 ratio of from 7.2 to 18, as determined by ASTM D-1238.

20 Other and preferred aspects of the invention are shown hereinafter, including the claims.

The improvements are most pronounced when the wall thickness of the injection molded article is generally greater than about 0.15 mm., and may be as

25 much as 1.5 mm or more, but is preferably not more than about 1.0 mm in thickness.

The interpolymers for use in the present invention have unimodal molecular weight distributions and can be made by using a coordination catalyst such as

30 a Ziegler-type or Phillips-type catalyst substantially as shown in U.S. Patents 4,250,288 and 4,314,912.

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Figures 1-4 are provided as visual aids in relating the present invention, and are discussed in are detail hereinafter.

5 In this disclosure, the expression "wall thickness" is used in deference to the fact that most of the injection-molded articles of interest in the present invention are containers of one kind or another that can be said to have "walls" which enclose the effective
10 interior of the container, whether or not the container has an upper "wall" or lid completely enclosing the container. A lid on a tumbler-shaped or bowl-shaped container, whether it be a friction-fitted lid or not, is also considered here as being a "wall" so far as
15 considering the thickness of the wall is concerned. The present invention is preferably and particularly useful in the making of various sizes of lids, such as the flanged snap-on lids used on food containers such as
20 plastic bowls for butter, oleo-margarine, cottage cheese, and the like.

Throughout this disclosure, "melt flow rate, (MFR)", "melt index (MI)", and "I₂" are all measured in
25 accordance with ASTM D-1238(190/2.16). "I₁₀" is measured in accordance with ASTM D-1238(190/10). Density is measured by ASTM D-792. "Environmental Stress Crack Resistance " (ESCR) was measured in accordance with the test described below.

30 The polymers of the present invention are also characterized by the ratio of the weight-average molecular weight to the number-average molecular weight (M_w/M_n). M_w/M_n was determined by using gel permeation
35 chromatography (GPC) at 145°C with trichlorobenzene as the solvent, a flow-rate of 2 ml/min. and a refractive

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index as the detector. The column set consisted of three eighteen inch columns containing Styragel™ packing having pore sizes of about 10^4 , 10^5 and 10^6 Angstroms. The GPC method was calibrated by using polystyrene standards. The Mw/Mn of polymers of the present invention ranged from 6.7 to 14.6. ("Styragel" is a trademark of Waters Associates, Inc.)

The polymers of this invention exhibit a unimodal molecular weight distribution as determined by gel permeation chromatography. The unimodal molecular weight distribution may be skewed on the high molecular weight or low molecular weight side of the molecular weight distribution. Figure 1 shows a typical unimodal molecular weight distribution of our invention which is skewed towards high molecular weight. Figure 2 shows an example of a bimodal molecular weight distribution which is not an example of this invention.

In a general sense, the amount of the 1-alkene in the interpolymer is dependent on the particular 1-alkene(s) employed, the amount being that which produces the critical combination of MFR, ratio of I_{10}/I_2 , and density. Preferably, the 1-alkene in the interpolymer is at least one of the group consisting of hexene, 4-methylpentene-1, and octene, most preferably octene. The percent of the 1-alkene in the interpolymer which produces the critical combination of properties is usually in the range of 1 to 10, most usually 3 to 8.

Regarding the critical properties, the preferred MFR is between 80 and 200 g/10 min., most preferably between 80 and 160 g/10 min., the preferred ratio of I_{10}/I_2 is at least 7.2, but less than 14, most

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preferably 7.2 to 10, and the density is most preferably between 0.925 and 0.940 g/cc.

5 The interpolymers used in the present invention in injection molded containers or lids exhibit an unpredicted increase in processability (as measured with spiral flow or the reciprocal of the log gas extrusion rheological processing index) at constant environmental stress crack resistance (ESCR) relative to the
10 commercially available interpolymer compositions of which we are aware or such as those which are disclosed in U.S. 4,192,935 and 4,294,794. The present interpolymer compositions also exhibit an unpredicted
15 improvement in environmental stress crack resistance when the processability is maintained constant relative to the commercially available interpolymer compositions that are referred to immediately above. Most of the commercially available LLDPE polymers of which we are
20 aware generally have melt flow rates in the range of 50 to 125 gms/10 minutes, I₁₀/I₂ ratios between 6.2 to 7.0 and densities in the range of 0.915 to 0.930. U.S. Patents 4,192,935 and 4,294,794 disclose interpolymer compositions having densities in the range of 0.94 to
25 0.96 gm/cc, melt flow rates in the range of 100 to 200 gms/10 minute and Mw/Mn ratios of less than 5 and the '794 patent claims the use of such polymers in the manufacture of containers having a wall thickness of
30 less than 0.7 mm.

