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(54) Title: HEAT SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY ETHYLENE COPOLYMERS

(57) Abstract

Laminar polyolefin film materials have a base film layer comprising a blend of an olefin polymer and up to 30 % by weight of at least one very low density copolymer of ethylene and a C_3 to C_2 alpha olefin comonomer copolymerizable with ethylene, and a heat sealable film layer present on one or both surfaces thereof comprising a very low density copolymer of ethylene and a copolymerizable C_5 to C_{12} alpha olefin comonomer. The ethylene copolymer constituents of the film are characterized as having a density in the range of about 0.88 g/cm^3 to 0.915 g/cm^3, a melt index in the range of 0.5 dg/min to 7.5 dg/min, a molecular weight distribution (M_w/M_n) of 1.5 to 3.5 and an essentially single melting point in the range of 60 °C to 115 °C, measured as a DSC peak T_m.

5   HEAT SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY
ETHYLENE COPOLYMERS

FIELD OF THE INVENTION

10   This invention relates to a laminar polyolefin film
having a base layer and at least one heat sealable layer
present on one or both surfaces of the base layer. More
specifically, the film has a base layer comprising a blend
of an olefin polymer and a very low density ethylene/alpha
15   monoolefin copolymer and a heat sealable layer comprising
a very low density copolymer of ethylene and a different
alpha monoolefin.

BACKGROUND OF THE INVENTION

         Films based on polyolefin polymers and copolymers are
20   widely used in packaging applications which require
sealing of the film to itself as the package is formed
and/or filled. This sealing may be accomplished using
adhesives such as low density polyethylene or
ethylene/vinyl acetate copolymers. When heat sealing is
25   used, it is important that the thermoplastic film be
readily heat sealable while also maintaining other
physical and mechanical properties such as resistance to
tearing, tensile strength and processability in high speed
packaging equipment.
30   In form/fill packaging operations, film is generally
first processed into a bag, a bottom being formed by
squeezing together two films, and subjecting the bottom to
a temperature above the seal initiation temperature under
pressure to seal the bottom of the bag. The bag is
35   subsequently filled with the goods to be packaged, and the
top is then sealed in a similar fashion.
         Film heat sealing is generally effected by means of
heated flat surfaces, between which film surfaces are

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forcefully pressed together at a temperature above the
seal initiation temperature of the film. When use is made
of equipment such as vertical form, fill and seal
machines, the bag is filled with the contents to be
5   packaged while the bottom seal is still hot. Cooling the
seal would entail too long a waiting time, thus
lengthening the cycle time and increasing operating costs.
Consequently, the film must be one which enables the
formation of a strong seal even as the seal formed is at
10 or near the seal formation temperature, i.e., it must have
good hot tack seal strength.
      There are several other desirable characteristics of
a heat sealable film which enable trouble free performance
in form fill and seal applications. First the film should
15 provide strong seals at a low temperature to minimize
energy requirements. Additionally, the film should allow
for strong seals over a broad temperature range so that
the film is more forgiving of heat sealing equipment
adjustments and inadequacies. Further, the film should
20 enable the development of seal strength almost immediately
(before cooling) so that the seal bears and secures the
weight of the wrapped product.
      Many commonly used plastic materials which are used
in the formation of film products could benefit from an
25 improvement of their heat sealing characteristics. For
example, crystalline polyolefin films such as
polypropylene films have found extensive use in the field
of packaging. Polypropylene films, in both oriented or
non-oriented form, are used widely in packaging
30 applications because of their superiority in mechanical
properties such as tensile strength, rigidity, surface
hardness, and optical properties such as gloss and
transparency, and in food hygiene properties such as
freedom from toxicity and odor. However, polypropylene
35 and other crystalline polyolefin films typically require
heat sealing initiation temperatures upwards of about
120ºC before adequate film seal strengths (at least 78.7
g/cm (200 g/inch), desirably 157.5 g/cm (400 g/inch) and

higher per specified settings for pressure and dwell time)
are obtained. Consequently, there has been considerable
development work to find ways that would allow the heat
sealing of polypropylene films at lower temperatures and
5   provide good hot tack seal strength. Such approaches have
included the use of coatings, blend components and
multiple film layers.

EP-A-0 221 726 discloses a film laminate prepared by
coextruding a base layer which may be a polyolefin,
10 particularly polypropylene or mixtures of polyolefins, and
a heat seal layer which may be a very low density
polyethylene (VLDPE) or a blend thereof with another
polyolefin. The publication also indicates that scrap
film may be recycled which could lead to structures where
15 the base layer would comprise a blend of polypropylene and
VLDPE. The VLDPE is described as having a density of 0.890
to 0.912 g/cc and a melt index of generally 0.8 g/10
minutes or less, and is said to be of low crystallinity
and produced in a low pressure process.

20   EP-A-0 247 897 discloses a film laminate comprising a
base layer which may contain polypropylene and at least
one heat-sealable film layer which may be based on a very
low density copolymer of ethylene and an alpha-monoolefin
such as octene-1.

25   US-A-4,764,404 discloses a multi layer package film
having adhered to one side of a base layer (aluminum,
polyamide or vinylidene chloride sheet) a composition
comprising a blend of polypropylene (40-70% by weight), a
second component which may be a copolymer of ethylene and
30 a different alpha olefin (5-35% by weight) and a third
elastomeric olefin polymer or copolymer (10-40% by
weight). The second component may be ethylene-based
copolymers available from Mitsui Petrochemical Company
Limited under the designations "TAFMER" A or P.

35   EP-A-0 341 091 discloses that certain linear low
density ethylene copolymers made in accordance with US-A-
4,612,300 using a Ziegler-Natta magnesium halide supported
catalyst have good heat seal properties for packaging

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applications. These copolymers may contain 7-40 wt % of a
C_5 to C_{12} alpha olefin and exhibit a density of 0.87 to
0.915.

5   US-A-Patent No. 4,291,092, 4,339,496, 4,340,640 and
4,340,641, all disclose a heat sealable packaging film
layer for a polypropylene substrate wherein the film layer
comprises a blend of a copolymer of ethylene and a higher
olefin and a copolymer of propylene and a higher olefin.
US-A-4,643,945 discloses the use of a linear low density
10   polyethylene in a heat sealable film composition.

