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(54) Titre : LDPE DESTINE A ETRE UTILISE COMME CONSTITUANT DE MELANGE DANS DES APPLICATIONS DE
FILM A CONTRACTION

(54) Title: LDPE FOR USE AS A BLEND COMPONENT IN SHRINKAGE FILM APPLICATIONS

(57) **Abrégé/Abstract:**

An ethylene-based polymer characterized as having a density from about 0.9 to about 0.94 grams per cubic centimeter, a molecular weight distribution (Mw/Mn) from about 4 to about 10, a melt index (I2) from about 0.05 to about 2 grams per 10 minutes, a gpcBR value greater than 0.05 as determined by a gpcBR Branching Index and a Y value greater than 0.4 is disclosed. This ethylene-based polymer is especially useful for blending with other polymers such as LLDPE. When converting the blends into film, especially shrink film, the film shows good optics, good shrink tension, high stiffness, high tensile modulus, and tensile strength. When this resin is blended at with a LLDPE on a blown film line, improvements are seen in haze, gloss, clarity, and MD and CD tear as compared to a comparative LDPE.



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(54) Title: LDPE FOR USE AS A BLEND COMPONENT IN SHRINKAGE FILM APPLICATIONS

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5 LDPE FOR USE AS A BLEND COMPONENT IN SHRINKAGE FILM
APPLICATIONS

BACKGROUND OF THE INVENTION

15 There are many types of polyethylene made and sold today. One type in particular is made by various suppliers and sold in large quantities. This polyethylene is called high pressure free radical low density polyethylene (usually called LDPE) and is usually made using a tubular reactor or an autoclave reactor or sometimes a combination. Sometimes polymer users blend LDPE with other polymers such as linear low density polyethylene (LLDPE) to try to modify properties such as flowability or processability.

20 We have now discovered new LDPE polymers which, especially when blended with LLDPE, can have improved shrinkage in combination with favorable stiffness, tensile strength, melt strength and optics, while maintaining other performance attributes.

SUMMARY OF THE INVENTION

25 In one embodiment, the invention is an ethylene-based polymer, preferably a homopolymer or a copolymer, characterized as having a density from about 0.9 to about 0.94 grams per cubic centimeter, a molecular weight distribution (M_w/M_n) from about 4 to about 10, preferably from about 4 to about 6, a melt index (I_2) from about 0.05 to about 2 grams per 10 minutes, preferably less than 0.8, more preferably less than 0.5 grams/10

5 minutes, a gpcBR value greater than 0.05 as determined by a gpcBR Branching Index and a GPC-LS characterization Y value greater than about 0.4, preferably greater than about 0.5. Preferably, the ethylene-based polymer has a melt strength at 190 °C in cN of greater than 9 cN. At least one film layer comprising the ethylene-based polymer can be made, especially wherein the film layer has a machine direction (MD) shrink tension
10 greater than 12 psi.

Preferably, the ethylene-based polymer has a cc GPC Mw in g/mol and a zero shear viscosity (η_o)(Pa*s) relationship $\log(\eta_o(\text{Pa*s at } 190^\circ\text{C})) > 12.333 * \log(\text{ccGPC Mw in g/mol}) - 56.367$, especially wherein the melt index of the ethylene-based polymer is less than 0.7 grams/10 minutes, preferably the $\log(\text{ccGPC Mw in g/mol})$ is greater than 4.88.

15 The ethylene-based polymer can be used in a composition comprising the ethylene-based polymer and at least one other natural or synthetic polymer, especially wherein the synthetic polymer is selected from the group consisting of linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and a low density polyethylene (LDPE), preferably wherein the synthetic polymer comprises LLDPE, more
20 preferably wherein the LLDPE comprises less than 50 percent by weight of the composition.

At least one film layer comprising the compositions made using the ethylene-based polymers can be made.

25 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of a process describing the elements of a disclosed tube reactor system 100;

Figure 2 is the light scattering gel permeation chromatography (LS-GPC) profile with an A1-type positive area segment;

5 Figure 3 is the light scattering gel permeation chromatography (LS-GPC) profile with an A2-type negative area segment;

 Figure 4 is the light scattering gel permeation chromatography (LS-GPC) profile with both A1 and A2 type area segments;

 Figure 5 is a schematic of the process used to make the examples of this
10 invention;

 Figure 6 is a schematic of the temperatures and reaction zones in the process used to make Example 1;

 Figure 7 is the GPC-LS Characterization Value (Y) vs. the molecular weight distribution by conventional calibration of the TDGPC for the examples of this invention
15 and comparative examples;

 Figure 8 is the log of the zero shear viscosity vs. the weight average molecular weight by conventional calibration of the TDGPC for the examples of this invention and comparative examples;

 Figure 9 is the total haze of blown films of Blends 1 through Blend 4;

20 Figure 10 is the 45 degree gloss and the clarity of blown films of Blends 1 through Blend 4;

 Figure 11 is the machine direction (MD) and cross direction (CD) tear of Blends 1 through Blend 4.

25 DETAILED DESCRIPTION OF THE INVENTION

 A LDPE (low density polyethylene) resin that would allow film converters to improve the shrinkage of films from their blown film lines when blended at 5 to 90% (weight basis) with a LLDPE (linear low density polyethylene) resin with general retention of mechanical properties would be useful.

5 Using the high pressure LDPE tubular technology, a resin is developed with relatively narrow molecular weight distribution (MWD). This resin when blown into film shows good optics, good shrink tension, high stiffness, high tensile modulus, and tensile strength. When this resin is blended at 80% (weight) with a LLDPE on a blown film line, improvements are seen in haze, gloss, clarity, and MD and CD tear as
10 compared to a comparative LDPE.

 The melt index of the LDPE ethylene-based polymer is from about 0.05 to about 50 g/10 minutes, preferably from about 0.05 to about 2 g/10 minutes. The density of the LDPE ethylenic based polymer is about 0.9 to about 0.94 g/cm³, preferably from about 0.923 to about 0.935 g/cm³. The LDPE ethylene-based polymer can have a melt strength
15 of from about 9 to about 40 cN. The LDPE ethylene-based polymers can have a MWD (Mw/Mn) of from about 4 to about 10, a Y value of about 0.4 to about 10, and a MD shrink tension from about 10 to 40 cN.

 The low density ethylene-based polymer may be a homopolymer of ethylene. The low density ethylene-based polymer may be an ethylene-based interpolymer
20 comprised of ethylene and at least one comonomer. Comonomers useful for incorporation into an ethylene-based interpolymer, especially an ethylene/ α -olefin interpolymer include, but are not limited to, propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, and mixtures thereof. Ethylene is frequently copolymerized with at least one C₃-C₂₀ α -olefin, such as propene, 1-butene, 1-hexene and 1-octene.

25 A low density ethylene-based polymer is disclosed that exhibits a relationship between the concentration-normalized light scattering (LS) response value and the molecular weight distribution as determined by conventional calibration that is different than that of other low density ethylene-based polymers. The difference is captured in a relationship called the Y value. The Y = LSCDF3 is determined by the GPC-LS
30 Characterization method, described *infra* in the Test Methods section. ("CDF" is the cumulative detector fraction.) The ethylene-based low density polymer has a Y value of about 0.4 to about 10.

5 Methods are well known in the art for using a tubular reactor to form low density
ethylene-based polymers. The process is a tubular polymerization reaction where a
process fluid partially comprised of ethylene is free-radically polymerized creating a
highly exothermic reaction. The reaction occurs under high operating pressure (1000 bar
to 4000 bar) in turbulent process fluid flow (hence low density ethylene-based polymers
10 also referred to as “high pressure” polymers) at maximum temperatures in the reactor of
160 °C to 360 °C, while the initial initiation temperature for the reaction is between 120
°C to 200 °C. At certain points along the tube, a portion of the heat produced during the
free-radical polymerization may be removed through the tube wall. Typical single-pass
conversion values for a tubular reactor range from about 20 - 40 percent. Tubular reactor
15 systems also include at least one monomer recycle loop to improve conversion efficiency.

For the purposes of describing the process, a non-limiting tubular polymerization
reaction system is shown in Figure 1. Tube reactor system 100 has a tube 2 with a length
typically from about 250 to about 2000 meters. The length and diameter of the tube
affects the residence time and velocity of the process fluid as well as the heat
20 addition/removal capacity of tube 2. Suitable, but not limiting, reactor lengths can be
between 100 and 3000 meters, and some between 500 and 2000 meters. Tube 2 also has
a working internal diameter from about 30 to about 100 mm based upon desired system
throughput, operational pressure range, and the degree of turbulent flow for mixing and
reaction. The working internal diameter may widen and narrow at points along tube 2 to
25 accommodate different portions of the process, such as turbulent mixing, injection of
reaction initiators and feeds, and process fluid throttling (i.e., accelerating process fluid
velocity at the expense of pressure loss).

Referring back to Figure 1 and tube reactor system 100, a primary compressor 4,
which may be a multi-stage compressor or two or more compressors running in parallel,
30 is connected at its intake side to a source of fresh monomer/comonomer feed called fresh
feed conduit 6 and a low pressure system recycle conduit 8. The low pressure system
recycle conduit 8 is one of two recycle loops feeding volatilized process fluid from the
refining section of the tube reactor system 100 back to the front of the process. In the
disclosed processes, the low pressure system recycle conduit 8 primarily contains

5 ethylene, but it may also contain unused comonomer and other process additives, such as residual chain transfer agents. The primary compressor 4 raises the pressure of process fluid to a pressure from about 20 bar to about 275 bar.

Still referring to Figure 1, a second compressor, in some cases called a hypercompressor 5, which may be a multi-stage compressor, is connected at its intake to
10 the discharge of the primary compressor 4 as well as to the second of the two recycle streams called the high pressure system recycle conduit 26. The hypercompressor 5 raises the pressure of the process fluid to an operating pressure of 1000 to 4000 bar.

The hypercompressor 5 of the disclosure may be a reciprocating plunger compressor due to the high compression ratio between the primary compressor outlet and
15 the reactor as well as the high reactor operating pressure of the process fluid. The hypercompressors can be a single-stage compressor for lower reactor operating pressures or multi-stage compressors with interstage cooling between some or all of the stages for higher reactor operating pressures.

The process fluid being discharged by the hypercompressor 5 does not flow in a
20 smooth, continuous manner but rather “pulses” with each stroke of the compressor. This occurs because the plunger within each stage intakes and discharges the compressible process fluid in a step-like manner. The resulting discharge flow pulses can result in pressure variations of $\pm 10\%$ or more in the operating pressure. A cycling discharge flow creating system pressure surges may have long-term negative effects on the mechanical
25 integrity of process units such as the hypercompressor, the discharge line(s), and the reactor. In turn, reduction in mechanical integrity of these subsystems can affect overall operation stability and reliability in terms of online operations while the process stability can be influenced by the flow and pressure pulsations. Furthermore, it is possible due to discharge line geometry that individual discharge strokes of separate plungers from the
30 same compressor (such as from a multi-stage compressor with several discharge points) may overlap each other (i.e., be partially or totally “in phase” with one another) resulting in an amplification in strength of the discharge pulsations upon combination in a common process fluid stream. It is good operational practice, therefore, to use static and active

5 mechanical devices such as orifices and pulsation dampeners in the compressor discharge line(s) to minimize not only pressure surges but to also minimize the effect of pressure pulse amplification in common discharge lines on the process and the reactor system equipment.

10 After pressurization by the hypercompressor 5, the process fluid is fed into tube 2 through conduit 12 as an upstream process feed stream. In some disclosed processes, the process fluid is split and fed to tube 2 at different feed locations. In such processes, part of the process fluid is fed to tube 2 through conduit 12 as an upstream process feed stream to the first reaction zone and the other parts (depending on the number of splits made in the process fluid) would be fed to tube 2 as downstream process feed streams to 15 the other reaction zones through various conduits 14. The other reaction zones are located lengthwise along tube 2 downstream of the first reaction zone. As previously stated, there may be more than one other reaction zone.

In processes where there are more than one reaction zone, one or more free-radical initiator or catalyst conduits 7 convey initiator or catalyst to tube 2 near or at the 20 beginning of each reaction zone. The injection of initiators or catalysts, depending upon the desired ethylene-based polymer adduct, at process operating conditions, start the reaction of monomer/comonomer materials. In disclosed processes, the main product of such a reaction is an ethylene-based polymer and heat. Initiator or catalyst may be added to each reaction zone to improve conversion of the monomer (and comonomer, if 25 included) in the process fluid as previously discussed. In a disclosed process, different initiators or catalysts may be added to the process fluid in different reaction zones to ensure the peak temperature is achieved close to the inspection point and to achieve various target peak temperatures.

Examples of free radical initiators used in the processes include oxygen-based 30 initiators such as organic peroxides (PO). Preferred initiators are t-butyl peroxy pivalate, di-t-butyl peroxide, t-butyl peroxy acetate, and t-butyl peroxy- 2- ethylhexanoate, and mixtures thereof. These organic peroxy initiators are used in conventional amounts of between 0.0001 and 0.01 weight percent based upon the weight of high pressure feed.

5 Suitable catalysts for use to polymerize other polymers which may be blended
with the new LDPE disclosed herein include any compound or combination of
compounds that is adapted for preparing polymers of the desired composition or type.
Both heterogeneous and homogeneous catalysts, and combinations thereof, may be
employed. In some embodiments, heterogeneous catalysts, including the well known
10 Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2
metal halides or mixed halides and alkoxides and the well known chromium or vanadium
based catalysts, may be used. In some embodiments, the catalysts for use may be
homogeneous catalysts comprising a relatively pure organometallic compound or metal
complex, especially compounds or complexes based on metals selected from Groups 3-10
15 or the Lanthanide series. If more than one catalyst is used in a system, it is preferred that
any catalyst employed not significantly detrimentally affect the performance of another
catalyst under the conditions of polymerization. Desirably, no catalyst is reduced in
activity by greater than 25 percent, more preferably greater than 10 percent under the
conditions of the polymerization. Examples of preferred catalyst systems may be found
20 in U.S. Patent Nos. 5,272,236 (Lai, et al.); 5,278,272 (Lai, et al.); 6,054,544 (Finlayson,
et al.); 6,335,410 (Finlayson, et al.); 6,723,810 (Finlayson, et al.); PCT Published
Application Nos. WO 2003/091262 (Boussie, et al.); 2007/136497 (Konze, et al.);
2007/136506 (Konze, et al.); 2007/136495 (Konze, et al.); and 2007/136496 (Aboelella,
et al.). Other suitable catalysts may be found in U.S. Patent Publication No.
25 2007/0167578 (Arriola, et al.).

 The free-radical polymerization reaction resulting in the disclosed ethylene-based
polymer adduct occurs in each reaction zone where initiator or catalyst is present. The
reaction is an exothermic reaction that generates a large quantity of heat. Without
cooling, the adiabatic temperature rise in the process fluid and the ethylene-based
30 polymer adduct (which absorbs and retains heat) would result in unfavorable reactions.
Such reactions may include ethylene decomposition (where ethylene and polyethylene
break down in a reaction accompanied by rapid increases in temperature into base
products).

5 In some processes, the temperature of the process fluid is reduced by removing
heat through the wall of tube 2 by inducing a heat flux with a heat removal medium. A
heat removal medium is a fluid used to absorb heat and remove it from the tube reaction
system 100, such as ethylene glycol, water, or air. When the heat removal medium is a
liquid, a heat exchanger 30, which may be as simple as a 1-1 cooling “jacket” or a
10 complex multipass refrigeration system, may be used to effect heat transfer and cool the
process fluid and the ethylene-based polymer adduct. Non-limiting examples of heat
exchangers and techniques for removing heat are described in Perry, Robert H., ed.,
Perry’s Chemical Engineers’ Handbook, Chp. 10, McGraw-Hill Book Co. (6th ed., 1984)
and McCabe, Warren L, *et al.*, *Unit Operations of Chemical Engineering*, McGraw-Hill,
15 Inc. (5th ed., 1993). When the heat removal medium is a gas, fans may be used to
convect the heat away from the reactor tube 2. The heat removal medium will have a
mass flow rate, an inlet temperature, and an outlet temperature. When the heat removal
medium is used to remove heat from the tube reaction system 100, the inlet temperature
of the heat removal medium into the heat exchanger 30 is lower than the outlet
20 temperature. The difference between the inlet and the outlet temperatures for a given
mass flow rate is reflective of the heat removed from the process given the heat capacity
of the heat removal medium and the ability of tube 2 to transfer heat to the heat removal
medium.