We have unexpectedly found that a plot of the environmental stress crack resistance as a function of the reciprocal of the log gas extrusion rheological processing index demonstrates, at a constant reciprocal
35 of the log gas extrusion rheological index, that certain LLDPE polymer with a broad molecular weight distribution

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has better environmental stress crack resistance than a LLDPE resin having a narrower molecular weight distribution. This relationship between environmental stress crack resistance, processing index and breadth of molecular weight distribution is very surprising in view of the prior art for other olefinic polymers.

Furthermore we have found that the above-mentioned plot demonstrates, at a constant environmental stress crack resistance, that a LLDPE resin with a broad molecular distribution has a larger reciprocal of the log gas extrusion rheological processing index than a LLDPE polymer having a narrower molecular weight distribution.

Processability of the LLDPE polymers was measured by using spiral flow length measurements and the gas extrusion rheological processing index. Processability is a function of the molecular weight and breadth of the molecular weight distribution of a polymer. A polymer processes easier when the molecular weight is low and the breadth of molecular weight distribution is broad. Since melt index is inversely related to the weight-average molecular weight, then a polymer processes easier with a large melt index. A polymer processes harder when the molecular weight is high and the breadth of the molecular weight distribution is narrow. Spiral flow is directly related to processability whereas the gas extrusion rheological processing index is inversely related to processability. Therefore, a large spiral flow length and a small gas extrusion rheological processing index means that the polymer processes easily.

Spiral flow length measurements were performed by molding the LLDPE polymers on a Reed 150-Ton injection molding machine equipped with a 0.159 centimeters (1/16 inch) nozzle tip. The spiral flow mold used had a cross-sectional dimension of 0.556 X 0.318 centimeters (0.219 x 0.125 inches) and a maximum flow length of 228.6 centimeters (90 inches). The temperature profile across the barrel is shown in Table I.

TABLE I
TEMPERATURE PROFILE ACROSS THE BARREL
DURING SPIRAL FLOW LENGTH MEASUREMENTS

	<u>Nozzle</u>	<u>Front</u>	<u>Middle</u>	<u>Back</u>	<u>Rear</u>
15	475°F	500°F	500°F	500°F	450°F
	246°C	260°C	260°C	260°C	246°C

All the conditions were held constant, except injection pressures. The pressures were varied from 400 to 800 pressure setting units which correspond to 48,262,600 to 162,027,800 dynes/cm² or 700 to 2350 psi. After each cm² pressure change, ten cycles were allowed to be completed before taking the next measurements. Ten specimens were taken at each pressure, measuring the spiral to the nearest 0.635 centimeter (0.25 inch). A mean and standard deviation were calculated from the ten values at each pressure setting. These data were used to generate linear plots which show the relative processability of each resin.

The rheological processing index is measured with a gas extrusion rheometer. The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L. V. Cancio in Polymer Eng. Sci., Vol. 17, no. 11 (1977)

on page 770 and in "Rheometers for Molten Plastics" by John M. Dealy, Van Nostrand Reinhold Co., 1982 on pp 97-99. The processing index is measured at a temperature of 190°C, at a nitrogen pressure of 1250 psi (8.6185 x 10⁷ dynes/cm²) and with a 20:1 L/D die. The 20:1 L/D die has a capillary orifice diameter of 0.0292 inches (0.0742 cm) and a capillary length of 0.6 inches (1.524 cm). The gas extrusion rheological processing index (PI) in millipoise units is calculated from the following equation:

$$PI = 1.05 \times 10^6 \text{ dynes/cm}^2 / (1000 \times \text{shear rate}).$$
where 1.05 x 10⁶ dynes/cm² is the shear stress at 1250 psi (8.6185 x 10⁷ dynes/cm²) and the shear rate at the wall (γ_w) is represented with the following equation:
$$\gamma_w = 32 Q' / \pi (60 \text{ sec/min}) (0.745) (\text{Dia} \times 2.54 \text{ cm/in})^3,$$
where Q' is the extrusion rate in grams/min. units, 0.745 is the density of polyethylene in the melt in gms/cm³ and Dia is the orifice diameter (measured in inches) of the capillary.

