EXHIBIT V

PART 13

CLAIMS

1. A process for preparing an ethylene polymer product, comprising the steps of:

(a) polymerizing a first homogeneous ethylene polymer using a first activated constrained geometry catalyst composition having a first reactivity such that the first polymer has a melt index of from 0.05 to 50 grams/10 minutes,

(b) polymerizing at least one second homogeneous ethylene polymer using a second activated constrained geometry catalyst composition having a second reactivity such that the second ethylene polymer has a melt index of from 0.05 to 50 grams/10 minutes, and

(c) combining from 50 to 95 weight percent of the first ethylene polymer with from 5 to 50 weight percent of the second ethylene polymer to form an ethylene polymer product.

2. A process for preparing an ethylene/alpha-olefin interpolymer product, comprising the steps of:

(a) polymerizing a first homogeneous ethylene/alpha-olefin interpolymer using a first activated constrained geometry catalyst composition having a first reactivity such that the first interpolymer has from 5 to 30 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point less than about 110°C,

(b) polymerizing at least one second homogeneous ethylene/alpha-olefin interpolymer using a second activated constrained geometry catalyst composition having a second reactivity such that the second ethylene/alpha-olefin interpolymer has from 2 to 10 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point greater than about 115°C, and

(c) combining from 50 to 95 weight percent of the first homogeneous ethylene/alpha-olefin interpolymer with from 5 to 50 weight percent of the second homogeneous ethylene/alpha-olefin interpolymer to form an ethylene/alpha-olefin interpolymer product.

3. The process of Claims 1 or 2 wherein the first activated constrained geometry catalyst composition comprises a titanium constrained geometry complex and an aluminoxane cocatalyst.

4. The process of Claims 1 or 2 wherein the second activated constrained geometry catalyst composition comprises a zirconium constrained geometry complex and an aluminoxane cocatalyst.

5. The process of Claims 1 or 2 wherein the second activated constrained geometry catalyst composition comprises a zirconocene constrained geometry complex and an aluminoxane cocatalyst.

6. The process of Claim 2 wherein (a) and (b) are performed substantially simultaneously in a common reactor.

7. The process of Claim 6 further comprising the steps of:

(d) mixing the first and second catalyst compositions together to form a catalyst mixture, and

(e) injecting the catalyst mixture into the common reactor.

8. The process of Claim 2 wherein (a) and (b) are performed separately in at least two reactors.

9. The process of Claim 8 wherein the two reactors comprise at least a first reactor and a second reactor and wherein the two reactors are operated in series.

10. The process of Claim 8 wherein the two reactors are operated in parallel.

11. The process of Claim 2 wherein the homogeneous ethylene/alpha-olefin interpolymer produced in step (a) has a melting point from 70°C to 110°C and wherein the homogeneous ethylene/alpha-olefin interpolymer produced in step (b) has a melting point from 115°C to 130°C.

12. The process of Claim 2 wherein at least one of the alpha-olefins is a C_2-C_{18} alpha-olefin.

13. The process of Claim 12 wherein at least one of the alpha-olefins is selected from the group consisting of ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.

14. The process of Claim 13 wherein the first and the second ethylene/alpha-olefin interpolymer each comprises a copolymer of ethylene and 1-octene.

15. The process of Claim 2 wherein either the first or the second activated constrained geometry catalyst compositions, or both, are chosen from constrained geometry catalyst components selected from the group consisting of titanium, vanadium, hafnium and zirconium.

16. The interpolymer product of Claim 2 wherein the first homogeneous ethylene/alpha-olefin interpolymer and the second homogeneous ethylene/alpha-olefin interpolymer are combined in amounts effective to yield an interpolymer product having a crystallization onset temperature at least about 5°C higher than the crystallization onset temperature of the interpolymer produced by the activated constrained geometry catalyst composition having the higher reactivity.

17. The interpolymer product of Claim 2 wherein the first homogeneous ethylene/alpha-olefin interpolymer and the second homogeneous ethylene/alpha-olefin interpolymer are combined in amounts effective to yield a crystallization onset temperature of at least about 110°C.

18. The interpolymer product of Claim 2 wherein the first and the second ethylene/alpha-olefin interpolymer each comprises a copolymer of ethylene and 1-octene.

19. A fabricated article made from the interpolymer product of Claim 16.

20. The fabricated article of Claim 19 selected from the group consisting of films, molded articles, and fibers.

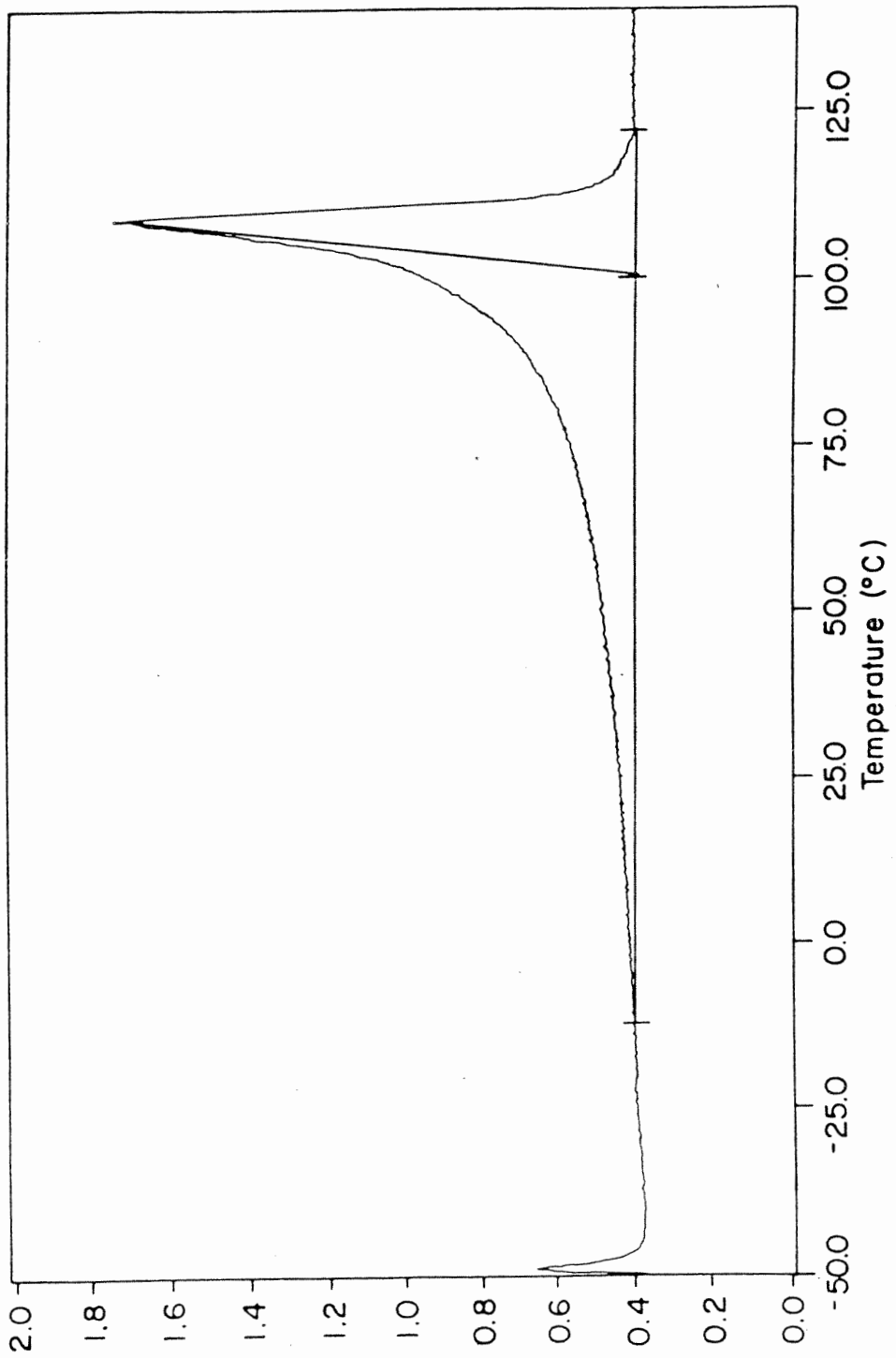
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Heat Flow (W/g)
-50.0
-25.0
0.0
25.0
50.0
75.0
100.0
125.0
Temperature (°C)

FIG. 1

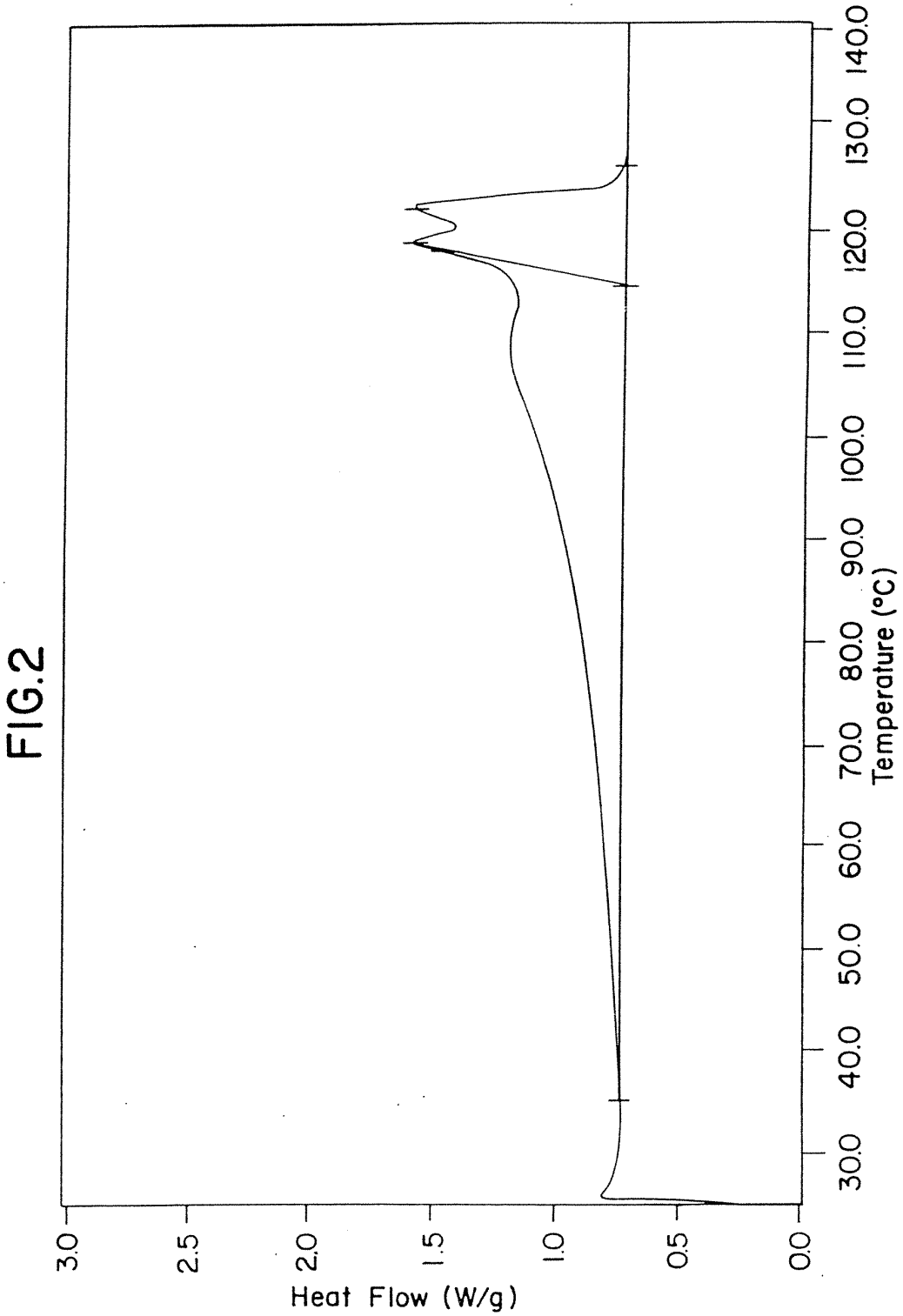
Heat Flow (W/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Temperature (°C)
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0