The prior art heat sealable films are not without
certain deficiencies. A need still exists in the industry
for a heat sealable layer having a seal initiation
temperature of about 110°C (225°F) or lower while the film
15   maintains good elevated temperature hot tack properties,
abrasion resistance, blocking resistance, good strength
and rigidity, and good film optical properties.

A class of highly active olefin catalysts known as
single site catalysts or metallocenes is well known
20   especially in the preparation of polyethylene and ethylene
copolymers. These catalysts, particularly those based on
group IVB transition metals such as zirconium, titanium
and hafnium, show extremely high activity in ethylene
polymerization. The metallocene catalysts are also highly
25   flexible in that, by manipulation of catalyst
substituents, catalyst composition and reaction
conditions, they can be made to provide polyolefins with
controllable molecular weights from as low as about 200
(useful in applications such as lube oil additives) to
30   about 1 million or higher as, for example, ultra high
molecular weight linear polyethylene. At the same time,
the molecular weight distribution of the polymers can be
controlled from extremely narrow (as in a polydispersity,
M_w/M_n of about 2), to broad (a polydispersity of about 8).
35   Teachings on these metallocene catalysts for the
polymerization of ethylene is found in EP-A-0 129 368 and
US-A-4,937,299. The metallocene catalyst may be used with
an activator such as an alumoxane which is formed when

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water reacts with trialkyl aluminum with the release of
methane, which alumoxane complexes with the metallocene
compound to form the catalyst; or with other types of
activators well known in the catalytic art. See for
5   example EP-A-0 277 003 and EP-A-0 277 004 both published
August 3, 1988. These publications describe ionic
activators, which ionize the metallocene on contact,
forming a metallocene cation associated with, but not
coordinated or only loosely coordinated to the remaining
10   ion of the ionizing compound. Further, useful to produce
polymers in polymerization process are the metallocene
catalyst components and catalyst systems described in US-
A-5,055,438, 5,057,475 and 5,096,867, EP-A-0 420 436 and
WO91/04257. These references relate to the metallocene
15   catalyst component being a monocylopentadienyl heteroatom
containing compound, which can be activated by the
alumoxane or the ionic compound described above.

        There are a number of structural variables in
polyolefins which affect the ultimate properties of the
20   polymer. Two of the most important are composition
distribution (CD) and molecular weight distribution (MWD).
Composition distribution (CD) refers to the distribution
of comonomer between copolymer molecules. This feature
relates directly to polymer crystallizability, optical
25   properties, toughness and many other important use
characteristics. Molecular weight distribution (MWD)
plays a significant role in melt processability as well as
the level and balance of physical properties achievable.
Molecular weight (MW) determines the level of melt
30   viscosity and the ultimately desired physical properties
of the polymer. The type and amount of comonomer affects
the physical properties and crystallizability of the
copolymer. All of these structural features (MW, MWD, CD,
comonomer type and amount) are readily controllable
35   through he use of metallocene catalysts as discussed in
EP-A-0 129 368 and US-A- 4,937,299.

        Metallocene catalyst are particularly attractive in
making tailored uniform and specialty copolymers. For

example, if a lower density ethylene copolymer is made
with a metallocene catalyst, such as very low density
polyethylene (VLDPE), a uniform copolymerization will
occur, as contrasted with the polymer produced by
5   copolymerization using conventional Ziegler Natta
catalysts.

SUMMARY OF THE INVENTION

The invention provides laminar polyolefin film
materials having a base film layer comprising a blend of
10 an olefin polymer and up to about 30% by weight of at
least one very low density copolymer of ethylene and a C_3
to C_{20} alpha monoolefin comonomer copolymerizable with
ethylene, the base layer having a heat sealable film layer
present on one or both surfaces thereof comprising a very
15 low density copolymer of ethylene and a copolymerizable C_3
to C_{20} alpha olefin comonomer, the film further
characterized in that the ethylene/alpha monoolefin
copolymer present in one of said layers is a copolymer of
ethylene and a C_6 to C_{10} alpha monoolefin which alpha
20 monoolefin differs from the alpha monoolefin present in
the ethylene copolymer of the other the layers. The
ethylene copolymer constituents of the film are
characterized as having a density in the range of 0.88
g/cm^3 to 0.915 g/cm^3, a melt index in the range of 0.5
25 dg/min to 7.5 dg/min, a molecular weight distribution
(M_w/M_n) of 1.5 to 3.5 and an essentially single melting
point in the range of 60°C to 115°C, measured as a DSC
peak T_m.

Films of this invention exhibit extremely good hot
30 tack seal strength at temperatures in the range of from
93.3°C to 143.3°C (200 to 290°F) thereby rendering them
extremely useful as packaging materials in high speed
packaging operations.

BRIEF DESCRIPTION OF THE DRAWINGS

35 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 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. 2 is a graph illustrating the correlation between dissolution temperature and composition used to convert the temperature scale to a composition scale.

FIG. 3 is a graph illustrating the method for calculating CDBI.

DETAILED DESCRIPTION OF THE INVENTION

The polyolefin component of the base (or core) material of the film of this invention is preferably selected from the group consisting of polypropylene, low density polyethylene, linear low density polyethylene, polybutene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4 to C_{12} alpha olefin as well as blends of two or more of these materials. The polyolefins which may be used as the major component in the base layer are distinguished from the VLDPE copolymers also contained in the film in that the former generally exhibit a density in excess of 0.915 g/cm^3.

The preferred polyolefin component of the base layer is crystalline polypropylene or random copolymers of propylene and another alpha olefin. Where random propylene copolymers are used as the base layer, the content of propylene is preferably in the range of from 88 to 99 mole percent, based on total moles, more preferably in the range of 90 mole percent to 94 mole percent. The preferred random copolymers consist of propylene copolymerized with 1 to 10 mole percent of ethylene.

The VLDPE's which may be used as the copolymer component of the base or sealing layers of the film of this invention are ethylene/alpha-monoolefin copolymers wherein the monoolefin can have from 3-20 carbon atoms such as ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1, and ethylene/propylene copolymers. These ethylene copolymers with prescribed range of comonomer levels can be prepared by polymerization of the

suitable olefins in the presence of supported or
unsupported single site catalysts systems. The preferred
range of comonomer level generally ranges from 4 to 15
mole percent.