 In some processes, chain transfer agents (CTAs) are added so as to blend as
25 homogeneously as possible with the process fluid before introduction to the tube 2.
Depending on the physical layout of the tube reactor system 100 and chemical
characteristics of the process fluid and the CTAs, such blending may be achieved by
injecting the CTAs at the inlet of the booster compressor 21 for the low pressure system
recycle conduit 8, in the inlet of the primary compressor 4, in the inlet of the
30 hypercompressor 5, at the outlet of the hypercompressor 5, at the inlet of the tube 2 or
together with the first peroxide injection. For the process shown in Figure 1, the CTAs
are injected into reaction system 100 via CTA source 23 at the inlet of the primary
compressor 4.

5 Although not shown in tube reactor system 100 to great detail in Figure 1, selective feeding of CTAs to the tube reactor 2 is possible. In some processes, the process fluid is split into an upstream process feed stream and at least one downstream process feed stream after pressurization by the hypercompressor 5. In such cases, the CTAs may be fed into tube 2 selectively by being injected into conduits 12 or 14 instead
10 of using the CTA source 23 as shown in Figure 1. In specific cases, the CTAs may be injected from CTA source 23 only into the upstream process feed stream via conduit 12. In processes where the hypercompressor 5 contains multiple stages or trains, the process fluid may be split into an upstream process feed and at least one downstream process feed stream at the inlet of the hypercompressor 5. In such cases, the CTAs may be selectively
15 fed from CTA source 23 into either the upstream process feed or at least one downstream process feed before pressurization by the hypercompressor 5, or, as previously stated, into conduits 12 or 14 after pressurization. This flexibility in the disclosed process regarding the injection of CTAs from CTA source 23 permits selective injection of CTAs only into the first reaction zone or only into some or all of the at least one other reaction
20 zones. It also permits the injection of different CTAs, including CTAs with different chain transfer constant (Cs) characteristics, to be injected from CTA source 23 into different zones to optimize reaction system performance and ethylene-based polymer adduct properties.

 In some processes, CTA source 23 may be comprised of several individual chain
25 transfer agent sources. Although not shown in Figure 1, the individual chain transfer agent sources may be distributed individually or combined into a common stream that is injected at a common point.

 Referring back to Figure 1 and the tube reactor system 100, a mixture of ethylene-based polymer formed from the reaction, unreacted monomer (and comonomer), and
30 unused feeds, such as solvents and CTAs, or degradation and side reaction products, passes from tube outlet 16 to the separations part of the process. The separating and recycling part of the tube reactor system 100 process includes a high-pressure separator (HPS) 18, which receives the product polymer and process fluid mixture from the outlet of tube 2. HPS 18 separates out most of the monomer from the ethylene-based polymer

5 adduct. The tails of HPS 18 conveys the polymer adduct and any remaining unreacted monomer/comonomer and other unused feeds that might be dissolved with the polymer adduct, to low-pressure separator (LPS) 20. The higher pressure lights stream passes through the high pressure system recycle conduit 26, which may include a refining system 24 to cool and purify the stream and purge inert gases, and rejoins the process
10 fluid passing from the primary compressor 4 to the hypercompressor 5.

Referring to Figure 1, LPS 20 separates any remaining monomer/comonomer and unused feeds from the polymer adduct by operating at slightly over atmospheric pressure or vacuum conditions. LPS 20 operates in a pressure range from about 4 to about 1.2 bar absolute to draw out entrained gases. The resulting ethylene-based polymer adduct, still
15 molten from processing, passes by the tails of LPS 20 to finishing steps, such as extrusion, quenching, and pelletization. The lights from LPS 20 pass through the low pressure system recycle conduit 8 where its pressure is boosted from around atmospheric pressure to at least the required pressure for proper operation of primary compressor 4. The low pressure booster compressor 21 may have a number of stages. The resulting
20 product polymer is degassed of volatile reactants and overall system efficiency is improved by the recycle of unused monomer to the front of reaction system 100.

The recycle streams in both the low pressure system recycle conduit 8 and the high pressure system recycle conduit 26 typically contain a portion of chain transfer agents. More often than not, the high pressure system recycle conduit 26 will often
25 contain a significant concentration of low-Cs chain transfer agent as it is not entirely consumed during the reaction process. In some disclosed processes, upon reaching steady-state production, the amount of fresh low-Cs CTA added to the process via CTA source 23 is relatively small compared to the amount present in the high and low pressure recycle conduits 26 and 8, respectively.

30 End-use products made using the disclosed ethylene-based polymers include all types of films (for example, blown, cast and extrusion coatings (monolayer or multilayer)), molded articles (for example, blow molded and rotomolded articles), wire and cable coatings and formulations, cross-linking applications, foams (for example,

5 blown with open or closed cells), and other thermoplastic applications. The disclosed
ethylene-based polymers are also useful as a blend component with other polyolefins,
such as the polymers described in US provisional serial number 61/165,065, DOWLEX
linear low density polyethylene (LLDPE), ENGAGE polyolefin elastomers, AFFINITY
polyolefin plastomers, INFUSE Olefin Block Copolymers, VERSIFY plastomers and
10 elastomers – all made by The Dow Chemical Company; and EXACT polymers,
EXCEED polymers, VISTAMAXX polymers – all made by ExxonMobil. ASTUTE and
SCLAIR made by Nova Chemicals also can be blended with the new LDPE disclosed
herein.

The types of films that make be produced as end-use products from the disclosed
15 ethylene-based polymers include lamination films, silage films, sealants, silobags, stretch
films, biaxially oriented polyethylene, display packaging, shrink films, overwraps,
masking films, release liners and heavy duty shipping sacks. Additionally, blown, cast
and extrusion coatings (monolayer or multilayer) also may be produced using the
disclosed ethylene-based polymers.

20

DEFINITIONS

The terms “blend” or “polymer blend” generally means a mixture of two or more
polymers. A blend may or may not be miscible (not phase separated at molecular level).
A blend may or may not be phase separated. A blend may or may not contain one or
25 more domain configurations, as determined from transmission electron spectroscopy,
light scattering, x-ray scattering, and other methods known in the art.

The term “comparable” means similar or like.

The term “composition” includes a mixture of materials which comprise the
composition as well as reaction products and decomposition products formed from
30 interaction and reaction between the materials of the composition.

5 The term “ethylene-based polymer” refers to a polymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers), and, optionally, may contain at least one comonomer. A homopolymer of ethylene is an ethylene-based polymer.

10 The term “ethylene/ α -olefin interpolymers” refers to an interpolymers that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers), and at least one α -olefin.

 The term “homopolymer” is a polymer that contains only a single type of monomer.

15 The term “interpolymers” refers to polymers prepared by the polymerization of at least two different types of monomers. The term interpolymers includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers, such as terpolymers.

20 The term “LDPE” may also be referred to as “high pressure ethylene polymer” or “highly branched polyethylene” and is defined to mean that the polymer is partly or entirely homopolymerized in autoclave or tubular reactors at pressures above 13,000 psig with the use of free-radical initiators, such as peroxides (see, for example, U.S. Patent No. 4,599,392 (McKinney, et al.)).

25 The term “polymer” refers to a compound prepared by polymerizing monomers, whether of the same or a different type of monomer. The term polymer embraces the terms “homopolymer” and “interpolymers”.

 The term “standard deviation” is a quantity which measures the spread or dispersion of the distribution from a mean value. *See* Perry, Robert H., ed., *Perry’s Chemical Engineers’ Handbook*, McGraw-Hill Book Co. (6th ed., 1984); *also* Miller, Irwin, *Probability and Statistics for Engineers*, Prentice Hall (4th ed., 1990).

30 The terms “steady state” and “steady state condition(s)” are a condition where properties of any part of a system are constant during a process. *See* Lewis, Richard J.,

- 5 Sr., *Hawley's Condensed Chemical Dictionary*, Wiley-Interscience (15th ed., 2007); also Himmelblau, David M., *Basic Principles and Calculations in Chemical Engineering*, Prentice Hall (5th ed., 1989).

The term "GPC-LS characterization Y value" is defined as the same as the term "LSCDF3" and calculated mathematically in Equations 14 -16 below.

10

TESTING METHODS

Density

- 15 Samples for density measurement are prepared according to ASTM D 1928. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

Melt Index

- Melt index, or I_2 , is measured in accordance with ASTM D 1238, Condition 190
20 °C/2.16 kg. I_{10} is measured with ASTM D 1238, Condition 190 °C/10 kg.

Melt Strength

- Melt strength is measured at 190 °C using a Göttfert Rheotens 71.97 (Göttfert Inc.; Rock Hill, SC), melt fed with a Göttfert Rheotester 2000 capillary rheometer
25 equipped with a flat entrance angle (180 degrees) of length of 30 mm and diameter of 2 mm. The pellets were fed into the barrel (L=300 mm, Diameter=12 mm), compressed and allowed to melt for 10 minutes before being extruded at a constant piston speed of 0.265 mm/s, which corresponds to a wall shear rate of 38.2 s^{-1} at the given die diameter. The extrudate passed through the wheels of the Rheotens located at 100 mm below the die
30 exit and was pulled by the wheels downward at an acceleration rate of 2.4 mm/s^2 . The force (in cN) exerted on the wheels was recorded as a function of the velocity of the

5 wheels (in mm/s). Melt strength is reported as the plateau force (cN) before the strand broke.

Zero Shear Viscosity

Specimens for creep measurements were prepared on a programmable
10 Tetrahedron bench top press. The program held the melt at 177°C for 5 minutes at a pressure of 10^7 Pa. The chase was then removed to the benchtop to cool down to room temperature. Round test specimens were then die-cut from the plaque using a punch press and a handheld die with a diameter of 25 mm. The specimen is about 1.8 mm thick.

Zero-shear viscosities are obtained via creep tests that were conducted on an AR-
15 G2 stress controlled rheometer (TA Instruments; New Castle, Del) using 25-mm-diameter parallel plates at 190°C. Two thousand ppm of antioxidant, a 2:1 mixture of IRGAFOS 168 and IRGANOX 1010 (Ciba Specialty Chemicals; Glattbrugg, Switzerland), is added to stabilize each sample prior to compression molding. At the testing temperature a compression molded sample disk is inserted between the plates and
20 allowed to come to equilibrium for 5 minutes. The upper plate is then lowered down to 50 μ m above the desired testing gap (1.5 mm). Any superfluous material is trimmed off and the upper plate is lowered to the desired gap. Measurements are done under nitrogen purging at a flow rate of 5 L/min. The default creep time is set for 5 hours.

A low shear stress of 20 Pa is applied for all of the samples to ensure that the
25 steady state shear rate is low enough to be in the Newtonian region. The resulting steady state shear rates are in the range of 10^{-3} to 10^{-4} s⁻¹ for all the samples in this study. Steady state is determined by taking a linear regression for all the data in the last 10% time window of the plot of $\log(J(t))$ vs. $\log(t)$, where $J(t)$ is creep compliance and t is creep time. If the slope of the linear regression is greater than 0.97, steady state is considered
30 to be reached, then the creep test is stopped. In all cases in this study the samples reached steady state within 5 hours. The steady state shear rate is determined from the slope of the linear regression of all of the data points in the last 10% time window of the plot of ϵ vs. t , where ϵ is strain. The zero-shear viscosity is determined from the ratio of the applied stress (20 Pa) to the steady state shear rate.

5 A small amplitude oscillatory shear test is conducted before and after the creep test on the same specimen from 0.1 to 100 rad/s at 10% strain. The complex viscosity values of the two tests are compared. If the difference of the viscosity values at 0.1 rad/s is greater than 5%, the sample is considered to have degraded during the creep test, and the result is discarded.

10

DSC

15 Differential Scanning Calorimetry (DSC) can be used to measure the melting and crystallization behavior of a polymer over a wide range of temperatures. For example, the TA Instruments Q1000 DSC, equipped with an RCS (refrigerated cooling system) and an autosampler is used to perform this analysis. During testing, a nitrogen purge gas flow of 50 ml/min is used. Each sample is melt pressed into a thin film at about 175 °C; the melted sample is then air-cooled to room temperature (~25 °C). A 3 - 10 mg, 6 mm
20 diameter specimen is extracted from the cooled polymer, weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis is then performed to determine its thermal properties.

 The thermal behavior of the sample is determined by ramping the sample temperature up and down to create a heat flow versus temperature profile. First, the
25 sample is rapidly heated to 180 °C and held isothermal for 3 minutes in order to remove its thermal history. Next, the sample is cooled to -40 °C at a 10 °C/minute cooling rate and held isothermal at -40 °C for 3 minutes. The sample is then heated to 150 °C (this is the “second heat” ramp) at a 10 °C/minute heating rate. The cooling and second heating curves are recorded. The cool curve is analyzed by setting baseline endpoints from the
30 beginning of crystallization to -20 °C. The heat curve is analyzed by setting baseline endpoints from -20 °C to the end of melt. The values determined are peak melting temperature (T_m), peak crystallization temperature (T_c), heat of fusion (H_f) (in Joules per gram), and the calculated % crystallinity for polyethylene samples using Equation 1:

5
$$\% \text{ Crystallinity} = ((H_f)/(292 \text{ J/g})) \times 100 \quad (\text{Eq. 1}).$$

The heat of fusion (H_f) and the peak melting temperature are reported from the second heat curve. Peak crystallization temperature is determined from the cooling curve.

Fourier Transform Infrared Spectroscopy (FTIR)

10 Unsaturations by FTIR were measured on a Thermo Nicolet model Nexus 470. The following procedures were followed:

- Methyls per 1000 C: ASTM D2238
- Trans per 1000 C: ASTM D6248
- Vinyls per 1000 C: ASTM D6248
- 15 • Vinylidenes per 1000C: ASTM D3124
- Carbonyl to thickness ratio. The ratio of the carbonyl area to thickness is determined as:

20
$$\frac{\text{Carbonyl Area}}{\text{Thickness}} = \frac{(\text{Area Between } 1710 - 1730 \text{ cm}^{-1})}{\text{Thickness in mm} \times ((\text{peak height at } 2665 \text{ cm}^{-1} - \text{peak height at } 2445 \text{ cm}^{-1})/2.71)} \quad (\text{Eq. 2})$$

Film Testing Conditions

The following physical properties are measured on the films produced:

- Total (Overall), Surface and Internal Haze: Samples measured for internal haze
25 and overall haze are sampled and prepared according to ASTM D 1003. Internal haze was obtained via refractive index matching using mineral oil on both sides of the films. A Hazegard Plus (BYK-Gardner USA; Columbia, MD) is used for testing. Surface haze is determined as the difference between overall haze and internal haze as shown in Equation 3. Surface haze tends to be related to the
30 surface roughness of the film, where surface haze increases with increasing

5 surface roughness. The surface haze to internal haze ratio is the surface haze value divided by the internal haze value as shown in Equation 4.

$$\text{Haze} = \text{Internal Haze} + \text{Surface Haze} \quad (\text{Eq. 3})$$

$$S/I = \text{Surface Haze/Internal Haze} \quad (\text{Eq. 4})$$

- 45° Gloss and 60° Gloss: ASTM D-2457.
- 10 • 1% Secant Modulus and 2% Secant Modulus in the MD (machine direction) and CD (cross direction): ASTM D-882.
- MD and CD Elmendorf Tear Strength: ASTM D-1922.
- MD and CD Tensile Strength: ASTM D-882.
- Dart Impact Strength: ASTM D-1709.
- 15 • Puncture Strength: Puncture is measured on an Instron Model 4201 with Sintech Testworks Software Version 3.10. The specimen size is 6" x 6" and 4 measurements are made to determine an average puncture value. The film is conditioned for 40 hours after film production and at least 24 hours in an ASTM controlled laboratory. A 100 lb load cell is used with a round specimen holder.
- 20 The specimen is a 4 inch circular specimen. The puncture probe is a ½ inch diameter polished stainless steel ball (on a 0.25 inch rod) with a 7.5 inch maximum travel length. There is no gauge length; the probe is as close as possible to, but not touching, the specimen. The crosshead speed used is 10"/minute. The thickness is measured in the middle of the specimen. The thickness of the film,
- 25 the distance the crosshead traveled, and the peak load are used to determine the puncture by the software. The puncture probe is cleaned using a "Kim-wipe" after each specimen.
- Shrink tension is measured according to the method described in Y. Jin, T. Hermel-Davidock, T. Karjala, M. Demirors, J. Wang, E. Leyva, and D. Allen,

5 “Shrink Force Measurement of Low Shrink Force Films”, SPE ANTEC
 Proceedings, p. 1264 (2008).

