EXHIBIT U

PART 4

In the thus obtained prepolymerization catalyst, the catalyst component (A) is supported in an amount in terms of transition metal atom, based on 1 g of the carrier, of 0.1 to 50 mg, preferably 0.3 to 30 mg, more preferably 0.5 to 20 mg. A molecular ratio (Al/M) of the catalyst components (B) and (C) in terms of Al atom to the catalyst component (A) in terms of the transition metal (M) is 5 to 200, preferably 10 to 150, more preferably 15 to 100.

The ethylene copolymers according to the present invention are obtained by copolymerizing ethylene with such an α-olefin having 3 to 20 carbon atoms as propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

In the second process for olefin polymerization according to the present invention, olefin is usually polymerized under the condition that the produced polymer exists in a solid state, for example in a gas phase or in slurry. In the slurry polymerization, an inactive hydrocarbon or the olefin itself may be used as a solvent.

Concrete examples of the hydrocarbon solvent include

aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane;

alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane;

aromatic hydrocarbons such as benzene, toluene and xylene; and

petroleum fractions such as gasoline, kerosene and gas oil. Of these hydrocarbons, preferred are aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions.

In the present invention, the slurry polymerization is carried out at a temperature of usually −50° to 100° C. preferably 0° to 90° C.

In the present invention, the gas phase polymerization is carried out at a temperature of usually 0° to 120° C., preferably 20° to 100° C.

In the slurry polymerization or gas phase polymerization of the invention, the concentration of the transition metal in the polymerization reaction system is usually 10^{-8} to 10^{-2} g atom/l, preferably 10^{-7} to 10^{-3} g atom/l.

Furthermore, in the polymerization of the invention, an aluminum oxy-compound or an aluminum compound similar to those used in the preparation of the catalyst components (B) and (C) may be added to the reaction system. During the polymerization, a ratio (Al/M) of the aluminum compound in terms of Al atom to the transition metal atom (M) (Al/M) is 5 to 300, preferably 10 to 200, more preferably 15 to 150.

The polymerization is carried out usually at a normal pressure to 100 kg/cm² preferably under an applied pressure condition of 2 to 50 kg/cm². The polymerization can be carried out either batchwise, semicontinuously or continuously.

Furthermore, the polymerization may also be carried out in not less than 2 steps having reaction conditions different from each other.

The solid catalyst for olefin polymerization of the present invention is illustrated below.

The first prepolymerized solid catalyst for olefin polymerization according to the present invention is formed by prepolymerizing olefin in a suspension or a gas phase in the presence of a solid catalyst comprising

[A] a fine particle carrier,

[B] a transition metal compound (designated as a nonbridge type transition metal compound hereinafter) comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually,

[C] a transition metal compound (designated as a bridge type transition metal compound) comprising at least two ligands each having a cyclopentadienyl skeleton, said at least two ligands being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group, and

[D] an organoaluminum oxy-compound.

The second prepolymerized solid catalyst for olefin polymerization according to the present invention is formed from the above-described components [A], [B], [C], [D], and [E] an organoaluminum compound.

The above-described carrier (iv) is used as the fine particle carrier [A].

There can be used as the nonbridge type transition metal compound [B] the same compound as the transition metal compound (E) described above comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually.

There can be used as the bridge type transition metal compound [C] the same compound as described above.

Furthermore, the same compound as described above is used as the organoaluminum oxy-compound [D].

Still furthermore, the same compound as described above is used as the organoaluminum compound [E].

The prepolymerized solid catalyst for olefin polymerization of the invention is prepared by mixing the fine particle carrier [A], the nonbridge type transition metal compound [B], the bridge type transition metal compound [C], the organoaluminum oxy-compound [D] and if necessary the organoaluminum compound [E] in an inactive hydrocarbon solvent, and introducing olefin for prepolymerization.

Though the mixing may be conducted in an arbitrarily selected order, the mixing and contacting is preferably conducted in the order of [A]→([E])→[D]→[B]→olefin→[C]→olefin, or [A]→([E])→[D]→olefin.

The prepolymerized solid catalyst for olefin polymerization of the invention may also be prepared by supporting the nonbridge type transition metal compound [B], the bridge type transition metal compound [C], the organoaluminum compound [D] and if necessary the organoaluminum compound [E] on the fine particle carrier [A], introducing olefin without a solvent, and carrying out prepolymerization.

When the components [A] to [D], and if necessary the component [E] are mixed, the component [B] and the component [C] are used in the total amount of usually 10^{-5} to 5×10^{-3} mol, preferably 5×10^{-5} to 10^{-3} mol based on 1 g of the component [A], and in the total concentration of about 10^{-4} to 2×10^{-2} mol/l, preferably 2×10^{-4} to 10^{-2} mol/l. The component [B] is used in an amount of 5 to 80 mol % preferably 7 to 70 mol %, more preferably 10 to 60 mol % based on the amount of the component [B] and the component [C] of 100 mol % in total.

The atomic ratio [Al/(transition metal)] of the aluminum in the component [D] to the transition metal in the components [B] and [C] is usually 10 to 500, preferably 20 to 200. The atomic ratio (Al_E/Al_D) Of the aluminum atoms (AL_E) in the component [E] used if necessary to the aluminum atoms (Al_D) in the component [D] is usually 0.02 to 3, preferably 0.05 to 1.5. The compo-

nents [A] to [D], and if necessary the component [E] are mixed at a temperature of usually −20° to 80° C., preferably 0° to 60° C., with a contact time of 1 to 200 minutes, preferably 5 to 120 minutes.

Olefin is prepolymerized in the presence of the components [A] to [D], and if necessary the component [E], described above. The prepolymerization is carried out with the transition metal compounds used in an amount of usually 10^{-4} to 2×10^{-2} mol/l, preferably 5×10^{-4} to 10^{-2} mol/l, at a temperature of −20° to 80° C., preferably 0° to 50° C., and for a period of 0.5 to 100 hours, preferably 1 to 50 hours.

Though olefin used in the prepolymerization is selected from the olefin used in the polymerization, ethylene is preferable.

In the prepolymerized solid catalyst for olefin polymerization of the invention obtained as described above, the transition metal is supported in an amount of 5×10^{-6} to 5×10^{-4} g atom, preferably 10^{-5} to 3×10^{-4} g atom, and aluminum is supported in an amount of 10^{-3} to 10^{-1} g atom, preferably 2×10^{-3} to 5×10^{-2} g atom, all the amounts being based on 1 g of the component [A].

Furthermore, the polymer is formed during the prepolymerization in an amount, based on 1 g of the fine particle carrier, of about 0.1 to 500 g, preferably 0.3 to 300 g, particularly preferably 1 to 100 g.

Concrete examples of the inactive hydrocarbon used as a solvent for the preparation of the solid catalyst for olefin polymerization of the invention include

- aliphatic hydrocarons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosene;
- alicyclic hydrocarbons such as cyclopentane, cyclohexane and methylcyclopentane;
- aromatic hydrocarbons such as benzene, toluene and xylene;
- halogenized hydrocarbons such as ethylene chloride, chlorobenzene and dichloromethane; and
- mixtures of these hydrocarbons.

In the polymerization of olefin with such the prepolymerized solid catalyst for olefin polymerization having a prepolymerized olefin as described above, the transition metal compounds [B] and [C] are desirably used in an amount (per liter of the polymerization volume) of usually 10^{-8} to 10^{-3} g atom, preferably 10^{-7} to 10^{-4} g atom in terms of the transition metal. In the polymerization, an organoaluminum compound and an aluminoxane may be used if necessary. Examples of the organoaluminum compound used in the polymerization include compounds similar to the organoaluminum compound [E] described above. The organoaluminum compound is used in an amount of 0 to 500 moles, preferably 5 to 200 moles based on 1 g atom of the transition metal.

The olefins which can be polymerized with such the prepolymerized catalyst for olefin polymerization include ethylene and α-olefins each having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene. In addition, styrene, vinylcyclohexane and dienes may also be employed.

In the present invention, the polymerization can be practiced either by a process for liquid phase polymerization such as solution polymerization and suspension polymerization, or by a process for gas phase polymerization.

In the process for liquid phase polymerization, the same inactive hydrocarbon solvent as employed in the catalyst preparation can be used, and the olefin itself can also be used as a solvent.

The olefin polymerization is carried out with such a catalyst as described above for olefin polymerization at a temperature of usually −50° to 150° C., preferably 0° to 100° C., at a pressure of usually a normal pressure to 100 kg/cm², preferably a normal pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Moreover, the polymerization may also be carried out in two or more steps having reaction conditions different from each other. The molecular weight of the produced olefin polymer can be adjusted either by placing hydrogen in the polymerization system, or by changing the polymerization temperature.

Furthermore, in the present invention, the catalyst for olefin polymerization may also contain components which are different from the above-mentioned components and which are useful for olefin polymerization.

The present invention is illustrated below with reference to examples, but it should be construed that the present invention is in no way limited to those examples.

In addition, the melt tension (abbreviated to MT sometimes hereinafter) in this specification is measured by a procedure described below.

The melt tension (MT) is determined by measuring the stress of a molten polymer while the polymer is being stretched at a constant rate. That is, there are used as samples for measurement fine particles of a produced polymer or a polymer obtained by dissolving the fine particles in decane once, and precipitating the dissolved powder with a methanol/acetone (volume ratio of 1/1) solution in a volume amount of not less than 5 times as much as that of decane, and the measurement was carried out using a MT measuring apparatus (manufactured by Toyoseiki Seisakusho K.K.) having a nozzle diameter of 2.09 mm and a nozzle length of 8 mm at a resin temperature of 190° C., an extrusion rate of 10 mm/min and a take-up speed of 10 to 20 m/min.

During measurement of the melt tension, ethylene copolymer samples are premixed with 0.1% by weight of 2,6-di-tert-butyl-p-cresol, a crosslinking stabilizer.

EXAMPLE 1

[Preparation of a catalyst component (A)]

A 400 ml glass flask purged with nitrogen was charged with 20 g of bis(indenyl)ethane and 200 ml of THF. The contents were cooled to −50° C. with stirring, and 100 ml of a solution of n-BuLi (1.6M solution) was added over a period of 50 minutes. Successively, the resultant mixture was stirred at −50° C. for 1 hour, and allowed to stand to be warmed to room temperature, whereby bis(indenyl)ethane became anionic. To the contents were added 100 ml of THF to form a homogeneous solution.

Another 1 liter glass flask purged with nitrogen was charged with 250 ml of THF, cooled to −50° C., and 16.54 g of zirconium tetrachloride was gradually added. The contents were warmed to 60° C., and stirred for 1 hour The anionic ligand prepared above was added dropwise. The resultant mixture was stirred at 60° C. for 3 hours, and filtered with a glass filter. The filtrate was condensed to 1/5 of the initial volume at room

temperature to precipitate a solid, which was separated by filtering with a glass filter, and the solid residue was washed with a hexane/ether (volume ratio of 1/1) solvent mixture, and dried under reduced pressure to obtain a catalyst component (A).

[Preparation of a catalyst component (B)]

A 400 ml flask thoroughly purged with nitrogen was charged with 37 g of $Al_2(SO_4)_3$-$14H_2O$ and 125 ml of toluene. The contents were cooled to 0° C., and 500 mmoles of trimethylaluminum diluted with 125 ml of toluene was added dropwise. The resultant mixture was warmed to 40° C., and the reaction was continued at the temperature for 48 hours. After the completion of the reaction, the reaction mixture was subjected to solid-liquid separation by filtering, and toluene was removed from the filtrate, whereby 9.1 g of a white solid catalyst component (B) was obtained.