5   The preferred single site catalyst systems preferably
used to produce the copolymers employed in films of the
invention are those wherein a transition metal compound is
activated with an activator preferably the transition
metal compound is of the formula $(LS)ZX_1X_2$

10   wherein Z is a group 3 to 10 transition metal, X_1 is an
anionic leaving group ligand or a non-coordination anion
leaving group, X_2 is a hydride or hydrocarbyl ligand, and
(LS) is a ligand system which completes the coordination
number of Z. Preferably the ligand system coordinated to

15   the transition metal (i) two cyclopentadienyl ligands,
each optionally substituted and the two optionally being
bridged with a bridging atom or group or (ii) a single,
optionally substituted, cyclopentadienyl ligand and a
heteroatom - containing ligand, the two ligands optionally

20   being bridged with a bridging atom or group.
Representative examples of such compounds may be found for
example in EP-A-0 129 368 and EP-A-0 420 436.

        The activator preferably employed is an aluminum
compound such as an alumoxane; or a non-coordinating anion

25   precursor such as described in EP-A-0 277 003 and EP-A-0
277 004.

        The low melting polymer ingredient utilized in the
base layer and heat seal layer of the film of the present
invention has a density in the range of 0.88 g/cm^3 to

30   0.915 g/cm^3. Preferably the density is in the range of
0.89 g/cm^3 to 0.91 g/cm^3. Densities above 0.90 g/cm^3 are
measured using standard accepted procedures. At densities
below 0.90 g/cm^3, the samples are additionally conditioned
by holding them for 48 hours at ambient temperature

35   (23ºC), prior to density measurement.
        The melt index (MI) of the ethylene/alpha-mono-
olefin copolymers of the present invention is in the range
of 0.5 dg/min to 7.5 dg/min. Preferably the MI is in the

range of 0.5 dg/min to 5.0 dg/min, and the most preferred
MI is in the range of 1.0 to 2.5 dg/min. MI as measured
herein is determined according to ASTM D-1238 (190/2.16).
High load MI is determined according to ASTM D-1238

5   (190/21.6). These copolymers also have a narrow molecular
weight distribution. The ratio of M_w/M_n is generally in
the range of 1.5 to 3.5, preferably in the range of 2.0 to
3.0.

The ethylene/alpha-monoolefin copolymers preferably

10 have an essentially single melting point characteristic
with a peak melting point (T_m) as determined by
Differential Scanning Colorimetry (DSC) in the range of
60°C to 115°C. More preferably the DSC peak T_m is in the
range of about 80°C to about 100°C. "Essentially single

15 melting point" as used herein means that at least about
80% by weight of the material corresponds to a single T_m
peak existing in the range of 60-115°C, and there is
essentially absent from the polymer any substantial
fraction of material which corresponds to a T_m peak found

20 at a temperature higher than 115°C, i.e., "essentially"
the bulk material content of the polymer corresponds to a
"single" melting point peak in the 60-115°C range, and
"essentially" no substantial fraction of the material has
a peak melting point in excess of 115°C, as determined by

25 DSC analysis.

DSC measurements are made on a Perkin Elmer System 7
Thermal Analysis System. Melting information reported are
second melting data i.e. the sample in heated at a
programmed rate of 10°C/min to a temperature above its

30 melting range. The sample is then cooled at a programmed
rate of 10°C/min to a temperature below its
crystallization range. The sample is then reheated (2nd
melting) at a programmed rate of 10°C/min.

The presence of higher melting peaks is detrimental

35 to film properties such as haze, and compromises the
chances for meaningful reduction in the seal initiation
temperature of the final film.

The composition distribution breadth index (CDBI) of

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such VLDPE copolymers will generally be in the range of 70
percent or higher. The CDBI is defined as the weight
percent of the copolymer molecules having a comonomer
content within 50 percent (i.e. ±50%) of the median total
5   molar comonomer content. The CDBI of linear polyethylene,
which does not contain a comonomer, is defined to be 100%.

The Composition Distribution Breadth Index (CDBI) is
determined via the technique of Temperature Rising Elution
Fractionation (TREF). CDBI determination clearly
10 distinguishes the VLDPE copolymers of this invention
(narrow composition distribution as assessed by CDBI
values generally above 70%) from VLDPE's available
commercially today which generally have a broad
composition distribution as assessed by CDBI values
15 generally less than 55%. The benefits to the subject
invention accrue through the specific use of VLDPE's of
narrow composition distribution. The CDBI of a copolymer
is readily calculated from data obtained from techniques
known in the art, such as, for example, temperature rising
20 elution fractionation as described, for example, Wild et
al., J. Poly. Sci, Poly, Phys, Ed., Vol.. 20, p. 441
(1982) and U.S. Patent No. 5,008,204.
Solubility Distribution is measured using a column of
length 164 cm and 1.8 cm ID (inner diameter) is packed
25 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
30 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
35 140°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

5 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

10 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

15 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 tetrachlorethylene solvent is pumped through the column at

20 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

25 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

30 Distribution Breadth Index (SDBI) is set forth below. Solubility distributions of two ethylene interpolymers are shown in FIG. 1. Here, for illustration purposes only, Sample X has a narrow solubility distribution and elutes over a narrow temperature range compared to Sample Y,

35 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

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(dissolving) at temperature T. The average dissolution
temperature, T_{ave}, is given by

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

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SDBI is calculated using the relation:

$$SDBI(°C) = [\int (T - T_{ave})^4 w(T) \, dT]^{1/4}$$

10   (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
15   FIG. 1 have SDBI values equal to 14.6°C and 29.4°C,
respectively. The preferred values of SDBI are less than
28°C and more preferred less than 25°C and even more
preferred less than 20°C.
      The composition distribution (CD) of a crystalline
20   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. FIG.
25   2 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
30   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
35   weight fractions given in FIG. 2 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

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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 FIG. 2
is applicable to any essentially random poly(ethylene-co-α
5   -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 versus composition
10 curve. As seen from the composition scale in FIG. 2,
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
15 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
20 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 FIG. 3. The median composition, C_{med},
corresponds to the composition at the point where the
25 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
30 values indicating broad CD. Thus, now referring back to
Figure 1, 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
35 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 copolymer.