FIG.2

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F10/02; C08F297/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 128 046 (EXXON RESEARCH AND ENGINEERING COMPANY) 12 December 1984 see the whole document & US,A,4 937 299 (cited in the application)	
A	EP,A,0 416 815 (THE DOW CHEMICAL COMPANY) 13 March 1991 see claims 1-25 & US,P,401 345 (cited in the application)	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13 APRIL 1993	17. 05. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	FISCHER B.R.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9211269
SA 68680

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 13/04/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0128046	12-12-84	AU-B- 581848	09-03-89
		AU-A- 2910784	13-12-84
		CA-A- 1231702	19-01-88
		DE-A- 3466880	26-11-87
		JP-A- 60035006	22-02-85
		US-A- 4937299	26-06-90
EP-A-0416815	13-03-91	AU-A- 6203990	07-03-91
		CA-A- 2024333	01-03-91
		JP-A- 3163088	15-07-91
		CN-A- 1049849	13-03-91

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08L 23/04, C09J 123/04 — A1

(11) International Publication Number: WO 93/03093

(43) International Publication Date: 18 February 1993 (18.02.93)

(21) International Application Number: PCT/US92/05924

(22) International Filing Date: 15 July 1992 (15.07.92)

(30) Priority data:
732,865 18 July 1991 (18.07.91) US

(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).

(72) Inventors: MEKA, Prasadarao ; 2730 Sandpebble Drive, Seabrook, TX 77586 (US). STEHLING, Ferdinand, Christian ; 214 Post Oak, Baytown, TX 77520 (US). TRUDELL, Barry, Colin ; 4123 Island Hills, Houston, TX 77059 (US). VAN DER SANDEN, Dirk, Germaine, Frans ; Hoogstraat 1d, B-1820 Perk (BE).

(74) Agents: SHER, Jaimes et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).

(81) Designated States: AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).

Published
With international search report.

(54) Title: HEAT SEALED ARTICLE

(57) Abstract

Heat sealed articles and heat sealable films comprising ethylene interpolymers having a narrow composition distribution and a narrow molecular weight distribution and blends of the ethylene interpolymers. The article and films have remarkably low heat seal initiation temperatures and may therefore be sealed at lower temperatures and higher speeds on commercial heat sealing equipment.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MN	Mongolia
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Faso	GN	Guinea	NO	Norway
BG	Bulgaria	GR	Greece	NZ	New Zealand
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	PT	Portugal
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland			SE	Sweden
CI	Côte d'Ivoire	KR	Republic of Korea	SK	Slovak Republic
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CS	Czechoslovakia	LK	Sri Lanka	SU	Soviet Union
CZ	Czech Republic	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America

TITLE: HEAT SEALED ARTICLE

This application is a Continuation-In-Part application of U.S. Application Serial No. 252,094 filed September 30, 1988 and U.S. Application Serial No. 732,865 filed July 18, 1991.

FIELD OF THE INVENTION

The present invention relates to a heat sealed article in which the heat sealed portion of the article is formed from interpolymers or blends thereof. In particular, the invention relates to the interpolymer compositions and interpolymer blend compositions where the interpolymers have a narrow composition distribution and a narrow molecular weight distribution. The interpolymers and especially the blends of the interpolymers exhibit excellent heat sealing and other physical properties. The interpolymers and the blends thereof may be used to make films, bags, pouches,

tubs, trays, lids, packages, containers and any article employing a heat seal.

BACKGROUND OF THE INVENTION

Many articles of manufacture employing heat seals are currently available in the marketplace. Generally, the seals on such articles may be employed by welding two separate portions of the article together. For example, plastic parts usefully employed in machines and toys may be constructed by joining together two individual plastic pieces by heating one or both of the plastic pieces, pressing them together, and then, allowing them to cool. Specifically, heat sealing is very important in packaging applications. Packages formed by a heat seal provide for the efficient transportation of a consumer item within the package, provide a display of the consumer item that promotes sales, and, in the food industry, the packaging is employed to preserve the freshness of the consumer item.

Various types of polymers are used to form articles, which include packages, that may be joined together or sealed by the application of heat and/or pressure. Polymers or blends of polymers used to make the articles are selected for use because they provide a strong seal, which is easily and rapidly formed by a single short application of heat and/or pressure. Occasionally, the entire heat sealed article is constructed from the same polymer or a blend of polymers. More often, the article is constructed of various areas or layers of different materials, and polymers which provide good heat sealing properties are utilized only in areas, or layers, where heat sealing will ultimately be necessary. This type of construction is employed because the articles, for instance multilayer films, should have desirable physical and mechanical

properties such as clarity, strength, resistance to puncture and tearing, in addition to heat sealing properties, and should be easily processed by high speed equipment. Many plastic materials are known to possess good physical and mechanical properties but often do not also possess good heat sealing properties. For example, polypropylene has good strength and clarity and is resistant to tearing, but does not readily form good seals at the temperatures which are preferred in commercial sealing machinery. Conversely, some polymers with good heat sealing properties do not have adequate strength or clarity.

The packaging art has therefore developed multiple layer articles such as multilayer films incorporating one or more layers of the same or different types of polymers that provide good mechanical and physical properties and providing one or more additional layers formed from polymers that provide the article of manufacture with good heat sealing properties. In this way, a film may be produced having a substrate layer of polypropylene provided for strength and clarity, and a layer of polyethylene to provide good heat sealing properties. Other articles, in addition to films, may be similarly constructed with a plurality of materials, each material selected to contribute to one or more of the desired properties of the final article.

Various types of polyethylene polymers are known in the art as having acceptable heat sealing properties. Low density polyethylene ("LDPE") is generally prepared at high pressure using free radical initiators and typically has a density in the range of 0.915-0.940 g/cm^3. LDPE is also known as "branched" polyethylene because of the relatively

large number of long chain branches extending from the main polymer backbone.

High density polyethylene ("HDPE") usually has a density in the range of greater than 0.940 to 0.960 g/cm^3. HDPE is prepared using a coordination catalyst, e.g., Ziegler-Natta type catalysts, at low or moderate pressures, but sometimes at high pressure. HDPE is generally linear without any substantial side chain branching. HDPE is a substantially crystalline polymer.

Linear low density polyethylene ("LLDPE") is generally prepared in the same manner as HDPE, but incorporates a relatively minor amount of an α-olefin comonomer such as butene, hexene or octene to introduce enough short chain branches into the otherwise linear polymer to reduce the density of the resultant polymer into the range of that of LDPE. The coordination catalysts used to interpolymerize ethylene and the α-olefins generally produce a LLDPE with a broad composition distribution, as hereinafter defined, and a relatively broad molecular weight distribution, i.e., Mw/Mn greater than about 3, wherein Mw is the weight average molecular weight and Mn is the number average molecular weight.

Commercial polymerization processes produce great numbers of polymer molecules simultaneously. The polymer molecules produced will not all have exactly the same molecular weight. Furthermore, when a comonomer is present, the resulting polymer molecules will not all have exactly the same amount of comonomer. As used herein, the terms "polymer", "polymers", "interpolymer" and "interpolymers" are used to refer to the group of polymer molecules produced at substantially the same polymerization conditions from catalysts having substantially the same composition and structure. Therefore, one

polymer differs from another polymer when the polymers are made from different types of catalysts, or when the polymers are produced from the same type of catalyst, but at different polymerization conditions. Polymerization conditions include the temperature and pressure of polymerization as well as the type and amount of comonomer present, if any, and the amount of hydrogen present, if any.

It is known in the prior art that interpolymers have relatively broad composition distributions. An interpolymer with a relatively broad composition distribution results because the number of α-olefin comonomer molecules incorporated into each polymer molecule differs. Generally, relatively low molecular weight polymer molecules will contain a relatively high proportion of the α-olefin comonomer, and the high molecular weight polymer molecules will contain a relatively low proportion of α-olefin comonomer. The polymer molecules of low comonomer content are relatively more crystalline and have a high melting temperature, whereas the high comonomer content polymer molecules are more amorphous and melt at a lower temperature. The presence of a component with a melting temperature that is too high is disadvantageous in many applications, for example, where heat sealing is required. On the other hand, the presence of too much comonomer in the lower melting component frequently results in a high quantity of extractables, low molecular weight polymers that are soluble in a solvent such as hexane or pentane, and this limits their use in food contact applications.

In the past, polyethylenes such as LLDPE also have a broad molecular weight distribution which can be undesirable in many respects. For example, LLDPE resins known previously in the art

contain relatively high molecular weight molecules that are subject to an orientation, which results in anisotropic properties in the machine direction compared to the transverse direction of a fabrication process. The higher molecular weight molecules having low comonomer content also have less desirable heat sealing properties. On the other hand, resins containing relatively lower molecular weight molecules, in which the comonomer is invariably concentrated, have better heat sealing properties but tend to exhibit high block and tackiness properties. These lower molecular weight, highly branched molecules also interfere with the proper function of certain additives compounded in the resin, increase the percentage of extractable polymer, and increase fouling in the polymerization plant. The relatively high α-olefin comonomer content of these low molecular weight polymer molecules causes such polymer molecules to be generally amorphous and to exude to the surface of fabricated parts, thereby producing an undesirable sticky surface.