[Preparation of a prepolymerized catalyst]

A 400 ml flask thoroughly purged with nitrogen was charged with 1.29 g of silica (F-948, from Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 20 ml of toluene to form a suspension. To the suspension was added 4.51 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes. Successively, 7.91 ml of a toluene solution of the catalyst component (B) prepared above (Al: 0.95 mole/liter) was added, and the mixture was stirred at room temperature for 30 minutes. Then, 72 ml of a toluene solution of the catalyst component (A) prepared above (Zr: 0.00298 mole/liter) was added, and the resultant mixture was stirred for 10 minutes. Then, 52 ml of decane was further added, and prepolymerized was carried out at 30° C. for 4 hours by continuously introducing ethylene at a normal pressure.

After the completion of the prepolymerization, the solvent was removed by decantation, and the residue was washed at 60° C. three times with 200 ml of hexane, and further washed at room temperature three times with 200 ml of hexane, whereby there was obtained a prepolymerized catalyst containing 8.5 mg of Zr, 160 mg of Al and 15 g of polyethylene based on 1 g of silica.

[Polymerization]

A stainless steel autoclave having a content volume of 2 liter and thoroughly purged with nitrogen was charged with 150 g of sodium chloride (special grade, from Wako Junyaku K.K.), and the contents were dried for 1 hour at 90° C. under reduced pressure. Thereafter, the system pressure was returned to a normal pressure by introducing a gas mixture of ethylene and 1-butene (1-butene content: 6.3 mol %), and the system temperature was lowered to 70° C.

To the autoclave was added the prepolymerized catalyst prepared above in an amount of 0.0075 mg atom in terms of zirconium and 1.13 mmoles of triisobutylaluminum.

Thereafter, 50 Nml of hydrogen and the gas mixture of ethylene and 1-butene described above were successively introduced, and polymerization reaction was started at the total pressure of 4 kg/cm^2-G, whereby the system temperature immediately rose to 80° C. Thereafter, the polymerization was carried out at 80° C. for 1 hour while the total pressure was being maintained at 4 kg/cm^2-G by feeding only the gas mixture.

After the completion of the polymerization, sodium chloride was removed from the reaction mixture by washing with water, and the remaining polymer was washed with methanol and dried overnight at 80° C. under reduced pressure, whereby there was obtained 116 g of an ethylene/1-butene copolymer containing 8.1% by weight of 1-butene constituent units and 2.8% by weight of a decane-soluble component at 23° C. having a MFR of 2.30 g/10 min measured at 190° C. and a load of 2.16 kg, a density of 0.915 g/cm^3, a melt tension (MT) of 5.3 g and a bulk specific gravity of 0.31 g/cm^3, and showing an endothermic curve having the maximum peak at 94° C. when measured by a differential scanning calorimeter (DSC).

EXAMPLE 2

[Preparation of a prepolymerized catalyst]

To 1.30 g of the same silica as used in Example 1 was added 20 ml of decane to form a suspension. To the suspension was added 3.24 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 17.1 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 1.03 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the resultant mixture was stirred for 15 minutes. To the mixture was added 50 ml of decane, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at a normal pressure. Thereafter, 100.5 ml of a toluene solution of the catalyst component (A) containing 0.00172 mole/liter of Zr, and the prepolymerization was continued at 30° C. for 4 hours. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 9.3 mg of zirconium, 190 mg of aluminum and 20 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 3.6 mol % of 1-butene, 10 Nml of hydrogen and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 70° C. for 2 hours, whereby there was obtained 88 g of an ethylene/1-butene copolymer containing 6.7% by weight of 1-butene constituent units and 0.25% by weight of a decane-soluble component, having a MFR of 0.48 g/10 min, a density of 0.922 g/cm^3, a melt tension of 11 g and a bulk specific gravity of 0.35 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

EXAMPLE 3

[Preparation of a prepolymerized catalyst]

To 3.0 g of the same silica as used in Example 1 was added 30 ml of decane to form a suspension. To the suspension was added 7.45 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 25 minutes.

Then, to the suspension was added 39.4 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 2.14 ml of a toluene solution of bis (methylcyclopentadienyl) zirco-

nium dichloride (Zr: 0.0465 mole/liter), and the resultant mixture was stirred for 10 minutes. To the mixture was added 100 ml of decane, and prepolymerization was carried out at 25° C. for 2.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, 166.4 ml of a toluene solution of the catalyst component (A) containing 0.00240 mole/liter of Zr, and the prepolymerization was continued at 30° C. for 5 hours. A subsequent procedure similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 8.2 mg of zirconium, 150 mg of aluminum and 20 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that 30 Nml of hydrogen was added, and that the prepolymerization catalyst described above was used, whereby there was obtained 149 g of an ethylene/1-butene copolymer containing 10.1% by weight of 1-butene constituent units and 3.1% by weight of a decane-soluble component, and having a MFR of 1.78 g/10 min, a density of 0.912 g/cm^3, a melt tension of 5.3 g and a bulk specific gravity of 0.36 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 94° C.

EXAMPLE 4

[Preparation of a prepolymerized catalyst]

To 1.49 g of the same silica as used in Example 1 was added 25 ml of decane to form a suspension. To the suspension was added 3.72 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 19.6 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 45 minutes.

Thereafter, to the suspension was added 2.13 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.0465 mole/liter), and the resultant mixture was stirred for 10 minutes. To the mixture was further added 75 ml of decane, and prepolymerization was carried out at 30° C. for 1.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, to the reaction mixture was added 51.9 ml of the toluene solution of the catalyst component (A) containing 0.00287 mole/liter of Zr and prepared in Example 1, and prepolymerization was continued at 30° C. for 4 hours. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 10.5 mg of zirconium, 190 mg of aluminum and 17 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 4.4 mol % of 1-butene, 30 Nml of hydrogen and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, whereby there was obtained 48 g of an ethylene/1-butene copolymer containing 6.5% by weight of 1-butene constituent units and 0.32% by weight of a decane-soluble component, having a MFR of 3.1 g/10 min, a density of 0.922 g/cm^3, a melt tension of 4.9 g and a bulk specific gravity of 0.36 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 115° C.

EXAMPLE 5

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 3.6 mol % of 1-butene, 30 Nml of hydrogen and the prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 70° C. for 1 hour, whereby there was obtained 95 g of an ethylene/1-butene copolymer containing 7.4% by weight of 1-butene constituent units and 0.18% by weight of a decane-soluble component, having a MFR of 0.075 g/10 min, a density of 0.920 g/cm^3 a melt tension of 42 g and a bulk specific gravity of 0.24 g/cm^3 and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

Comparative Example 1

[Preparation of a prepolymerized catalyst]

To 3.14 g of the same silica as used in Example 1 was added 25 ml of decane to form a suspension, and 13.1 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter) was added to the suspension. The resultant mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 36.5 ml of a toluene solution of an organoaluminum oxy-compound (Al: 1.79 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 20 minutes.

Thereafter, to the suspension was added 10.9 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0480 mole/liter), and the resultant mixture was stirred for 30 minutes. To the mixture was further added 100 ml of decane, and prepolymerization was carried out at 30° C. for 4.5 hours by continuously introducing ethylene at a normal pressure. A subsequent washing operation similar to that of Example 1 was conducted to obtain a prepolymerization catalyst containing 7.6 mg of zirconium, 190 mg of aluminum and 9.7 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.1 mol % of 1-butene and the above-described prepolymerized catalyst in an amount of 0.015 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm^2-G, whereby there was obtained 137 g of an ethylene/1-butene copolymer containing 7.2% by weight of 1-butene constituent units and 1.1% by weight of a decane-soluble component, having a MFR of 1.29 g/10 min, a density of 0.920 g/cm^3, a melt tension of 1.9 g and a bulk specific gravity of 0.37 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 114° C.

EXAMPLE 6

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there was used a polymerization catalyst in an amount of 0.003 mg atom in terms of zirconium and 0.54 mmole in terms of triisobutylaluminum, and that polymerization of only ethyl-

ene was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm^2-G, whereby there was obtained 121 g of an ethylene polymer having a MFR of 0.29 g/10 min, a melt tension of 17.5 g and a bulk specific gravity of 0.32 g/cm^3.

EXAMPLE 7

[Polymerization]

A procedure similar to that of Example 3 was repeated except that there were used a gas mixture containing 3.9 mol % of 1-butene, 50 Nml of hydrogen and the prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, and that polymerization was carried out at the total pressure of 2.5 kg/cm^2-G, whereby there was obtained 119 g of an ethylene/1-butene copolymer containing 7.0% by weight of 1-butene constituent units and 0.35% by weight of a decane-soluble component, having a MFR of 1.97 g/10 min, a density of 0.920 g/cm^3, a melt tension of 4.6 g and a bulk specific gravity of 0.36 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

EXAMPLE 8

[Polymerization]

A polymerization procedure similar to that of Example 4 was repeated except that there were used 50 Nml of hydrogen and a prepolymerized catalyst in an amount of 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 85° C. and the total pressure of 7 kg/cm^2-G, whereby there was obtained 141 g of an ethylene/1-butene copolymer containing 6.8% by weight of 1-butene constituent units and 0.67% by weight of a decane-soluble component, having a MFR of 1.99 g/10 min, a density of 0.920 g/cm^3, a melt tension of 6.0 g and a bulk specific gravity of 0.37 g/cm^3.

EXAMPLE 9

[Preparation of a prepolymerized catalyst]

To 1.11 g of the same silica as used in Example 1 was added 15 ml of toluene to form a suspension. To the suspension was added 7.76 ml of a toluene solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes. Then, to the suspension was added 13.6 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 35 minutes. Thereafter, to the suspension was added 162.0 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00228 mole/liter), and the resultant mixture was stirred for 30 minutes. To the mixture was added 100 ml of decane, and prepolymerization was carried out at 30° C. for 5 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 20.6 mg of zirconium, 310 mg of aluminum and 27 g of polyethylene based on 1 g of silica.

[Polymerization]

A glass autoclave having a content volume of 1.5 liters and thoroughly purged with nitrogen was charged with 1 Liter of decane, and an ethylene and hydrogen gas mixture was introduced at a flow rate of 250 liter/hr and 1 liter/hr, respectively. The system temperature was raised to 75° C., and to the autoclave was added a mixture of 0.5 mmole of triisobutylaluminum and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium. Thereafter, polymerization was carried out at 75° C. and a normal pressure for 3 hours while the above-mentioned gas mixture was being fed continuously, whereby polymerization progressed in a slurry state.

After the completion of the polymerization, the resultant polymer was recovered by filtering, and dried overnight at 80° C. under reduced pressure to obtain 16.9 g of an ethylene polymer having a MFR of 1.18 g/10 min and a melt tension of 6.5 g.

EXAMPLE 10

[Preparation of a catalyst]

A 100 ml egg-plant type flask thoroughly purged with nitrogen was charged with 20 ml of decane, 27.9 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.716 mole/liter) and 37.3 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00268 mole/liter), and the contents were stirred for 5 minutes. Toluene was distilled off from the mixture over a period of 2 hours using an evaporator at room temperature under reduced pressure. The resultant precipitated solid product was recovered by filtering, washed with hexane, and dried at room temperature under reduced pressure to obtain a solid catalyst having an Al/Zr atomic ratio of 112.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that only the solid catalyst component prepared above was used as a catalyst component in an amount of 0.005 mg atom in terms of zirconium, and that ethylene homopolymerization was carried out at 85° C. for 1 hour at the total pressure of 8 kg/cm^2-G, whereby 26.4 g of an ethylene homopolymer having a MFR of 0.42 g/10 min and a melt tension of 12.0 g was obtained.