Utilizing a metallocene catalyst, the VLDPE copolymers useful as the low melting polymers of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

A slurry polymerization process generally uses super-atmospheric pressures and temperatures in the range of 40-100°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 an alkane, 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.

Alternatively, the VLDPE copolymer 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 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 or recirculated so as to maintain the particles at a temperatures of 50°C-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 any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge,

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and used without further deactivation or catalyst removal.

The VLDPE copolymers of the present invention can also be produced in accordance with a high pressure process by polymerization ethylene in combination with

5   other monomers such as butene-1, hexene-1, octene-1, or 4-methylpentene-1 in the presence of the catalyst system comprising a cyclopentadienyl-transition metal compound and an alumoxane compound. In the high-pressure process, the polymerization temperature would generally be above

10   120°C but below the decomposition temperature of the polymer product and that the polymerization pressure would generally be above 500 bar (kg/cm^2) although other temperature and pressure conditions may also be employed. In those situations wherein the molecular weight of the

15   polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in producing copolymers employed

20   in films of this invention.

The blend composition of the film base layer contains from 1 to 30 percent by weight of the VLDPE copolymer component, more preferably from 5 to 25 percent by weight of VLDPE, each based on the total weight of olefin polymer

25   forming the base film layer.

The VLDPE copolymer which is applied to one or both surfaces of the base film layer to form a heat sealable layer may possess the same physical and chemical characteristics and may be made by the same processes as

30   described above with respect to the VLDPE component of the base layer, except that it differs in composition from the copolymers contained in the base layer.

It has been found that the excellent results in terms of hot tack seal strength are achieved where the VLDPE

35   component of a first layer which may be the base layer or heat sealable layer is a copolymer of ethylene and a C_3 to C_{20} alpha-monoolefin and the VLDPE component of the other layer is a copolymer of ethylene and a C_6 to C_{10} alpha-

monoolefin which differs from the alpha-monoolefin
comonomer present in the VLDPE of the first layer. In the
more preferred embodiments of the invention, the C_6 to C_{10}
alpha-monoolefin-containing copolymer is used as the heat

5   seal layer and the different C_3 to C_{20} alpha-monoolefin-
containing copolymer is used as a component in the base
layer.

These materials provide an excellent balance of
adhesion to the substrate base film without the need to

10 employ an inter disposed anchor or tie layer such as
polyvinylidene chloride or ethylene/vinyl acetate
copolymers, and also possess the requisite high hot tack
seal strength required for modern high speed packaging
applications. Best results in terms of adhesion and hot

15 tack seal strength are achieved with laminar structures
wherein the VLDPE copolymer component of the base layer is
an ethylene/butene-1 copolymer and the heat seal coating
layer comprises a copolymer of ethylene with either
hexene-1 or octene-1.

20 The percent hexane extractables for the low melting
polymer VLDPE ingredients of the present invention are low
enough to allow for applications in the food industry.
Preferably, for food packaging applications, products
having extractables 5 percent and under would be utilized.

25 The heat sealable films of the present invention may
be manufactured using film fabrication technologies well
known in the art. For example, the base film may be
extruded into film using a flat die or blown extruded into
film using a tubular die, and the heat seal layer formed

30 thereon by solvent deposition, lamination or coextrusion
techniques. A preferred method of manufacture is via
coextrusion wherein a molten layer of the heat seal
material is applied to the surface of an extruded cast
film of the base layer. These laminar films may

35 optionally be further oriented (either uniaxially or
biaxially) using technologies well known to those skilled
in the art.

The laminar film structure of the present invention

may have an overall thickness in the range of from .00127
cm (0.5 mil) to 0.0127 cm (5 mil), with a preferred
thickness of .0019 cm (0.75 mil) to 0.00635 cm (2.5 mil).
The heat seal coating layer may constitute from 3 to 50%
5   of this overall thickness, more preferably from 10 to 25%
of the overall thickness, present on one or both sides of
the base layer.

The VLDPE copolymer component of the base layer may
also comprise a mixture of compositionally different VLDPE
10   components within the scope of this invention. This is
particularly the case because the VLDPE component of the
base layer differs compositionally from the VLDPE
component of the heat seal layer. Scrap trim recycled to
the extruder and mixed with virgin polymer used to make
15   the base layer will result in a base layer which contains
a mixture of these VLDPE copolymers. Thus, in a preferred
embodiment wherein the heat sealable layer comprises a
VLDPE copolymer of ethylene and hexene-1 and the base
layer contains a VLDPE copolymer of ethylene and butene-1,
20   recycle of scrap trim back to the extruder would result in
a base layer containing a mixture of the ethylene/butene-1
and ethylene/hexene-1 copolymers, along with the major
polyolefin component of the base layer.

The polymer components used to fabricate the films of
25   the present invention may also contain appropriate amounts
of other additives normally included in such compositions.
These include slip agents such as talc, antioxidants,
fillers, dyes, pigments, radiation stabilizers and like
additives.
30   The film products made in accordance with the present
invention are useful in a wide variety of bag and pouch
applications in which heat sealability is important. Bag
and pouch forming include, but are not limited to
horizontal form-fill-and-seal, and vertical form-fill-and-
35   seal.
Some key properties of the final film are heat
sealability and seal strength, hot tack strength, tensile
strength, film rigidity, haze and gloss, low extractables,

and abrasion resistance.

EXAMPLE I

**Preparation of VLDPE-EB-1 (1.6 MI, Density of 0.8895,
butene-1 Comonomer)**

5   A catalyst is prepared by adding 5.1 liters of a 10%
solution of trimethylaluminum in heptane into a dry and
oxygen-free 1.67 l (two-gallon) reactor equipped with a
mechanical stirrer. A sample of 800 g of undehydrated
silica gel, containing 12.3% water, is slowly added into
10   the reactor. After the addition is complete, the mixture
is stirred at ambient temperature for one hour. A 20 g
sample of di-(n-butylcyclopentadienyl) zirconium
dichloride slurried in 30 liters of heptane is then added
into the reactor and the mixture is allowed to react at
15   ambient temperature for 30 minutes. The reactor is then
heated to 65°C, while a nitrogen gas is purged through the
reactor to remove the solvent. The nitrogen purging is
stopped when the mixture in the reactor turns into a free-
flowing powder.