Previously known blends of polyethylenes designed to improve one or more of the properties of the blend relative to its blend components or relative to polyethylene homopolymers in the past have also suffered from the drawbacks mentioned above. For example, incorporating a blend component with a high average comonomer content to reduce crystallinity and improve heat sealability generally results in an increase of extractables and adversely affects other properties so that the full advantage of the blend is not realized.

Further, International Application WO 90/0314 published April 5, 1990 discloses interpolymer blends made from components having a narrow molecular weight distribution and a narrow

composition distribution. It also mentions in general terms that such blends may have improved properties such as tear and tensile strength. However, this publication by no means makes available or suggests the surprising and unexpected finding that heat sealed articles may be formed from a select group of ethylene interpolymers and blends under conditions of temperature and contact pressure which enable the formation of good seals at commercially advantageous temperatures and processing times.

In the past, heretofore this present invention as discussed above, no way has been found to achieve the desired uniform distribution of comonomer in polymers giving such polymers and blends thereof excellent heat sealing properties while maintaining other desirable physical properties. Therefore, there is a need for a polymer or a blend of polymers selected so as to distribute the comonomer appropriately and uniformly throughout all of the polymer molecules.

SUMMARY OF THE INVENTION

This invention relates to articles of manufacture exhibiting improved heat seal properties formed from interpolymers each having a narrow molecular weight distribution and a composition distribution breadth index of at least 50% and blends of these interpolymers. In particular, the interpolymers can be ethylene interpolymers or blends of ethylene interpolymers useful for forming single or multilayer films used in a variety of packaging applications. Each individual group of ethylene interpolymers has a narrow molecular weight distribution and a narrow composition distribution. Specifically, the particular ethylene interpolymers and blends thereof are selected to yield superior properties in the resulting heat sealable or heat

sealed article of this present invention. Broadly, the blends used in articles of manufacture of this invention comprise a plurality of linear ethylene interpolymer components where each component has a composition distribution breadth index (CDBI) (later described) of 50% or higher. The phrase "narrow composition distribution" or "narrow CD" is used herein to denote a polymer with a CDBI of 50% or higher. The preferred heat sealable polymer blends are substantially free of blend components having both a higher average molecular weight and a lower average comonomer content than that of any other polyethylene component in the blend. The components for each blend can be selected so that the resultant blend has plural modality with respect to molecular weight distribution, comonomer content, or both.

In another aspect, the components for the blend are linear ethylene interpolymers having narrow molecular weight and narrow composition distribution mentioned above and the blend components are selected from one of the following groups: (1) linear ethylene interpolymer blend components having substantially the same average molecular weight but different average comonomer contents; (2) linear ethylene interpolymer blend components having substantially the same average comonomer content but different average molecular weights; and (3) linear ethylene interpolymer blend components having different average molecular weights and comonomer contents in which the blend components, taken serially in order of increasing average molecular weight, have an increasing comonomer content.

In still another aspect, the linear ethylene interpolymer blend components have the narrow molecular weight and composition distribution mentioned above, and when the linear ethylene

interpolymer blend components are taken serially in order of increasing average molecular weight, each succeeding component has substantially the same or a higher average comonomer content than each preceding component in said series.

In another aspect, the invention provides a heat sealable linear ethylene interpolymer blend having plural modality with respect to comonomer content, a narrow molecular weight distribution such that $M_w/M_n \leq 3$ and an overall composition distribution breadth index less than 50%.

In still another aspect, the invention provides a linear ethylene interpolymer blend having plural modality with respect to molecular weight so that the blend has a broad overall molecular weight distribution such that $M_w/M_n > 3$ and a CDBI $\geq$ 50%.

In still another aspect, the invention provides a blend of linear ethylene interpolymers of plural modality with respect to both comonomer content and molecular weight, comprising a plurality of components having a narrow molecular weight distribution such that $M_w/M_n \leq 3$ for each component, and each component taken serially in order of increasing average molecular weight, has an increasing average comonomer content.

In a still further aspect of the invention, there is provided a linear ethylene interpolymer blend of plural modality with respect to both comonomer content and molecular weight which comprises a plurality of components having a composition distribution breadth index of 50% or more, wherein the components taken serially in order of increasing comonomer content, have an increasing average molecular weight.

The heat sealed article of this invention may be formed by pressing at least two portions of the article together at a temperature sufficient to

soften at least one of the article portions. The article portion which has been softened by heat is formed from ethylene interpolymers having a CDBI of at least 50% or from a polymer blend comprising a plurality of the ethylene interpolymers as blend components. Although it is sufficient if only one of the article portions being heated and pressed to form a heat seal is formed from the ethylene interpolymers or blends of the ethylene interpolymers, it is preferable for all article portions directly involved in the heat seal to be formed from the ethylene interpolymers or blends thereof.

The heat sealed article so formed may, in one aspect, be a sealed container comprising a body and a sealing member secured thereto, wherein the sealing member comprises a seal layer comprising one of the group of ethylene interpolymers having a narrow composition distribution and a blend of a plurality of said ethylene interpolymers as blend components.

A heat sealable article in accordance with the invention, is, in one aspect, a film comprising ethylene interpolymers having a CDBI of at least 50% and a narrow molecular weight distribution or a polymer blend comprising a plurality of said ethylene interpolymers as blend components.

The invention also includes the interpolymers and interpolymer blends having heat sealing properties for use in heat sealing applications comprising:

a plurality of linear ethylene interpolymer blend components, each component having a narrow molecular weight distribution such that M_w/M_n is less than or equal to 2.5 and a composition distribution breadth index of 50% or greater. The blend components are selected from one of the groups

consisting essentially of blend components having essentially:

(1) the same average molecular weight but different average comonomer content, or,

(2) the same average comonomer content but different average molecular weights, or,

(3) different average molecular weights and comonomer contents wherein said components, taken serially in order of increasing average molecular weight have an increasing comonomer content, or,

(4) a combination thereof;

wherein the density of the interpolymer blend is from about 0.875 to 0.94 g/cm^3.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing aspects, features, and advantages of the invention will become clearer and more fully understood when the following detailed description is read in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic illustration of different blends made from poly(ethylene-co-α-olefin) blend components having narrow molecular weight and composition distributions.

Fig. 2 illustrates the broad molecular weight distribution and broad composition distribution of a typical prior art LLDPE.

Fig. 3 illustrates the narrow molecular weight distribution and narrow composition distribution of an exemplary blend component used in the present invention.

Fig. 4 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to an embodiment of

the invention in which the blend components have about the same molecular weight but differing comonomer contents.

Fig. 5 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to another embodiment of the invention in which the blend components have about the same comonomer content but differing molecular weights.

Fig. 6 illustrates the molecular weight distribution and composition distribution of an exemplary LLDPE blend according to yet another embodiment of the invention in which the comonomer contents of the blend components increases as the molecular weight increases.

Fig. 7 is a graph of the relationship between seal strength and sealing temperature for films made from prior art polymers.

Fig. 8 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention.

Fig. 9 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention.

Fig. 10 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention.

Fig. 11 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention.

Fig. 12 is a graph of the relationship between seal strength and sealing temperature for films according to the invention compared to a prior art polyethylene.

Fig. 13 is a cross-sectional view of a sealed container according to the invention.

Fig. 14 is a cross-sectional view of a film, or lid or sealing member according to the invention.

Fig. 15 is a graph of the solubility distribution and composition distribution of a copolymer (X) having a narrow SDBI and CDBI and copolymer (Y) having a broad SDBI and CDBI.

Fig. 16 is a graph illustrating the correlation between dissolution temperature and composition used to convert the temperature scale to a composition scale.

Fig. 17 is a graph illustrating the method for calculating CDBI.

DETAILED DESCRIPTION OF THE INVENTION

The linear ethylene interpolymers of the present invention may be homopolymers of ethylene or higher interpolymers of a major proportion of ethylene and a minor proportion of comonomer. If a comonomer is used, the ethylene is generally polymerized in a proportion of 70-99.99, typically 70-97, and often 70-80, 80-90, 83-99.99 or 90-95, mole percent of the interpolymerized monomers with 0.01-30, typically 3-30, and often 20-30, 10-20, 0.01-17 or 5-10, mole percent comonomer. Contemplated blend components may have a density in the range of 0.85 to 0.96 g/cm^3 and generally include elastomer blend components in the density range of about 0.875-0.900 g/cm^3, very low density polyethylene blend components in the density range of about 0.900-0.915 g/cm^3, and linear, low density polyethylene blend components in the density range of about 0.915-0.940 g/cm^3. Ethylene interpolymers having a density in the high density polyethylene range above about 0.940 g/cm^3 are also contemplated as being suitably employed in the invention.

Suitable comonomers interpolymerized with the ethylene to obtain the ethylene interpolymer

herein generally include monomers which may be copolymerized with ethylene to obtain the comonomer distribution desired in the blend component. A preferred class of comonomers are the α-olefins having 3 to about 12 carbon atoms, such as propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecane and the like. Other suitable comonomers include vinyl cyclohexane, norbornene, vinyl cyclohexene, and other diene comonomers such as 1,3-butadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,5-hexadiene and the like. The ethylene interpolymer may include one or more of such comonomers, i.e. it may be copolymer, terpolymer, etc.

The molecular weight of the ethylene interpolymers may range from one thousand to one million or more depending on the particular end use, preferably 10^4-10^6, and especially 2 X 10^4 - 5 X 10^5. As used herein, the terms "average molecular weight" and "molecular weight" refer to weight average molecular weight unless otherwise indicated. The molecular weight of resulting polymers may be varied by adjusting the amount of hydrogen gas that is added to the polymerization reaction. Generally, a higher molecular weight polymer results when the hydrogen concentration is lower, and lower molecular weight polymer is produced when the hydrogen concentration is higher. Therefore, by selecting the proper amount of hydrogen, one can produce polymer of desired molecular weight.

The ethylene interpolymers preferably have a composition distribution ("CD") such that the composition distribution breadth index ("CDBI") is at least 50%, more preferably at least 60% and most preferably at least 70%. The CDBI is defined as the

weight percent of the ethylene interpolymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. For instance if the median total molar comonomer content of a certain group of ethylene interpolymers is found to be 4 mole percent, the CDBI of that group of interpolymers would be the weight percent of ethylene interpolymers having a molar comonomer concentration from 2 to 6 mole percent. If 55 wt% of the ethylene interpolymers had a molar comonomer content in the 2 to 6 mole percent range, the CDBI would be 55%. The CDBI of linear homopolymer polyethylene, which does not contain a comonomer, is defined to be 100%. The CDBI of a copolymer is readily calculated by data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, in U.S. Patent 5,008,204 or in Wild et al., J. Poly. Sci, Poly. Phys. Ed., vol. 20, p. 441 (1982), both of which are hereby fully incorporated herein by reference.