The following described examples are for illustration purposes, but the invention is not limited to only the particular examples described.

Some of the LLDPE polymers were molded into lids on a Reed 150-Ton injection molding machine equipped with a two-cavity, single plate, hot-runner mold. The 502 lids which are 13.0175 centimeters in diameter had a panel thickness of 0.58 mm. The standard molding conditions used for each resin are summarized in Table II.

35

TABLE II
150 TON INJECTION MOLDING MACHINE
RUN CONDITIONS WHEN USING 502 MOLD

	<u>BARREL TEMP.</u>	<u>°F</u>
5	Nozzle Zone	475
	Front Extension Zone	500
	Front Zone	500
10	Center Zone	500
	Rear Zone	450
	Melt	455-460
15	TIMERS	SECONDS
	Injection Standard	1.0
	Injection Fast	0.0
	Injection Hold	0.0
20	Screw Delay	0.0
	Cure	3.0
	Clamp Open	0.5
	Cycle Time	6.4
25	CHILLER	DATA
	Supply Temp.	50°F
30	Thermostat Temp.	50°F
	Pump Pressure	+ 2,757,920 dynes/cm ² (+ 40 psi)
35		

TABLE II (continued)
 150 TON INJECTION MOLDING MACHINE
 RUN CONDITIONS WHEN USING 502 MOLD

5	<u>BARREL TEMP.</u>	<u>°F</u>
	PRESSURE SETTINGS	POTENTIOMETER SETTINGS
	Low Close Pressure	400
10	Injection Hold Pressure	775
	Injection Standard Pressure	750
	Injection Fast Pressure	800
15		
	PRESSURE READINGS	DYNES/CM ² (PSI)
	Back Pressure	3,447,400 (50)
20		
	CONTROL SETTINGS	POTENTIOMETER SETTINGS
	Screw Stop	090
25	Injection Standard Speed	2
30		
35		

Because the change of molding parameters (i.e. injection times, temperatures, pressures, total cycle times) influences the final properties that a molded lid possesses, the cycle time for each resin was not
5 optimized, but rather the conditions were held constant so that the manufacturing variables would not interfere with the resin evaluations. To one skilled in the art of injection molding, all molding machines are known to
10 be independent of each other. Therefore, these molding conditions cannot be construed as those standard to the industry.

The environmental stress crack resistance of the lids was determined by the following ESCR test using
15 CRISCO oil. Eighteen lids were collected from cavity one for each resin. Each lid was inverted, folded and placed in a sample holder at a width of 4.445 centimeters. The lids and holders were submerged in
20 commercially available edible liquid vegetable oil known as CRISCO oil at room temperature. Failure was recorded as the time required for a crack to propagate from the edge of the rim to the gate. The time F50 in minutes, where half of the lids failed, was recorded.

25 The gull wing tear strength in units of grams of force per meter (gf/m) of the lids was determined according to ASTM D-1004. Specimens were cut from the panel of the lids made from each of the polymers of
30 Table IV.

To confirm that processing index accurately represents processability, twenty-nine LLDPE polymers having melt flow rates from 23 to 121 grams/10 min., and
35 I10/I2 ratios from 6.2 to 13.4, spiral flow length measurements at a pressure of 3.45×10^7 dynes/cm² (or

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550 psi) were shown to be linearly and inversely related to the log gas extrusion rheological processing indexes measured at a shear stress of 1.05×10^6 dynes/cm². The relationship between the spiral flow length and log gas extrusion rheological processing index is represented by the following equation:

$$\text{Spiral Flow Length} = -93.5319 \times \text{Log Processing Index} + 72.2735$$

where spiral flow length is expressed in centimeters and the processing index is expressed in millipoise. This relationship is illustrated in Figure 3. In addition to the gas extrusion rheological processing index (PI) and spiral flow length for the twenty-nine LLDPE polymers, density, melt index and I_{10}/I_2 are summarized in Table III.