20   The polymerization was conducted in a 40.64cm (16-
inch) diameter fluidized gas phase reactor. Ethylene,
butene-1 and nitrogen were fed continuously into the
reactor to maintain a constant production rate. Product
was periodically removed from the reactor to maintain the
25   desired bed weight. The polymerization conditions are
shown below.

Gas Phase Polymerization

Temperature	(137 °F)	58.3 °C
Total Pressure	(300 psia)	2068.5kPa
Gas Velocity	(1.58ft/sec)	.482 m/sec
Catalyst Feed Rate		7.0 g/hr
Butene-1 Feed Rate	(5.3lb./hr)	2.4 kg/hr Production
Rate (26 lb/hr)	11.8 kg/hr	

The polymerized product had a Melt Index (dg/min.) of 1.60
35   and a Density (g/cm^3) of 0.8895.

EXAMPLE 2

**Preparation of VLDPE-EB-2 (2.3 MI, Density of 0.8970,
butene-1 comonomer)**

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The process of Example 1 was repeated as set forth therein except that the polymerization conditions were as shown below:

Gas Phase Polymerization

5
Temperature	(129 °F)	53.9°C
Total Pressure	(300 psia)	2068.5 kPa
Gas Velocity	(1.59 ft/sec)	.485 m/sec
Catalyst Feed Rate		7.0 g/hr
Butene-1 Feed Rate	(2.9 lb./hr)	1.32 kg/hr
10 Production Rate | (19 lb./hr) | 8.62 kg/hr |

The polymerized product had a Melt Index (dg/min.) of 2.30 and a Density (g/cm³) of 0.8970.

EXAMPLE 3

Preparation of VLDPE-EH (1.5 MI, Density of 0.905, hexene-
15 1 comonomer)

The catalyst for polymerizing this ethylene copolymer was prepared as follows. A 800 gram quantity of silica gel and a 2700 ml. aliquot of methylalumoxane/toluene solution (10%) were placed in a 1.67 l (two-gallon)
20 reactor and allowed to react at ambient temperature for one hour. A 21.6 gram quantity of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 300 ml of toluene was added into the reactor and the mixture was allowed to react at 65°C for 30 minutes. The
25 reactor was then heated at 75°C while nitrogen gas was purged through the reactor to remove the solvent. The heating and nitrogen purging were stopped when the mixture in the reactor turned into a free-flowing powder.

The polymerization was conducted in a 40.6 cm (16-
30 inch) diameter fluidized bed gas-phase reactor. Ethylene, hexene-1 and nitrogen were fed continuously into the reactor to maintain a constant production rate. Product was periodically removed from the reactor to maintain the desired bed weight. the polymerization conditions are
35 shown below:

Gas Phase Polymerization

| Temperature | (158 °F) | 70°C |
| Total Pressure | (300 psia) | 2068.5kPa |

Gas Velocity   (1.22 ft/sec)   .372 m/sec
Catalyst Feed Rate   3.0 g/hr
Hexene-1 Feed Rate   (3.1 lb./hr)   1.41 kg/hr
Production Rate   (20 lb./hr)   9.1 kg/hr

5   The polymerized product had a measured Melt Index (dg/min)
of 1.5 and a density of 0.905 g/cm³.

EXAMPLES 4-12

A series of coextruded unoriented films were produced
on a compounding extruder to produce AB type laminar films
10   comprising a base film layer having an average thickness
of .0041 cm (1.6 mil) and a single heat sealable coating
layer having an average thickness of .0010 cm(.4 mils),
i.e., the coating layer constituted about 20% of the
thickness of the composite film. The composition of the
15   base films was polypropylene, a propylene/ethylene random
copolymer or a mixture of one of the above with a VLDPE
copolymer of ethylene and butene-1 as prepared in Examples
1 and 2. The composition of the coating layer was either
a VLDPE copolymer of ethylene and butene-1 or a VLDPE
20   copolymer of ethylene and hexene-1 as prepared in
accordance with Example 3. The composition of these
various layers is identified in Table 1.

As used in Table 1, "PEC" is a crystallizable random
copolymer of propylene having a MFI of 5.0 dg/min and
25   containing abut 5 wt % ethylene. It has a DSC peak
melting temperature of about 132°C and is available
commercially from Exxon Chemical Company as Escorene™ PD-
9282. PP is a crystallizable polypropylene homopolymer
having an MFI of about 2.3 dg/min and is available from
30   Exxon Chemical Company under the designation Esorcene™
PP4092. The material identified as EB-1 is a VLDPE
copolymer of ethylene and butene-1 as prepared in Example
1 having a MFI of 1.60 dg/min and a density of 0.8895
g/cm³. The material designated as EB-2 is a VLDPE
35   prepared in Example 2 with a MFI of 2.30 dg/min and a
density of 0.8970 g/cm³. The material designated EH is a
VLDPE copolymer of ethylene and hexene-1 as prepared in
Example 3 having an MFI of 1.5 dg/min and a density of

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0.905 g/cm^3.

The material designated EVA is a copolymer of ethylene and vinyl acetate (28% by weight vinyl acetate content) having an MFI of 3.1 dg/min.

5   Heat seal data and hot tack seal strengths of the various film formulations and configurations were evaluated using a Thellar Model EB Heat Sealer. Under this test, the heat seal sides of the coated films are brought into contact and seals are attempted to be formed

10   at various temperatures from 60°C to 148.9°C in -12.22 °C (140°F to 300°F in 10°F) increments. The dwell time and pressures applied during sealing generally ranges from about 0.25 to 0.5 seconds and 448.2 kPa-551.6 kPa (65 psi-80 psi) respectively. The times and pressures employed

15   are indicated in Table 1.