Solubility Distribution is measured using a column of length 164 cm and 1.8 cm ID (inner diameter) is packed with non-porous glass beads (20-30 mesh) and immersed in a temperature programmable oil bath. The bath is stirred very vigorously to minimize temperature gradients within the bath, and the bath temperature is measured using a platinum resistance thermometer. About 1.6 g of polymer is placed in a sample preparation chamber and repeatedly evacuated and filled with nitrogen to remove oxygen from the system. A metered volume of tetrachlorethylene solvent is then pumped into the sample preparation chamber, where it is stirred and heated under 3 atmospheres pressure at 140°C to obtain a polymer solution of about 1 percent concentration. A metered volume of this solution,

100 cc is then pumped into the packed column thermostated at a high temperature, 120°C.

The polymer solution in the column is subsequently crystallized by cooling the column to 0°C at a cooling rate of ~20°C/min. The column temperature is then maintained at this temperature for 25 min. at 0°C. The elution stage is then begun by pumping pure solvent, preheated to the temperature of the oil bath, through the column at a flow rate of 27 cc/min. Effluent from the column passes through a heated line to an IR detector which is used to measure the absorbance of the effluent stream. The absorbance of the polymer carbon-hydrogen stretching bands at about 2960 cm^{-1} serves as a continuous measure of the relative weight percent concentration of polymer in the effluent. After passing through the infrared detector the temperature of the effluent is reduced to about 110°C, and the pressure is reduced to atmospheric pressure before passing the effluent stream into an automatic fraction collector. Fractions are collected in 3°C intervals. In the elution stage pure tetrachloroethylene solvent is pumped through the column at 0°C at 27 cc/min for 25 min. This flushes polymer that has not crystallized during the cooling stage out of the column so that the percent of uncrystallized polymer (i.e. the percent of polymer soluble at 0°C) can be determined from the infrared trace. The temperature is then programmed upward at a rate of 1.0°C/min. to 120°C. A solubility distribution curve, i.e. a plot of weight fraction of polymer solubilized as a function of temperature, is thus obtained.

The procedure for calculating the Solubility Distribution Breadth Index (SDBI) is set forth below.

Solubility distributions of two ethylene interpolymers are shown in Figure 15. Here, for illustration purposes only, Sample X has a narrow solubility distribution and elutes over a narrow temperature range compared to Sample Y, which has a broad solubility distribution. A solubility distribution breadth index (SDBI) is used as a measure of the breadth of the solubility distribution curve. Let $w(T)$ be the weight fraction of polymer eluting (dissolving) at temperature T. The average dissolution temperature, T_{ave}, is given by

$$T_{ave} = \int T\, w(T)dT, \text{ where } \int w(T)dT = 1.$$

SDBI is calculated using the relation:

$$SDBI(^{\circ}C) = \sqrt[4]{(T - T_{ave})^4 w(T)dT}.$$

(SDBI is thus analogous to the standard deviation of the solubility distribution curve, but it involves the fourth power rather than the second power to $T - T_{ave}$). Thus, for example, the narrow solubility distribution Sample X and the broad solubility distribution Sample Y in Figure 15 have SDBI values equal to 14.6 and 29.4°C, respectively.

The preferred values of SDBI are less than 28°C and more preferred less than 25°C and evern more preferred less than 20°C.

The composition distribution (CD) of a crystalline interpolymer is determined as follows. The composition and number average molecular weight, M_n, of fractions collected in various narrow temperature intervals for several poly(ethylene-co-butene)'s was determined by C13 NMR and size exclusion chromatography, respectively. Figure 16 is a plot of mole percent comonomer vs. elution

temperature for fractions having M_n > 15,000. The curve drawn through the data points is used to correlate composition with elution temperature for temperatures greater than 0°C. The correlation between elution temperature and composition becomes less accurate as the M_n of a fraction decreases below 15,000. Such errors can be eliminated by direct measurement of the composition of effluent fractions by C13 NMR. Alternatively, the elution temperature-composition calibration for high molecular weight fractions given in Figure 16 may be corrected based on the M_n of effluent fractions and an experimentally established correlation between M_n and elution temperature that applies for M_n < 15,000. However, it is assumed that such low molecular weight molecules are present to a negligible extent and that any errors caused are negligible. A correlation curve such as the one in Figure 16 is applicable to any essentially random poly(ethylene-co-α-olefin) provided, however, that the α-olefin is not propylene.

The temperature scale of a solubility distribution plot can thus be transformed to a composition scale, yielding a weight fraction of polymer vs. composition curve. As seen from the composition scale in Figure 16, Sample X contains molecules spanning a narrow composition range, whereas Sample Y contains molecules spanning a wide composition range. Thus, Sample X has a narrow composition distribution whereas Sample Y has a broad composition distribution.

A quantitative measure of the breadth of the composition distribution is provided by the Composition Distribution Breadth Index (CDBI). CDBI is defined to be the percent of polymer whose composition is within 50% of the median comonomer composition. It is calculated from the composition

distribution cure and the normalized cumulative integral of the composition distribution curve, as illustrated in Figure 17. The median composition, C_{med}, corresponds to the composition at the point where the cumulative integral equals 0.5. The difference between the values of the cumulative integral at compositions 0.5 C_{med} and 1.5 C_{med} (71 - 29, or 42%, in this example) is the CDBI of the copolymer. CDBI values fall between zero and one, with large values indicating narrow CD and low values indicating broad CD. Thus, now referring back to Figure 15, the narrow and broad CD copolymers have CDBI's equal to 95.5% and 42%, respectively. It is difficult to measure the CD and CDBI of copolymers having very low comonomer content with high accuracy so the CDBI of polyethylenes with densities greater than 0.94 g/cc is defined to be equal to 100%. Unless otherwise indicated, terms such as "comonomer content", "average comonomer content" and the like refer to the bulk comonomer content of the indicated ethylene interpolymer on a molar basis.

The ethylene interpolymers of this present invention preferably have a narrow molecular weight distribution (MWD). The term "narrow MWD" means that the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n) is less than or equal to 3.0. Particularly preferred are the ethylene interpolymers having a very narrow MWD, i.e. M_w/M_n less than or equal to 2.5, and especially about equal to 2. Molecular weight distributions of ethylene interpolymers are readily determined by techniques known in the art, such as, for example, size exclusion chromatography.

A graphical illustration of an exemplary narrow MWD, narrow CD ethylene interpolymer is seen in Fig. 3. In this three-dimensional figure, the Y-

axis is the molecular weight, the X-axis is the molar comonomer content, and the Z-axis represents the incidence or weight proportion of molecules. As can be seen, the MWD and the CD of the ethylene interpolymer are narrow and appear as relatively sharp peaks in Fig. 3. In contrast, the MWD/CD diagram for a typical conventional LLDPE, seen in Fig. 2, shows a broad MWD and a broad CD, and the comonomer content tends to decrease as the molecular weight increases. In each blend of the present invention, one or more of the properties of the blend are improved by appropriate selection and combination of narrow CD and narrow MWD ethylene interpolymer blend components. In one embodiment, for example, tear strength may be controlled by blending linear polyethylene resins having about the same average molecular weight but with different average comonomer contents. Such a blend is illustrated as line B in Fig. 1. In another embodiment, the comonomer contents of the linear polyethylene blend components are the same, but molecular weights are varied, as illustrated by line C in Fig. 1. In still further embodiments illustrated by lines D, E and F in Fig. 1, the blend components taken serially in order of increasing molecular weight, or in order of increasing molar comonomer content, have the same or higher comonomer content or molecular weight, respectively.

As used herein, two or more blend components have substantially the same molecular weight if the resulting MWD of the blend thereof is similarly narrow to the MWD of each blend component, i.e. the value of M_w/M_n of the resulting blend is less than or equal to about 3.0, preferably less than about 2.5. Conversely, two or more blend components have a different average molecular weight if the overall M_w/M_n of the resulting blend is

relatively greater than for each such blend component, i.e., the M_w/M_n of the blend is greater than 3.0.

As used herein, two or more blend components have a different comonomer content if the overall CDBI of the resulting blend is relatively less than that of each such blend component, i.e., the overall CDBI of the blend is less than 50%. Conversely, two or more blend components have substantially the same molar comonomer content if the resulting CD of the blend thereof is similarly narrow with respect to each blend component, i.e., the resulting blend has a CDBI of 50% or greater. It is readily appreciated that the CD and MWD of a blend can depend on the relative proportions of each blend component employed therein. It is specifically contemplated that blend components may have the "same" molecular weight for purposes of one blend, but not for the purpose of another blend, e.g., wherein the components would result in the blend having an MWD less than or greater than 3.0 depending on the proportion of each blend component. Similarly, blend components may have a "different" comonomer content for purposes of one blend, but not for the purposes of another blend, e.g., wherein the components would result in the final blend having CDBI less than or greater than 50% depending on the proportion of each blend component.

The molecular weight and composition distribution of a bimodal blend of the invention is illustrated graphically in Fig. 4. It is seen from this MWD/CD diagram that the comonomer content of each of the blend components is different, while the molecular weight of each blend component is about the same. The comonomer content of ethylene interpolymers may be varied by adjusting the amount of comonomer fed to the polymerization reactor. If

more comonomer is fed to the reactor, more comonomer will be incorporated in the resulting interpolymer. The comonomer content of resulting interpolymers may be measured directly by NMR spectroscopy or correlated by density. Generally, when more comonomer is incorporated in the resulting polymer, the density of the polymer will decrease.

The blend of Fig. 4 corresponds to line B of Fig. 1. In contrast, a similar graph for typical conventional LLDPE is seen in Fig. 2, and line A of Fig. 1. These figures show that the lower molecular weight fractions contain more of the comonomer than the higher molecular weight fractions. The lower molecular weight molecules which contain relatively high comonomer concentrations as in this conventional LLDPE can cause undesirable effects such as poor surface properties, high block and tackiness, cling development, high levels of extractables, and fouling of polymerization plants. In the present invention, such effects are minimized and properties are enhanced by providing heat sealed articles comprising ethylene interpolymers or comprising ethylene interpolymer blends of the type illustrated in Curve B, C, D, E, and F.