- % Free Shrink: A single layer square film with a dimension of 10.16 cm × 10.16
 cm is cut out by a punch press from a film sample along the edges of the machine
 direction (MD) and the cross direction (CD). The film is then placed in a film
 10 holder and the film holder is immersed in a hot-oil bath at 150 °C for 30 seconds.
 The holder is then removed from the oil bath. After oil is drained out, the length
 of film is measured at multiple locations in each direction and the average is taken
 as the final length. The % free shrink is determined from Equation 5.

$$\frac{(\text{Initial Length}) - (\text{Final Length})}{\text{Initial Length}} \times 100 \quad (\text{Eq. 5})$$

15

Triple Detector Gel Permeation Chromatography (TDGPC)

The Triple Detector Gel Permeation Chromatography (3D-GPC or TDGPC)
 system consists of a Waters (Milford, Mass) 150C high temperature chromatograph
 (other suitable high temperature GPC instruments include Polymer Laboratories
 20 (Shropshire, UK) Model 210 and Model 220) equipped with an on-board differential
 refractometer (RI). Additional detectors can include an IR4 infra-red detector from
 Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, Mass.) 2-angle laser
 light scattering (LS) detector Model 2040, and a Viscotek (Houston, Tex.) 150R 4-
 capillary solution viscometer. A GPC with these latter two independent detectors and at
 25 least one of the former detectors is sometimes referred to as “3D-GPC” or “TDGPC”
 while the term “GPC” alone generally refers to conventional GPC. Depending on the
 sample, either the 15° angle or the 90° angle of the light scattering detector is used for
 calculation purposes. Data collection is performed using Viscotek TriSEC software,
 Version 3, and a 4-channel Viscotek Data Manager DM400. The system is also equipped
 30 with an on-line solvent degassing device from Polymer Laboratories (Shropshire, United
 Kingdom).

5 Suitable high temperature GPC columns can be used such as four 30 cm long
Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron
mixed-pore-size packing (MixA LS, Polymer Labs). The sample carousel compartment
is operated at 140 °C and the column compartment is operated at 150 °C. The samples
are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The
10 chromatographic solvent and the sample preparation solvent contain 200 ppm of
trichlorobenzene (TCB). Both solvents are sparged with nitrogen. The polyethylene
samples are gently stirred at 160 °C for four hours. The injection volume is 200
microliters. The flow rate through the GPC is set at 1 ml/minute.

 The GPC column set is calibrated by running 21 narrow molecular weight
15 distribution polystyrene standards. The molecular weight (MW) of the standards ranges
from 580 to 8,400,000, and the standards are contained in 6 “cocktail” mixtures. Each
standard mixture has at least a decade of separation between individual molecular
weights. The standard mixtures are purchased from Polymer Laboratories. The
polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular weights
20 equal to or greater than 1,000,000 and 0.05 g in 50 mL of solvent for molecular weights
less than 1,000,000. The polystyrene standards were dissolved at 80 °C with gentle
agitation for 30 minutes. The narrow standards mixtures are run first and in order of
decreasing highest molecular weight component to minimize degradation. The
polystyrene standard peak molecular weights are converted to polyethylene molecular
25 weight using Equation 6 (as described in Williams and Ward, *J. Polym. Sci.*, Polym.
Letters, 6, 621 (1968)):

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (\text{Eq. 6}),$$

where M is the molecular weight of polyethylene or polystyrene (as marked), and B is
equal to 1.0. It is known to those of ordinary skill in the art that A may be in a range of
30 about 0.38 to about 0.44 and is determined at the time of calibration using a broad
polyethylene standard, as outlined in the gpcBR Branching Index by the 3D-GPC
method, *infra*, and specifically Equations 11-13. Use of this polyethylene calibration
method to obtain molecular weight values, such as the molecular weight distribution

5 (MWD or M_w/M_n), and related statistics, is defined here as the modified method of Williams and Ward.

The systematic approach for the determination of multi-detector offsets is performed in a manner consistent with that published by Balke, Mourey, *et al.* (Mourey and Balke, *Chromatography Polym.*, Chapter 12, (1992)) (Balke, Thitiratsakul, Lew, 10 Cheung, Mourey, *Chromatography Polym.*, Chapter 13, (1992)), optimizing triple detector log (weight average molecular weight M_w and intrinsic viscosity) results from Dow 1683 broad polystyrene (American Polymer Standards Corp.; Mentor, OH) or its equivalent to the narrow standard column calibration results from the narrow polystyrene standards calibration curve. The molecular weight data is obtained in a manner 15 consistent with that published by Zimm (Zimm, B.H., *J. Chem. Phys.*, 16, 1099 (1948)) and Kratochvil (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used in the determination of the molecular weight is obtained from the mass detector area and the mass detector constant derived from a suitable linear polyethylene homopolymer, or one 20 of the polyethylene standards of known weight average molecular weight. The calculated molecular weights are obtained using a light scattering constant derived from one or more of the polyethylene standards mentioned and a refractive index concentration coefficient, dn/dc , of 0.104. Generally, the mass detector response and the light scattering constant should be determined from a linear standard with a molecular weight in excess of about 25 50,000 daltons. The viscometer calibration can be accomplished using the methods described by the manufacturer or alternatively by using the published values of suitable linear standards such as Standard Reference Materials (SRM) 1475a, 1482a, 1483, or 1484a. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd virial coefficient effects (concentration effects on molecular weight).

30

gpcBR Branching Index by 3D-GPC

In the 3D-GPC configuration, the polyethylene and polystyrene standards can be used to measure the Mark-Houwink constants, K and α , independently for each of the

5 two polymer types, polystyrene and polyethylene. These can be used to refine the Williams and Ward polyethylene equivalent molecular weights in application of the following methods.

The gpcBR branching index is determined by first calibrating the light scattering, viscosity, and concentration detectors as described previously. Baselines are then
 10 subtracted from the light scattering, viscometer, and concentration chromatograms. Integration windows are then set to ensure integration of all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the refractive index chromatogram. Linear polyethylene standards are then used to establish polyethylene and polystyrene Mark-
 15 Houwink constants as described previously. Upon obtaining the constants, the two values are used to construct two linear reference conventional calibrations for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution volume, as shown in Equations 7 and 8:

$$M_{PE} = \left(\frac{K_{PS}}{K_{PE}} \right)^{1/\alpha_{PE}+1} \cdot M_{PS}^{\alpha_{PS}+1/\alpha_{PE}+1} \quad (\text{Eq. 7})$$

$$20 \quad [\eta]_{PE} = K_{PS} \cdot M_{PS}^{\alpha+1} / M_{PE} \quad (\text{Eq. 8})$$

The gpcBR branching index is a robust method for the characterization of long chain branching as described in Yau, Wallace W., “Examples of Using 3D-GPC – TREF for Polyolefin Characterization”, *Macromol. Symp.*, 2007, 257, 29-45. The index avoids the slice-by-slice 3D-GPC calculations traditionally used in the determination of g’
 25 values and branching frequency calculations in favor of whole polymer detector areas. From 3D-GPC data, one can obtain the sample bulk absolute weight average molecular weight ($M_{w, Abs}$) by the light scattering (LS) detector using the peak area method. The method avoids the slice-by-slice ratio of light scattering detector signal over the concentration detector signal as required in a traditional g’ determination.

5 With 3D-GPC, absolute weight average molecular weight (“ $M_{w, Abs}$ ”) and intrinsic viscosity are also obtained independently using Equations 9 and 10:

$$M_w = \sum_i w_i M_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \frac{\sum_i C_i M_i}{\sum_i C_i} = \frac{\sum_i LS_i}{\sum_i C_i} = \frac{LS \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 9})$$

The area calculation in Equation 9 offers more precision because as an overall sample area it is much less sensitive to variation caused by detector noise and 3D-GPC settings on baseline and integration limits. More importantly, the peak area calculation is not affected by the detector volume offsets. Similarly, the high-precision sample intrinsic viscosity (IV) is obtained by the area method shown in Equation 10:

$$IV = [\eta] = \sum_i w_i IV_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \frac{\sum_i C_i IV_i}{\sum_i C_i} = \frac{\sum_i DP_i}{\sum_i C_i} = \frac{DP \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 10}),$$

where DP_i stands for the differential pressure signal monitored directly from the online viscometer.

To determine the gpcBR branching index, the light scattering elution area for the sample polymer is used to determine the molecular weight of the sample. The viscosity detector elution area for the sample polymer is used to determine the intrinsic viscosity (IV or $[\eta]$) of the sample.

20 Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a or an equivalent, are determined using the conventional calibrations (“cc”) for both molecular weight and intrinsic viscosity as a function of elution volume, per Equations 11 and 12:

$$M_{w_{cc}} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \sum_i w_i M_{cc,i} \quad (\text{Eq. 11})$$

$$5 \quad [\eta]_{cc} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \sum_i w_i IV_{cc,i} \quad (\text{Eq. 12}).$$

Equation 13 is used to determine the gpcBR branching index:

$$gpcBR = \left[\left(\frac{[\eta]_{cc}}{[\eta]} \right) \cdot \left(\frac{M_w}{M_{w,cc}} \right)^{\alpha_{PE}} - 1 \right] \quad (\text{Eq. 13}),$$

wherein $[\eta]$ is the measured intrinsic viscosity, $[\eta]_{cc}$ is the intrinsic viscosity from the conventional calibration, M_w is the measured weight average molecular weight, and $M_{w,cc}$ is the weight average molecular weight of the conventional calibration. The weight average molecular weight by light scattering (LS) using Equation (9) is commonly referred to as “absolute weight average molecular weight” or “ $M_{w, Abs}$ ”. The $M_{w,cc}$ from Equation (11) using conventional GPC molecular weight calibration curve (“conventional calibration”) is often referred to as “polymer chain backbone molecular weight”, “conventional weight average molecular weight”, and “ $M_{w, GPC}$ ”.

All statistical values with the “cc” subscript are determined using their respective elution volumes, the corresponding conventional calibration as previously described, and the concentration (C_i) derived from the retention volume molecular weight calibration. The non-subscripted values are measured values based on the mass detector, LALLS, and viscometer areas. The value of K_{PE} is adjusted iteratively until the linear reference sample has a gpcBR measured value of zero. For example, the final values for α and Log K for the determination of gpcBR in this particular case are 0.725 and -3.355, respectively, for polyethylene, and 0.722 and -3.993 for polystyrene, respectively.

Once the K and α values have been determined using the procedure discussed previously, the procedure is repeated using the branched samples. The branched samples are analyzed using the final Mark-Houwink constants as the best “cc” calibration values and Equations 9 - 12 are applied.

5 The interpretation of gpcBR is straight forward. For linear polymers, gpcBR
calculated from Equation 13 will be close to zero since the values measured by LS and
viscometry will be close to the conventional calibration standard. For branched
polymers, gpcBR will be higher than zero, especially with high levels of long chain
10 calculated $M_{w,cc}$, and the calculated IV_{cc} will be higher than the measured polymer IV. In
fact, the gpcBR value represents the fractional IV change due the molecular size
contraction effect as the result of polymer branching. A gpcBR value of 0.5 or 2.0 would
mean a molecular size contraction effect of IV at the level of 50% and 200%,
respectively, versus a linear polymer molecule of equivalent weight.

15 For these particular Examples, the advantage of using gpcBR in comparison to a
traditional “g” index” and branching frequency calculations is due to the higher precision
of gpcBR. All of the parameters used in the gpcBR index determination are obtained
with good precision and are not detrimentally affected by the low 3D-GPC detector
response at high molecular weight from the concentration detector. Errors in detector
20 volume alignment also do not affect the precision of the gpcBR index determination.

GPC-LS Characterization

Analysis of a concentration-normalized LS chromatogram response curve for a
particular sample using a pre-determined molecular weight range is useful in
differentiating embodiment polymers from analogous and commercially available
25 comparative low density ethylene-based polymers.

The “GPC-LS Characterization” parameter, Y, is designed to capture the unique
combination of MWD and the GPC-LS profile for a specific material. Figures 2 – 4
provide the examples and the guide for using the GPC-LS Characterization method to
identify inventive embodiments.

30 An ethylene-based polymer that has long chain branching, such as low density
ethylene-based polymers, can be differentiated by using an analysis technique called
“GPC-LS Characterization”. In the GPC-LS Characterization method, the determination

5 is made using the light scattering (LS) detector response for a sample processed by a conventionally calibrated 3D-GPC (“cc-GPC”) over a range of molecular weights of the sample. The molecular weights of the sample are converted to logarithm values for scaling purposes. The LS response is “concentration-normalized” so the LS response can be compared between samples, as it is known in the art that the unnormalized LS signals
 10 can vary greatly from sample to sample without normalization. When plotted, the logarithm values of range of the cc-GPC molecular weights and the concentration-normalized LS values form a concentration-normalized LS chromatogram curve such as shown in Figures 2 – 4.

Once the concentration-normalized LS chromatogram curve is available, the
 15 determination of the GPC-LS Characterization value is straightforward. In the GPC-LS Characterization method, a GPC-LS Characterization value (Y) is determined using the following equations:

$$Y = \text{LSCDF3} \quad (\text{Eq. 14})$$

$$\text{LSCDF3} = \text{Abs}((A/B) / \text{SF}) \quad (\text{Eq. 15})$$

$$20 \quad \text{SF} = \text{A Slope Function} = \text{Abs}(x) + 0.05 \quad (\text{Eq. 16})$$

where Abs() is the mathematical absolute value function.

Essentially, the GPC-LS Characterization value is a relationship between two associated areas (A and B) and an indexed slope of a line (x) between two points on the concentration-normalized LS chromatogram curve at the logarithmic values of two
 25 specified cc-GPC molecular weight values. The specified cc-GPC molecular weight values attempt to bracket a molecular weight fraction that is known to contain polymer chains with long chain branching.

The first step in the analysis is generation of the concentration-normalized LS chromatogram curve representing concentration-normalized LS response values versus
 30 the logarithmic values of cc-GPC molecular weights for the polymer being examined.

5 The second step is to draw a straight line between two points on the concentration-normalized LS chromatogram curve. The straight line and the points will provide the basis for the determination of areas A and B. The two points, a first point and a second point, are located on the concentration-normalized LS chromatogram curve and represent the concentration-normalized LS response values (a first and a second
10 concentration-normalized LS response values) at the logarithm values for two cc-GPC molecular weight values (a first and a second logarithmic cc-GPC molecular weight values). The first point (for example, Intercept 1 on Figure 2) is defined as being on the concentration-normalized LS chromatogram curve (representing the first concentration-normalized LS response value) corresponding to the logarithm value of cc-GPC
15 molecular weight 200,000 grams/mole (representing the first logarithmic cc-GPC molecular weight value), which is a value of approximately 5.3010. The second point (Intercept 2 on Figure 2) is defined as being on the concentration-normalized LS chromatogram curve at the concentration-normalized LS response value (representing the second concentration-normalized LS response value) corresponding to a logarithm value
20 of cc-GPC molecular weight 1,150,000 grams/mole (representing the second logarithmic cc-GPC molecular weight value), which is a value of approximately 6.0607. It is known in the art that differentiation in long chain branching typically is shown around 1M (1×10^6) grams/mole cc-GPC molecular weight.

 The third step is to determine the area A between the straight line and the
25 concentration-normalized LS chromatogram curve between the two logarithmic cc-GPC molecular weight values. Area A is defined as being the value of A1 plus A2. In preferred embodiments, the area A is defined for the range of values between the logarithm value of cc-GPC molecular weight 200,000 grams/mole and the logarithm value of cc-GPC molecular weight 1,150,000 grams/mole.

30 A1 is defined as the area bound between the straight line and the normalized LS chromatogram curve where the concentration-normalized LS response value of the straight line is greater than the concentration-normalized LS response value for the concentration-normalized LS chromatogram curve between the two logarithmic cc-GPC molecular weight values.

5 As can be seen in Figure 2, the area defined as A1 fills the entire range between the two logarithmic cc-GPC molecular weights; therefore $A = A1$. In many cases the straight line will be “above” the concentration-normalized LS chromatogram curve for the logarithmic cc-GPC molecular weight range and will not intersect with the concentration-normalized LS chromatogram curve except at Intercepts 1 and 2. In these
10 cases, $A = A1 =$ a positive value, and $A2 = 0$.

A2 is defined as the inverse of A1. A2 is the area bound between the straight line and the concentration-normalized LS chromatogram curve where the concentration-normalized LS response of the straight line is less than the concentration-normalized LS response for the concentration-normalized LS chromatogram curve between the two
15 logarithmic cc-GPC molecular weight values. For the example shown in Figure 3, A2 is the area between the concentration-normalized LS response curve and the straight line between Intercepts 1 and 2. In these cases, $A = A2 =$ a negative value, and $A1 = 0$.