EXAMPLE 11

[Polymerization]

A polymerization procedure similar to that in Example 10 was repeated except that 100 Nml of hydrogen was added, whereby 34.0 g of an ethylene homopolymer having a MFR of 3.10 g/10 min and a melt tension of 5.0 g was obtained.

Comparative Example 2

[Polymerization]

A polymerization procedure similar to that in Example 9 was repeated except that there were used toluene as a solvent, and an ethylene, 1-butene (both being polymerization monomers) and hydrogen gas mixture at a flow rate of 285 liter/hr, 15 liter/hr and 2 liter/hr, respectively and that copolymerization was carried out for 20 minutes, whereby polymerization progressed in a solution state. After the completion of the polymerization, the resultant polymer was recovered by precipitating it in a large amount of methanol, and dried overnight at 130° C. under reduced pressure, whereby there was obtained 33.1 g of an ethylene/1-butene copolymer containing 6.5% by weight of 1-butene constituent units, having a MFR of 1.44 g/10 min, a density of 0.922 g/cm^3 and a melt tension of 2.1 g.

Comparative Example 3

[Polymerization]

A polymerization procedure similar to that in Example 9 was repeated except that the flow rates of ethylene and hydrogen in the gas mixture were altered to 100 liter/hr and 5 liter/hr, respectively, that there were used as catalyst components 3.42 ml of a toluene solution of the organoaluminum oxy-compound (Al: 1.46 mole/liter) and 0.33 ml of a toluene solution of ethylenebis(indenyl)-zirconium dichloride (Zr: 0.00150 mole/liter), and that ethylene homopolymerization reaction was carried for 80 minutes, whereby the polymerization progressed in a cloudy state. After the completion of the polymerization, the resultant polymer was recovered by precipitating it in a large amount of methanol, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 8.2 g of an ethylene copolymer having a MFR of 0.72 g/10 min and a melt tension of 2.9g.

Example 12

[Preparation of a prepolymerized catalyst]

An 8 liter flask thoroughly purged with nitrogen was charged with 55.4 g of silica (TG-20643, manufactured by Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 1 liter of decane to form a suspension. To the suspension was added 46 mmoles of triisobutylaluminum diluted with 50 ml of decane, and the mixture was stirred at room temperature for 10 minutes.

Successively, 140 ml of a toluene solution of the catalyst component (ii) (manufactured by Schering Co., Ltd.) prepared above (Al: 1.65 mole/liter) was added, and the mixture was stirred at room temperature for 10 minutes. Then, 36.9 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.05 mole/liter) was added, and the mixture was stirred for 15 minutes. Then, prepolymerization was carried out at 30° C. for 3.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, there were successively added 2 liters of decane, 279 ml of the catalyst component (ii), 2.79 liters of the catalyst component (i) (Zr: 0.00264 mole/liter) prepared in Example 1, and 23.4 ml of triisobutylaluminum diluted with 50 ml of decane, and prepolymerization was carried out at 30° C. for 4 hours.

After the completion of the prepolymerization, the solvent was removed by decantation, washed at 60° C. 3 times with 5 liters of hexane, and further washed 3 times at room temperature with 5 liters of hexane, whereby there was obtained a prepolymerized catalyst containing 11 mg of Zr, 190 mg of Al and 16 g of polyethylene based on 1 g of silica.

[Polymerization]

Copolymerization of ethylene with 1-hexene was carried out using a continuous fluidized bed gas phase polymerization equipment at a polymerization temperature of 80° C. and the total pressure of 20 kg/cm^2-G by continuously feeding the above-described prepolymerization catalyst at a rate of 0.1 mmole/hr in terms of zirconium and 15 mmole/hr in terms of triisobutylaluminum, and also continuously supplying ethylene, 1-hexene, hydrogen and nitrogen to maintain the following constant gas composition during polymerization: a 1-hexene/ethylene volume ratio of 0.015 and a H_2/ethylene volume ratio of 6.3×10^{-3}. The polymer yield was 6.0 kg/hr.

The thus obtained polymer contained 10.7% by weight of 1-hexene constituent units and 0.53% by weight of a decane-soluble component measured at 23° C., had a MFR of 1.60 g/10 min, a density of 0.922 g/cm^3 a melt tension (MT) of 6.6 g and a bulk specific gravity of 0.38 g/cm^3 and showed an endothermic curve (measured by DSC) with the maximum peak at 112.1° C.

The results are shown in Tables 1 and 2.

TABLE 1

	Polymerization Conditions								
Example	Catalyst component (mg atom-Zr)		(i-Bu)$_3$Al (mmole)	Total pressure (kg/cm^2-G)	1-Butene (mol %)	H_2 (Nml)	Temp. (°C.)	Time (h)	Note
1	(Ex. 1)	0.0075	1.13	4	6.3	50	80	1	
2	(Ex. 2)	0.0050	0.75	4	3.6	10	70	2	
3	(Ex. 3)	0.0075	1.13	4	6.3	30	80	1	
4	(Ex. 4)	0.0050	0.50	4	4.4	30	80	1	
5	(Ex. 1)	0.0050	0.75	4	3.6	30	70	1	
6	(Ex. 1)	0.0030	0.54	8	—	50	85	1	
7	(Ex. 3)	0.0050	0.50	2.5	3.9	50	80	1	
8	(Ex. 4)	0.0050	0.75	7	4.4	50	85	1	
9	(Ex. 9)	0.0050	0.50	normal pressure	—	(1 l/h)	75	3	Ethylene 250 l/h
10	(Ex. 10)	0.0050	—	8	—	50	85	1	
11	(Ex. 10)	0.0050	—	8	—	100	85	1	
12	(Ex. 12) (0.1 mmole/h)		(15 mmole/h)	20	—	—	80	—	
Comp. Ex. 1	(Comp. Ex. 1)	0.0150	0.75	8	6.1	50	85	1	
Comp. Ex. 2	(Ex. 9)	0.0050	0.50	normal pressure	(15 l/h)	(2 l/h)	75	0.33	Ethylene 285 l/h
Comp. Ex. 3	(Comp. Ex. 3)	0.0005	5.00	normal pressure	—	(5 l/h)	75	0.33	Ethylene 100 l/h

TABLE 2

Example	Yield (g)	1-Butene content (wt. %)	Polymerization results: MFR (g/10 min.)	Density (g/cm³)	Decane-sol. component (wt. %)	Melt tension (g)	DSC max. peak temp. (°C.)	Bulk sp. gr. (g/cm³)
1	116	8.1	2.30	0.915	2.8	5.3	94	0.31
2	88	6.7	0.48	0.922	0.25	11	103	0.35
3	149	10.1	1.78	0.912	3.1	5.3	94	0.36
4	48	6.5	3.10	0.922	0.32	4.9	115	0.24
5	95	7.4	0.075	0.920	0.18	42	103	0.32
6	121	—	0.29	—	—	17.5	—	0.36
7	119	7.0	1.97	0.920	0.35	4.6	103	0.37
8	141	6.8	1.99	0.920	0.67	6.0	—	—
9	16.9	—	1.18	—	—	6.5	—	—
10	26.4	—	0.42	—	—	12.0	—	—
11	34.0	—	3.10	—	—	5.0	—	—
12	(6.0 kg/h)	10.7 (1-hexene content)	1.60	0.922	0.53	6.6	112.1	0.38
Comp. Ex. 1	137	7.2	1.29	0.920	1.1	1.9	114	—
Comp. Ex. 2	33.1	6.5	1.44	0.922	—	2.1	—	—
Comp. Ex. 3	8.2	—	0.72	—	—	2.9	—	—

Comparative Example 4

[Preparation of a prepolymerized catalyst]

Comparative Example 1 was repeated except that 13.1 ml of a toluene solution of bis(cyclopentadienyl)-zirconium dichloride (Zr: 0.04 mole/liter) was used in place of the toluene solution of bis(methylcyclopentadienyl)-zirconium dichloride to obtain a prepolymerized catalyst containing 8.7 mg of zirconium, 290 mg of aluminum and 7.7 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.7 mol % of 1-butene and the prepolymerized catalyst obtained above in an amount of 0.01 mg atom in terms of zirconium and 0.25 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm²-G, whereby there was obtained 75 g of an ethylene/1-butene copolymer containing 6.9% by weight of 1-butene constituent units and 1.5% by weight of a decane-soluble component, having a MFR oil 2.63 g/10 min, a density of 0.922 g/cm³ and a melt tension of 1.3 g, and showing an endothermic curve (measured by DSC) with the maximum peak at 114° C.

Comparative Example 5

[Preparation of a prepolymerized catalyst]

To 1.05 g of the same silica as used in Example 1 was added 20 ml of decane to form a suspension in a 400 ml glass flask. To the suspension was added 2.62 ml of a decane solution of triisobutylaluminum (Al: 1 mole/-liter), and the resultant mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 4.87 ml of a toluene solution of an organoaluminum oxy-compound [prepared by removing toluene from a toluene solution of a methylaluminoxane manufactured by Schering Co., Ltd. and redissolving the residue in toluene (Al: 1.79 mole/liter)], and the resultant mixture was stirred at room temperature for 35 minutes.

Thereafter, to the suspension was added 16.2 ml of a toluene solution of bis(n-butylcyclopentadienyl)zirconium dichloride (Zr: 0.0108 mole/liter), and the mixture was stirred for 30 minutes. Then, 75 ml of decane was further added to the mixture, and prepolymerization was carried out at 30° C. for 4 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 9.3 mg of zirconium, 150 mg of aluminum and 18 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.9 mol % of 1-butene and the prepolymerized catalyst obtained above in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm²-G, whereby there was obtained 147 g of an ethylene/1-butene copolymer containing 9.6% by weight of 1-butene constituent units and 1.5% by weight of a decane-soluble component, having a MFR of 2.45 g/10 min, a density of 0.910 g/cm³ and a melt tension of 0.95 g, and showing an endothermic curve (measured by DSC) with the maximum peak at 109° C.

Comparative Example 6

A glass autoclave having a content volume of 1.5 liter and thoroughly purged with nitrogen was charged with 1 liter of toluene, and ethylene, 1-butene and hydrogen in a mixture were introduced thereinto at a flow rate of 285 liter/hour, 15 liter/hour and 2 liter/hour, respectively. The system temperature was raised to 70° C. and polymerization was started after introducing 0.5 mmole of triisobutylaluminum and the prepolymerized catalyst prepared in Example 1 in an amount of 0.005 mg atom in terms of zirconium.

Polymerization was carried out for 20 minutes at 75° C. and a normal pressure by continuously introducing the above-mentioned gas mixture, whereby the polymerization progressed while dissolving the produced polymer in toluene. After the completion of polymerization, the resultant polymer was precipitated by pouring the polymer solution in methanol.

Then, the precipitated polymer was recovered by filtering, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 33.1 g of an ethylene/1-butene copolymer having a MFR of 1.44 g/10 min, a density of 0.922 g/cm³ and a melt tension (MT) of 2.1 g.

Comparative Example 7

A glass autoclave having a content volume of 1.5 liter and thoroughly purged with nitrogen was charged with 1 liter of toluene, and ethylene, 1-butene and hydrogen in a mixture were introduced at a flow rate of 285 liter/-hour, 15 liter/hour and 5 liter/hour, respectively. The system temperature was raised to 70° C. and polymerization was initiated by introducing the organoaluminum oxy-compound prepared in Example 1 in an amount of 5.0 mg atom in terms of aluminum and the catalyst component (i) in an amount of 0.0005 mg atom in terms of zirconium.