As an example of the embodiment of Curve B, it has been found that a 50-50 blend of a first LLDPE having a 6.4 mole% 1-butene content and a M_w of 80,400 (M_w/M_n = 2.3; CDBI ≈67%; MI (melt index) = 4.0 dg/min; density = 0.9042 g/cm^3) with a HDPE having a 0.0 mole% 1-butene content and a M_w of 76,700 (M_w/M_n = 2.8; CDBI ≈100%; MI = 5.0 dg/min; density = 0.9552 g/cm^3) has an Elmendorf tear strength of 210 g/mil. Surprisingly, this blend is enhanced in contrast to the tear strengths of 111 and 48 g/mil for the respective first and second blend components. Further, a 25-75 blend of these same components has a further enhanced Elmendorf

tear strength of 227 g/mil. This result is quite surprising and unexpected because including a higher proportion of the second LLDPE resin with the lower tear strength in the blend increases the tear strength of the resulting blend, rather than decreasing the tear strength as would be expected from polyethylene produced according to the prior art.

In another embodiment exemplified in Fig. 5 and line C of Fig. 1, a multimodal MWD is obtained by blending linear polyethylene components each having narrow molecular weight and composition distributions, and about the same comonomer content, but differing molecular weights. The MWD of such blends improves the melt processability and rheological characteristics thereof, for example, the blends may be formulated to have high extrusion rates, high bubble stability, high shear sensitivity, and reduced draw resonance. On the other hand, the optical, mechanical and surface properties of individual blend components are generally substantially retained or improved in the blends, for example tear strength, modulus, yield strength, clarity, gloss, haze, heat sealability, hot tack and the like are improved and blocking is reduced. Moreover, such blends have lower portions of solvent extractable polymer molecules than prior art copolymers having similar molecular weight distribution. Desirable molecular weight and composition distributions may be obtained by separately making the appropriate ethylene interpolymer components and then blending the different components together, or by polymerization of the blend components simultaneously in the same reactor or in multiple reactors.

The higher molecular weight fraction containing relatively less comonomer in conventional

LLDPE may cause an anisotropic morphology during fabrication processing known as "row nucleated" or "shish-ka-bob" morphology. This anisotropic morphology is believed to contribute to poor toughness in articles crystallized from flowing melts. In the present invention, the anisotropy may be minimized by providing a blend with lower concentrations of such higher molecular weight molecules with a relatively low comonomer content and by incorporating the comonomer in the blend components as indicated in blends B, C, D, E and F.

In another embodiment as exemplified by Fig. 6 and line D of Fig. 1, the blend includes components having narrow molecular weight and composition distributions, but differing average molecular weights and average comonomer contents. However, in contrast to conventional LLDPE as illustrated in line A of Fig. 1 and in Fig. 2, the blend of this embodiment has a greater comonomer content in the higher molecular weight fractions or blend components than in the lower molecular weight fractions or blend components. These distributions are obtained, for example, by blending narrow MWD, narrow CD linear polyethylene resins which, taken serially in order of increasing molecular weight, have an increasing comonomer content. It is also contemplated that the blend may include two or more blend components having the same molecular weight as illustrated by line F in Fig. 1, in which case such components would be included in the serial ordering secondarily in order of their increasing average comonomer content. Also, the presence of two or more blend components having the same comonomer content is also contemplated as being within the purview of this embodiment, as illustrated by line E in Fig. 1, provided that there is included either at least one blend component having a higher comonomer

content and molecular weight or at least one blend component having a lower comonomer content and lower molecular weight than any of the blend components having the same comonomer content. In this embodiment, the blend is preferably substantially free of blend components having both a higher molecular weight and a lower comonomer content than any component present in the blend.

Such a blend has heat sealing properties which are significantly superior to prior art blends and conventional LLDPE resins in which the comonomer content generally decreases in proportion to increasing molecular weight components or fractions. The isotropy and toughness of films made from such blends are also improved by minimizing the anisotropic shish-ka-bob or row-nucleated morphology ordinarily caused by a low concentration of comonomers present in the higher molecular weight molecules of conventional LLDPE resins. Moreover, such blends have other desirable properties such as, for example, reduced blocking, reduced coefficients of friction, and lower extractables, in comparison to conventional heat sealable LLDPE resins.

Preferred blends according to the invention generally have a density in the range of 0.88 to 0.94 g/cm^3, and a melt index (MI) (MI by ASTM D-1238) in the range of 0.5 to 2.0. Particularly, one preferred blend may be prepared by combining two different ethylene interpolymer components. The first component is a high molecular weight ethylene interpolymer with a density of 0.88 to 0.92 g/cm^3 and a MI of 0.05 to 2. The second component is a low molecular weight ethylene interpolymer witn a density of 0.91 to 0.96 g/cm^3 and a MI of 50 to 1000. The combination of 50 to 70 wt% of the first component with 30 to 50 wt% of the second component will result in an excellent heat sealing blend.

The linear polyethylene blend components of the invention may be prepared by use of catalyst systems of the metallocene type known to provide ethylene interpolymers with both narrow CD and narrow MWD. Cyclopentadienylide catalyst systems using a metallocene complex in conjunction with an alumoxane cocatalyst or reaction product thereof are suitable for preparing the ethylene interpolymers utilized individually or as blends in the invention. The metallocene catalyst may be represented by the general formula $(C_p)_mMR_nR'_p$ wherein C_p is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IVB, or VB transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M. Various forms of the catalyst system of the metallocene type may be used for polymerization to prepare the polymer components of the present invention including those of the homogeneous or the heterogeneous, supported catalyst type wherein the catalyst and alumoxane cocatalyst are together supported or reacted together onto an inert support for polymerization by gas-phase, high pressure, slurry, or solution polymerization.

The cyclopentadienyls of the catalyst may be unsubstituted or substituted with hydrogen or hydrocarbyl radicals. The hydrocarbyl radicals may include alkyl, alkenyl, aryl, alkylaryl, arylalkyl, and like radicals containing from about 1-20 carbon atoms or where 2 carbon atoms of cyclopentadienyl are joined together to form a C_4-C_6 ring. Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like. Exemplary halogen substituents include

chlorine, bromine, fluorine and iodine. Of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the like. Illustrative, but non-limiting examples of the metallocene catalyst useful in preparing the polymers of the present invention include bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopentadienyl)zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)titanium methyl iodide, bis(cyclopentadienyl)titanium ethyl bromide, bis(cyclopentadienyl)titanium phenyl bromide, bis(cyclopentadienyl)titanium phenyl iodide, bis(cyclopentadienyl)zirconium methyl bromide, bis(cyclopentadienyl)zirconium methyl iodide, bis(cyclopentadienyl)zirconium methyl iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopentadienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopentadienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium ethyl iodide,

bis(cyclopentadienyl)zirconium phenyl bromide, bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl metallocenes such as cyclopentadienyltitanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienylzirconium trimethyl, cyclopentadienylhafnium triphenyl, cyclopentadienylhafnium trineopentyl, and cyclopentadienylhafnium trimethyl.

Other metallocenes which may be usefully employed to prepare the polymer components of the invention include the monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH_2 and derivatives of this reagent such as bis(cyclopentadienyl)Ti=CH_2 · $Al(CH_3)_3$, $(Cp_2TiCH_2)_2$, $Cp_2TiCH_2CH(CH_3)CH_2$, Cp_2Ti-$CHCH_2CH_2$ wherein Cp represents a cyclopentadienyl; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride and other dihalide complexes; silicon, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or

dichloride and other dihalide complexes and the like.

Additional zirconocene catalysts useful according to the present invention include bis(cyclopentadienyl) zirconium dimethyl; bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl) zirconium methylchloride, pentamethylcyclopentadienyl zirconium trichloride, pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethylcyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopentadienes, such as bis(ethylcyclopentadienyl)zirconium dimethyl, bis(Ã-phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, bis(n-butyl-cyclcopentadienyl)zirconium dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl, bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)zirconium di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl and dihalide complexes of the above; silicon, phosphorus, and carbon bridged cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl ethylene bridged bis(tetrahydroindenyl) zirconium dimethyl or dihalide, carbenes represented by the formula $Cp_2Zr{=}CHP(C_6H_5)_2CH_3$, and derivatives of these compounds such as $Cp_2ZrCH_2CH(CH_3)CH_2$.

Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)vanadium dichloride, bis(cyclopentadienyl)vanadium dichloride and the like are illustrative of other metallocenes.

The alumoxanes are polymeric aluminum compounds which can be represented by the general formula $(R\text{-}Al\text{-}O)_n$ which is a cyclic compound and $R(R\text{-}Al\text{-}O\text{-})_nAlR_2$, which is a linear compound. In the general formula R is a C_1-C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 2 to about 20. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained.

The alumoxane can be prepared in various ways. Preferably, alumoxane is prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in the form of a moist solvent. In an alternative method, the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate.

Preferably, the alumoxane is prepared in the presence of a hydrated ferrous sulfate as described in U.S. Patent 4,665,208 incorporated herein by reference. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with ferrous sulfate represented by the general formula $FeSO_4 \cdot 2\ 7H_2O$. The ratio of ferrous sulfate to aluminum trimethyl is desirably about 1 mole of ferrous sulfate for 6 to 7 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The ratio of aluminum in the alumoxane to total metal in the metallocenes can be in the range of about 0.5:1 to about 10,000:1, and preferably about 5:1 to about 1000:1.

Various inorganic oxide supports may be used for supported catalyst systems to prepare interpolymers and blend components of the present invention. The polymerization is generally carried out in the temperature range of about 0-160°C, or even higher. This temperature range is not meant to be exclusive for preparing the interpolymer and blend components of the invention. They may be prepared by any technique resulting in the structure set forth. Atmospheric, sub-atmospheric, or super-atmospheric pressure conditions have been used for the polymerization using the metallocene catalyst described above. It is generally preferred to use catalyst compositions at a concentration so as to provide from about 1 ppm to about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of transition metal based on the weight of monomers in the polymerization of the ethylene polymers.

A slurry polymerization process generally uses super-atmospheric pressures and temperatures in the range of 40-110°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

In a modification, the polymer components of the present invention may be formed by gas-phase polymerization. A gas-phase process utilizes super-atmospheric pressure and temperatures in the range of about 50°-120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst

and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced at a controlled constant temperature or recirculated so as to maintain the particles at a temperature of 50°-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other impurities. Polymer product can be withdrawn continuously or semi-continuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by a suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, separated from residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal. The polymer obtained can be extruded into water and cut into pellets or other suitable comminuted shapes as is known in the art. Also known in the art, pigments, antioxidants and other additives may be added to the polymer.