In some embodiments, as can be seen in Figure 4, the straight line may intersect with the concentration-normalized LS chromatogram curve in at least one other point
20 besides Intercepts 1 and 2 (see Figure 4 at “Additional Intersection Point”). In such situations, A1 is determined as previously defined. For the example shown in Figure 4, A1 would be the positive area between the concentration-normalized LS chromatogram curve and the straight line between the logarithm cc-GPC molecular weight value of approximately 5.8 to the logarithm value of cc-GPC molecular weight 200,000
25 grams/mole. In such situations, A2 is determined as previously defined. For the example shown in Figure 4, A2 is the negative area between the concentration-normalized LS response curve and the straight line between the logarithm cc-GPC molecular weight value of approximately 5.8 to the logarithm value of cc-GPC molecular weight 1,150,000 grams/mole.

30 In calculating a total value for A, A is again defined as the area A1 (positive value) plus the area A2 (negative value). In some embodiments, as can be seen graphically in Figure 4, the total value for A can again be either positive or negative.

5 The fourth step is to determine the area B under the concentration-normalized LS chromatogram curve for the logarithmic cc-GPC molecular weight range. B is defined as the area under the concentration-normalized LS chromatogram curve between the two logarithmic cc-GPC molecular weight values. Area B does not depend upon the analysis of area A.

10 The fifth step is to determine the value of x, the slope indexing value. The value of the x is an indexing factor that accounts for the slope of the straight line established for determining areas A and B. The value of x is not the slope of the straight line; however, it does represent a value reflective of the difference between Points 1 and 2. The value of x is defined by Equation 17:

$$15 \quad x = \frac{\frac{LSresponse_{(Point\ 2, CN)} - LSresponse_{(Point\ 1, CN)}}{LSresponse_{(Point\ 2, CN)}}}{\log MW_{(Point\ 2, ccGPC)} - \log MW_{(Point\ 1, ccGPC)}} \quad (\text{Eq. 17}),$$

where “LS response” terms are the concentration-normalized (CN) LS response values for Intercepts 1 and 2, respectively, and “log MW” terms are the logarithmic cc-GPC molecular weights for Intercepts 1 and 2, respectively. In some embodiments, the straight line may intersect the normalized LS chromatogram curve at least once between
20 Intercepts 1 and 2.

Finally, once x, A, and B are established, the GPC-LS Characterization value (Y) is determined using the previously presented Equations 14 - 16, repeated below:

$$Y = LSCDF3 \quad (\text{Eq. 14})$$

$$LSCDF3 = \text{Abs}(A/B / SF) \quad (\text{Eq. 15})$$

$$25 \quad SF = A \text{ Slope Function} = \text{Abs}(x) + 0.05 \quad (\text{Eq. 16})$$

where, Abs() is the mathematical absolute value function.

Process Information Related to Examples 1 – 6 (Ex. 1 – 6) and Comparative Example 9 (CE9).

5 In discussing the Examples and Comparative Examples, several terms are defined. There are six Example compositions and sets of process information for their creation: Examples 1 - Example 6. There is one Comparative Example composition and set of process information. The same process train was used to create Comparative Example 9 and Example 1 – Example 6.

10 When process conditions are discussed and compared, the process conditions may be referred to by their product designation (e.g., process conditions for producing Example 1 product may be referred to as “the process of Example 1”).

 Example 1 – Example 6 as well as Comparative Example 9 are produced on the same process reaction system; therefore, in referring to the same equipment between the
15 runs, the physical process and its units are analogous to one another. Figure 5 is a simple block diagram of the process reaction system used to produce the aforementioned Examples and Comparative Examples.

 The process reaction system in Figure 5 is a partially closed-loop dual recycle high-pressure, low density polyethylene production system. The process reaction system
20 is comprised of a fresh ethylene feed conduit 1; a booster/primary compressor “BP”, a hypercompressor “Hyper”, a three zone tube reactor which is made up of 144 high pressure tubes that are 9.14 meters long. The tube reactor consists of a first reaction feed zone; a first peroxide initiator conduit 3 connected to a first peroxide initiator source #11; a second peroxide initiator conduit 4 connected to the second peroxide initiator source
25 12; a third peroxide initiator conduit 5 connected to a second peroxide initiator source 12; cooling jackets (using high pressure water) are mounted around the outer shell of the tube reactor and preheater; a high pressure separator “HPS”; a high pressure recycle line 7; a low pressure separator “LPS”; a low pressure recycle line 9; and a chain transfer agent (CTA) feed system 13.

30 The tube reactor further comprises three reaction zones demarcated by the location of the peroxide injection points. The tube reactor has a length of about 1316 meters. The first reaction zone feed is attached to the front of the tube reactor at 0 meters and feeds a portion of the process fluid into the first reaction zone. The first reaction

5 zone starts at injection point #1 (box 3 of Figure 5), which is located about 120 meters
downtube of the front of the tube reactor and ends at injection point #2 (box 4 of Figure
5). The first peroxide initiator is connected to the tube reactor at injection point #1 (box 3
of Figure 5). The second reaction zone starts at injection point #2 (box 4 of Figure 5),
which is about 520 meters downtube from the front of the tube reactor. The second
10 reaction zone ends at injection point #3 (box 5 of Figure 5). The third reaction zone starts
at injection point #3 (box 5 of Figure 5), which is located about 890 meters downtube
from the front of the tube reactor.

The preheater, which is the first 13 tubes starting at 0 meters, and all of the
reaction zones have an inner tube diameter of 5 centimeters. For all the Examples and the
15 Comparative Example 100% of the fresh ethylene and ethylene recycles are directed to
the first reaction zone via the first reaction zone feed conduit. This is referred to as an all
front gas tubular reactor.

For all the Examples and the Comparative Example, a mixture containing t-butyl
peroxy-2 ethylhexanoate (TBPO), di-t-butyl peroxide (DTBP), tert-butyl peroxyvalate
20 (PIV) and an iso-paraffinic hydrocarbon solvent (boiling range >179°C) is used as the
initiator mixture for the first injection point. For injection points #2 and #3, a mixture
containing only DTBP, TPO and the iso-paraffinic hydrocarbon solvent are used. Table
1 shows the flows of the peroxide initiator and solvent solution used for each of the
Examples and the Comparative Example. Note that in order to maintain reaction stability
25 for the Examples at the low reaction temperatures, or peak temperatures less than 290°C,
the front peroxide mix (source 11 of Figure 6) must contain higher concentrations of
TBPO and less PIV as shown in Table 1.

Table 1: Peroxide initiator flows in kilograms per hour at each injection point for
Examples 1 – 6 (Ex. 1 – Ex. 6) and Comparative Example 9 (CE9).

| Material | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 | CE9 |
|---------------------------------------|-------|-------|-------|-------|-------|-------|------|
| TBPO Flow (Injection Point 1) (kg/hr) | 1.85 | 2.03 | 1.97 | 1.99 | 2.01 | 1.93 | 0.90 |
| DTBP Flow (Injection Point 1) (kg/hr) | 0.62 | 0.68 | 0.66 | 0.66 | 0.67 | 0.64 | 0.78 |

| | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|
| PIV Flow (Injection Point 1) (kg/hr) | 0.62 | 0.68 | 0.66 | 0.66 | 0.67 | 0.64 | 2.69 |
| Solvent Flow (Injection Point 1) (kg/hr) | 12.31 | 13.52 | 13.14 | 13.28 | 13.40 | 12.86 | 18.03 |
| TBPO Flow (Injection Point 2) (kg/hr) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.71 |
| DTBP Flow (Injection Point 2) (kg/hr) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.71 |
| Solvent Flow (Injection Point 2) (kg/hr) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 16.28 |
| TBPO Flow (Injection Point 3) (kg/hr) | 0.60 | 0.63 | 0.62 | 0.69 | 0.66 | 0.62 | 0.39 |
| DTBP Flow (Injection Point 3) (kg/hr) | 0.60 | 0.63 | 0.62 | 0.69 | 0.66 | 0.62 | 0.39 |
| Solvent Flow (Injection Point 3) (kg/hr) | 13.74 | 14.55 | 14.26 | 15.82 | 15.16 | 14.26 | 9.02 |

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For all Examples and the Comparative Example, 1-butene is used as the CTA. The 1-butene is injected into the ethylene stream at the discharge drum of the first stage booster. The composition of the CTA feed to the process is adjusted between the Comparative Example and Example 1 – Example 6. This is done to control the melt index of the product. The 1-butene CTA is selected based on its ability to narrow the molecular weight distribution of the final product when compared to other CTAs used in this technology.

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For Example 1 – Example 6, peroxide injection #2 (Source 12 of Figure 5) is turned off resulting in a two peak reactor configuration. The peak temperatures for Example 1 – Example 6 for each of the two reaction zones are then decreased to reduce the overall reactor temperature. The lower overall reactor temperature served to narrow the molecular weight distribution and to increase the product density, two properties which are key in relating to film properties of the ultimate use of this LDPE in one case as a shrink resin in which good optics and good stiffness, respectively, are important. The low reactor temperature coupled with the CTA choice are both key for the production of a high clarity, narrow molecular weight distribution product with a higher density.

The reactor tube process conditions used to manufacture Example 1 – Example 6 and Comparative Example 9 are given in Table 2.

5 Table 2: Process conditions used to make Example 1 – Example 6 (Ex. 1 – Ex. 6) and Comparative Example 9 (CE9).

Note that BW stands for boiling water.

| Process Variables | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 | CE9 |
|--------------------------------------|---------|--------|--------|--------|---------|---------|---------|
| Reactor Pressure (psig) | 38,300 | 38,300 | 38,300 | 38,300 | 38,300 | 38,300 | 38,300 |
| Zone 1 Initiation Temp (°C) | 125 | 148 | 148 | 148 | 125 | 125 | 125 |
| Zone 1 Peak Temp (°C) | 285 | 285 | 285 | 285 | 285 | 285 | 300 |
| Zone 2 Initiation Temp (°C) | none | none | none | none | none | none | 256 |
| Zone 2 Peak Temp (°C) | none | none | none | none | none | none | 300 |
| Zone 3 Initiation Temp (°C) | 208 | 214 | 211 | 207 | 203 | 207 | 258 |
| Zone 3 Peak Temp (°C) | 285 | 285 | 285 | 285 | 285 | 285 | 290 |
| Fresh ethylene Flow (lb/hr) | 22,500 | 21,300 | 20,200 | 22,500 | 23,300 | 22,800 | 26,000 |
| Total ethylene flow (lb/hr) | 101,000 | 99,900 | 100 | 100 | 101,000 | 101,000 | 101,000 |
| Ethylene Conversion (%) | 20 | 20 | 21 | 21 | 21 | 21 | 25 |
| Polyethylene Production Rate (lb/hr) | 20,100 | 20,275 | 21,170 | 21,378 | 21,478 | 20,836 | 25,100 |
| 1-Butene Flow (lb/hr) | 161 | 120 | 125 | 135 | 178 | 166 | 145 |
| Ethylene Purge Flow (lb/hr) | 400 | 500 | 500 | 500 | 400 | 400 | 400 |
| Recycle 1-Butene Conc. (wt%) | 1 | 0 | 0 | 1 | 1 | 1 | 0 |
| BW Drum Press. System 1 (psig) | 140 | 140 | 140 | 140 | 140 | 140 | 140 |
| BW Drum Temp. System 1 (°C) | 180 | 180 | 180 | 180 | 180 | 180 | 180 |
| BW Drum Press. System 2 (psig) | 140 | 140 | 140 | 140 | 140 | 140 | 140 |
| BW Drum Temp. System 2 (°C) | 180 | 180 | 180 | 180 | 180 | 180 | 180 |
| BW Drum Press. System 3 (psig) | 265 | 240 | 240 | 240 | 265 | 265 | 270 |
| BW Drum Temp. System 3 (°C) | 209 | 204 | 204 | 204 | 209 | 209 | 210 |

Note that from Table 2 and Figure 6, BW system 1 goes to Zone 3, BW system 2 goes to zones 4, 5, and 6, and BW system 3 goes to Zone 1 and 2. Figure 6 show the temperature profiles of the tube reactor showing the reactor details of Example 1 and the reaction zones with respect to the peroxide injections. The x-axis shows the joint location between tubes and the y-axis is the temperature for the reaction and for the boiling water.

Thermocouples are used to measure the reaction temperature down the tube during production. The reaction peaks for each zone are controlled by adjusting peroxide flows to each of the reaction zones. The peak temperatures are then used to control the molecular weight distribution and density of the product.

Characterization of Example 1 – Example 6 and Comparative Example 9

Characterization properties of Example 1 – Example 6 and Comparative Example 9 are shown in Table 3. From Table 3, the examples of this invention are generally lower in melt index, higher in density, higher in melting point, higher in heat of fusion, higher in crystallinity, higher in crystallization temperature, comparable to or higher in melt strength, and higher in zero-shear viscosity than the comparative example. The increased density is advantageous in terms of increased stiffness of this material in a film composition when the film needs to be stiff in order for the film to be cut, for example, to be used in a shrink film. The higher density also maintains the rigidity of the film as it is being pulled in a semimolten state after going through a shrink tunnel. The changes in the thermal properties are in many cases a reflection of this higher density. The lower melt index of these resins is very favorable in terms of increased shrink tension in a resulting film as is the higher melt strength and zero-shear viscosity.

Table 3: Melt index, density, DSC (thermal) properties of peak melting temperature (T_m), heat of fusion, % crystallinity and peak cooling temperature (T_c), melt strength, and zero shear viscosity of Example 1 – 6 and Comparative Example 9.

| Description | Melt Index (I ₂ at 190 °C) | Density (g/cc) | T_m (°C) | Heat of Fusion (J/g) | % Crystallinity | T_c (°C) | Melt strength at 190 °C (cN) | Zero Shear Viscosity (Pa-s) |
|-------------|---------------------------------------|----------------|------------|----------------------|-----------------|------------|------------------------------|-----------------------------|
| Example 1 | 0.43 | 0.9244 | 113.0 | 152.7 | 52.3 | 101.3 | 11.8 | 46,773 |
| Example 2 | 0.37 | 0.9244 | 113.0 | 155.6 | 53.3 | 101.4 | 10.2 | 53,691 |
| Example 3 | 0.44 | 0.9244 | 113.3 | 157.2 | 53.8 | 101.2 | 11.5 | 42,744 |
| Example 4 | 0.68 | 0.9245 | 113.3 | 156.6 | 53.6 | 101.0 | 9.6 | 25,272 |
| Example 5 | 0.72 | 0.9243 | 113.1 | 154.7 | 53.0 | 101.2 | 11.2 | 27,005 |
| Example 6 | 0.61 | 0.9241 | 113.1 | 154.8 | 53.0 | 101.3 | 11.5 | 30,788 |
| CE9 | 0.87 | 0.9232 | 112.2 | 150.8 | 51.6 | 99.0 | 10.8 | 23,680 |

5 Table 4 shows unsaturation properties of Example 1 – Example 6 and Comparative Example 9. The Examples in general show slightly higher trans, similar to slightly lower vinyl levels, lower methyl levels, lower vinylidene levels, and lower carbonyl to thickness ratios than the comparative example.

Table 4: FTIR properties of Example 1 – Example 6 and Comparative Example 9.

| Description | Trans / 1000C | Vinyls / 1000C | Methyls / 1000C | Vinylidenes / 1000C | Carbonyl to Thickness Ratio |
|-------------|---------------|----------------|-----------------|---------------------|-----------------------------|
| Example 1 | 0.114 | 0.074 | 14.0 | 0.047 | 0.310 |
| Example 2 | 0.089 | 0.062 | 14.1 | 0.044 | 0.433 |
| Example 3 | 0.094 | 0.063 | 14.5 | 0.047 | 0.429 |
| Example 4 | 0.102 | 0.068 | 14.2 | 0.041 | 0.485 |
| Example 5 | 0.107 | 0.08 | 14.8 | 0.049 | 0.320 |
| Example 6 | 0.123 | 0.076 | 14.4 | 0.047 | 0.350 |
| CE 9 | 0.079 | 0.073 | 17.7 | 0.057 | 0.590 |

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Table 5 shows the melt index, density, zero-shear viscosity, and TDGPC properties of Example 1 – Example 6 and Comparative Example 1 – Comparative Example 19. For the TDGPC and zero-shear viscosity results, additional comparative examples have been

chosen to show the uniqueness of the Examples as compared to the Comparative Examples. These data are shown in Table 5 and plotted in Figure 7. As shown in Figure 7, the inventive examples show a unique relationship with $Y = \text{LSCDF3}$ and also with M_w/M_n . In particular, the inventive examples have a much higher Y than any of the comparative samples and in general have a lower M_w/M_n . The Y is between about 0.4 and about 10. The unique structure as demonstrated by their high GPC-LS characterization Y values of the inventive embodiments is clearly shown in Table 5, where a large number of LDPE resins of similar MI range are compared. The comparative examples in Table 5 cover a MI range from 0.17 to 0.87. The comparative examples in Table 5 also covers a broad range of branching level with gpcBR values ranging from about 0.86 to about 2.02. The comparative examples in Table 5 also cover a broad range of molecular weights with the cc- M_w values ranging from about 75,000 to about 140,000 g/mol.