The polymerization was carried out for 20 minutes at 75° C. and a normal pressure while the above-described gas mixture was being continuously introduced, whereby the polymerization progressed while dissolving the produced polymer in toluene. A subsequent operation similar to that in Comparative Example 4 was repeated to obtain 44.1 g of an ethylene/1-butene copolymer having a MFR of 1.08 g/10 min, a density of 0.928 g/cm^3 and a melt tension (MT) of 2.0 g.

EXAMPLE 13

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

A 400 ml glass flask thoroughly purged with nitrogen was charged with 1.38 g of silica (F-498, manufactured by Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 20 ml of decane to form a suspension. To the suspension was added 3.24 ml of a decane solution of triisobutylaluminum (Al: 1 mole/-liter), and the contents were stirred at room temperature for 30 minutes.

To the suspension was added 18.8 ml of a toluene solution of an organoaluminum oxy-compound (prepared by drying methylaluminoxane manufactured by Schering Co., Ltd, and redissolving the residue in toluene, Al: 0.864 mole/liter), and the mixture was further stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 1.03 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the mixture was stirred for 10 minutes. Then, 50 ml of decane was further added, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at a normal pressure.

Thereafter, 100.5 ml of of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00172 mole/liter) was added, and the prepolymerization was continued at 30° C. for 4 hours.

After the completion of the prepolymerization, the solvent was removed by decantation, and the residue was washed 3 times at 60° C. with 250 ml of hexane and then 3 times at room temperature with 250 ml of hexane, whereby there was obtained a prepolymerized solid catalyst containing 9.5 mg atom of zirconium, 0.66 g atom of aluminum and 1750 g of polyethylene.

[Polymerization]

A stainless steel autoclave having a content volume of 2 liters and thoroughly purged with nitrogen was charged with 150 g of sodium chloride (special grade, from Wako Junyaku K.K.), and the contents were dried for 1 hour at 90° C. under reduced pressure. Thereafter, the system pressure was returned to a normal pressure by introducing ethylene, and the system temperature was held at 70° C. Thereafter, the autoclave was charged with a premixture of 0.3 mmole of triisobutylaluminum and the above-described solid catalyst in an amount of 0.003 mg atom in terms of zirconium.

Then, 50 Nml of hydrogen was introduced at first, and then ethylene was further introduced into the autoclave at a system temperature of 70° C. so that the total pressure became 8 kg/cm^2-G, and polymerization was initiated.

Thereafter, the polymerization was carried out at 85° C. for 1 hour while the total pressure was being maintained at 8 kg/cm^2-G by introducing only ethylene. After the completion of the polymerization, sodium chloride was removed from the contents by washing with water. The remaining polymer was washed with methanol, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 142 g of a polymer having a bulk specific gravity of 0.43 g/cm^3, a MFR of 0.65 g/10 min measured at 190° C. and a load of 2.16 kg, a melt tension (MT) of 10 g and an average particle size of 410 μm.

EXAMPLE 14

To 1.12 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 2.8 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 35 minutes.

Then, to the suspension was added 10.8 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 0.864 mole/liter), and the mixture was further stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 1.34 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the contents were stirred for 30 minutes. Furthermore, 50 ml of decane was added, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at normal pressure. Thereafter, to the reaction mixture was added 71.3 ml of a toluene solution of ethylenebis-(indenyl)zirconium dichloride (Zr: 0.00183 mole/liter), and the prepolymerization was continued at 30° C. for 3.5 hours. A subsequent operation similar to that in Example 13 was conducted to obtain a solid catalyst containing 9.6 mg atom of zirconlure, 0.66 g atom of aluminum and 2100 g of polyethylene based on 100 g of silica.

[Polymerization]

The procedure of Example 13 was repeated to obtain 88 g of a polymer having a bulk specific gravity of 0.42 g/cm^3, a MFR of 0.60 g/10 min and an average particle size of 380 μm.

EXAMPLE 15

[Preparation of a solid catalyst (zirconium catalyst)]

To 3.0 g of the same silica as used in Example 13 was added 30 ml of decane to form a suspension. To the suspension was added 7.45 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 17.6 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 2.14 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.0465 mole/liter), and the contents were stirred for 5 minutes. To the mixture was

further added 100 ml of decane, and prepolymerization was carried out at 25° C. for 2.5 hours by continuously introducing ethylene at a normal pressure continuously. Then, there was added 166.4 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.0024 mole/liter), and the prepolymerization was further continued at 30° C. for 5 hours. A subsequent operation similar to that in Example 13 was conducted, and there was obtained a prepolymerized solid catalyst containing 9.0 mg atom of zirconium, 0.55 g atom of aluminum and 2000 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 13 was repeated except that 0.54 mmole of triisobutylaluminum was used, and that the catalyst component was injected with ethylene into the autoclave having an internal pressure of 6.5 kg/cm^2, whereby there was obtained 124 g of a polymer having a bulk specific gravity of 0 41 g/cm^3 a MFR of 0 58 g/10 min, a melt tension (MT) of 13 g and an average polymer particle size of 400 μm.

Comparative Example 8

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 3.05 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 7.61 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 11.9 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 10.9 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0465 mole/liter), and the mixture was stirred for 30 minutes. Then, 100 ml of decane was further added, and prepolymerization was carried out at 30° C. for 3.5 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that in Example 13 was repeated, whereby there was obtained a solid catalyst containing 12.0 mg atom of zirconium, 0.71 g atom of aluminum and 790 g of polyethylene based on 100 g of silica. ps [Polymerization]

The polymerization procedure in Example 15 was repeated except that the prepolymerized solid catalyst obtained above was used in an amount of 0.015 mg atom in terms of zirconium to obtain 70 g of a polymer having a specific bulk gravity of 0.42 g/cm^3 and a MFR of 0.69 g/10 min.

Comparative Example 9

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 1.16 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 4.05 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 3.17 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 80.5 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.0024 mole/liter), and the mixture was stirred for 30 minutes. Then, 50 ml of decane and 90 ml of toluene were further added, and prepolymerization was carried out at 30° C. for 3 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that in Example 13 was repeated, whereby there was obtained a prepolymerized solid catalyst containing 8.9 mg atom of zirconium, 0.56 g atom of aluminum and 1000 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 15 was repeated to obtain 123 g of a polymer having a specific bulk gravity of 0.36 g/cm^3, a MFR of 0.44 g/10 min and a polymer average particle size of 370 μm.

EXAMPLE 16

[Polymerization]

The polymerization procedure in Example 13 was repeated except that there were used a gas mixture of ethylene and 1butene (1-butene content: 3.9 mol %) in place of ethylene, 30 Nml of hydrogen, 0.75 mmole of triisobutylaluminum and the solid catalyst component prepared in Example 3 in an amount of 0.0075 mg atom in terms of zirconium, and that the polymerization temperature and total pressure were set at 80° C. and 2.5 kg/cm^2-G, respectively, whereby there was obtained 172 g of a polymer having a bulk specific gravity of 0.38 g/cm^3, a MFR of 0.82 g/10 min, a melt tension (MT) of 9 g and a density of 0.918 g/cm^3.

EXAMPLE 17

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 1.49 g of the same silica as in Example 13 was added 25 ml of decane to form a suspension. To the suspension was added 3.72 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 8.09 ml of the same organoaluminum oxy-compound as in Example 13 (Al: 2.30 mole/liter), and the contents were further stirred at room temperature for 45 minutes.

Thereafter, to the suspension was added 2.13 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0465 mole/liter), and the contents were stirred for 10 minutes. To the mixture was further added 75 ml of decane, and prepolymerization was carried out at 30° C. for 1.5 hours by continuously introducing ethylene at a normal pressure. Thereafter, to the reaction mixture was added 51.9 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00287 mole/liter), and the prepolymerization was continued at 30° C. for 4 hours, whereby there was obtained a prepolymerized solid catalyst containing 11.5 mg atom of zirconium, 0.71 g atom of aluminum and 1700 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 13 was repeated except that there were used a gas mixture of ethylene and 1-butene (1-butene content: 4.4 mol %) in place of ethylene, 30 Nml of hydrogen, 0.5 mmole of triisobutylaluminum and the prepolymerized solid catalyst component prepared above in an amount of 0.005 mg atom in terms of zirconium, whereby there was obtained 137 g of a polymer having a bulk specific gravity of 0.39 g/cm^3, a MFR of 0.53 g/10 min, a melt tension (MT) of 12 g and a density of 0.917 g/cm^3.

What is claimed is:

1. An ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms, which is characterized in that:

(A) the ethylene copolymer has a density (d) of 0.87 to 0.94 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the endothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400(d) - 250.$$

2. The ethylene copolymer as claimed in claim 1, wherein the ethylene copolymer comprises the constituent units derived from ethylene in an amount of 70 to 96% by weight, and the constituent units derived from an α-olefin in an amount of 4 to 30% by weight.

* * * * *


PATENT & TRADEMARK OFF.
1995

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/378,998	01/27/95	CHUM P	C-40.121-AB

15M2/1214

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

WU, D EXAMINER	
ART UNIT	PAPER NUMBER
1505	20

DATE MAILED: 12/14/95

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents

PTOL-90 (Rev. 6/84)

1 - PATENT APPLICATION FILE COPY

CHUM P C-40,121-AB

WU, D

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office

Address : COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
			1505

12/14/95

EXAMINER	
ART UNIT	PAPER NUMBER
	20

DATE MAILED:

NOTICE OF ABANDONMENT

This application is abandoned in view of:

1. ☒ Applicant's failure to respond to the Office letter, mailed 4-18-95 .
2. ☐ Applicant's letter of express abandonment which is in compliance with 37 C.F.R. 1.138.
3. ☐ Applicant's failure to timely file the response received _____ within the period set in the Office letter.
4. ☐ Applicant's failure to pay the required issue fee within the statutory period of 3 months from the mailing date of _____ of the Notice of Allowance.

   ☐ The issue fee was received on _____ .

   ☐ The issue fee has not been received in Allowed Files Branch as of _____ .

   In accordance with 35 U.S.C. 151, and under the provisions of 37 C.F.R. 1.316(b), applicant(s) may petition the Commissioner to accept the delayed payment of the issue fee if the delay in payment was unavoidable. The petition must be accompanied by the issue fee, unless it has been previously submitted, in the amount specified by 37 C.F.R. 1.17 (l), and a verified showing as to the causes of the delay.

   If applicant(s) never received the Notice of Allowance, a petition for a new Notice of Allowance and withdrawal of the holding of abandonment may be appropriate in view of Delgar Inc. v. Schuyler, 172 U.S.P.Q. 513.

5. ☐ Applicant's failure to timely correct the drawings and/or submit new or substitute formal drawings by _____ as required in the last Office action.
   ☐ The corrected and/or substitute drawings were received on _____ .
6. ☐ The reason(s) below.

David W. Wu

DAVID W. WU
PRIMARY EXAMINER
GROUP 1500

PTO-1432 (REV. 5-83)

PTO/SB/68
Approved for use through 10/31/99. OMB 06
Patent and Trademark Office: U.S. DEPARTMENT OF COM
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control

REQUEST FOR ACCESS OF ABANDONED APPLICATION UNDER 37 CFR 1.14

In re Application of	
Application Number: 054,379	Filed: 4-23-93
Group Art Unit:	Examiner:

PROCESSED BY
JUN 18 1998
FIII

Paper No. #21

Assistant Commissioner for Patents
Washington, DC 20231

I hereby request access under 37 CFR 1.14(a)(3)(iv) to the application file record of the above-identified ABANDONED application, which is: (CHECK ONE)

___ (A) referred to in United States Patent Number 5747554, column _____,

___ (B) referred to in an application that is open to public inspection as set forth in 37 CFR 1.11, i.e., Application No. _____, filed _____, on page _____ of paper number _____,

___ (C) an application that claims the benefit of the filing date of an application that is open to public inspection, i.e., Application No. _____, filed _____, or

___ (D) an application in which the applicant has filed an authorization to lay open the complete application to the public.