The blends of the present invention are prepared by blending the desired components in the desired proportions using conventional blending techniques and apparatus, such as, for example, screw-type extruders, Banbury mixers, and the like. Alternatively, the blends may be made by direct polymerization, without isolation of the blend components, using, for example, two or more catalysts in one reactor, or by using a single catalyst and two or more reactors in series or parallel. The blend may also be compounded with various conventional additives known in the art such as, for example, antioxidants, UV stabilizers, pigments, fillers, slip additives, block additives,

and the like. The blend preferably does not contain any blend components in proportions which would significantly adversely affect any improved properties desired to be obtained by blending the LLDPE resins.

Ethylene interpolymers with narrow CD and narrow MWD may be formed as described above. The ethylene interpolymers may be used to form articles with particularly desirable heat sealing properties. In particular, the ethylene interpolymers may be processed into films which will possess particularly desirable heat sealing and other physical characteristics. Different ethylene interpolymer components, each having a narrow CD and narrow MWD, may be combined to form a polymer blend of ethylene interpolymers having particularly preferred heat sealing characteristics. The ethylene interpolymers are individually selected so that the resulting blend is essentially free of blend components having both a higher average molecular weight and a lower average comonomer content than that of any other blend component.

A blend having a narrow CD and a narrow MWD is made by blending two or more ethylene interpolymers selected so that the blend has a CDBI of at least 50% and a MWD (M_w/M_n) $\leq$ 3. A blend having a narrow CD and a broad MWD is made by blending two or more ethylene interpolymers selected so that the blend has a CDBI of at least 50% and a MWD > 3. A blend having a broad CD and a narrow MWD is made by blending two or more ethylene interpolymers selected so that the blend has a CDBI of less than 50% and a MWD $\leq$ 3. Also, an interpolymer having a narrow CD and a narrow MWD can be blended with a polymer having a CDBI of less than 50% and a MWD > 3.0.

The ethylene interpolymers may be used to form any commercial article where heat sealing is important or necessary. For example, the ethylene interpolymers and blends thereof may be used to form films which are in turn formed into bags or pouches by heat sealing techniques known in the art. The heat sealable film may also be used in packaging as the sealing material, for example, the film may be placed over the opening of a container, and then secured to the container by the application of heat. This technique may be used to seal perishable items, such as food, into paper, plastic, glass, ceramic or metallic containers. The technique may also be used to package consumer items in attractive sales displays and to secure items for transportation.

The articles described herein are said to be formed from ethylene interpolymers and blends thereof. The articles may comprise other materials, especially in portions of the article that will not be utilized for heat sealing. In the portions of the article that are used for heat sealing, the language "formed from" is intended to mean "comprising." All articles or portions of articles described herein may also be constructed to consist essentially of the inventive ethylene interpolymers or blends thereof, in more preferred embodiments. In other words, the heat sealing portion of any article described herein may consist essentially of the inventive ethylene interpolymers and blends thereof.

The ethylene interpolymers may be formed into films by methods well known in the art. For example, the polymers may be extruded in a molten state through a flat die and then cooled. Alternatively, the polymers may be extruded in a molten state through an annular die and then blown and cooled to form a tubular film. The tubular film

may be axially slit and unfolded to form a flat film. The films of the invention may be unoriented, uniaxially oriented or biaxially oriented.

The films of the invention may be single layer or multiple-layer films. The multiple-layer films may consist of one or more layers formed from ethylene interpolymers and blends thereof. The films may also have one or more additional layers formed from other materials such as other polymers, polypropylene, polyester and EVOH for instance, metal foils, paper and the like.

Multiple-layer films may be formed by methods well known in the art. If all layers are polymers, the polymers may be coextruded through a coextrusion feedblock and die assembly to yield a film with two or more layers adhered together but differing in composition. Multiple-layer films may also be formed by extrusion coating whereby a substrate material is contacted with the hot molten polymer as the polymer exits the die. For instance, an already formed polypropylene film may be extrusion coated with an ethylene interpolymer film as the latter is extruded through the die. Extrusion coating is particularly useful when the ethylene interpolymer heat seal layer is to be applied to substrates that are woven or knitted from natural or synthetic fibers or yarns, e.g., textiles, or substrates made from non-polymer materials such as glass, ceramic, paper or metal.

Multiple-layer films may also be formed by combining two or more single layer films prepared as described above. For instance, a polypropylene substrate film may be combined with an ethylene interpolymer heat seal film yielding a two layer film that would have the strength properties of polypropylene and the heat sealing characteristic of the ethylene interpolymer film. The two layers of a

film so formed may be adhered together with an adhesive or by the application of heat and pressure.

There are several important characteristics of a good heat sealing polymer. One important characteristic is the heat seal initiation temperature. This is the temperature to which the polymer must be heated before it will undergo useful bonding to itself under pressure. Therefore, heat sealing temperatures above the seal initiation temperature result in heat seals with considerable and measurable seal strength. Relatively lower heat seal initiation temperatures are desirable in commercial heat sealing equipment. The lower temperatures provide for faster operation of the equipment because the polymer need not be heated to as great a temperature to make the seal. Also, cooling of the seal to attain adequate strength will be faster.

Another important characteristic is the seal strength plateau on-set temperature. This is the lowest temperature to which the polymer must be heated to obtain a seal with the maximum strength after cooling that is possible with the particular materials being sealed. As heat sealing temperature is gradually raised above the seal initiation temperature, the resulting seals are stronger. The seal strength continues to increase with increasing sealing temperature up to a point where increased sealing temperature no longer provides increased seal strength. This temperature is the seal strength plateau on-set temperature. More importantly, the seal strength plateau on-set temperature is usually the lowest heat sealing temperature that will yield a heat seal that fails solely by tearing and not by peeling alone or by peeling and tearing. When a heat seal fails by peeling, the two sealed surfaces separate cleanly.

When a seal fails in this manner, the seal strength is usually low. When a seal fails by peeling and tearing the two sealed surfaces undergo considerable stretching or elongation during separation. When a seal fails by tearing, the failure occurs not in the seal itself but in the material around the seal. The maximum seal strength is reached when failure is solely by tearing. Since the mode of seal failure changes at the seal strength plateau on-set temperature, a visual indication of the seal failure modes may be used to determine the plateau on-set temperature. Commercial sealing equipment may be operated at higher speeds if the seal strength plateau on-set temperature is lower for the same reasons discussed above with respect to seal initiation temperature.

A third important characteristic is the sealing window which is the range of temperatures acceptable for forming a seal. The sealing window determines the acceptable range of operating temperatures where seal strength remains essentially constant. The low temperature in the range is the plateau on-set temperature and the upper temperature in the range is the temperature where the seal strength begins to decrease or the polymer begins to degrade. Since it is often difficult or impossible to maintain commercial sealing equipment at exactly the same temperature throughout a commercial sealing run, a broader range of acceptable sealing temperatures makes it easier to assure that all heat seals made will have acceptable strength.

The heat sealed article may be formed by pressing at least two portions of the article together at a temperature sufficient to soften at least one of the article portions. The article portion which has been softened by heat is formed from ethylene interpolymers having a CDBI of at

least 50% or from a polymer blend comprising a plurality of the ethylene interpolymers as blend components. Although it is sufficient if only one of the article portions being heated and pressed to form a heat seal is formed from the ethylene interpolymers or blends of the ethylene interpolymers, it is preferable for all article portions directly involved in the heat seal to be formed from the ethylene interpolymers or blends thereof. Other portions of the article may be constructed of other materials.

The heat sealing temperature must be high enough to soften the interpolymers so that they will stick to the material to which they are being sealed. The heat sealing temperature may range as high as the melting temperature of the interpolymers or even higher, but at temperatures this high the sealing contact time must be shortened.

The seals are formed by heating one or both of the article portions to the necessary temperature, pressing the article portions together for a time sufficient to cause them to meld together, at least partially, and then cooling the seal. The pressure needed to join the portions will depend on the article shape, the thickness of the sealing layer, the composition of the sealing layer and the temperature at which the seal is made. The heat sealed article so formed may be a sealed container comprising a body and a sealing member secured thereto, wherein the sealing member comprises a seal layer comprising one of the group of ethylene interpolymers having a narrow composition distribution and a blend of a plurality of said ethylene interpolymers as blend components.

The body, as described previously, may be constructed with any number of different materials such as paper, plastic, glass, ceramics, metals and

textiles. The body can be constructed with walls that are impervious to liquids and/or gasses or the body may be constructed to allow the passage of liquids and/or gasses. The body may also be constructed with one or more portals to allow passage of small items through the body wall or to allow the consumer to inspect the item stored in the container without removing the item from the container. Figure 13 represents a cross-section of a sealed container, showing a container body 132 and a sealing member 134 which define a sealed chamber 136. The sealed container may also have a flange 138, to provide extra surface area for making a heat seal.

In commercial applications, the open chamber 136 is filled with the item to be packaged and the sealing member 134 is then pressed against the flange 138. The sealing member 134, the flange 138 or both may be preheated prior to contact or one or both may be heated after contact. In any event, the sealing member 134 is pressed against flange 138 at a temperature sufficient to soften the sealing member 134. After sealing member 134 has been pressed against flange 138 under heat and pressure sufficient to form a heat seal, the heat and pressure are removed and the sealed area is cooled. The resulting article is a sealed container with the consumer item sealed in chamber 136.

As discussed above, the sealing member may be constructed solely from the inventive ethylene interpolymers and blends thereof, or the sealing member may be a multilayer film. If the sealing member is constructed from more than one material, the inventive ethylene interpolymers, or blends thereof, need be utilized only in the areas where the heat seal will be formed. For example, the sealing member may be constructed as shown in Figure

14, which is a cross-section of a two-layer film. The sealing member 144 may be constructed of a substrate layer 143 and a heat sealing layer 145.

REFERENTIAL EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following referential examples are offered as related to actual tests performed in the practice of this invention, and illustrate the surprising and unexpected heat seal property of the interpolymers and blends thereof of this present invention and are not intended as a limitation on the scope of the invention.

EXAMPLE I

An ethylene copolymer resin was prepared according to the prior art and is identified herein as Sample No. A. Sample A was prepared in a fluidized bed gas phase reactor employing a titanium transition metal catalyst as described below. The gas phase reaction was carried out at 83°C reaction temperature, an ethylene pressure of 130 psia, a hydrogen/ethylene mole ratio of 0.0556, a butene/ethylene mole ratio of 0.0263 and a residence time of 2.4 hours. A comonomer of 4.82 mole % butene was incorporated in the resulting polymer.