Table 5: Melt index (190 °C), density, melt strength, zero shear viscosity (η_0), and TDGPC properties of Examples and Comparative Examples used in Figure 7.

| # | Melt Index | Density (g/cc) | Melt strength (cN) | η_0 (190 °C, Pa-s) | cc-GPC Mn (g/mol) | cc-GPC Mw (g/mol) | cc-GPC Mz (g/mol) | cc-GPC Mw/Mn | Mw(LS-abs) / Mw(cc-GPC) | IVw dl/g | LCBf | g' | gpcBR | Y |
|-------|------------|----------------|--------------------|-------------------------|-------------------|-------------------|-------------------|--------------|-------------------------|----------|-------|-------|-------|--------|
| Ex. 1 | 0.43 | 0.9244 | 11.8 | 46,773 | 16,650 | 84,700 | 270,300 | 5.09 | 2.10 | 1.009 | 1.560 | 0.640 | 1.354 | 0.755 |
| Ex. 2 | 0.37 | 0.9244 | 10.2 | 53,691 | 17,170 | 87,290 | 285,700 | 5.08 | 2.12 | 1.008 | 1.654 | 0.637 | 1.406 | 0.502 |
| Ex. 3 | 0.44 | 0.9244 | 11.5 | 42,744 | 17,520 | 83,640 | 253,900 | 4.77 | 2.16 | 1.023 | 1.437 | 0.650 | 1.340 | 0.531 |
| Ex. 4 | 0.68 | 0.9245 | 9.6 | 25,272 | 16,560 | 77,960 | 241,200 | 4.71 | 2.11 | 0.992 | 1.455 | 0.658 | 1.248 | 0.761 |
| Ex. 5 | 0.72 | 0.9243 | 11.2 | 27,005 | 16,520 | 80,570 | 277,700 | 4.88 | 2.07 | 0.967 | 1.643 | 0.648 | 1.336 | 0.829 |
| Ex. 6 | 0.61 | 0.9241 | 11.5 | 30,788 | 16,930 | 84,710 | 318,300 | 5.00 | 2.03 | 0.961 | 1.952 | 0.633 | 1.380 | 0.760 |
| CE1 | 0.37 | 0.9276 | 12.6 | 46,130 | 17,980 | 90,540 | 292,400 | 5.04 | 2.45 | 1.054 | 1.420 | 0.642 | 1.705 | 0.363 |
| CE2 | 0.24 | 0.9215 | 15.1 | 125,156 | 14,730 | 111,700 | 429,400 | 7.58 | 2.26 | 1.083 | 1.671 | 0.617 | 1.783 | 0.094 |
| CE3 | 0.49 | 0.9274 | 11.8 | 54,010 | 17,210 | 100,010 | 368,800 | 5.81 | 1.94 | 1.091 | 0.979 | 0.684 | 1.147 | -0.253 |
| CE4 | 0.32 | 0.9251 | 11.5 | 67,069 | 17,530 | 97,740 | 352,100 | 5.58 | 2.51 | 1.061 | 1.745 | 0.622 | 1.861 | 0.168 |
| CE5 | 0.63 | 0.9262 | 11.6 | 35,524 | 13,860 | 103,210 | 424,700 | 7.45 | 1.84 | 1.027 | 0.870 | 0.697 | 1.446 | -0.145 |
| CE6 | 0.70 | 0.9269 | 11.6 | 31,862 | 15,240 | 98,540 | 354,800 | 6.47 | 2.02 | 1.040 | 1.146 | 0.673 | 1.514 | -0.111 |
| CE7 | 0.64 | 0.9283 | 13.2 | 34,548 | 16,250 | 94,790 | 379,100 | 5.83 | 1.87 | 1.023 | 1.008 | 0.688 | 1.202 | -0.341 |
| CE8 | 0.47 | 0.9272 | 13.3 | 49,383 | 18,270 | 100,240 | 362,300 | 5.49 | 1.95 | 1.108 | 0.900 | 0.688 | 1.306 | -0.355 |
| CE9 | 0.87 | 0.9232 | 10.7 | 23,680 | 13,840 | 94,240 | 340,400 | 6.81 | 2.10 | 0.959 | 1.949 | 0.615 | 1.617 | 0.393 |
| CE10 | 0.78 | 0.9232 | 11.9 | 15,625 | 17,920 | 85,740 | 259,900 | 4.78 | 1.87 | 1.006 | 1.207 | 0.656 | 1.184 | 0.106 |
| CE11 | 0.75 | 0.9240 | 9.6 | 15,468 | 20,290 | 74,810 | 160,000 | 3.69 | 1.66 | 1.005 | 1.167 | 0.668 | 0.856 | 0.170 |
| CE12 | 0.23 | 0.9189 | 21.8 | 129,786 | 15,390 | 130,530 | 474,600 | 8.48 | 2.59 | 1.167 | 2.024 | 0.561 | 2.016 | -0.045 |
| CE13 | 0.26 | 0.9179 | 25.8 | 134,228 | 14,850 | 140,380 | 477,100 | 9.45 | 2.47 | 1.174 | 2.261 | 0.545 | 2.016 | -0.086 |
| CE14 | 0.26 | 0.9251 | 18.6 | 88,928 | 18,490 | 111,420 | 346,000 | 6.03 | 1.83 | 1.114 | 1.446 | 0.612 | 1.372 | -0.193 |
| CE15 | 0.85 | 0.9240 | 13.1 | 25,355 | 13,720 | 94,170 | 380,500 | 6.86 | 2.26 | 0.964 | 1.841 | 0.624 | 1.867 | 0.239 |
| CE16 | 0.71 | 0.9202 | 14.1 | 18,921 | 22,980 | 84,050 | 202,800 | 3.66 | 1.99 | 1.036 | 1.412 | 0.628 | 1.291 | -0.005 |
| CE17 | 0.17 | 0.9225 | 16.6 | 154,799 | 17,400 | 115,550 | 423,300 | 6.64 | 2.51 | 1.098 | 2.135 | 0.584 | 1.852 | 0.063 |
| CE18 | 0.61 | 0.9269 | 13.37 | 39,393 | 14,300 | 96,890 | 347,100 | 6.78 | 2.07 | 1.051 | 1.274 | 0.651 | 1.504 | -0.668 |
| CE19 | 0.28 | 0.9276 | 15.6 | 94,652 | 14,690 | 108,330 | 363,600 | 7.37 | 2.13 | 1.103 | 1.346 | 0.636 | 1.575 | -0.228 |

5 Table 5 also shows the zero-shear viscosities of the examples and comparative examples. The zero-shear viscosity is plotted vs. the weight average molecular weight as determined by conventional calibration as shown in Figure 8. The examples of this invention have a higher zero-shear viscosity for a given weight average molecular weight as determined by conventional calibration. This is advantageous in terms of improved
10 shrinkage properties for the example resins and in general improved melt strength properties. As shown in Figure 8, the examples of this invention fall above a line given by Equation (18):

$$\text{Log}(\eta_0, \text{Pa-s}, 190^\circ\text{C}) = 12.333\text{Log}(\text{ccGPCMw (g/mol)}) - 56.367 \quad (\text{Eqn. 18})$$

15 where the zero-shear viscosity is obtained via a creep test at 190°C via the method described above, and the ccGPC Mw value is determined by the conventional GPC method also as described above.

Films of LDPE

20 Films of Example 1 – Example 6 and Comparative Example 9 are made on a 6” die with a LLDPE type screw. No internal bubble cooling is used. General blown film parameters used to produce the blown film are shown in Table 6. The temperatures show the temperatures closest to the pellet hopper (Barrel 1) and in increasing order as the polymer is being extruded through the die (melt temperature). The film properties are
25 shown in Table 7. The examples of the invention show very low haze, especially Example 2 which is a lower melt index material in which case it is usually difficult to obtain good haze properties. Additionally, the good optics properties of the films are reflected in the high gloss and clarity values. The examples of the invention show a low internal haze, making them suitable for inner layers of co-extruded structures to impart
30 good optical properties. The examples show good dart and puncture properties. The secant modulus values are high in general as compared to the comparative example.

- 5 Example 1 and 3 show very high % CD shrink which is especially advantageous when this LDPE is used in a collation shrink type film. The MD shrink tension values as well as the CD shrink tension values are also very high for the examples of this invention, again reflecting the usefulness of these examples in shrink films.

Table 6: Blown film fabrication conditions for Example 1 – Example 6 and Comparative

- 10 Example 9 samples with physical property results shown in Table 7.

| Parameter | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 5 | Ex. 6 | CE9 |
|--------------------------|-------|-------|-------|-------|-------|-------|
| Blow up ratio (BUR) | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Output (lb/hr) | 188.4 | 187.9 | 188.4 | 189.8 | 189 | 187.9 |
| Film Thickness (mil) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Die Gap (mil) | 40 | 40 | 40 | 40 | 40 | 40 |
| Air Temperature (°F) | 52 | 45 | 46 | 49 | 51 | 49 |
| Temperature Profile (°F) | | | | | | |
| Barrel 1 | 310 | 375 | 375 | 310 | 310 | 310 |
| Barrel 2 | 330 | 425 | 425 | 330 | 330 | 330 |
| Barrel 3 | 350 | 420 | 390 | 350 | 350 | 350 |
| Barrel 4 | 380 | 420 | 420 | 380 | 380 | 380 |
| Barrel 5 | 379 | 420 | 420 | 380 | 380 | 379 |
| Screen | 421 | 440 | 419 | 421 | 420 | 420 |
| Adapter | 420 | 440 | 440 | 420 | 420 | 420 |
| Rotator | 420 | 440 | 440 | 420 | 420 | 420 |
| Lower Die | 427 | 450 | 450 | 421 | 423 | 420 |
| Upper Die | 421 | 450 | 453 | 420 | 421 | 423 |
| Melt Temperature | 434 | 448 | 447 | 432 | 432 | 429 |

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Table 7: Physical properties of film with process conditions shown in Table 6.

| | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 5 | Ex. 6 | CE 9 |
|---|--------|--------|--------|--------|--------|--------|
| Clarity (%) | 97 | 99 | 98 | 98 | 98 | 97 |
| Gloss 45 degree (%) | 83 | 91 | 88 | 86 | 86 | 84 |
| Gloss 60 degree (%) | 117 | 132 | 123 | 127 | 125 | 120 |
| Haze (%) | 5.72 | 4.81 | 5.54 | 5.11 | 5.12 | 5.64 |
| Haze - Internal (%) | 1.56 | 1.55 | 1.54 | 1.81 | 1.82 | 2.29 |
| Haze - Surface (%) | 4.16 | 3.25 | 4.00 | 3.30 | 3.30 | 3.35 |
| Surface/Internal Haze | 2.67 | 2.10 | 2.59 | 1.82 | 1.81 | 1.46 |
| Dart A (g) | 112 | 124 | 109 | 103 | 109 | 115 |
| Puncture (ft-lb/in ³) | 62 | 66 | 62 | 54 | 59 | 60 |
| Secant Modulus 1% CD (Psi) | 34,949 | 39,415 | 40,834 | 24,686 | 20,516 | 28,732 |
| Secant Modulus 2% CD (Psi) | 30,097 | 33,305 | 34,398 | 27,765 | 26,759 | 25,822 |
| Secant Modulus 1% MD (Psi) | 32,888 | 36,262 | 36,799 | 24,871 | 19,823 | 26,917 |
| Secant Modulus 2% MD (Psi) | 28,642 | 31,753 | 31,666 | 26,823 | 24,992 | 24,019 |
| Elmendorf Tear CD (g) | 421 | 566 | 507 | 478 | 471 | 335 |
| Elmendorf Tear MD (g) | 260 | 283 | 334 | 364 | 352 | 349 |
| Ultimate Tensile - CD (Psi) | 3,464 | 3,679 | 3,736 | 2,917 | 3,543 | 3,197 |
| Toughness - CD (ft*lb/in ³) | 1,010 | 1,142 | 1,221 | 882 | 1,114 | 937 |
| Ultimate Elongation - CD (%) | 583 | 603 | 626 | 554 | 633 | 576 |
| Yield Strain - CD (%) | 14 | 14 | 14 | 15 | 14 | 14 |
| Yield Strength - CD (Psi) | 1,847 | 2,054 | 2,177 | 1,847 | 1,849 | 1,732 |
| Ultimate Tensile - MD (Psi) | 3,351 | 4,380 | 4,203 | 3,612 | 3,371 | 3,554 |
| Toughness - MD (ft*lb/in ³) | 780 | 1,147 | 1,043 | 952 | 825 | 833 |
| Ultimate Elongation - MD (%) | 366 | 442 | 406 | 448 | 399 | 379 |
| Yield Strain - MD (%) | 110 | 33 | 28 | 107 | 111 | 73 |
| Yield Strength - MD (Psi) | 2,408 | 2,240 | 2,166 | 2,247 | 2,283 | 2,366 |
| % MD Shrink at 150 °C | 79 | 72 | 72 | 77 | 72 | 79 |
| % CD Shrink at 150 °C | 30 | 16 | 24 | 16 | 19 | 18 |
| Shrink Tension MD (Psi) | 16.4 | 12.6 | 13.3 | 13.1 | 12.6 | 10.9 |
| Shrink Tension CD (Psi) | 1.2 | 1.0 | 1.2 | 0.8 | 1.1 | 0.7 |

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5 Films of LDPE in Blends with LLDPE

Blends of LDPE and LLDPE were made and film was blown from these blends. Table 8 shows the two LLDPE resins used in these blends, Table 9 shows the two LDPE resins used in these blends, and Table 10 shows the 4 blends made from the resins of Table 8 and Table 9.

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Table 8: Descriptions of LLDPE1 – LLDPE 2. DOWLEX and ELITE are Trademarks of The Dow Chemical Company.

| LLDPE | Description | Target I ₂ (190 °C) | Target Density (g/cc) |
|---------|---------------------|--------------------------------|-----------------------|
| LLDPE 1 | DOWLEX XUS 61528.58 | 0.50 | 0.9274 |
| LLDPE 2 | ELITE 5111G | 0.85 | 0.9255 |

15 Table 9: Descriptions of LDPE Example 1 and Comparative Example 2.

| LDPE | I ₂ (190 °C) | Density (g/cc) |
|-----------|-------------------------|----------------|
| Example 1 | 0.43 | 0.9244 |
| CE2 | 0.24 | 0.9215 |

Table 10: Descriptions of blends made into blown films.

| Blend | Description |
|---------|-----------------------------|
| Blend 1 | 80% CE2 / 20% LLDPE 1 |
| Blend 2 | 80% Example 1 / 20% LLDPE 1 |
| Blend 3 | 80% CE2 / 20% LLDPE 2 |
| Blend 4 | 80% Example 1 / 20% LLDPE 2 |

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Films of Blend 1 – Blend 4 are made on a 6” die with a LLDPE type screw. No internal bubble cooling is used. General blown film parameters used to produce the blown film are shown in Table 11. The temperatures show the temperatures closest to the pellet hopper (Barrel 1) and in increasing order as the polymer is being extruded through the die (melt temperature). The film properties are shown in Table 12. Blend 2 and Blend 4, each containing Example 1, as compared to Blend 1 and Blend 3, respectively, show good optics (low haze, high gloss and clarity). The haze of these samples is shown in Figure 9 and the 45 degree gloss and clarity are shown in Figure 10. Figure 11 shows improvements in MD tear and CD tear of the inventive blends as compared to the comparative blends.