Test results are shown in Table 1. As is evident from the data in Table 1, film compositions within the scope of this invention (Examples 8 and 9) exhibited hot tack strengths in excess of 246.1g/cm (625 g/in) over a

20   sealing temperature of 115.6°C to 132.2°C (240 to 270°F) and over 275.6g/cm (700g/in) at sealing temperatures of 115.5°C (240°F). This is in marked contrast to other formulations outside the scope of the present invention wherein the sealing layer and base layer each contain a

25   VLDPE copolymer of ethylene and butene-1 or a copolymer of ethylene and vinyl acetate.

TABLE 1

EX	Base Film / Composition	VLDPE Coat. Comp.	Dwell Time (sec)	Seal kPa/ (psi)	Seal Strength g/cm/(g/IN) At °C/(°F)								
					93.3/200°	93.3/200°	98.9/210°	104.4/220°	110/230°	115.6/240°	121.1/250°	126.7/260°	132.2/270°
4	100%PEC /--	EB-1	0.5	462/(67)	<9.84/<25	<9.84/<25	9.84/25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25
5	80%PEC/20%EB-1	EB-1		482.7/(70)	9.84/25	9.84/25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25
6	80%PP/20%EB-1	EB-1	0.5	482.7/(70)	NS*	NS	<9.84/<25	9.84/25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25
7	100%PEC /---	EB-2	0.5	482.7/(70)	NS	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25	<9.84/<25
8	100%PP/ ---	EB-2	0.5	462/(67)	NS	<9.84/<25	9.84/25	9.84/25	29.5/75	9.84/25	9.84/25	9.84/25	9.84/25
9	80%PP/20%EB-1	EH	0.25	482.7/(70)	NS	39.4/100	167.3/425	>275.6/>700	>275.6/>700	>275.6/>700	>275.6/>700	>275.6/>700	>275.6/>700
10	80%PP/20%EB-1	EH	0.5	524/(76)	9.84/25	88.6/225	147.6/375	216.5/550	>275.6/>700	246.1/625	265.7/675	265.7/675	265.7/675
11	100%PEC/---	EVA	0.5	482.7/(70)	(Max Seal Strength at 160°F; <9.84/<25 above 93.3°C(200°F))								
12	100%PEC/---	EVA	0.25	482.7/(70)	(Max Seal Strength at 170°F; <75 above 93.3°C (200°F))								

*NS MEANS NO SEAL

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CLAIMS

1.   A multiple layer heat sealable film comprising a
base layer and a heat sealable layer superimposed on one
or both sides of said base layer wherein:

    i) the base layer comprises a blend of (a) an olefin
    polymer having a density in excess of 0.915 g/cm^3 and
    (b) from 1 to 30 weight percent based on base layer
    polymer content of a copolymer (1) of ethylene and a
    C_3 to C_{20} alpha monoolefin comonomer, said copolymer
    (1) having a density of from 0.88 to 0.915 g/cm^3, a
    melt index of from 0.5 to 7.5 dg/min, a molecular
    weight distribution of no greater than 3.5 and a
    composition distribution breadth index greater than
    70 percent;

    ii) the heat sealable layer comprises a copolymer,
    (2) of ethylene and a C_3 to C_{20} alpha-monoolefin
    comonomer, the copolymer (2) having a density of from
    0.88 to 0.915 g/cm^3, a melt index of from 0.5 to 7.5
    dg/min, a molecular weight distribution of no greater
    than 3.5 and a compositional breath index greater
    than 70 percent,

the film further characterized in that one of the
copolymer (1) and (2) is a copolymer of ethylene and a C_6
to C_{10} alpha-monoolefin comonomer which alpha-monoolefin
comonomer differs from the alpha-monoolefin comonomer
present in the others of the copolymers (1) and (2).

2.   The film of claim 1 wherein copolymer (1) and/or
copolymer (2) has a density of from 0.89 to 0.91.

3.   The film of claim 1 or 2 wherein copolymer (1)
and/or copolymer (2) has a molecular weight distribution
of from 2.0 to 3.0 and/or a melt index of from 0.5 to 5.0

4.   The film of any preceding claim wherein

copolymer (1) and/or copolymer (2) has an essentially
single melting point characteristic with a DSC peak
melting point of from 60 to 115°C.

5.   The film in accordance with any preceding claim
having a thickness of from .00127 cm (0.5 mil) to .0127 cm
(5.0 mils).

6.   The film in accordance with any preceding claim
wherein the heat sealable layer constitutes from 3 to 50%
of the thickness of said film.

7.   The film in accordance with any preceding claim
wherein the ethylene copolymer present in each layer
contains from 4 to 15 mole percent of said comonomer.

8.   The film of claim 1 wherein the copolymer of
ethylene and C_6 to C_{10} alpha-monoolefin is present in the
heat sealable layer.

9.   The film in accordance with claim 6 wherein the
heat sealable layer comprises a copolymer of ethylene and
hexene-1 or ethylene and octene-1.

10.   The film in accordance with any preceding claim
wherein the base layer comprises a copolymer of ethylene
and butene-1.

11.   The film in accordance with any preceding claim
wherein the olefin polymer component of the base layer
comprises polypropylene, random copolymers of propylene
with up to 15 mole % of a C_2 or C_4-C_{12} alpha olefin, low
density polyethylene, linear low density polyethylene,
high density polyethylene, polybutene , crystallizable
random copolymer of propylene and ethylene or a mixture or
two or more thereof.

12.   The film in accordance with any preceding claim

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wherein the or each of the ethylene copolymers (1) and (2)
are prepared using a single site catalyst system.

13.   A process for fabricating a heat sealed package
comprising:

(a)   providing a film according to any preceding
claim;

(b)   forming a shaped article from the film such that
two heat sealable layers thereof are in contact; and

(c)   applying to the contact region conditions of
temperature and pressure sufficient to bond the heat
sealable layers together, to form the desired package.

14.   The process of claim 13 wherein the bonding
conditions include a temperature of from 98.9°C to 132.2°C
(210 to 270°F).