Please direct any correspondence concerning this request to the following address:

_____

_____

_____

Cantwell & Paxton
Signature

6-18-98
Date

V. Williams
Typed or printed name

FOR PTO USE ONLY
Approved by: A. Day (initials)
Unit: F.I.I.4

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual

PTO/SB/88
Approved for use through 10/31/98. OMB 00
Under the Paperwork ction Act of 1995, no persons are required to respond to a Pat nd Trademark Office; U.S. DEPARTMENT OF COM ction of information unless it displays a valid OMB control

REQUEST FOR ACCESS OF ABANDONED APPLICATION UNDER 37 CFR 1.14

RECEIVED BY
OCT 21998
FIII

In re Application of	
Application Number: 08/378998	Filed: 1-27-95
Group Art Unit:	Examiner:

Paper No. #22

Assistant Commissioner for Patents
Washington, DC 20231

I hereby request access under 37 CFR 1.14(a)(3)(iv) to the application file record of the above-identified ABANDONED application, which is: (CHECK ONE)

V (A) referred to in United States Patent Number 5,677,383, column _____;

___ (B) referred to in an application that is open to public inspection as set forth in 37 CFR 1.11, i.e., Application No. _____, filed _____, on page _____ of paper number _____;

___ (C) an application that claims the benefit of the filing date of an application that is open to public inspection, i.e., Application No. _____, filed _____, or

___ (D) an application in which the applicant has filed an authorization to lay open the complete application to the public.

Please direct any correspondence concerning this request to the following address:

_____

_____

_____

Cantwell Paxton
Signature

Oct 2 - 1998
Date

CANTWELL PAXTON
Typed or printed name

FOR PTO USE ONLY

Approved by: _____
(initials)

Unit: _____

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the indi case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

PTO/SB/68 (11-86)
Approved for use through 10/31/99. OMB 0651-0031
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of ... no persons are required to respond to a collection of infor... unless it displays a valid OMB control number.

REQUEST FOR ACCESS OF ABANDONED APPLICATION UNDER 37 CFR 1.14(a)

In re Application of	
CHUM ET AL	
Application Number	**Filed**
08/378998	1/27/95
Group Art Unit	**Examiner**
1505	[illegible]

Paper No. 23

Assistant Commissioner for Patents
Washington, DC 20231

I hereby request access under 37 CFR 1.14(a)(3)(iv) to the application file record of the above-identified ABANDONED application, which is: (CHECK ONE)

✓ (A) referred to in United States Patent Number 5677383, column _____.

___ (B) referred to in an application that is open to public inspection as set forth in 37 CFR 1.11, i.e., Application No. _____, filed _____, on page _____ of paper number _____,

___ (C) an application that claims the benefit of the filing date of an application that is open to public inspection, i.e., Application No. _____, filed _____, or

___ (D) an application in which the applicant has filed an authorization to lay open the complete application to the public.

Please direct any correspondence concerning this request to the following address:

_____

_____

_____

Betty Byrd
Signature

12/7/98
Date

BETTY BYRD
Typed or printed name

FOR PTO USE ONLY

Approved by: [illegible] (Initials)

Unit: 1111

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231

?

PTO/SB/31 (07-03)
Approved for use through 7/31/2003. OMB 0651-0033
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

In re Application of

Bring completed form to:
File Information Unit
Crystal Plaza Three, Room 1D01
2021 South Clark Place
Arlington, VA
Telephone: (703) 308-2733

RECEIVED
JAN 22 2004
File Information Unit

Application Number	Filed
08/378,998	1/27/95

Paper No. #24

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. _____, page, _____ line _____.

United States Patent Number 6111023, column _____, line, _____ or

WIPO Pub. No. _____, page _____, line _____.

Related Information about Access to Pending Applications (37 CFR 1.14):

Direct access to pending applications is not available to the public but copies may be available and may be purchased from the Office of Public Records upon payment of the appropriate fee (37 CFR 1.19(b)), as follows:

For published applications that are still pending, a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

For unpublished applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the pending application as originally filed.

Pat Fellenz
Signature

1/22/04
Date

Pat Fellenz
Typed or printed name

0008104
Registration Number, if applicable

703-624-0743
Telephone Number

FOR PTO USE ONLY

Approved by: Pak (Initials)

Unit: FILE

This collection of information is required by 37 CFR 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including preparation, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the

PTO/SB/68 (07-03)
Approved for use through 7/31/2003. OMB 0651-0031
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

In re Application of: Churn et al

Application Number: 08/378,998 | Filed: 1/27/95

Bring completed form to:
File Information Unit
Crystal Plaza Three, Room 1D01
2021 South Clark Place
Arlington, VA
Telephone: (703) 308-2733

Paper No. 25

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. _____, page, _____ line _____.

United States Patent Number 5,847,053, column _____, line, _____ or

WIPO Pub. No._____, page _____, line _____.

Related Information about Access to Pending Applications (37 CFR 1.14):

Direct access to pending applications is not available to the public but copies may be available and may be purchased from the Office of Public Records upon payment of the appropriate fee (37 CFR 1.19(b)), as follows:

For published applications that are still pending, a member of the public may obtain a copy of:
the file contents;
the pending application as originally filed; or
any document in the file of the pending application.

For unpublished applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
the file contents;
the pending application as originally filed; or
any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
the pending application as originally filed.

BA Harris
Signature

3/23/05
Date

BA Harris
Typed or printed name

Registration Number, if applicable

703-415-0602
Telephone Number

FOR USE ONLY
RECEIVED
Approved by: MAR 23 2005 (initials)
Unit: File Information Unit

This collection of information is required by 37 CFR 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. BRING TO: File Information Unit, Crystal Plaza Three, Room 1D01, 2021 South Clark Place, Arlington, VA.

Under the Paperwork Reduction Act of 1995 persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

In re Application of

Application Number: 08/378998 | Filed: 1-27-95

Art Unit: 2626

Bring completed form to:
File Information Unit
Crystal Plaza Three, Room 1091
2021 South Clark Place
Arlington, VA
Telephone: (703) 308-2733

OCT 26 2005

Paper No. _____

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. _____, page _____ line _____.

United States Patent Number 6111043, column _____, line _____ or

WIPO Pub. No. _____, page _____, line _____.

Related Information about Access to Pending Applications (37 CFR 1.14):

Direct access to pending applications is not available to the public but copies may be available and may be purchased from the Office of Public Records upon payment of the appropriate fee (37 CFR 1.19(b)), as follows:

For published applications that are still pending, a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

For unpublished applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the pending application as originally filed.

Signature

10-26-05
Date

Wayne Cortes
Typed or printed name

Registration Number, if applicable

415-1077
Telephone Number

FOR PTO USE ONLY

Approved by: _____ (Initials)

OCT 26 2005

Unit: _____

This collection of information is required by 37 CFR 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. BRING TO: File Information Unit, Crystal Plaza Three, Room 1091, 2021 South Clark Place, Arlington, VA.

PTO/SB/66 (07-03)
Approved for use through 7/31/2006. OMB 0651-0031
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

RECEIVED
JUL 05 2006
File Information Unit

Bring completed form to:
File Information Unit
Crystal Plaza Three, Room 1D01
2021 South Clark Place
Arlington, VA
Telephone: (703) 308-2733

In re Application of

Application Number 08/378,998 Filed JAN 27, 1995

Paper No. #27

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. 08/378,998, page _____, line _____,

United States Patent Number 5617383, column _____, line _____, or

WIPO Pub. No. _____, page _____, line _____.

Related Information about Access to Pending Applications (37 CFR 1.14):

Direct access to pending applications is not available to the public but copies may be available and may be purchased from the Office of Public Records upon payment of the appropriate fee (37 CFR 1.19(b)), as follows:

For published applications that are still pending, a member of the public may obtain a copy of:
the file contents;
the pending application as originally filed; or
any document in the file of the pending application.

For unpublished applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
the file contents;
the pending application as originally filed; or
any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
the pending application as originally filed.

Signature

7/5/06
Date

Typed or printed name

Registration Number, if applicable

703-518-0210
Telephone Number

FOR PTO USE ONLY
Approved by: JUL 05 2006 (initials)
Unit E.I.C.

This collection of information is required by 37 CFR 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. BRING TO: File Information Unit, Crystal Plaza Three, Room 1D01, 2021 South Clark Place, Arlington, VA.

PTO/SB/88 (07-03)
Approved for use through 7/31/2006. OMB 0651-0031
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

RECEIVED
JUL 12 2006
File Information Unit

Bring completed form to:
File Information Unit
Crystal Plaza Three, Room 1D01
2021 South Clark Place
Arlington, VA
Telephone: (703) 305-9723

In re Application of

Application Number	Filed
08/378998	1/27/95

Paper No. #28

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. _____, page, _____ line _____,

United States Patent Number 5677383, column _____, line, _____ or

WIPO Pub. No._____, page _____, line _____.

Related Information about Access to Pending Applications (37 CFR 1.14):

Direct access to pending applications is not available to the public but copies may be available and may be purchased from the Office of Public Records upon payment of the appropriate fee (37 CFR 1.19(b)), as follows:

For published applications that are still pending, a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

For unpublished applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the file contents;
- the pending application as originally filed; or
- any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain a copy of:
- the pending application as originally filed.

Signature

Typed or printed name Garcia

Registration Number, if applicable

703 413 0600
Telephone Number

7/12/06
Date

FOR PTO USE ONLY

RECEIVED
JUL 12 2006
File Information Unit

Approved by: _____ (initials)

Unit: _____

This collection of information is required by 37 CFR 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. BRING TO: File Information Unit, Crystal Plaza Three, Room 1D01, 2021 South Clark Place, Arlington, VA.

PTO/SB/68 (11-04)
Approved for use through 7/31/2006. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR ACCESS TO AN ABANDONED APPLICATION UNDER 37 CFR 1.14

RECEIVED
NOV 22 2006
File Information Unit

Bring completed form to:
File Information Unit, Room 2E04
2900 Crystal Drive
Arlington, VA 22202-3514
Telephone: (703) 308-2733

In re Application of
PAK-WING STEVE CHUM

Application Number	Filed
08/378,998	JAN. 27, 1995

Paper No. 29

I hereby request access under 37 CFR 1.14(a)(1)(iv) to the application file record of the above-identified ABANDONED application, which is not within the file jacket of a pending Continued Prosecution Application (CPA) (37 CFR 1.53(d)) and which is identified in, or to which a benefit is claimed, in the following document (as shown in the attachment):

United States Patent Application Publication No. 6,111,023, page, _____ line _____,

United States Patent Number _____, column _____, line, _____ or

WIPO Pub. No._____, page _____, line _____.

Related Information About Access to Applications Maintained in the Image File Wrapper System (IFW) and Access to Pending Applications in General

A member of the public, acting without a power to inspect, cannot order applications maintained in the IFW system through the FIU. If the member of the public is entitled to a copy of the application file, then the file is made available through the Public Patent Application Information Retrieval system (Public PAIR) on the USPTO internet web site (www.uspto.gov). Terminals that allow access to Public PAIR are available in the Public Search Room. The member of the public may also be entitled to obtain a copy of all or part of the application file upon payment of the appropriate fee. Such copies must be purchased through the **Office of Public Records** upon payment of the appropriate fee (37 CFR 1.19(b)).