Table 11: Blown film fabrication conditions for Blend 1 – Blend 4 with physical property results shown in Table 12.

| Parameter | Blend 1 | Blend 2 | Blend 3 | Blend 4 |
|--------------------------|---------|---------|---------|---------|
| Blow up ratio (BUR) | 2.5 | 2.5 | 2.5 | 2.5 |
| Output (lb/hr) | 150.8 | 150.4 | 150.5 | 150.0 |
| Film Thickness (mil) | 2.0 | 2.0 | 2.0 | 2.0 |
| Die Gap (mil) | 70 | 70 | 70 | 70 |
| Air Temperature (°F) | 45 | 45 | 46 | 46 |
| Temperature Profile (°F) | | | | |
| Barrel 1 | 375 | 375 | 375 | 375 |
| Barrel 2 | 425 | 425 | 425 | 425 |
| Barrel 3 | 420 | 420 | 420 | 420 |
| Barrel 4 | 421 | 420 | 420 | 420 |
| Barrel 5 | 421 | 420 | 440 | 420 |
| Screen | 439 | 440 | 441 | 440 |
| Adapter | 440 | 439 | 432 | 440 |
| Rotator | 443 | 451 | 450 | 449 |
| Lower Die | 449 | 450 | 450 | 450 |
| Upper Die | 448 | 450 | 450 | 450 |
| Melt Temperature | 473 | 470 | 466 | 463 |

5 Table 12: Physical properties of films made with process conditions shown in Table 11.

| | Blend 1 | Blend 2 | Blend 3 | Blend 4 |
|--|---------|---------|---------|---------|
| Clarity (%) | 86 | 94 | 91 | 97 |
| Gloss 45 degree (%) | 62 | 77 | 64 | 80 |
| Gloss 60 degree (%) | 74 | 102 | 81 | 111 |
| Haze (%) | 11.76 | 8.26 | 10.96 | 7.71 |
| Haze - Internal (%) | 1.48 | 3.75 | 1.79 | 2.76 |
| Haze - Surface (%) | 10.28 | 4.51 | 9.17 | 4.95 |
| Surface/Internal Haze | 6.95 | 1.20 | 5.13 | 1.79 |
| Dart A (g) | 202 | 136 | 217 | 142 |
| Puncture (ft-lb/in ³) | 51 | 50 | 84 | 79 |
| Secant Modulus 1% CD (Psi) | 53,178 | 51,486 | 47,730 | 50,611 |
| Secant Modulus 2% CD (Psi) | 42,794 | 42,043 | 38,922 | 40,473 |
| Secant Modulus 1% MD (Psi) | 43,741 | 45,150 | 41,866 | 44,659 |
| Secant Modulus 2% MD (Psi) | 37,470 | 37,819 | 34,879 | 36,785 |
| Elmendorf Tear CD (g) | 335 | 601 | 423 | 637 |
| Elmendorf Tear MD (g) | 149 | 201 | 159 | 266 |
| Ultimate Tensile - CD (Psi) | 3,588 | 3,810 | 4,402 | 3,949 |
| Toughness - CD (ft*lb/in ³) | 994 | 1,176 | 1,302 | 1,228 |
| Ultimate Elongation - CD (%) | 597 | 663 | 691 | 680 |
| Yield Strain - CD (%) | 10 | 13 | 12 | 15 |
| Yield Strength - CD (Psi) | 1,754 | 1,832 | 1,712 | 1,825 |
| Ultimate Tensile - MD (Psi) | 4,099 | 4,098 | 4,355 | 4,191 |
| Toughness - MD (ft*lb/in ³) | 616 | 952 | 1,052 | 1,044 |
| Ultimate Elongation - MD (%) | 222 | 363 | 377 | 396 |
| Yield Strain - MD (%) | 109 | 114 | 116 | 111 |
| Yield Strength - MD (Psi) | 3,721 | 3,064 | 3,235 | 2,949 |
| % MD Shrink at 150 °C | 81.3 | 78.3 | 79.3 | 77.4 |
| % CD Shrink at 150 °C | 26.2 | 19.3 | 26.2 | 22.2 |
| Shrink Tension MD (Psi) | 36.3 | 23.4 | 27.8 | 20.2 |
| Shrink Tension CD (Psi) | 1.1 | 0.9 | 0.6 | 0.5 |
| Density (g/cc) | 0.9234 | 0.9256 | 0.9231 | 0.9249 |
| I ₂ (190 °C) | 0.20 | 0.33 | 0.26 | 0.40 |
| I ₁₀ 190 °C | 3.35 | 4.72 | 4.42 | 5.64 |
| I ₁₀ /I ₂ (190 °C) | 16.46 | 14.37 | 17.25 | 14.09 |

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5 What is claimed is:

1. An ethylene-based polymer characterized as having a density from about 0.9 to about 0.94 grams per cubic centimeter, a molecular weight distribution (M_w/M_n) from about 4 to about 10, a melt index (I_2) from about 0.05 to about 2 grams per 10 minutes, a gpcBR value greater than 0.05 as determined by a gpcBR Branching Index and a GPC-
 10 LS characterization Y value greater than about 0.4, wherein the GPC-LS characterization Y value is determined according to the following formula;

$$Y = \text{Abs}(A/B / (\text{Abs}(x)+0.05))$$

wherein A is the area between (a) a straight line between a first intercept point and a second intercept point at the two logarithmic cc-GPC molecular weight values located on
 15 the concentration-normalized LS chromatogram curve, and (b) the concentration-normalized LS chromatogram curve between the two logarithmic cc-GPC molecular weight values, and wherein B is the area under the concentration-normalized LS chromatogram curve between the two logarithmic cc-GPC molecular weight values; and wherein x is determined according to the following formula:

$$20 \quad x = \frac{\frac{LSresponse_{(Point\ 2,CN)} - LSresponse_{(Point\ 1,CN)}}{LSresponse_{(Point\ 2,CN)}}}{\log MW_{(Point\ 2,ccGPC)} - \log MW_{(Point\ 1,ccGPC)}}$$

wherein $LSresponse_{(Point\ 2,CN)}$ is the concentration-normalized (CN) LS response value for Intercept 2, corresponding to logarithmic cc-GPC molecular weight value of 6.0607, $LSresponse_{(Point\ 1,CN)}$ is the concentration-normalized (CN) LS response value for Intercept 1, corresponding to the logarithmic cc-GPC molecular weight value of 5.3010,
 25 and $\log MW_{(Point\ 2,ccGPC)}$ is the logarithmic cc-GPC molecular weight for Intercept 2, corresponding to the logarithmic cc-GPC molecular weight value 6.0607, $\log MW_{(Point\ 1,ccGPC)}$ is the logarithmic cc-GPC molecular weight for Intercept 1 corresponding to the logarithmic cc-GPC molecular weight value of 5.3010; and wherein Abs() is the mathematical absolute value function.

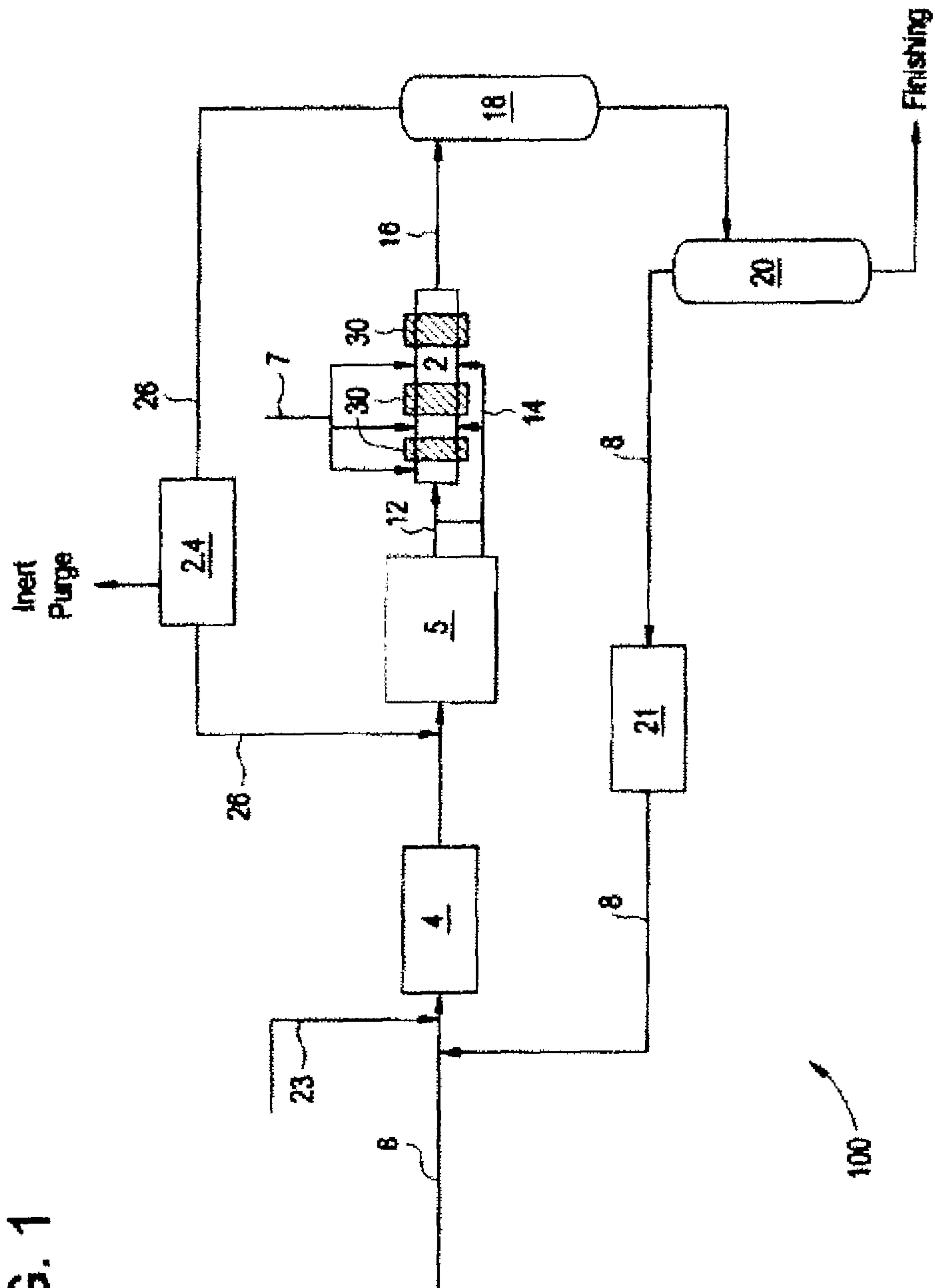
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- 5 2. The ethylene-based polymer of claim 1, where the ethylene-based polymer is a homopolymer.
3. The ethylene-based polymer of claim 1, where the ethylene-based polymer is a copolymer.
4. The ethylene-based polymer of claim 1, where the Y value is greater than about
10 0.5.
5. The ethylene-based polymer of claim 1, where the melt index is less than 0.8 grams/10 minutes.
6. The ethylene-based polymer of claim 1, where the melt index is less than 0.5 grams/10 minutes.
- 15 7. The ethylene-based polymer of claim 1 where the molecular weight distribution (M_w/M_n) of the ethylene-based polymer composition is from about 4 to about 6.
8. A composition comprising the ethylene-based polymer of claim 1 and at least one other natural or synthetic polymer.
9. The composition of claim 9 wherein the synthetic polymer is selected from the
20 group consisting of linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and low density polyethylene (LDPE).
10. The composition of claim 9 wherein the synthetic polymer comprises LLDPE.
11. The composition of claim 11 wherein the LLDPE comprises less than 50 percent by weight of the composition.
- 25 12. At least one film layer comprising the composition of claim 10.
13. The polymer of claim 1, wherein the polymer has a cc GPC Mw in g/mol and a zero shear viscosity (η_o)(Pa*s) relationship $\log(\eta_o(\text{Pa*s at } 190^\circ\text{C})) > 12.333 * \log(\text{ccGPC Mw in g/mol}) - 56.367$.

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- 5 14. The polymer of claim 14, wherein the melt index is less than 0.7 grams/10
minutes.
15. The polymer of claim 14, wherein the log (ccGPC Mw in g/mol) is greater than
4.88.
16. The polymer of claim 1, wherein the polymer has a melt strength at 190 °C in cN
10 of greater than 9 cN.
17. At least one film layer comprising the ethylene-based polymer of claim 1.
18. The film layer according to claim 17, wherein the film layer has a machine
direction (MD) shrink tension greater than 12 psi.

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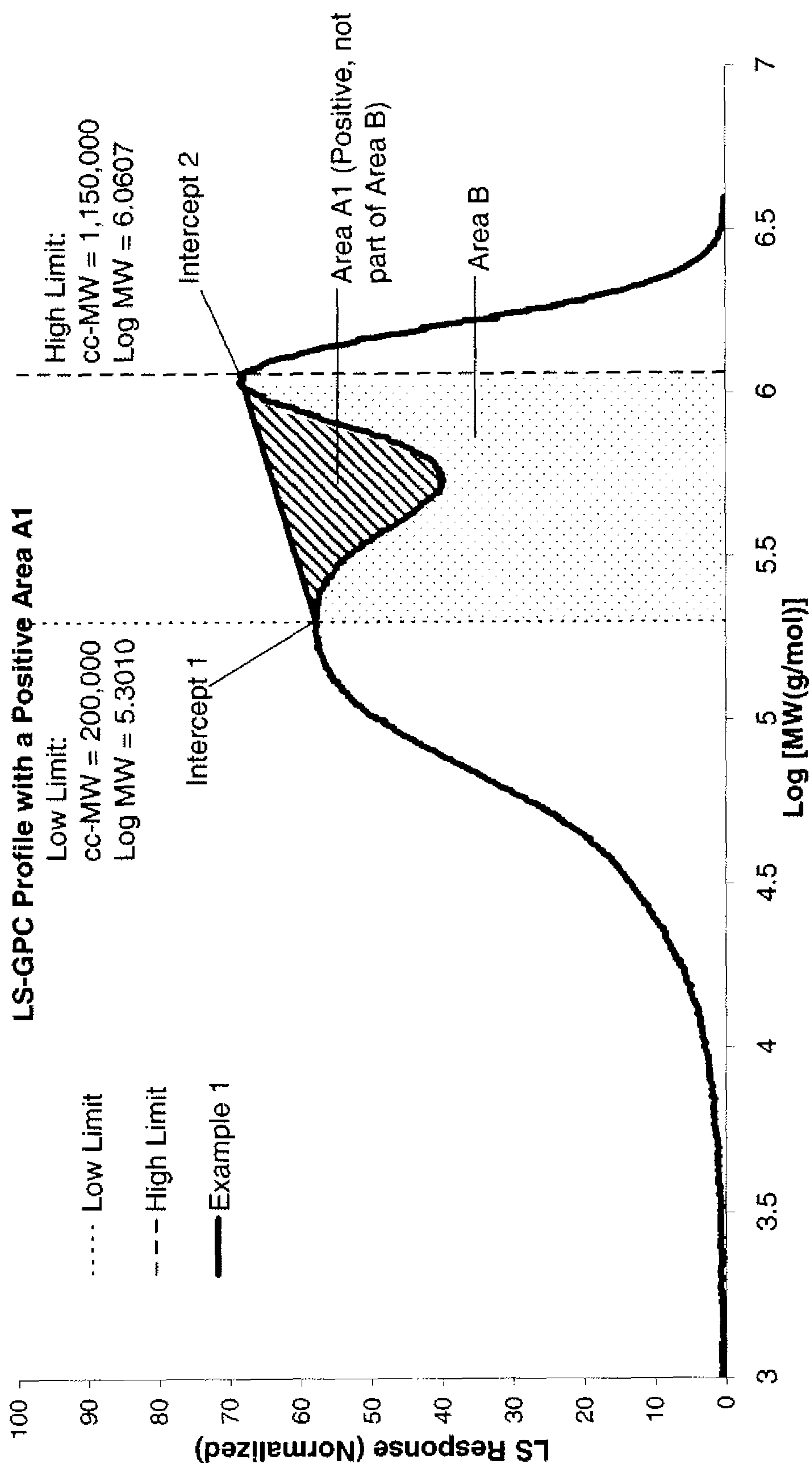