15.   The process according to claim 13 or 14 which
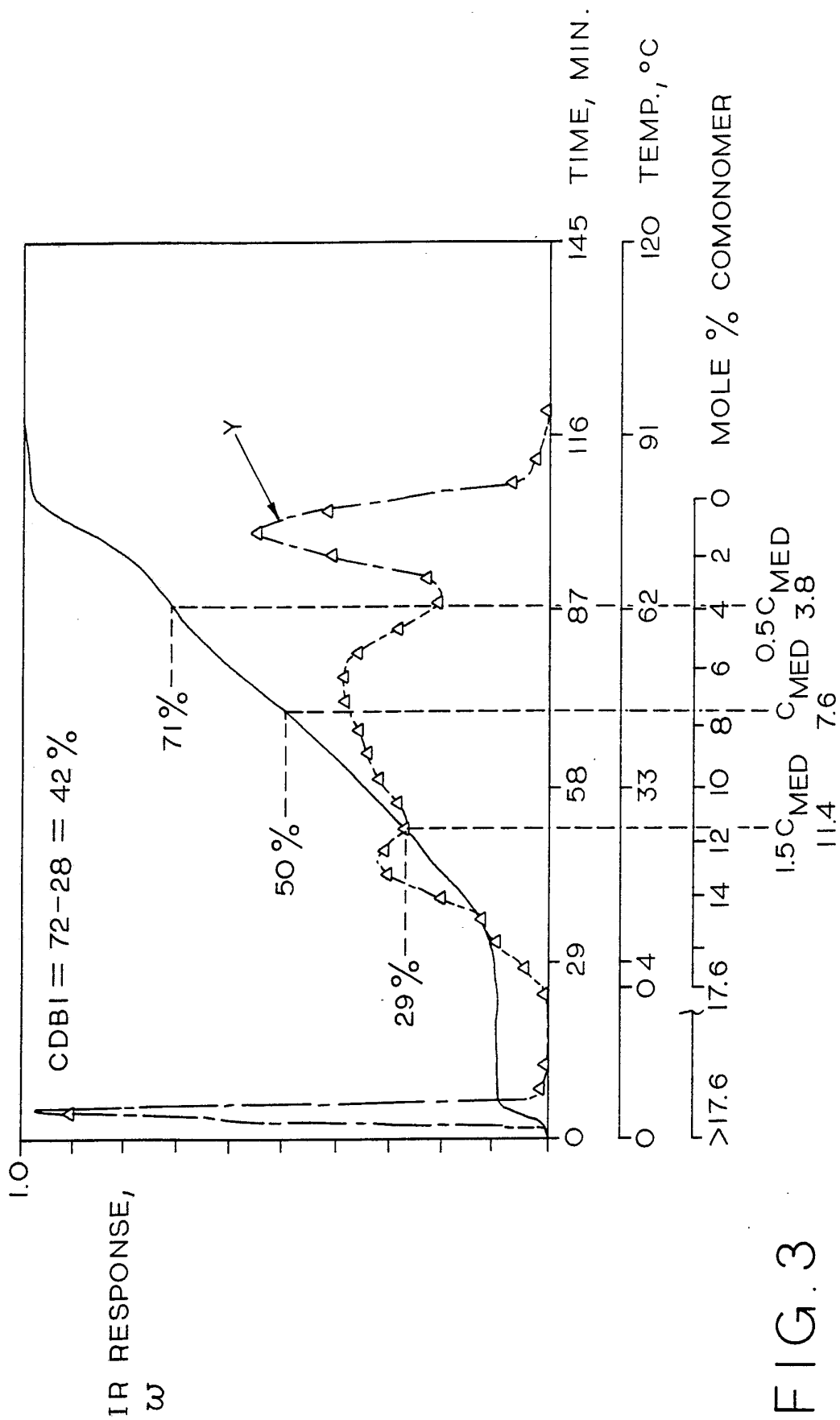comprises a horizontal or vertical form-fill and seal
process.
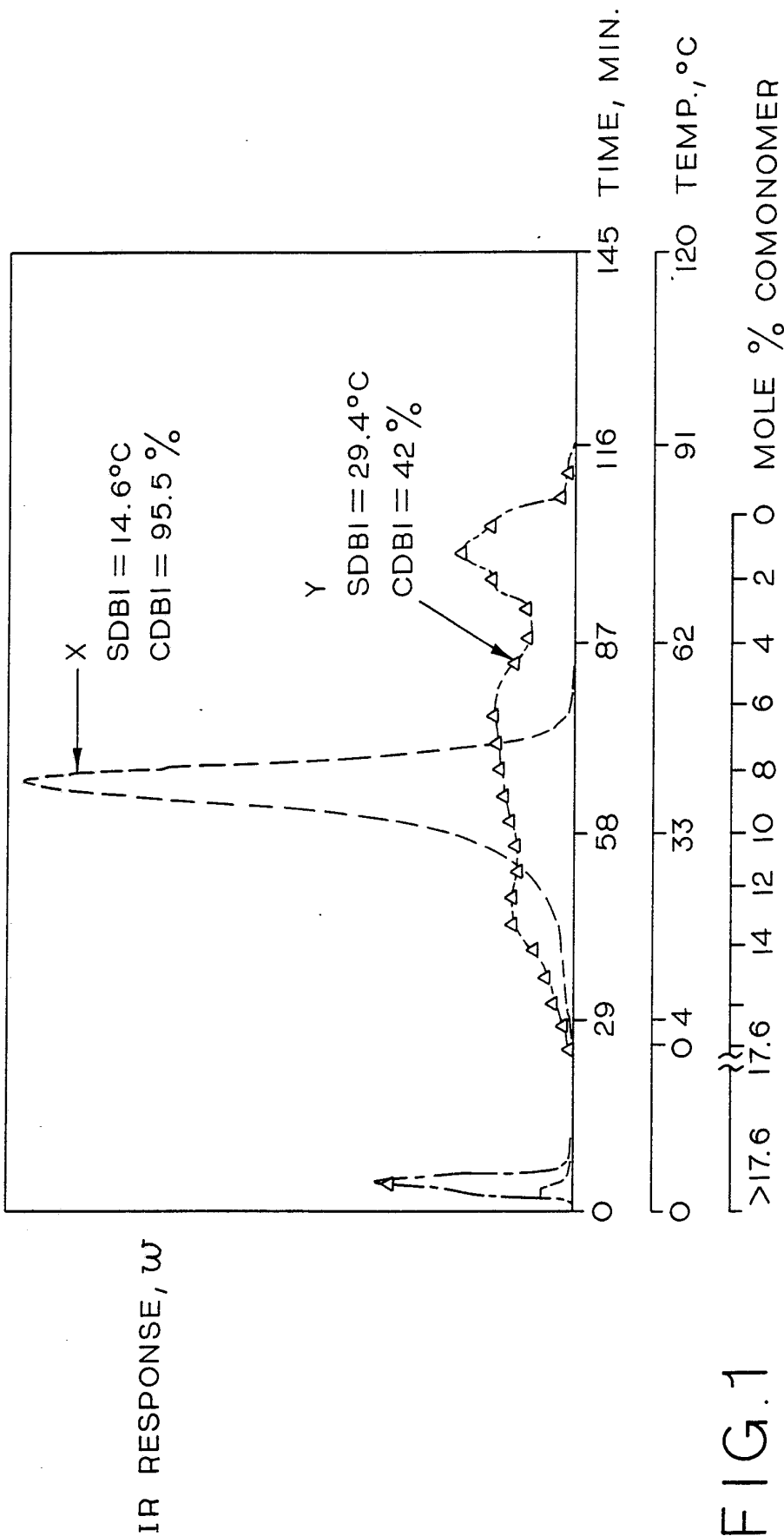
FIG.1
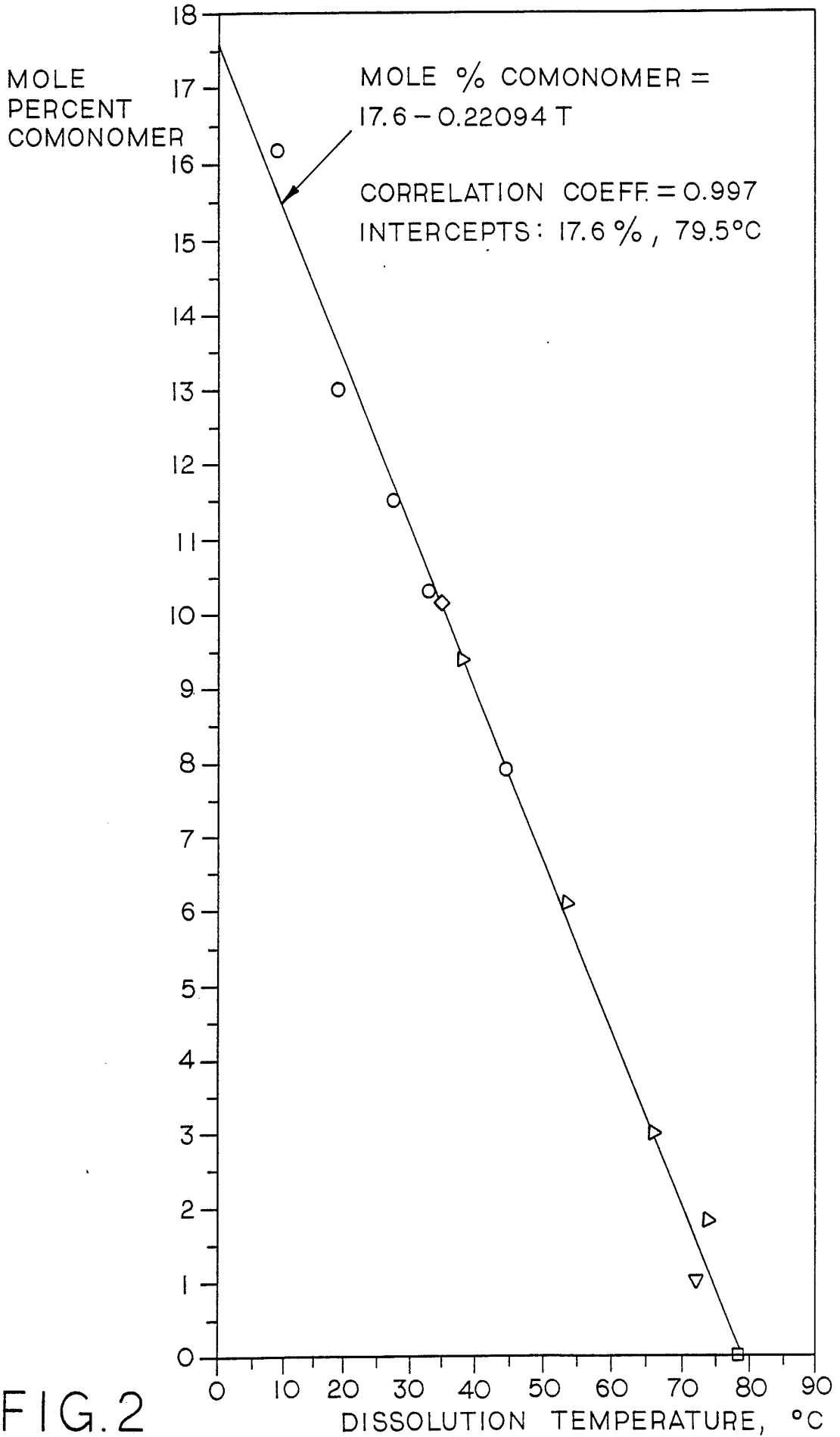
FIG.2