For **published** applications that are still pending, a member of the public may obtain **a copy** of: the file contents; the pending application as originally filed; or any document in the file of the pending application.

For **unpublished** applications that are still pending:

(1) If the benefit of the pending application is claimed under 35 U.S.C. 119(e), 120, 121, or 365 in another application that has: (a) issued as a U.S. patent, or (b) published as a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain **a copy** of: the file contents; the pending application as originally filed; or any document in the file of the pending application.

(2) If the application is incorporated by reference or otherwise identified in a U.S. patent, a statutory invention registration, a U.S. patent application publication, or an international patent application publication in accordance with PCT Article 21(2), a member of the public may obtain **a copy** of the pending application as originally filed.

SPS
Signature

11-22-06
Date

SPECIALIZED PATENT SERVICES
Typed or printed name

0002180
Registration Number, if applicable

(703) 415-1555
Telephone Number

FOR PTO USE ONLY

Approved by: DB (initials)

Unit: _____

This collection of information is required by 37 CFR 1.11 and 1.14. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **BRING TO: File Information Unit, Room 2E04, 2900 Crystal Drive, Arlington, Virginia.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

US006111023A

United States Patent [19]

Chum et al.

[11] Patent Number: 6,111,023

[45] Date of Patent: *Aug. 29, 2000

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum; George W. Knight**, both of Lake Jackson; **Ronald P. Markovich**, Friendswood; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/927,393**

[22] Filed: **Aug. 27, 1997**

Related U.S. Application Data

[63] Continuation of application No. 08/544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of application No. 08/378,998, Jan. 27, 1995, abandoned, which is a continuation of application No. 08/054,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of application No. 07/776,130, Oct. 15, 1991, Pat. No. 5,272,236, which is a continuation-in-part of application No. 07/939,281, Sep. 2, 1992, Pat. No. 5,278,272.

[51] **Int. Cl.**[7] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320; 526/160, 161, 352

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,983,704	5/1961	Roedel .	
3,179,720	4/1965	Hillmer .	
3,231,636	1/1966	Synder et al. .	
3,340,328	9/1967	Brindell et al. .	
3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,914,342	10/1975	Mitchell .	
3,998,914	12/1976	Lillis et al. .	
4,205,021	5/1980	Morita et al. .	
4,230,831	10/1980	Sakurai et al. .	
4,263,422	4/1981	Lowery, Jr. et al. .	
4,320,088	3/1982	Nicco .	
4,330,639	5/1982	Matsuura et al. .	
4,346,834	8/1982	Mazumdar .	
4,374,227	2/1983	Michie, Jr. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al. .	
4,438,238	3/1984	Fukushima et al. .	
4,461,873	7/1984	Bailey et al. .	
4,469,752	9/1984	Yoshimura et al. .	
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,542,199	9/1985	Kaminsky et al. .	
4,659,685	4/1987	Coleman, III et al. .	
4,668,752	5/1987	Tominari et al. .	
4,701,432	10/1987	Welborn, Jr. .	
4,752,597	6/1988	Turner .	
4,770,912	9/1988	Furrer et al. .	
4,786,688	11/1988	Thiersault et al. .	
4,789,714	12/1988	Cozewith et al. .	
4,801,652	1/1989	Mizutani et al. .	
4,804,714	2/1989	Olivo .	
4,828,906	5/1989	Nishimura et al. .	
4,837,262	6/1989	Jeon et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,939,217	7/1990	Stricklen .	
4,981,760	1/1991	Naito et al. .	
4,987,212	1/1991	Morterol et al. .	
5,001,206	3/1991	Bashir et al. .	
5,026,798	6/1991	Canich .	
5,028,663	7/1991	Chung .	
5,032,651	7/1991	McDaniel et al. .	
5,041,501	8/1991	Shirodkar .	
5,047,468	9/1991	Lee et al. .	
5,055,438	10/1991	Canich .	
5,077,255	12/1991	Welborn .	
5,082,902	1/1992	Gurevitch et al. .	
5,084,540	1/1992	Albizzati et al. .	
5,091,228	2/1992	Fujii et al. .	
5,177,147	1/1993	Spenadel et al. .	
5,189,106	2/1993	Morimoto et al. .	
5,206,075	4/1993	Hodgson, Jr. .	
5,210,142	5/1993	Kale et al. .	
5,218,071	6/1993	Tsutsui et al. .	
5,266,392	11/1993	Land et al. .	
5,272,016	12/1993	Ralph .	
5,272,236	12/1993	Lai et al. .	
5,278,272	1/1994	Lai et al. .	
5,350,807	9/1994	Pettijohn et al. .	
5,374,700	12/1994	Tsutsui et al. .	
5,376,439	12/1994	Hodgson et al. .	
5,395,471	3/1995	Obijeski et al. .	
5,395,810	3/1995	Shamshoum et al. .	
5,408,004	4/1995	Lai et al. .	
5,444,145	8/1995	Brant et al. .	
5,464,905	11/1995	Tsutsui et al. .	
5,519,091	5/1996	Tsutsui et al. .	
5,530,065	6/1996	Farley et al. .	
5,656,696	8/1997	Yamamoto et al. .	
5,663,236	9/1997	Takahashi et al. .	
5,677,383	10/1997	Chum et al.	525/240

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada .
0 374 695	6/1990	European Pat. Off. .

(List continued on next page.)

OTHER PUBLICATIONS

Modern Methods of Polymer Characterization, pp. 103–112, (1991) "Measurement of Long–Chain Branch Frequency in Synthetic Polymers", by Alfred Rudin.

(List continued on next page.)

Primary Examiner—David W. Wu
Assistant Examiner—R. Harlan

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

US005677383A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,677,383

[45] Date of Patent: Oct. 14, 1997

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **544,497**

[22] Filed: **Oct. 18, 1995**

Related U.S. Application Data

[63] Continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,479, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,998,914	12/1976	Lillis et al.	260/897
4,205,021	5/1980	Morita et al. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al.	525/240
4,438,238	3/1984	Fukushima et al.	525/240
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,668,752	5/1987	Tominari et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,981,760	1/1991	Naito et al.	428/523
4,987,212	1/1991	Morterol et al. .	
5,026,798	6/1991	Canich .	
5,055,438	10/1991	Canich .	
5,084,540	1/1992	Albizzati et al. .	
5,189,106	2/1993	Morimoto et al.	525/240
5,206,075	4/1993	Hodgson, Jr.	428/216
5,218,071	6/1993	Tsutsui et al.	526/348
5,272,236	12/1993	Lai et al.	526/348.5
5,278,272	1/1994	Lai et al.	526/348.5
5,374,700	12/1994	Tsutsui et al.	526/348.3
5,395,471	3/1995	Obijeski et al.	156/244.11
5,395,810	3/1995	Shamshoum et al.	502/113
5,408,004	4/1995	Lai et al.	525/240
5,444,145	8/1995	Brant et al.	526/348.3

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada	C08F 4/16
0416815A2	3/1991	European Pat. Off. .	
0 447 035 A3	9/1991	European Pat. Off.	C08F 297/08
9003414	4/1990	WIPO .	
WO 90/03414 A1	4/1990	WIPO	C08L 23/08
WO 93/03093 A1	2/1993	WIPO	C08L 23/04
WO 93/08221 A2	4/1993	WIPO	C08F 10/00
WO 93/13143 A1	7/1993	WIPO	C08F 10/02
WO 94/06857 A1	3/1994	WIPO	C08L 23/04
WO 94/12568 A1	6/1994	WIPO	C08L 23/08
WO 95/13321 A1	5/1995	WIPO	C08L 23/04

OTHER PUBLICATIONS

Journal of Polymer Science, Part A, vol. 1 (pp. 2869–2880 (1963)), "Long–Chain Branching Frequency in Polyethylene" by J. E. Guillet.

Polymer Preprints, Amer. Chem. Society, vol. 12, No. 1, pp. 277–281 (Mar. 1971), "Evidence of Long–Chain Branching in High Density Polyethylene" by E. E. Drott and R. A. Mendelson.

Journal of the American Chemical Society, 98:7, pp. 1729–1742 (Mar. 31, 1976) "Structure and Chemistry of Bis(cyclopentadienyl)–MLn Complexes" by Joseph W. Lauher and Roald Hoffman.

Polymer Engineering and Science, vol. 16, No. 12, pp. 811–816 (Dec. 1976), "Influence of Long–Chain Branching on the Viscoelastic Properties of Low–Density Polyethylenes" by L. Wild, R. Ranganath, and D. Knobeloch.

Angew. Chem. Int. Ed. Engl., pp. 630–632 (1976) vol. 15, No. 10, "Halogen–Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature" by Arne Andresen et al.

Advances in Organometallic Chemistry, pp. 99–148, vol. 18, (1980) "Ziegler–Natta Catalysis" by Hansjorg Sinn and Walter Kaminsky.

Angew. Chem. Int. Ed. Engl., pp. 390–393, vol. 19 No. 5 (1980) "Living Polymers' on Polymerization with Extremely Productive Ziegler Catalysts" by Hansjorg Sinn, Walter Kaminsky, Hans–Jurgen Vollmer, and Rudiger Woldt.

Polymer Bullentin, 9, pp. 464–469 (1983) "Halogen Free Soluble Ziegler Catalysts with Methylalumoxan as Catalyst" by Jens Herwig and Walter Kaminsky.

Makromol. Chem., Rapid Commun., 4, pp. 417–421 (1983) "Bis(cyclopentadienyl)zirkon–Verbingungen und Aluminoxan als Ziegler–Katalysatoren fur die Polymerisation und Copolymerisation von Olefinen" by Walter Kaminsky et al.

ANTEC Proceedings, pp. 306–309 (1983), "Analysis of Long Chain Branching in High Density Polyethylene" by J.K. Hughes.

(List continued on next page.)

Primary Examiner—David W. Wu

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

18 Claims, 2 Drawing Sheets

US005677383A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,677,383

[45] Date of Patent: Oct. 14, 1997

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **544,497**

[22] Filed: **Oct. 18, 1995**

Related U.S. Application Data

[63] Continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,998,914	12/1976	Lillis et al.	260/897
4,205,021	5/1980	Morita et al. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al.	525/240
4,438,238	3/1984	Fukushima et al.	525/240
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,668,752	5/1987	Tominari et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,981,760	1/1991	Naito et al.	428/523
4,987,212	1/1991	Morterol et al. .	
5,026,798	6/1991	Canich .	
5,055,438	10/1991	Canich .	
5,084,540	1/1992	Albizzati et al. .	
5,189,106	2/1993	Morimoto et al.	525/240
5,206,075	4/1993	Hodgson, Jr.	428/216
5,218,071	6/1993	Tsutsui et al.	526/348
5,272,236	12/1993	Lai et al.	526/348.5
5,278,272	1/1994	Lai et al.	526/348.5
5,374,700	12/1994	Tsutsui et al.	526/348.3
5,395,471	3/1995	Obijeski et al.	156/244.11
5,395,810	3/1995	Shamshoum et al.	502/113
5,408,004	4/1995	Lai et al.	525/240
5,444,145	8/1995	Brant et al.	526/348.3

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada	C08F 4/16
0416815A2	3/1991	European Pat. Off. .	
0 447 035 A3	9/1991	European Pat. Off.	C08F 297/08
9003414	4/1990	WIPO .	
WO 90/03414 A1	4/1990	WIPO	C08L 23/08
WO 93/03093 A1	2/1993	WIPO	C08L 23/04
WO 93/08221 A2	4/1993	WIPO	C08F 10/00
WO 93/13143 A1	7/1993	WIPO	C08F 10/02
WO 94/06857 A1	3/1994	WIPO	C08L 23/04
WO 94/12568 A1	6/1994	WIPO	C08L 23/08
WO 95/13321 A1	5/1995	WIPO	C08L 23/04

OTHER PUBLICATIONS

Journal of Polymer Science, Part A, vol. 1 (pp. 2869–2880 (1963)), "Long–Chain Branching Frequency in Polyethylene" by J. E. Guillet.