FIG. 2

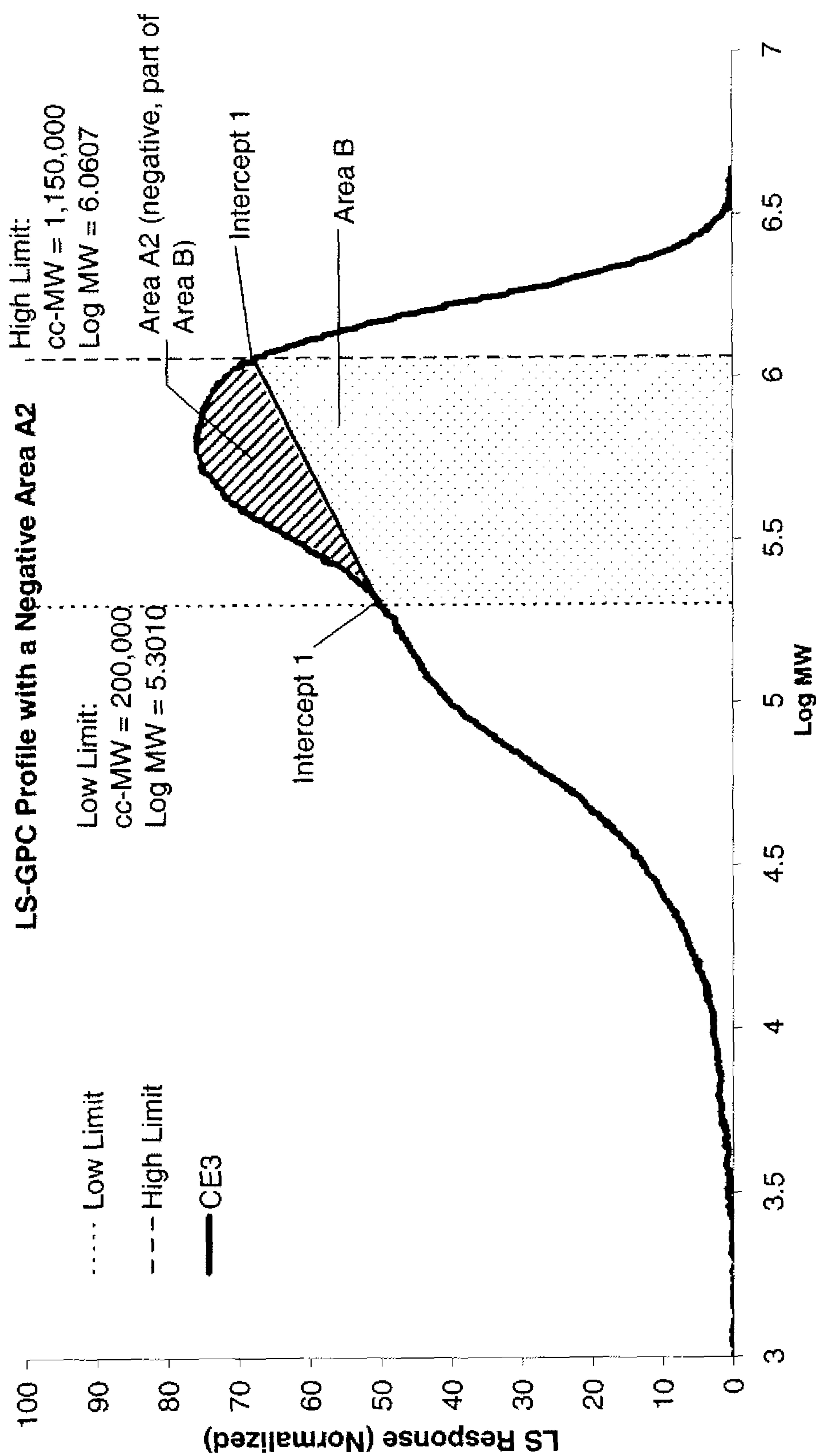


FIG. 3

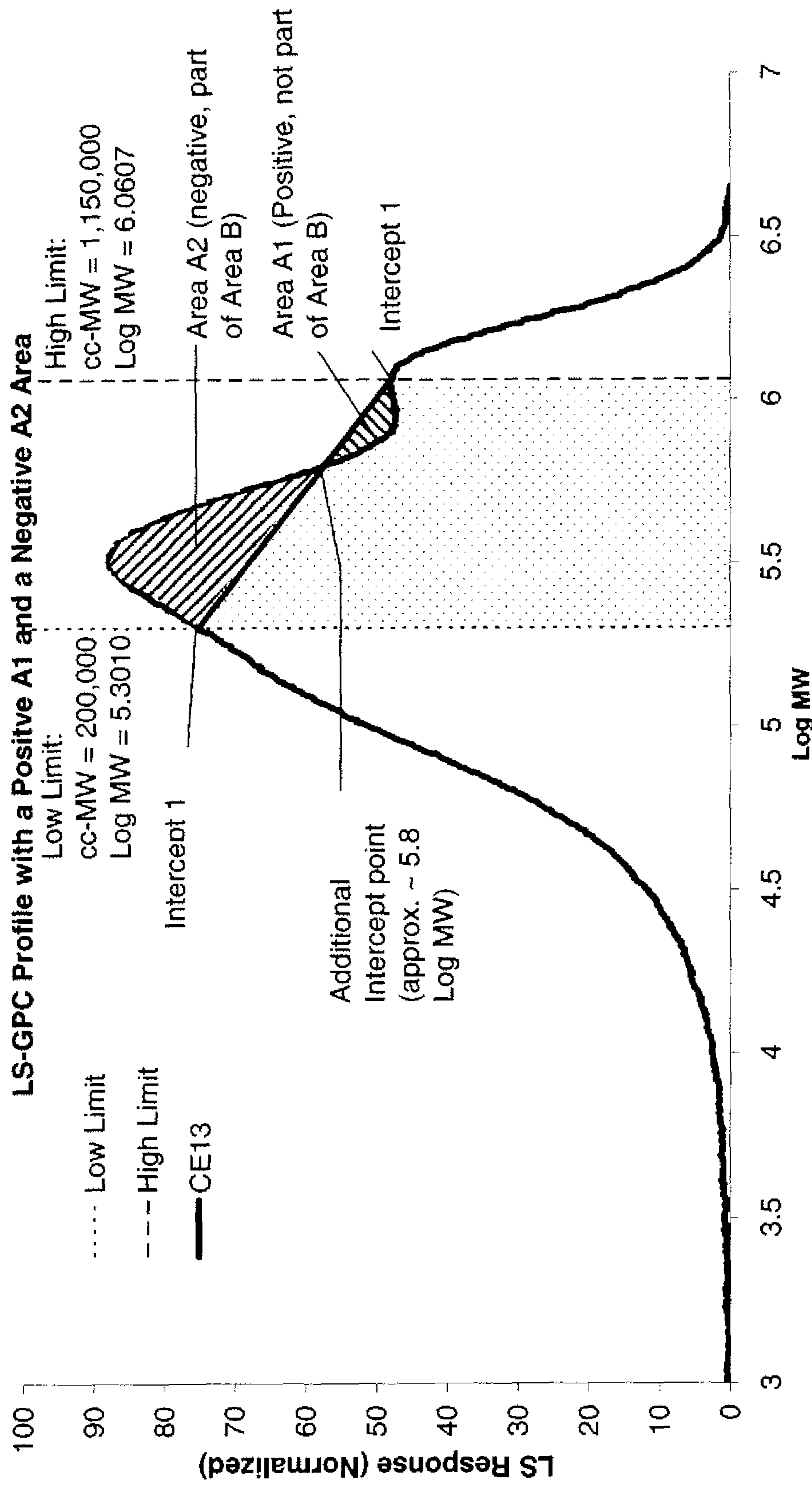


FIG. 4

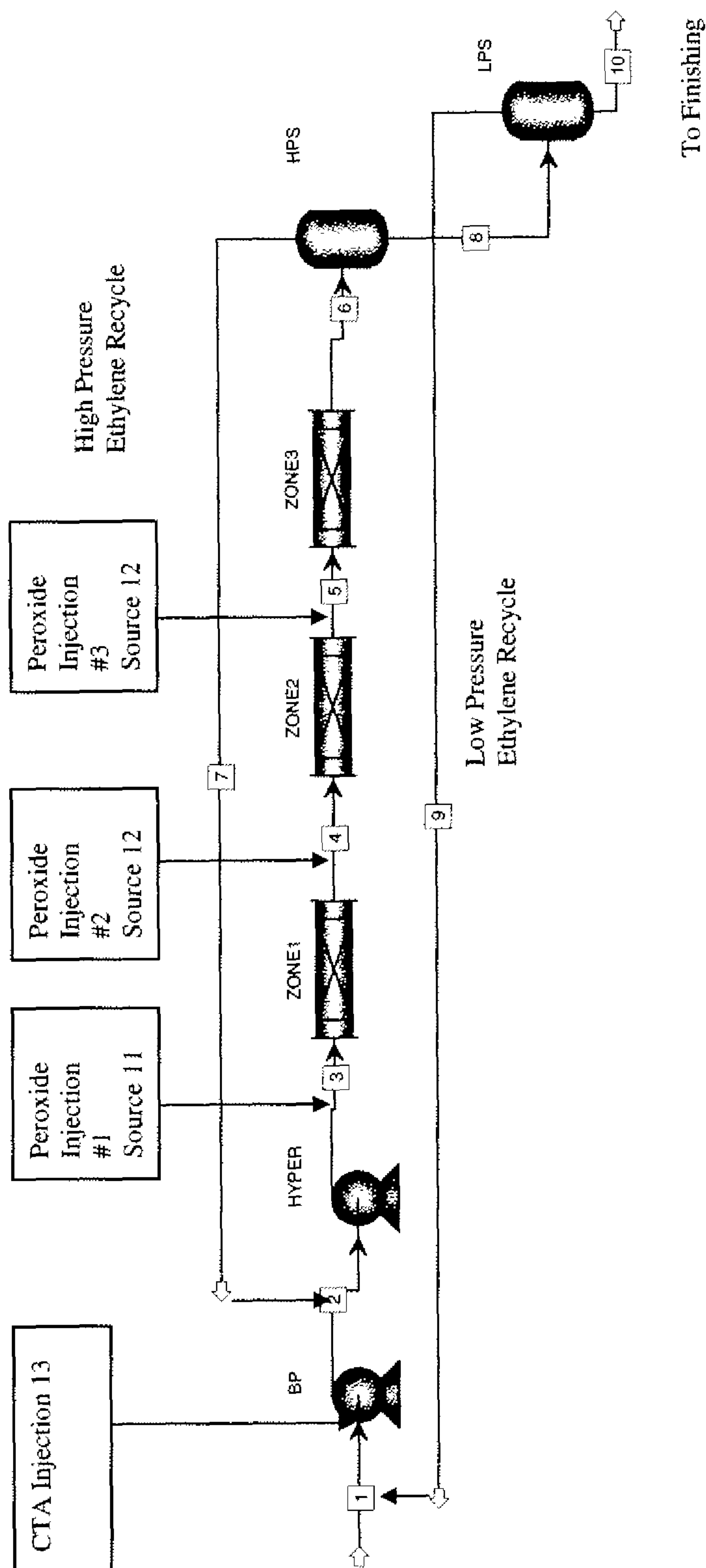


FIG. 5

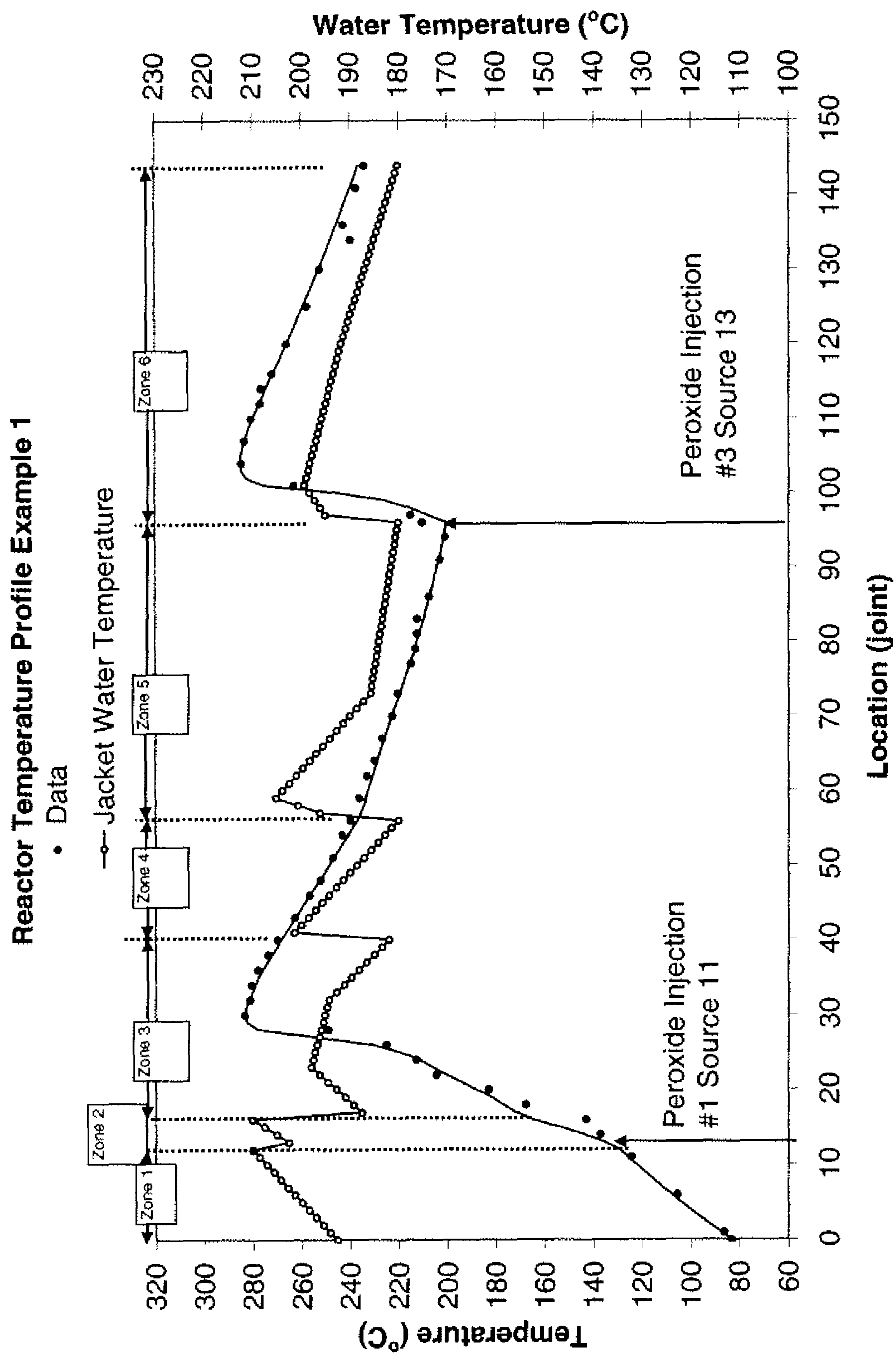


FIG. 6