FIG. 3

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 B32B27/32;   C08L23/10;   C09J123/16

II. FIELDS SEARCHED

Minimum Documentation Searched[7]	
Classification System	Classification Symbols
Int.Cl. 5	C09J ; C08L ; B32B

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[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	US,A,4 837 084 (WARREN) 6 June 1989 see column 1, line 67 - column 2, line 5; claims 1,2,4,6 ---	1-15
Y	EP,A,0 144 999 (IDEMITSU PETROCHEMICAL COMPANY LIMITED) 19 June 1985 see page 7, paragraph 2; claims. ---	1-15
A	EP,A,0 129 368 (EXXON RESEARCH AND ENGINEERING COMPANY) 27 December 1984 cited in the application see the whole document ---	1,12
P,Y	WO,A,9 214 784 (EXXON CHEMICAL PATENTS) 3 September 1992 see claims ---	1-15

-/--

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
18 FEBRUARY 1993	0 4. 03. 93

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	DE JONGE S.J.P.

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

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,Y	EP,A,0 474 376 (W.R. GRACE & CO.) 11 March 1992 see claims ---	1-15
A	EP,A,0 247 897 (EXXON CHEMICAL PATENTS) 2 December 1987 cited in the application see the whole document -----	1-15

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

US 9210618
SA 68218

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