A second copolymer known in the art was prepared in a liquid slurry phase reaction and designated as Sample No. B. The slurry phase reaction temperature used to prepare Sample No. B was 83°C, the pressure of ethylene in the reactor was 130 psia, the hydrogen/ethylene mole ratio in the reactor was 0.0556, and the residence time was 2.4 hours. A comonomer of 3.2 mole % butene was incorporated in the resulting polymer. The prior art transition metal catalyst was prepared in accordance with procedures outlined in U.S. patent 4,719,193 which is incorporated herein by reference.

Silica was calcined at 600°C and then treated with triethylaluminum in a mixture of isopentane at 25°C. Magnesium dichloride was then reacted with titanium trichloride in the presence of aluminum trichloride and tetrahydrofuran (THF) solvent at 60°C. The resulting reaction product was contacted in THF solvent at 50°C with the treated silica prepared as noted above. The resulting product was treated with a mixture of diethylaluminum chloride and tri n-Hexyl aluminum in isopentane at 50°C to yield the catalyst used to prepare Sample B.

The physical properties of the resulting polymers are set forth in Table I below. The melt index (MI) is measured according to ASTM D-1238 and is the number of grams of polymer extruded in ten minutes under a weight of 2.16 kg at a temperature of 190°C.

The tear resistance (TR) is measured by the Elmendorf Pendulum method according to ASTM D-1922 (PL-007). Tear resistance is measured in (Kg/cm) in the machine direction (MD) and in the transverse directions (TD) because the films show different behavior in different directions. Intrinsic tear (IT) is measured according to ASTM 922.

Dart impact resistance (DIR) is measured by the free falling dart method according to ASTM D-1709-75, Method A (PL-002). Dart impact resistance is measured in (gm/mil).

Haze is measured according to ASTM D-1003-61 Procedure A and Gloss is measured according to ASTM D-2457-70, AST D-523-80. Both Haze and Gloss are measured by percent (%). Haze is not the same as Gloss. Gloss is the shine of the film seen by reflected light. The Haze of a film is inversely related to the clarity of the film.

Hexane Extractables (HE) is measured according to the procedure set forth by the Food and

TABLE I

Polymer Properties

Sample No.	Density (g/cm³)	MI (g/10 min @ 190°C)	MW (X 10^3)	MWD (MW/Mn)	CDBI	SCBI (°C)	Comonomer B = Butene H = Hexene (mole %)	TR (Kg/cm)	DIR (gm/mil)	IT (Kg/cm)	Haze (%)	Gloss (%)	HE (%)
A	0.9168	1.0	109.2	5.65	38	28.6	B/4.82	-	-	-	-	-	-
B	0.911	1.0	106.6	5.9	46	-	B/3.2	-	-	-	-	-	-
1	0.9065	5	81.5	3.5	56	27.9	B/4.82	26	80	64	0.9	98	3.5
2	0.9099	5	81.0	4.3	38	34.9	B/5.7	80	60	100	2.4	90	2.1
3	0.9089	5	79.0	4.1	57	27.5	B/5.93	28	100	64	0.5	101	4.0
4	0.9074	5	79.0	4.1	58	27.7	B/5.93	24	70	64	1.0	97	3.6
5	0.9102	5	86.0	5.0	34	37.7	B/4.82	24	40	28	1.2	97	8.1
6	0.909	5	80.0	4.6	38	32.2	B/6.61	65	170	140	1.6	94	2.3
7	0.9045	5	75.0	5.0	-	-	B/6.16	24	110	68	0.7	98	1.1
8	0.9049	5	80.0	2.0	-	-	B/9.1	-	-	-	-	-	-
9	0.9104	1.7	96.5	2.16	50	24.1	H/5.4	-	-	-	-	-	-
10	0.9147	4.0	84.3	2.2	50	22.7	B/5.48	-	-	-	-	-	-

Drug Administration as described in 21 CFR § 1.77.1520(d)(3)(ii) measured in percent (%).

EXAMPLE II

A silica supported transition metal catalyst according to the invention was prepared in the following manner. About 100 grams of high surface area (Davison 952) silica, was dehydrated by heating the silica to 800°C for about five hours and maintaining a flow of dry nitrogen over the silica. The dry silica was then slurried with 500 ml of dry toluene at 25°C under a nitrogen atmosphere in a 2500 ml round-bottom flask equipped with a magnetic stirrer. Thereafter, 250 ml of methyl alumoxane in toluene (1.03 mole/liter in aluminum) was added dropwise over about 15 minutes with constant stirring of the silica slurry. Stirring was subsequently continued for 30 minutes while maintaining the temperature of the flask at 25°C. A toluene solution containing 2.00 grams of bis(n-butylcyclopentadienyl)zirconium dichloride was added to the alumoxane treated silica slurry dropwise over 15 minutes. Stirring was maintained constantly during the addition and for one additional half hour while maintaining the temperature of the slurry at 65°C. Thereafter, toluene was decanted and the solids were recovered and dried under a vacuum for four hours. Analysis of the catalyst indicated that it contained 4.5 wt% aluminum and 0.63 wt% zirconium.

Catalysts prepared in the manner described above was then used for a gas phase reaction under the conditions indicated in Table II. During each polymerization reaction, the indicated amount of ethylene mixed with nitrogen was added to the reactor along with the indicated amount of hydrogen. The reaction time to make each polymer was about two to four hours. The reaction temperature was

maintained as indicated in Table II and the indicated amount of comonomer was added at the start of the reaction. After each reaction, polymer particles were separated from the rest of the reaction mixture. The resulting molecular weight and density of each blend component is also set forth in Table II and properties of the blends are set forth in Table I.

Samples A and B described above in Example I and have a comonomer distribution in relationship to molecular weight as represented by line A of Figure 1. Sample 1 was prepared to have a narrow CD and a broad MWD and contain a majority of high molecular weight component. The distribution of comonomer in relation to molecular weight for Sample 1 would lie along line C of Figure 1.

Sample 2 was blended to have a broad CD and a broad MWD with a minority of high molecular weight, low density component. A distribution plot for Sample 2 would lie along line D of Figure 1.

Sample 3 was blended to have a narrow CD, and a broad MWD and have a majority of high molecular weight component. The distribution figure for Sample 3 would lie along line C of Figure 1.

Sample 4 has a narrow CD, and a broad MWD and contains a minority of high molecular weight component. A representation of the comonomer distribution would appear as line C in Figure 1.

Sample 5 has a broad composition distribution and a broad molecular weight distribution and comprises a minority of high molecular weight high density component. This sample was blended to mimic prior art polymers. The distribution for Sample 5 would lie along line A of Figure 1.

Sample 6 has a broad CD and a broad MWD and contains a majority of a high molecular weight, low

density component. A distribution for Sample 6 would lie along line D in Figure 1.

Sample 7 has a broad CD and a narrow MWD and equal amounts of high and low density components. The distribution for Sample 7 would lie along line B of Figure 1.

Sample 8 has a narrow CD and a narrow MWD and has only one interpolymer component of 80,000 molecular weight and 0.9049 density.

Sample 9 is a single interpolymer with a narrow CD and a narrow MWD. Sample 9 has a high molecular weight of about 96,500 and a 0.9104 density.

Sample 10 is also a single interpolymer component sample with a narrow CD and a narrow MWD. Sample 10 has a 84,300 molecular weight and a 0.9147 density.

TABLE II

Blend Component	Reaction H2 Conc. (ppm)	Reaction Ethylene (mole %)	Reaction Comonomer (mole %)	Reaction Temp. (°C)	Product Comonomer (mole %)	Product MW (X 10³)	Product Density (g/cm³)	CDBI (%)	SDBI (%)
1'	1450	52.0	B/5.0	145	8.22	20	0.912	-	-
1"	115	52.0	B/1.75	145	5.48	115	0.907	-	-
2'	84	42.0	B/6.45	111.7	16.82	190	0.876	62	-
2"	460	52.0	B/2.85	145	4.16	34	0.925	71	24.0
3'	120	41.8	B/2.8	148	4.82	119	0.909	-	-
3"	1310	52.0	B/5.0	145	6.35	22.7	0.912	-	-
4'	895	52.0	B/5.0	145	7.06	31	0.912	-	-
4"	66	41.7	B/2.49	147.3	4.82	143	0.908	-	-
5'	670	41.3	B/5.62	144.9	11.11	31	0.898	68	21.0
5"	73	69.7	B/0.32	188.1	0.01	171	0.938	-	-
6'	269	41.5	B/6.8	140	10.37	115	0.893	71	25.3
6"	800	52.0	B/1.4	145	2.66	27.5	0.945	65	25.2
7'	475	41.5	B/5.17	145	7.19	76	0.897	-	-
7"	185	52.0	B/1.45	145	4.36	78	0.922	-	-
8					9.1	80.0	0.905	-	-
9					5.4/11	96.5	0.910	-	-
10					5.48	84.3	0.915	-	-

EXAMPLE III

The films made from Samples A and B were made on a 1" inch Egan Blown Film Line, (Tower Flight Model) with a blown ratio of 4:1. The films produced each had a thickness of approximately 2.0 mils (50 microns). The blends for samples numbered 1-8 were each homogenized on a large Werner Pfleiderer model ZSK-57 twin screw compounding extruder. Films from each of the resins so blended were then made on a 1-inch Killion Mini Cast Film Line, Model KLB 100 into films having a thickness of 1.5 to 2.0 mils (37.5 to 50 microns) in thickness. Samples 9 and 10 each comprised only one polymer component and therefore did not require blending. Films from Samples 9 and 10 were made on a 2-inch Collin Film Cast Line.

Heat seals were made from the films on a laboratory scale Theller Model EB heat sealer. A dwell time of about one second and a sealing pressure of 50 N/cm^2 was used for making the seals. The seals on the films were made in the transverse direction for both the blown and cast films and the heat sealing anvils were insulated from the heat sealing film by a Mylar film. The Mylar film is very stable at normal heat sealing temperatures and is easily removed from the heat sealing polymer after the seal has been made. The seals were aged for 24 hours before testing them for strength.

For the strength test, the sealed samples were cut into 1 inch (2.54 cm) wide pieces and then strength tested using an Instron instrument at a strain rate of 508 mm/min and a 2 inch (5.08 cm) jaw separation. The free ends of the sample are fixed in jaws, and then the jaws are separated at the strain rate until the seal fails. The peak load at seal break is measured and the seal strength is

calculated by dividing the peak load by the sample width.

The heat seal initiation temperature was determined by measuring the seal strengths of each sample sealed at various temperatures and then extrapolating from a plot of seal strength versus temperature to find the lowest temperature at which some seal strength is present. This same plot can be used to determine the temperature at which a seal strength of 2 N/cm occurs. The plot can also be used to determine the plateau on-set temperature and the sealing temperature window. Values for these measured properties of prior art and inventive heat sealed films are given in Table III.