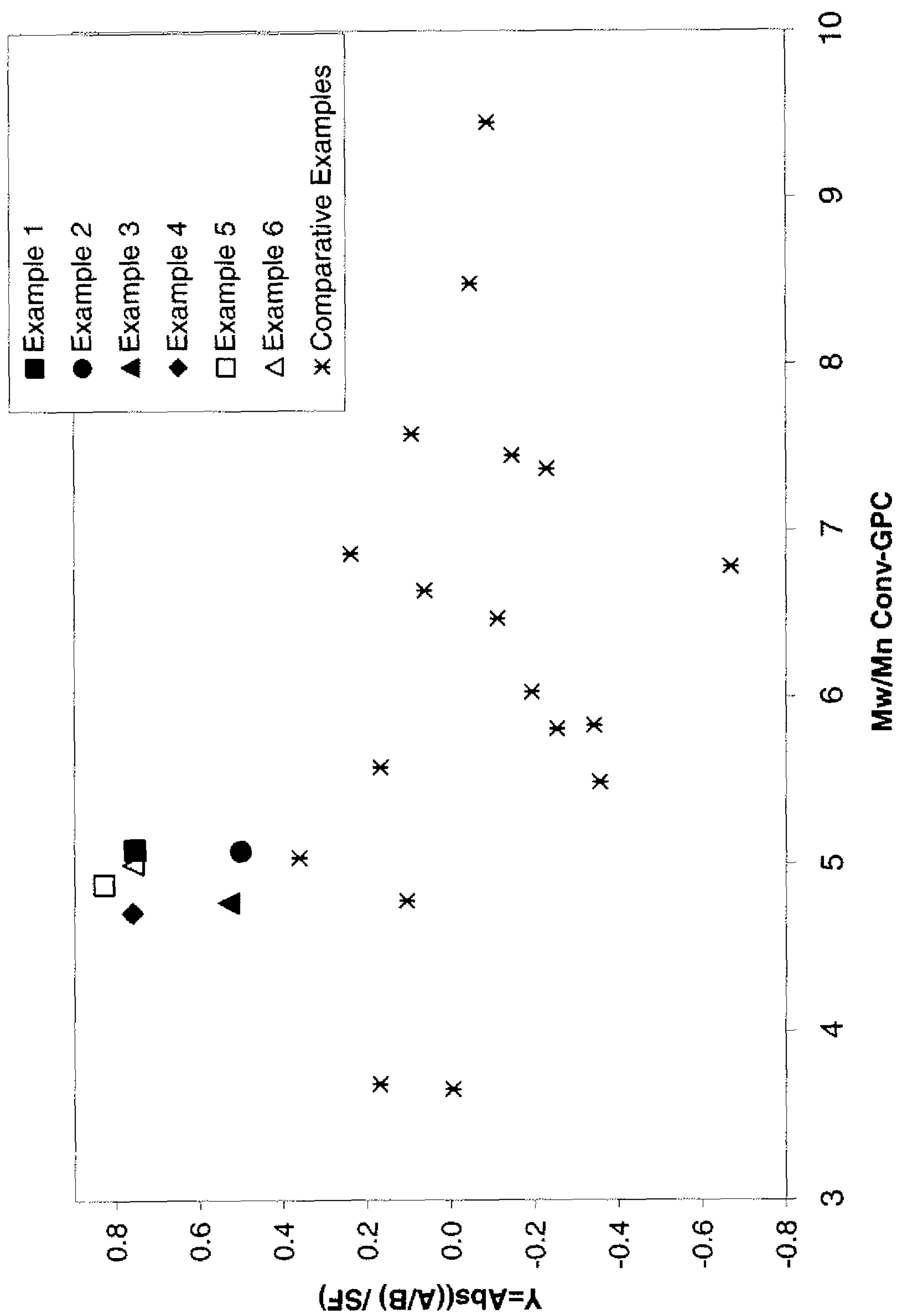


FIG. 7

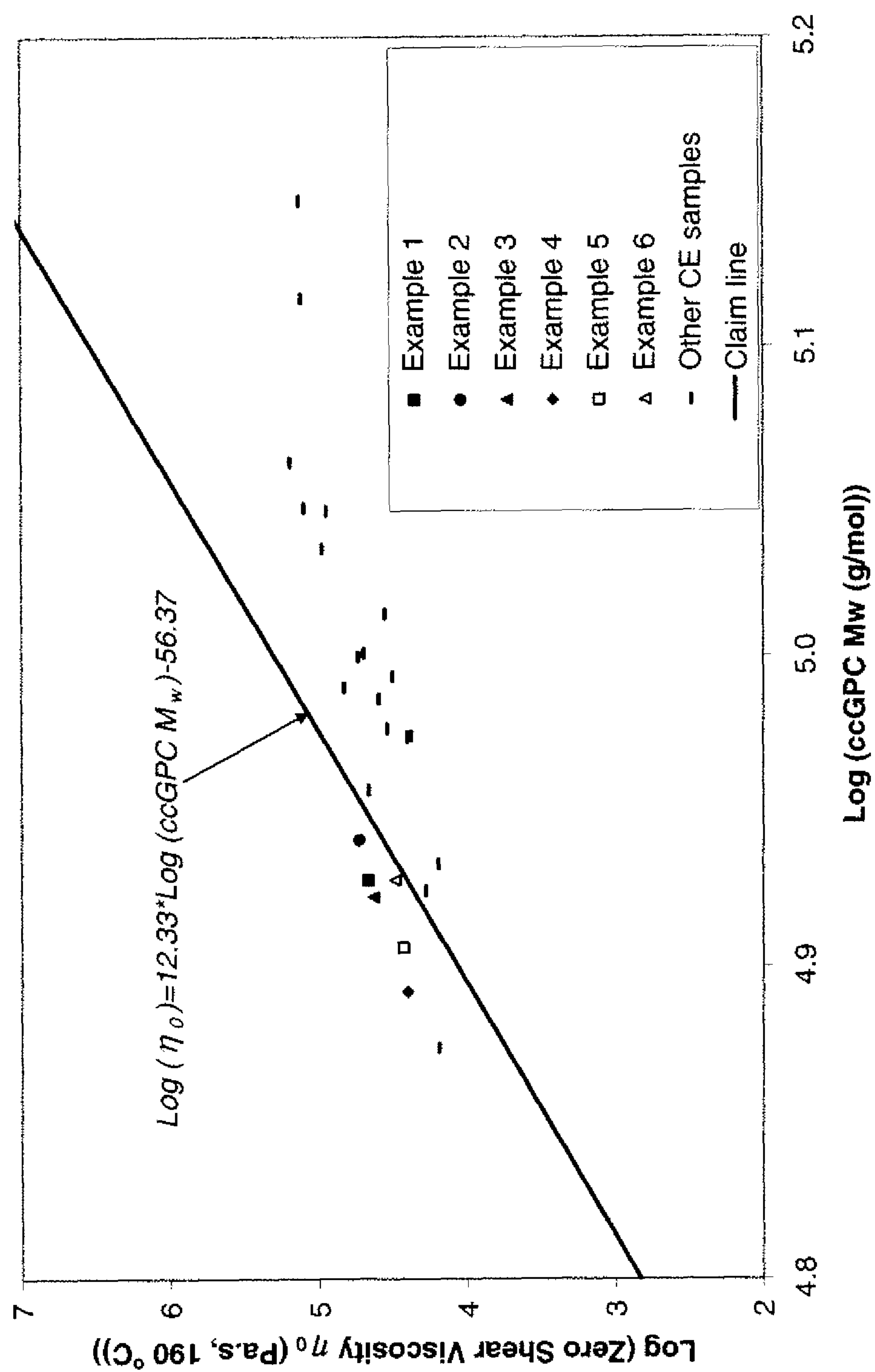


FIG. 8

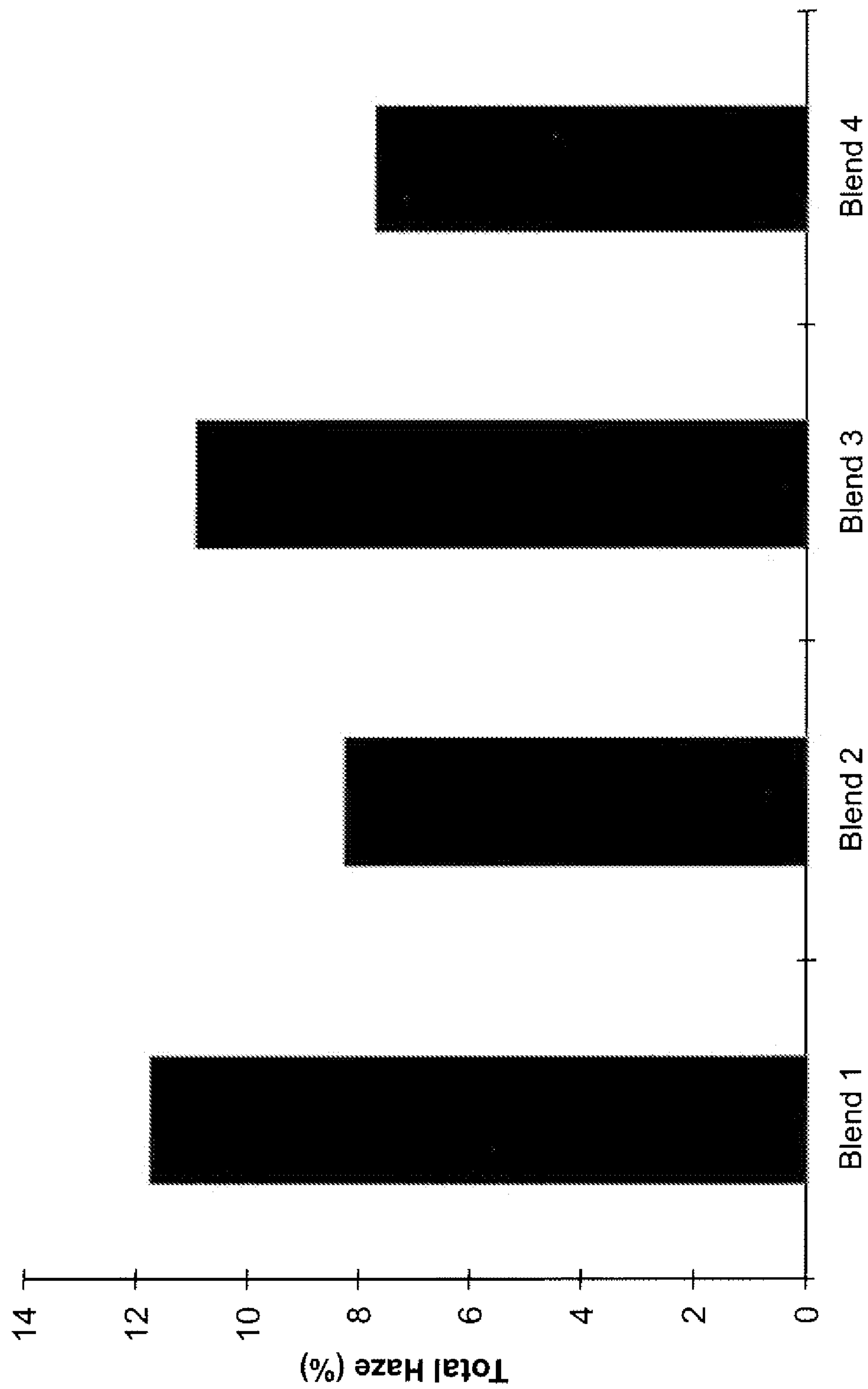


FIG. 9

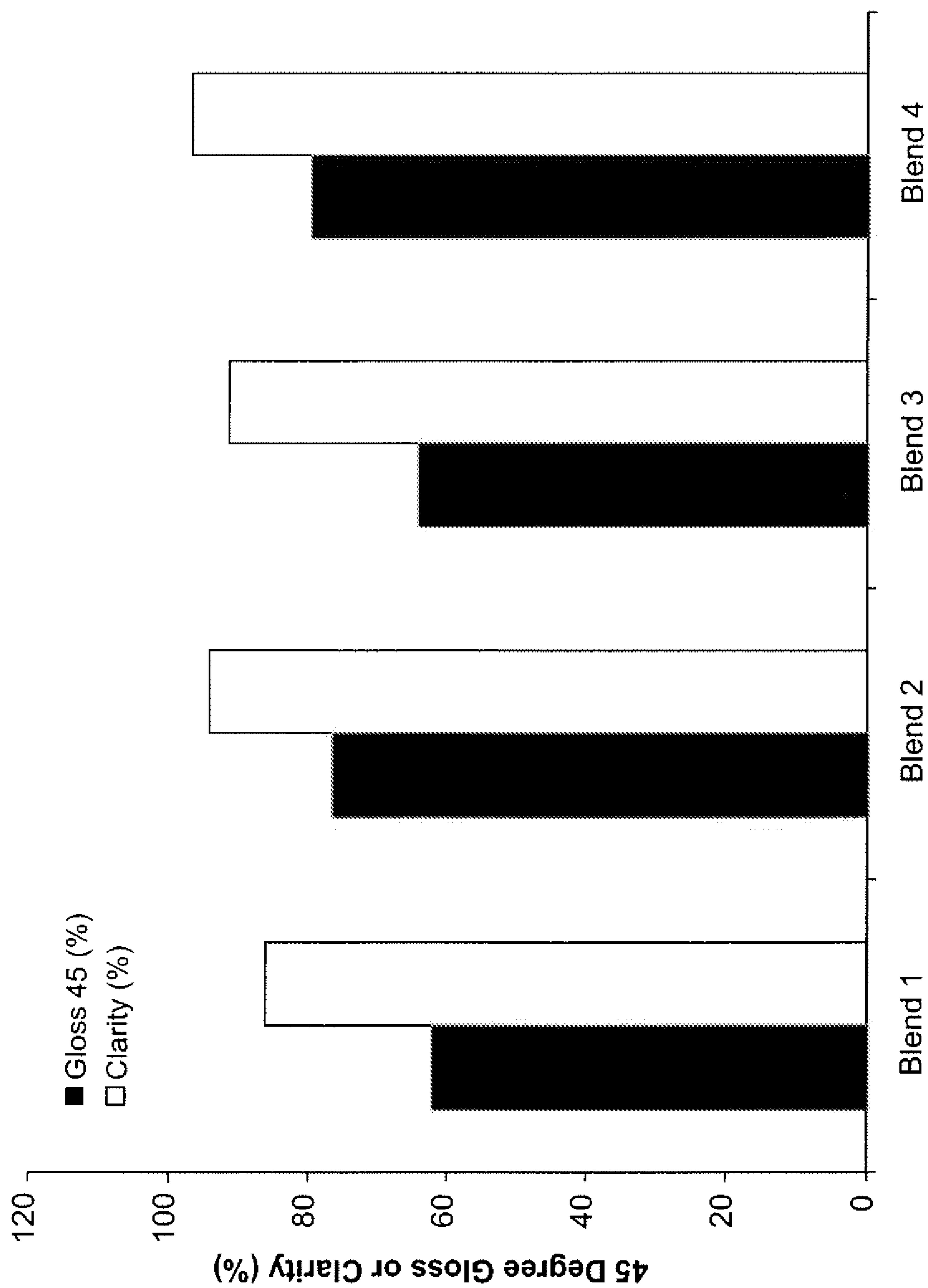


FIG. 10

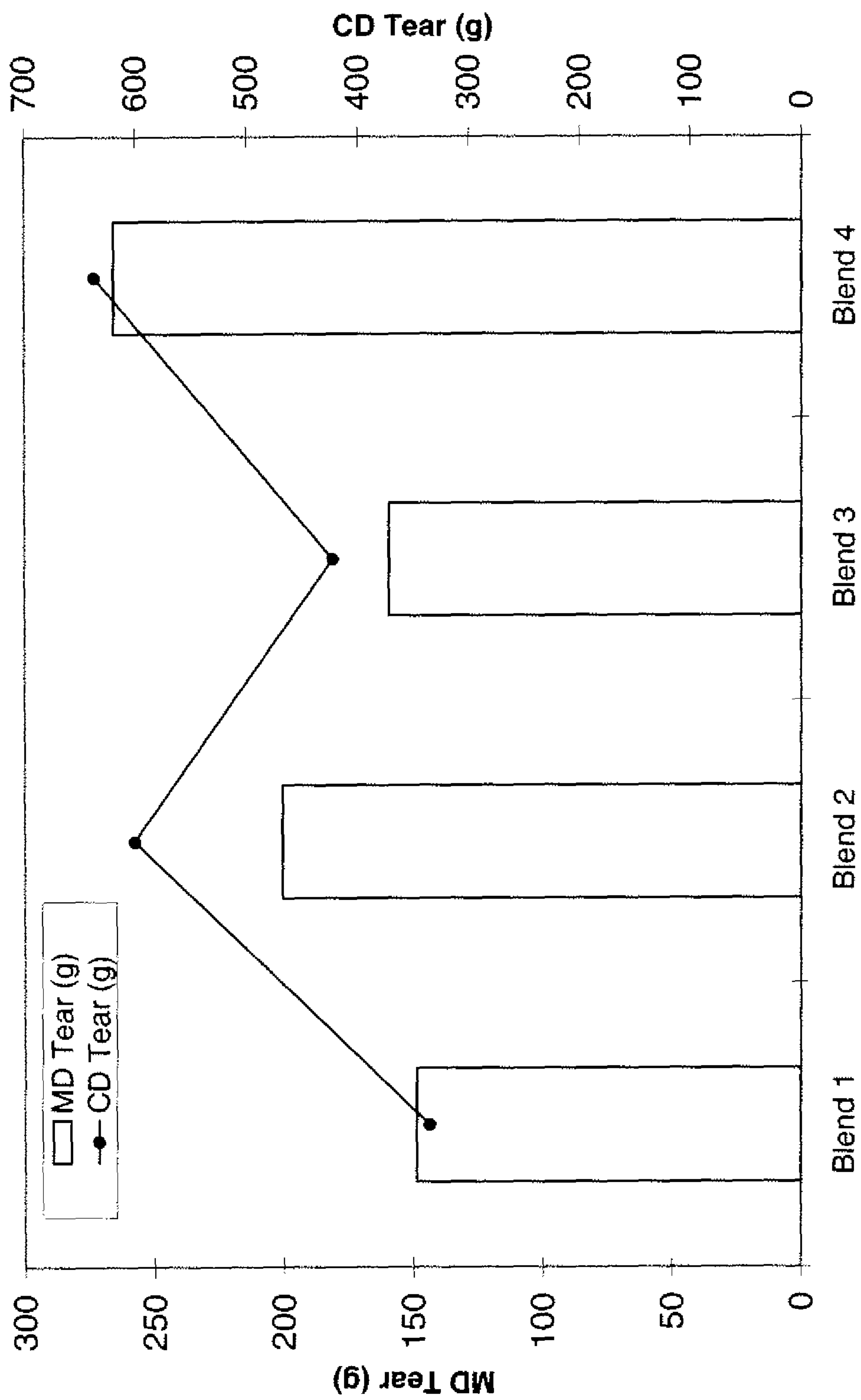


FIG. 11