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TABLE III
 TWENTY-NINE LLDPE POLYMERS HAVING DENSITY FROM 0.908
 TO 0.9325 GRAMS/CC, MELT FLOW RATES FROM 23 TO 121
 GRAMS/10 MINUTES AND I₁₀/I₂ RATIOS FROM 6.2 TO 13.4

	<u>Resin</u>	<u>Density^a</u>	<u>Melt Index^b</u>	<u>I₁₀/I₂</u>	<u>PI_c</u>	<u>Spiral Flow Length^d</u>
5	A	0.9183	23	7.5	1.38	62
10	B	0.9270	85	6.6	0.41	110
	C	0.9317	98	6.2	0.38	115
	D	0.9318	121	6.6	0.30	128
	E	0.9280	46	7.1	0.71	83
15	F	0.9325	91	7.0	0.35	114
	G	0.9086	35	8.7	0.67	85
	H	0.9097	29	7.6	1.04	71
	I	0.9158	47	8.0	0.60	93
20	J	0.9165	88	8.3	0.26	129
	K	0.9144	100	12.0	0.10	166
	L	0.9320	83	13.4	0.13	152
	M	0.9320	82	12.2	0.13	151
25	N	0.9302	82	7.9	0.31	118
	O	0.9284	59	8.5	0.44	103
	P	0.9292	60	8.0	0.47	110
	Q	0.9292	64	7.7	0.44	103
30	R	0.9296	65	7.8	0.45	103
	S	0.9296	64	7.3	0.46	102
	T	0.9306	60	7.3	0.50	97
	U	0.9310	75	7.2	0.41	108

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TABLE III (continued)
 TWENTY-NINE LLDPE POLYMERS HAVING DENSITY FROM 0.908
 TO 0.9325 GRAMS/CC, MELT FLOW RATES FROM 23 TO 121
 GRAMS/10 MINUTES AND I₁₀/I₂ RATIOS FROM 6.2 TO 13.4

	<u>Resin</u>	<u>Density</u> ^a	<u>Melt Index</u> ^b	<u>I₁₀/I₂</u>	<u>PI</u> ^c	<u>Spiral Flow Length</u> ^d
5	V	0.9309	75	7.3	0.41	107
10	W	0.9309	77	7.4	0.41	110
	X	0.9306	87	7.0	0.33	120
	Y	0.9307	89	7.5	0.34	116
	Z	0.9307	85	7.4	0.37	114
15	AA	0.9316	84	6.9	0.37	114
	AB	0.9316	86	6.8	0.38	114
	AC	0.9317	86	7.3	0.36	114

a Density units are grams per cubic centimeter.

b Melt index units are grams/10 minutes.

20 c PI is an abbreviation for the processing index obtained with the gas extrusion rheometer. PI was measured at a shear stress of 1.05×10^6 dynes/cm². The processing index units are millipoise.

25 d The spiral flow length was measured in units of centimeters at a pressure of 500 psi or 3.45×10^7 dynes/cm².

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TABLE IV
 CRISCO* Oil Environmental Stress Crack
 Resistance and Gull Wing Tear Strength of
 Ten LLDPE Ethylene/Octene Interpolymers

	<u>Resin</u>	<u>ESCR F50 (min.)</u>	<u>Gull Wing Tear (gf/m)**</u>
5	B	1280	884
	C	896	895
10	D	311	870
	Le	153	830
	Me	150	830
	Ne	1207	888
15	ye	1254	929
	ze	1615	929
	AA	1164	939
	AB	1131	949

20

- e An example of this invention
 * The word "CRISCO" is a trademark of
 Proctor & Gamble
 ** Gull Wing Tear Strength was measured
 in units of grams of force per meter
 (gf/m).

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The invention is best illustrated by Figure 4.
 Figure 4 shows the relationship between the inverse of
 the log gas extrusion rheological processing index and
 the CRISCO oil environmental stress crack resistance for
 30 the ten LLDPE interpolymers in Table IV. In Figure 4,
 the x's represent runs having I₁₀/I₂ ratios in the range
 of 6.65 ± 0.25, the o's represent runs having I₁₀/I₂
 ratios of 7.6 ± 0.3 and the "+" on the graph represents
 35 2 runs of I₁₀/I₂ ratios of about 12.8 ± 0.6.

In Figure 4, the CRISCO oil environmental stress crack resistance (ESCR) is shown by the diagonal line to decrease rapidly as the inverse of the log gas extrusion rheological processing index is increased for each group of interpolymers. Because the inverse of the log gas extrusion rheological processing index is directly related to the processing performance of the interpolymers, this shows that increased processability is achievable only with severe reductions in ESCR. This trend is consistent with the plot of melt flow index versus time-to-failure from an environmental stress crack resistance test on page 355 of "Fracture Behavior of Polymers," Elsevier Applied Science Publishers, 1983, by A. J. Kinlock and R. J. Young.