Polymer Preprints, Amer. Chem. Society, vol. 12, No. 1, pp. 277–281 (Mar. 1971), "Evidence of Long–Chain Branching in High Density Polyethylene" by E. E. Drott and R. A. Mendelson.

Journal of the American Chemical Society, 98:7, pp. 1729–1742 (Mar. 31, 1976) "Structure and Chemistry of Bis(cyclopentadienyl)–MLn Complexes" by Joseph W. Lauher and Roald Hoffman.

Polymer Engineering and Science, vol. 16, No. 12, pp. 811–816 (Dec. 1976), "Influence of Long–Chain Branching on the Viscoelastic Properties of Low–Density Polyethylenes" by L. Wild, R. Ranganath, and D. Knobeloch.

Angew. Chem. Int. Ed. Engl., pp. 630–632 (1976) vol. 15, No. 10, "Halogen–Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature" by Arne Andresen et al.

Advances in Organometallic Chemistry, pp. 99–148, vol. 18, (1980) "Ziegler–Natta Catalysis" by Hansjorg Sinn and Walter Kaminsky.

Angew. Chem. Int. Ed. Engl., pp. 390–393, vol. 19 No. 5 (1980) "Living Polymers' on Polymerization with Extremely Productive Ziegler Catalysts" by Hansjorg Sinn, Walter Kaminsky, Hans–Jurgen Vollmer, and Rudiger Woldt.

Polymer Bullentin, 9, pp. 464–469 (1983) "Halogen Free Soluble Ziegler Catalysts with Methylalumoxan as Catalyst" by Jens Herwig and Walter Kaminsky.

Makromol. Chem., Rapid Commun., 4, pp. 417–421 (1983) "Bis(cyclopentadienyl)zirkon–Verbingungen und Aluminoxan als Ziegler–Katalysatoren fur die Polymerisation und Copolymerisation von Olefinen" by Walter Kaminsky et al.

ANTEC Proceedings, pp. 306–309 (1983), "Analysis of Long Chain Branching in High Density Polyethylene" by J.K. Hughes.

(List continued on next page.)

Primary Examiner—David W. Wu

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

18 Claims, 2 Drawing Sheets

JUL 0 5 2006
File Information Unit

RECEIVED
JUL 03 2006
File Information Unit

RECEIVED
JUL 0 2006
File Information Unit

PATENT APPLICATION FEE DETERMINATION RECORD

Effective October 1, 1994

Application or Docket Number: 378 998

CLAIMS AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE	SMALL ENTITY FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY FEE
BASIC FEE				365.00	OR		730.00
TOTAL CLAIMS	15 minus 20 =	* —	x$11=		OR	x$22=	
INDEPENDENT CLAIMS	2 minus 3 =	* —	x38=		OR	x76=	
MULTIPLE DEPENDENT CLAIM PRESENT			+120=		OR	+240=	
			TOTAL		OR	TOTAL	730

* If the difference in column 1 is less than zero, enter "0" in column 2

CLAIMS AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	* 17	Minus	** 20	= —
Independent	* 4	Minus	*** 3	= 1
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				

SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
x$11=		OR	x$22=	
x38=		OR	x76=	76
+120=		OR	+240=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	76

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				

SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
x$11=		OR	x$22=	
x38=		OR	x76=	
+120=		OR	+240=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT C

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA
Total	*	Minus	**	=
Independent	*	Minus	***	=
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				

SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
x$11=		OR	x$22=	
x38=		OR	x76=	
+120=		OR	+240=	
TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in colu
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."
*** If the Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."
The Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

FORM PTO-875
(Rev. 10/94)

Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

PTO 1130 (REV 11/91) U.S. DEPARTMENT OF COMMERCE– PATENT & TRADEMARK OFFICE

PACE DATA ENTRY CODING SHEET

08/054379

1ST EXAMINER [signature] DATE 6/4/93

2ND EXAMINER LM DATE 8/17/93

APPLICATION NUMBER	TYPE APPL	FILING DATE MONTH	DAY	YEAR	SPECIAL HANDLING	GROUP ART UNIT	CLASS	SHEETS OF DRAWING
	1	04	28	93	0	1503	528	2

TOTAL CLAIMS	INDEPENDENT CLAIMS	SMALL ENTITY?	FILING FEE	FOREIGN LICENSE	ATTORNEY DOCKET NUMBER
30	4	0	1134	Y	C401216

CONTINUITY DATA

CONTINUITY CODE	STATUS CODE	PARENT APPPLICATION SERIAL NUMBER	PARENT PATENT NUMBER	PARENT FILING DATE MONTH	DAY	YEAR
03	2	07761130		10	15	91

PCT/FOREIGN APPLICATION DATA

FOREIGN PRIORITY CLAIMED	COUNTRY CODE	PCT/FOREIGN APPLICATION SERIAL NUMBER	FOREIGN FILING DATE MONTH	DAY	YEAR

TITLE OF INVENTION
ATTORNEY REGISTRATION NUMBERS
CORRESPONDENCE NAME AND ADDRESS
APPLICANT/INVENTOR DATA
AUTHORITY CODE
FAMILY NAME
GIVEN NAME
CITY
NAME SUFFIX
STATE/CTRY CODE
AUTHORITY CODE
FAMILY NAME
GIVEN NAME
CITY
NAME SUFFIX
STATE/CTRY CODE
MORE

Form PTO 1130
(REV 2/94)

PACE DATA ENTRY CODING SHEET

U.S. DEPARTMENT OF COMMERCE
Patent and Trademark Office

1ST EXAMINER Dilla — DATE 2/23/95

2ND EXAMINER — DATE

APPLICATION NUMBER	TYPE APPL	FILING DATE MONTH	DAY	YEAR	SPECIAL HANDLING	GROUP ART UNIT	CLASS	SHEETS OF DRAWING
08/378998	2	01	27	95	0	1503	526	2

TOTAL CLAIMS	INDEPENDENT CLAIMS	SMALL ENTITY?	FILING FEE	FOREIGN LICENSE	ATTORNEY DOCKET NUMBER
15	2	0	730	1	C-40,121-AB

CONTINUITY DATA

CONT CODE	STATUS CODE	PARENT APPLICATION SERIAL NUMBER	PCT APPLICATION SERIAL NUMBER	PARENT PATENT NUMBER	PARENT FILING DATE MONTH	DAY	YEAR
02	3	08/054,379	PCT/		04	28	93
12	3	07/776,130	PCT/		10	15	91
			PCT/				
			PCT/				
			PCT/				

PCT/FOREIGN APPLICATION DATA

FOREIGN PRIORITY CLAIMED	COUNTRY CODE	PCT/FOREIGN APPLICATION SERIAL NUMBER	FOREIGN FILING DATE MONTH	DAY	YEAR

Case 1:05-cv-00737-JJF Document 157-5 Filed 09/03/2008 Page 32 of 62

EXHIBIT PAGE 000220

TITLE OF INVENTION
ATTORNEY REGISTRATION NUMBERS
CORRESPONDENCE NAME AND ADDRESS
APPLICANT/INVENTOR DATA
AUTHORITY CODE
FAMILY NAME
GIVEN NAME
CITY
NAME SUFFIX
STATE/CTRY CODE
AUTHORITY CODE
FAMILY NAME
GIVEN NAME
CITY
NAME SUFFIX
STATE/CTRY CODE
MORE

2

PATENT APPLICATION FEE DETERMINATION RECORD

Effective October 1, 1992

Application or Docket Number: 054379

CLAIMS AS FILED - PART I

1111

	(Column 1) NUMBER FILED		(Column 2) NUMBER EXTRA	SMALL ENTITY RATE	SMALL ENTITY FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY FEE
FOR								
BASIC FEE					$355.00	OR		$710.00
TOTAL CLAIMS	30	minus 20 =	* 10	x$11=		OR	x$22=	220
INDEPENDENT CLAIMS	4	minus 3 =	* 1	x 37=		OR	x 74=	74
MULTIPLE DEPENDENT CLAIM PRESENT				+115=		OR	+230=	
				TOTAL		OR	TOTAL	1004

* If the difference in column 1 is less then zero, enter "0" in column 2

CLAIMS AS AMENDED - PART II

AMENDMENT A

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
Total	* 15	Minus	** 30	= —	x$11=		OR	x$22=	
Independent	* 2	Minus	*** 4	—	x 37=		OR	x 74=	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+ 115=		OR	+230=	
					TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

AMENDMENT B

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
Total	*	Minus	**	=	x$11=		OR	x$22=	
Independent	*	Minus	***	=	x 37=		OR	x 74=	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+ 115=		OR	+ 230=	
					TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