A qualitative rank of the performance of each of the samples further indicates the advantages of heat seals made from the inventive interpolymers over those of the prior art. Prior art type polymers are represented by Samples No. A and B and rank at the top of the order depicted in Table IV. The samples at the top of the Table require the highest heat sealing temperatures for the indicated level of seal strength. They are therefore the least desirable of the samples ranked in Table IV. Samples at the bottom of the Table require the lowest heat sealing temperature required for achieving the indicated level of seal strength and are therefore most desirable. Sample No. 5 was blended to mimic the composition distribution of prior art polymers, and as can be seen from Table IV, the properties of Sample No. 5 are about as poor as those of prior art polymers.

The 2 N/cm seal strength, while chosen arbitrarily, does provide some indication of the minimum temperature necessary to provide commercially useful heat seals. As Tables III and IV show, the invention provides seals with 2 N/cm

seal strengths at heat sealing temperatures of 95°C or less, 90°C or less, or even 85°C or less. The prior art samples A and B, and sample 5 blended to mimic the prior art required heat sealing temperatures of greater than 95°C in order to produce a seal of 2 N/cm seal strength. All of the inventive blends required 95°C or less. These temperatures are significantly below the temperatures required for sealing prior art polymers, even though in absolute terms they differ by only a few degrees Centigrade. This small reduction in absolute heat sealing temperature can result in significant improvement in commercial heat sealing processes. As mentioned before, the lower seal temperature provides for faster sealing and greater productivity per heat sealing machine.

TABLE III

Sample No.	Seal Initiation Temperature (°C)	2N/cm Temp. (°C)	Plateau On-Set (°C)	Sealing Window (°C) (170°-On-Set Temperature)
A	105	109	126	44
B	93	96	123	47
1	86	88	120	50
2	90	95	125	45
3	80	84.5	115	55
4	84	92	115	55
5	105	108	130	40
6	87	89	125	45
7	85	86	120	50
8	84	89	122	48
9	82	84.5	112	58
10	91	91.5	113	57

TABLE IV

Sample Rank Based on Temperature Necessary for the Indicated Seal Strength

Temperature	Seal Initiation 2N/cm		Plateau On-set	
highest	A	A	5	5
	5	5	A	A
	B	B	2	2
	10	2	6	6
	2	4	B	B
	6	10	8	8
	1	6	1	1
	7	8	7	7
	4	1	3	3
	8	7	4	4
	9	3	10	10
lowest	3	9	9	9

Although all of the resins according to the invention provide improved heat sealing properties, samples numbered 1, 3, 6, 7, 8 and 9 are far superior than the prior art polymers as indicated by the data in Tables III and IV. They form seals of 2 N/cm strength at sealing temperatures of 90°C or less. Samples 3 and 9 form such seals at 85°C or less. A further indication of the superiority of the inventive heat seals made from the particularly described polymers is graphically indicated in Figures 7-12. Figure 7 represents the sealing curve of two prior art polymers, Samples A and B. The graphs represent the seal strength of a heat seal measured in N/cm with respect to the temperature (°C) at which the seal was made. For comparison, the curve for Sample A appears in all of the Figures 7-11.

Figure 8 represents the curves for samples numbered 1, 2 and 3 and graphically depicts the advantages of samples 1, 2 and 3 over the prior art. The curves for the inventive samples begin at lower temperatures, thus indicating the lower seal initiation temperature achieved through the use of the narrow CD and narrow MWD polymers or blends thereof. The strength of the seal formed with these inventive polymers is greater at the same heat sealing temperature as compared to the prior art polymer A. For example, in Figure 8, at 100°C sealing temperature, it is apparent that samples numbered 1, 2 and 3 have remarkably higher seal strength than the prior art polymer of Sample A. For instance, the seal strength of Sample A at 100°C as determined from the figure is less than 1 N/cm, whereas the seal strength for Sample No. 3 is above 6 N/cm. This Figure shows the remarkably improved seal strength of a film according to the invention at a relatively low sealing temperature.

Figure 9 represents samples numbered 4, 5 and 6 compared to Sample A. This figure shows further that Sample No. 5, which was blended to mimic prior art type polymers, has a sealing curve substantially the same as that of prior art polymers. In comparison, samples numbered 4 and 6 exhibit the beneficial properties as described in the specification. Namely, samples numbered 4 and 6 have greater seal strength at the same sealing temperature in comparison to the prior art polymers represented by Sample A. For instance, at 100°C, the seal strength for Sample No. 6 is above 4 N/cm while the seal strength for Sample No. A is below 1 N/cm.

Figure 10 represents the advantages of samples numbered 7 and 8 compared to the prior art polymer. The figure shows that samples 7 and 8 exhibit the same desirable qualities as described in this application. Namely, low seal initiation temperature and a greater seal strength at lower sealing temperatures. Again for comparison, the inventive polymers exhibit remarkably higher seal strength at 100°C sealing temperature than is exhibited by the prior art polymer. The inventive resins have seal strengths of 4 N/cm or greater compared to less than 1 N/cm for the prior art polymer.

Figure 11 represents the seal strength data for samples numbered 9 and 10 in comparison with the prior art Sample A. The same advantages for samples 9 and 10 are apparent and include remarkably higher seal strength at a sealing temperature of 100°C. Samples numbered 9 and 10 have a seal strength of almost 6 N/cm at 100°C compared to less than 1 N/cm for the prior art polymer.

Figure 12 represents the seal strength data for samples numbered 1, 3 and 9 in comparison with

prior art Sample B. This plot shows the same heat sealing advantages of the invention, i.e. lower heat seal initiation temperature and greater seal strength at a given heat sealing temperature, in comparison to the prior art.

The commercial advantages to be obtained through the use of the inventive type of heat sealing articles is apparent from the figures. The inventive articles may be adequately sealed at temperatures of less than 120°C, 110°C, or 100°C, and yet retain adequate strength in the seal thus formed. In comparison prior art polymers sealed at 100°C, 110°C or even 120°C and higher may not yield seals of substantial strength. It is therefore possible to use the inventive materials in commercial lines operating at a sealing temperature as low as 100°C or less. An operating temperature of 100°C is substantially lower than normal commercial sealing operating temperatures. With sealing temperatures as low as 100°C, substantial increases in heat sealing speed may be achieved and therefore the output of a heat sealing unit may be remarkably increased by use of the inventive heat sealing materials. At the higher heat sealing temperatures used for sealing prior art materials, the invention provides the advantage of faster sealing. Since the properties of the interpolymers or blends of interpolymers provide for faster heat sealing, greater numbers of seals may be made on existing heat sealing equipment.

While the present invention has been described and illustrated by reference to particular embodiments thereof, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For instance, the catalyst system may comprise various other transition metal

metallocenes that are activated by alumoxane and/or ionic activators as the cocatalyst to produce interpolymers having a narrow molecular weight distribution and narrow composition distribution. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

What is claimed is:

1. An article of manufacture having a seal region formed by pressure contact of first and second article portions of a temperature sufficient to soften at least one portion wherein at least the first portion comprises an ethylene interpolymer or blend of ethylene interpolymers, the blend or each interpolymer being selected to have a composition distribution breadth index (CDBI) as herein before defined of at least 50% such that the portions are sealably contacted at a seal initiation temperature less than 93°C.

2. The article according to claim 1 wherein at least the first portion comprises a film and optionally the second portion comprises a like film or a layer comprising a polymer other than said interpolymer or interpolymer blend, a metal foil, paper or textile.

3. The article according to claim 1 or 2 when in the form of (i) a multilayer film or (ii) a sealed container comprising (a) a body, optionally of molded polyolefin, and (b) a sealing member having or comprising a seal layer sealed to the body and constituting the first article portion, said sealing member optionally further comprising a supporting substrate adhered to the seal layer or optionally being a film of at least two layers one of which is the seal layer and another of which is a supporting substrate.

4. The article in accordance with any preceding claim wherein the CDBI is at least 70%.

5. The article in accordance with any preceding claim wherein the blend or each interpolymer has a comonomer content of from 0.01 to 17 mole percent.

6. The article in accordance with any preceding claim wherein the molecular weight distribution of the blend or each interpolymer is 2.5 or less.

7. The article in accordance with any preceding claim wherein the blend or each interpolymers has a density of from 0.875 to 0.96 g/cm^3, preferably from 0.89 to 0.93 g/cm^3, and a weight average molecular weight in the range of 10,000 to 1,000,000, preferably from 40,00 to 200.000.

8. The article in accordance with any preceding claim wherein the polymer blend is essentially free of blend components having both a higher average molecular weight and a lower average comonomer content than that of any other blend component.

9. The article in accordance with any preceding claim wherein the polymer blend comprises ethylene interpolymer components having substantially:

(1) the same average molecular weight but different average comonomer content, or,

(2) the same average comonomer content but different average molecular weights, or,

(3) different average molecular weights and comonomer contents wherein said components, taken serially in order of increasing average molecular weight have an increasing comonomer content, or,

(4) a combination thereof.

10. The article in accordance with any of claims 1 to 8 wherein said polymer blend has a broad

molecular weight distribution and optionally a narrow composition distribution.

11. The article in accordance with any preceding claim wherein the polymer blend has a density of from 0.88 to 0.94 g/cm^3, preferably from 0.90 to 0.92 g/cm^3, and a melt index (MI) of from 0.5 to 20, preferably a weight average molecular weight of form 40,000 to 200,000.

12. The article in accordance with claim 11 wherein the polymer blend comprises 50 to 70 wt% of a high molecular weight component with a density of 0.88 to 0.92 g/cm^3 and a MI of 0.05 to 2, and 30 to 50 wt% of a low molecular weight component with a density of 0.91 to 0.96 g/cm^3 and a MI of 50 to 1000.

13. A method of forming a heat seal by pressing at least two article portions together at a temperature sufficient to soften at least one of the article portions wherein at least one of the article portions is formed from an ethylene interpolymer having a composition distribution breadth index (CDBI) of at least 50%, or a polymer blend comprising a plurality of said ethylene interpolymers, and wherein said heat seal has a heat seal initiation temperature of less than 93°C.

14. The use of an ethylene interpolymer having a CDBI of at least 50%, or a blend comprising two or more such interpolymers, as a sealing portion in an article having first and second portions comprising a sealed region where sealing is initiated at a temperature less than 93°C.

15. The article, method or use according to any preceding claim wherein the seal initiation temperature is in the range 80°C to below 93°C.

16. The article, method or use according to any preceding claim wherein the seal has a plateau-on-set temperature in the range of 110°C to below 123°C.