Figure 4 shows that broadening the molecular weight distribution beyond an I_{10}/I_2 of 7.2 disrupts this trend by allowing the practitioner to achieve better ESCR at equivalent processability or achieve better processability at constant ESCR. As can be seen in the figure however, this effect diminishes somewhat as the molecular weight distribution increases beyond an I_{10}/I_2 of 12.

CLAIMS :

1. A process for preparing linear low density polyethylene (LLDPE) ~~wherein LLDPE~~ articles having wall thicknesses in the range of 0.15 to 1.5 mm are made by injection-molding of molten LLDPE polymer ~~wherein~~ ^{characterized in that} the LLDPE has the following combination of properties:

- 5 (i) a sufficient amount of at least one copolymerized C5-C12 alpha-olefin to produce a density in the range of 0.91 to 0.945 gm/cc;
- (ii) a melt flow rate in the range of 60 to 200 gms./10 minutes as determined by ASTM D-1238, and
- 10 (iii) an I₁₀/I₂ ratio of from 7.2 to 18, as determined by ASTM D-1238.

2. The process of Claim 1 wherein the LLDPE polymer has a melt flow rate which is in the range of 80

15 to 200 gms./10 minutes.

3. The process of Claim 1 wherein the LLDPE polymer contains a sufficient amount of hexene, 4-methyl pentene-1, and/or octene-1 copolymerized

20 therein to produce a density in the range of 0.91 to 0.945 gm/cc.

4. The process of Claim 1 wherein the alpha-

25 olefin comprises octene-1.



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5. The process of Claim 1 wherein the LLDPE has an I_{10}/I_2 ratio of from 7.2 to 14.

5 6. The process of Claim 1 wherein the LLDPE article comprises a container and/or a lid for a container.

10 7. The process of Claim 1 wherein the LLDPE article is a lid for a container.

15 8. The process of Claim 1 wherein the LLDPE article has wall thicknesses in the range of 0.15 to 1 mm.

15 9. The process of Claim 1 wherein the LLDPE polymer is an ethylene/octene-1 copolymer and wherein
20 (i) the octene-1 is present in sufficient amounts to provide a density in the range of 0.915 to 0.94 gm/cc;
(ii) a melt flow rate in the range of 80 to 160 gms/10 minutes; and
(iii) an I_{10}/I_2 ratio in the range of 7.2 to 10.

25 10. The process of Claim 1 wherein the LDPE polymer ethylene/hexene-1 copolymer and wherein (i) the hexene-1 is present in sufficient amounts to provide a density in the range of 0.915 to 0.94 gm/cc;
30 (ii) a melt flow rate in the range of 80 to 160 gms/10 minutes; and
(iii) an I_{10}/I_2 ratio in the range of 7.2 to 10.

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11. An injection-molded article prepared by the process of Claim 1.

5 12. The article of Claim 11 wherein said wall thickness is in the range of 0.15 to 1 mm and the LLDPE polymer has an Environmental Stress crack Resistance (ESCR) greater than 100 minutes as determined by used a liquid edible vegetable oil.

10 13. The article of Claim 11 wherein the article is a container, a lid, or a container and lid.

15 14. The article of Claim 11 wherein the density of the LLDPE polymer is in the range of 0.91 to 0.94 gm/cc.

15 15. The article of Claim 11 wherein the alpha-olefin is at least one of hexene-1, 4-methyl pentene-1, and octene-1.

20 16. The article of Claim 11 wherein the alpha-olefin is octene-1.

25 17. The article of Claim 11 wherein the alpha-olefin is hexene-1.

18. The article of Claim 11 wherein the melt flow rate is in the range of 80 to 160.

30 19. The article of Claim 11 wherein the I₁₀/I₂ ratio is in the range of 7.2 to 14.

35 ~~20. The article of Claim 11 wherein the I₁₀/I₂ ratio is in the range of 7.2 to 10.~~



20. The article of Claim 11 wherein the I_{10}/I_2 ratio is in the range of 7.2 to 10.

21. A process as claimed in Claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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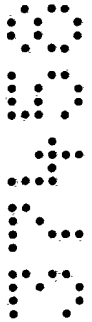
DATED: 3 January 1991

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

THE DOW CHEMICAL COMPANY

David B Fitzpatrick



Vertical text on the right margin, possibly a reference or filing number.

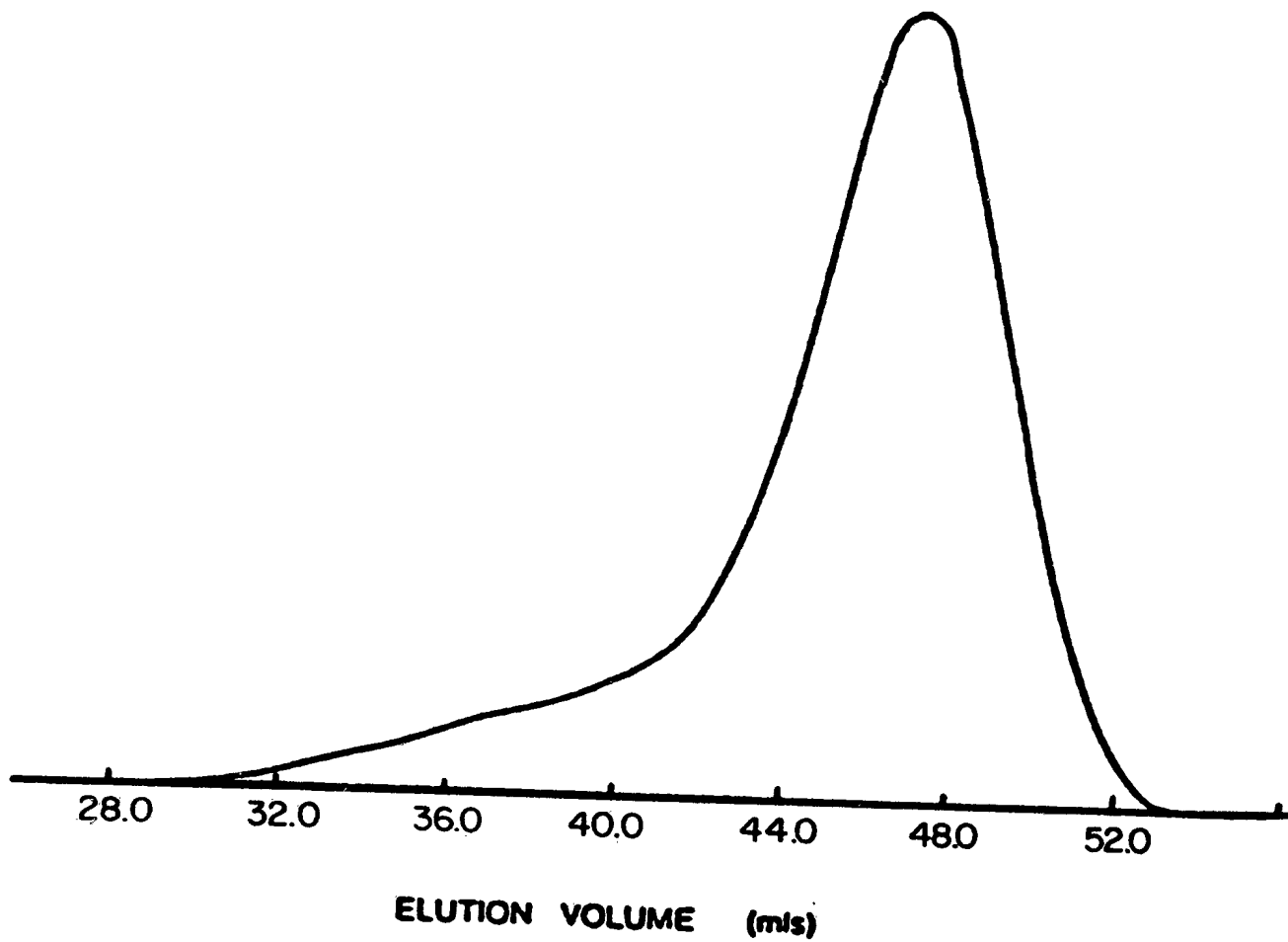


FIG. 1

SUBSTITUTE SHEET

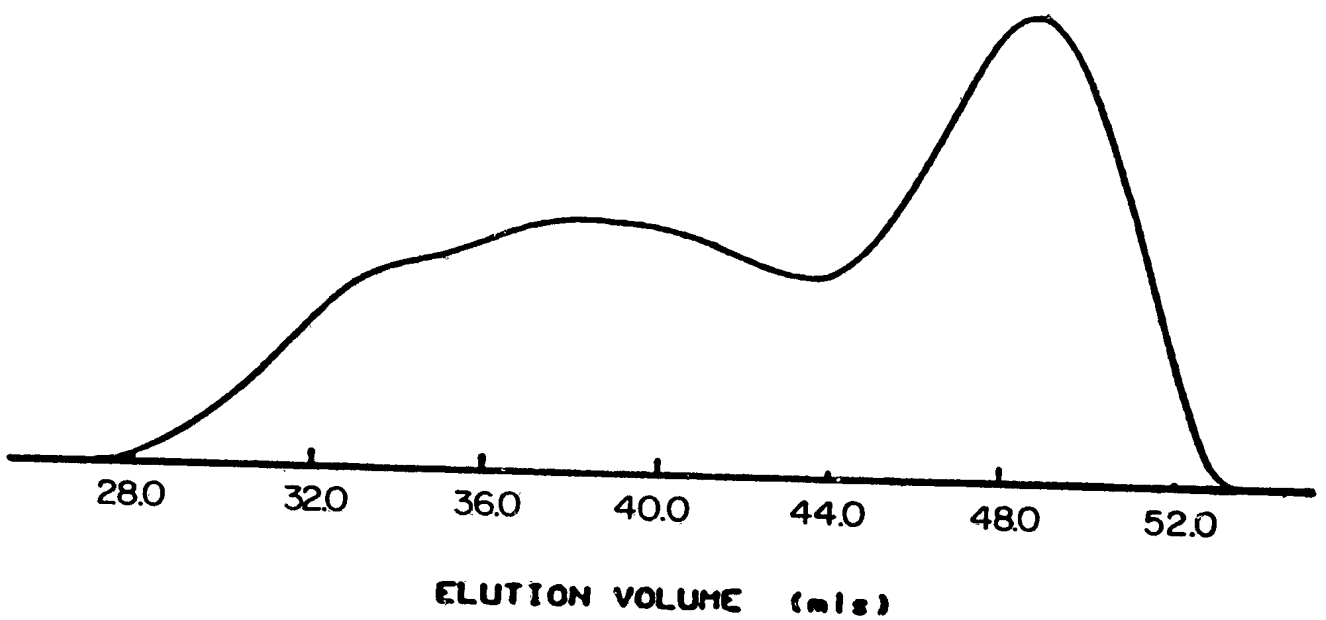


FIG. 2

SUBSTITUTE SHEET

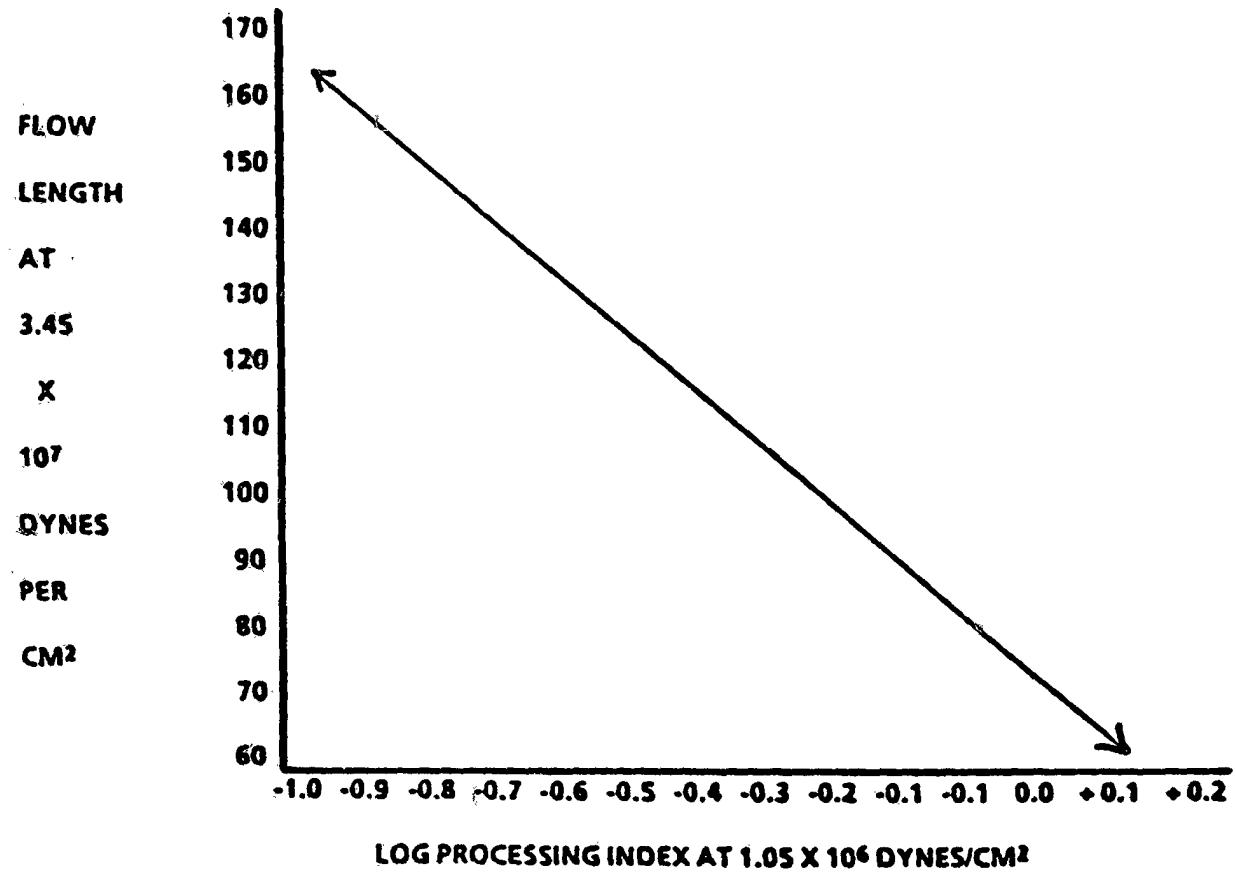


FIG. 3

SUBSTITUTE SHEET

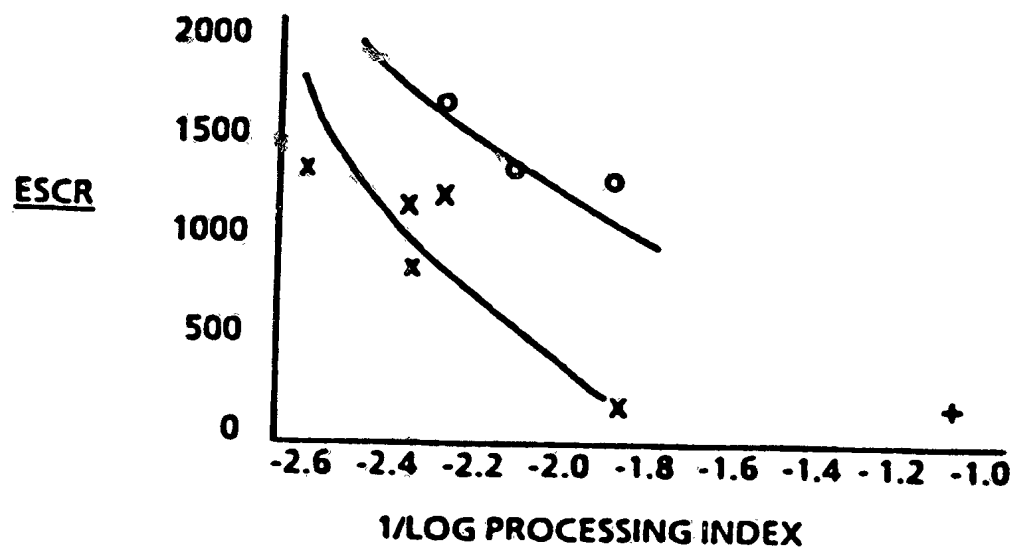


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/02083**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. 4 C08F 210/02		
US Cl 428/34.7, 34.8, 35.5, 35.7, 36.92, 523		
II. FIELDS SEARCHED		
Minimum Documentation Searched †		
Classification System	Classification Symbols	
US	428/34.7, 34.8, 35.5, 35.7, 36.92, 523	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ‡		
III. DOCUMENTS CONSIDERED TO BE RELEVANT †		
Category †	Citation of Document, †† with indication, where appropriate, of the relevant passages †‡	Relevant to Claim No. †§
A	US, A, 4,192,935 (Lovell) 11 March 1980	1-20
<p>* Special categories of cited documents: †</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		

IV. CERTIFICATION

Date of the Actual Completion of the International Search

02 August 1989

Date of Mailing of this International Search Report

20 AUG 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

W. J. Van Saen
W. J. Van Saen