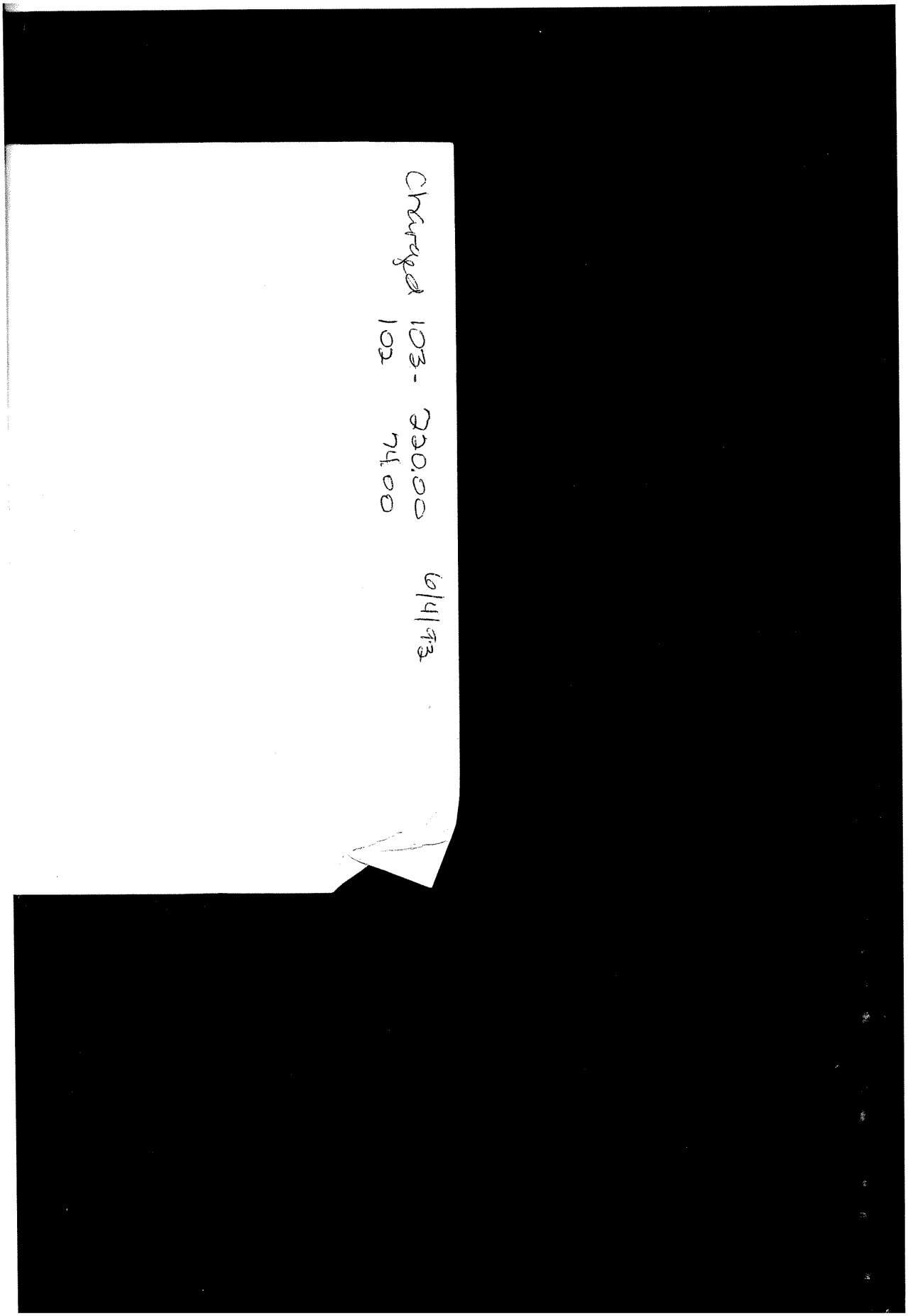
AMENDMENT C

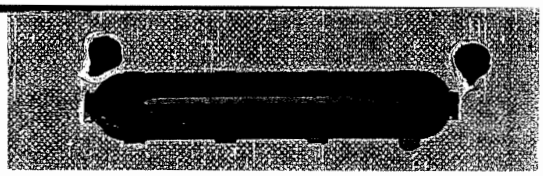
	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE	SMALL ENTITY ADDITIONAL FEE	OR	OTHER THAN SMALL ENTITY RATE	OTHER THAN SMALL ENTITY ADDITIONAL FEE
Total	*	Minus	**	=	x$11=		OR	x$22=	
Independent	*	Minus	***	=	x 37=		OR	x 74=	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+115=		OR	+230=	
					TOTAL ADDIT. FEE		OR	TOTAL ADDIT. FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

FORM PTO-875
(Rev.10-92)

Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE


Charged 103-201
00074 230.00
6/14/13



SEARCHED

Class	Sub.	Date	Exmr.
525	240	11-16-93	WA

INTERFERENCE SEARCHED

Class	Sub.	Date	Exmr.

SEARCH NOTES

	Date	Exmr.

(RIGHT OUTSIDE)

Staple Issue Slip Here

POSITION		ID NO.	DATE
CLASSIFIER		7	5-24-93
EXAMINER		341	6/4/93
TYPIST		323	8/26
VERIFIER		320	
CORPS CORR.			
SPEC. HAND		408	8/17/93
FILE MAINT.		407	6-17-93
DRAFTING			

INDEX OF CLAIMS

Claim Final	Claim Original	Date 93 11 10	Date 94 7 26
	1	✓	✓
	2		
	3		
	4		
	5		
	6		
	7		
	8	✓	✓
	9	~	
	10		
	11		
	12		
	13		
	14		
	15		
	16	✓	
	17	✓	✓
	18		
	19		
	20		
	21		
	22		
	23	✓	✓
	24	✓	
	25		
	26		
	27		
	28		
	29		
	30		
	31		
	32		
	33		
	34		
	35		
	36		
	37		
	38		
	39		
	40		
	41		
	42		
	43		
	44		
	45		
	46		
	47		
	48		
	49		
	50		

SYMBOLS

✓	Rejected
=	Allowed
- (Through numberal)	Canceled
+	Restricted
N	Non-elected
I	Interference
A	Appeal
O	Objected

Claim Final	Claim Original	Date
	51	
	52	
	53	
	54	
	55	
	56	
	57	
	58	
	59	
	60	
	61	
	62	
	63	
	64	
	65	
	66	
	67	
	68	
	69	
	70	
	71	
	72	
	73	
	74	
	75	
	76	
	77	
	78	
	79	
	80	
	81	
	82	
	83	
	84	
	85	
	86	
	87	
	88	
	89	
	90	
	91	
	92	
	93	
	94	
	95	
	96	
	97	
	98	
	99	
	100	

(LEFT INSIDE)

US005847053A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,847,053

[45] Date of Patent: Dec. 8, 1998

[54] **ETHYLENE POLYMER FILM MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **834,050**

[22] Filed: **Apr. 11, 1997**

Related U.S. Application Data

[63] Continuation of Ser. No. 544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/08**

[52] **U.S. Cl.** **525/240**

[58] **Field of Search** 525/240

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,983,704	5/1961	Roedel .	
3,179,720	4/1965	Hillmer .	
3,231,636	1/1966	Synder et al. .	
3,340,328	9/1967	Brindell et al. .	
3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,914,342	10/1975	Mitchell .	
3,998,914	12/1976	Lillis et al. .	
4,205,021	5/1980	Morita et al. .	
4,230,831	10/1980	Sakurai et al. .	
4,263,422	4/1981	Lowery, Jr. et al. .	
4,320,088	3/1982	Nicco .	
4,330,639	5/1982	Matsuura et al. .	
4,346,834	8/1982	Mazumdar .	
4,374,227	2/1983	Michie, Jr. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al. .	
4,438,238	3/1984	Fukushima et al. .	
4,461,873	7/1984	Bailey et al. .	
4,469,752	9/1984	Yoshimura et al. .	
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,542,199	9/1985	Kaminsky et al. .	
4,659,685	4/1987	Coleman, III et al. .	
4,668,752	5/1987	Tominari et al. .	
4,701,432	10/1987	Welborn, Jr. .	
4,752,597	6/1988	Turner .	
4,770,912	9/1988	Furrer et al. .	
4,786,688	11/1988	Thiersault et al. .	
4,789,714	12/1988	Cozewith et al. .	
4,801,652	1/1989	Mizutani et al. .	
4,804,714	2/1989	Olivo .	
4,828,906	5/1989	Nishimura et al. .	
4,837,262	6/1989	Jeon et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,939,217	7/1990	Stricklen .	

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada .
0 374 695	6/1990	European Pat. Off. .
0 416 815	3/1991	European Pat. Off. .
0416815A2	3/1991	European Pat. Off. .
0 436 328	7/1991	European Pat. Off. .
0 447 035	9/1991	European Pat. Off. .
0 503 791	9/1992	European Pat. Off. .
0 572 034	12/1993	European Pat. Off. .
0 598 626	5/1994	European Pat. Off. .
0 662 989	7/1995	European Pat. Off. .
0 735 090	2/1996	European Pat. Off. .

(List continued on next page.)

OTHER PUBLICATIONS

Modern Methods of Polymer Characterization, pp. 103–112, (1991) "Measurement of Long–Chain Branch Frequency in Synthetic Polymers", by Alfred Rudin.

The Journal of Chemical Physics, vol. 17, No. 12, Dec. (1949), pp. 1301–1314, "The Dimensions of Chain Molecules Containing Branches and Rings", by Bruno H. Zimm and Walter H. Stockmayer.

Antec 93—Be In That Number, New Orleans, May 9–13, (1993), vol. II, "Dow Constrained Geometry Catalyst Technology (CGCT): New Rules For Ethylene α–Olefin Interpolymers–controlled Rheology Polyolefins", pp. 1188–1192, by S. Lai and G.W. Knight.

Journal of Rheology, (1986), pp. 340–341, 344–345, 348–349, 352–353, 356–357, "Wall Slip in Viscous Fluids and Influence of Materials of Construction", by A.V. Ramamurthy.

Rheometers for Molten Plastics, (1982), pp. 97–99, by John Dealy.

Polymer Engineering and Science, vol. 17, No. 11, Nov. (1977), pp. 769–774, "Correlation of Low Density Polyethylene Rheological Measurements with Optical and Processing Properties", by M. Shida, R.N. Shroff, and L.V. Cancio.

"A Review of High Resolution Liquid ^{13}Carbon Nuclear Magnetic Resonance Characterizations of Ethylene–Based Polymers", *JMS–Rev. Macromol. Chem. Phys.*, C29(2&3), pp. 201–317, (1989) by James C. Randall.

(List continued on next page.)

Primary Examiner—David W. Wu

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

US006111023A

United States Patent [19]

Chum et al.

[11] Patent Number: 6,111,023

[45] Date of Patent: *Aug. 29, 2000

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**; **George W. Knight**, both of Lake Jackson; **Ronald P. Markovich**, Friendswood; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/927,393**

[22] Filed: **Aug. 27, 1997**

Related U.S. Application Data

[63] Continuation of application No. 08/544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of application No. 08/378,998, Jan. 27, 1995, abandoned, which is a continuation of application No. 08/054,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of application No. 07/776,130, Oct. 15, 1991, Pat. No. 5,272,236, which is a continuation-in-part of application No. 07/939,281, Sep. 2, 1992, Pat. No. 5,278,272.

[51] **Int. Cl.**[7] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320; 526/160, 161, 352

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,983,704	5/1961	Roedel .	
3,179,720	4/1965	Hillmer .	
3,231,636	1/1966	Synder et al. .	
3,340,328	9/1967	Brindell et al. .	
3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,914,342	10/1975	Mitchell .	
3,998,914	12/1976	Lillis et al. .	
4,205,021	5/1980	Morita et al. .	
4,230,831	10/1980	Sakurai et al. .	
4,263,422	4/1981	Lowery, Jr. et al. .	
4,320,088	3/1982	Nicco .	
4,330,639	5/1982	Matsuura et al. .	
4,346,834	8/1982	Mazumdar .	
4,374,227	2/1983	Michie, Jr. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al. .	
4,438,238	3/1984	Fukushima et al. .	
4,461,873	7/1984	Bailey et al. .	
4,469,752	9/1984	Yoshimura et al. .	
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,542,199	9/1985	Kaminsky et al. .	
4,659,685	4/1987	Coleman, III et al. .	
4,668,752	5/1987	Tominari et al. .	
4,701,432	10/1987	Welborn, Jr. .	
4,752,597	6/1988	Turner .	
4,770,912	9/1988	Furrer et al. .	
4,786,688	11/1988	Thiersault et al. .	
4,789,714	12/1988	Cozewith et al. .	
4,801,652	1/1989	Mizutani et al. .	
4,804,714	2/1989	Olivo .	
4,828,906	5/1989	Nishimura et al. .	
4,837,262	6/1989	Jeon et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,939,217	7/1990	Stricklen .	
4,981,760	1/1991	Naito et al. .	
4,987,212	1/1991	Morterol et al. .	
5,001,206	3/1991	Bashir et al. .	
5,026,798	6/1991	Canich .	
5,028,663	7/1991	Chung .	
5,032,651	7/1991	McDaniel et al. .	
5,041,501	8/1991	Shirodkar .	
5,047,468	9/1991	Lee et al. .	
5,055,438	10/1991	Canich .	
5,077,255	12/1991	Welborn .	
5,082,902	1/1992	Gurevitch et al. .	
5,084,540	1/1992	Albizzati et al. .	
5,091,228	2/1992	Fujii et al. .	
5,177,147	1/1993	Spenadel et al. .	
5,189,106	2/1993	Morimoto et al. .	
5,206,075	4/1993	Hodgson, Jr. .	
5,210,142	5/1993	Kale et al. .	
5,218,071	6/1993	Tsutsui et al. .	
5,266,392	11/1993	Land et al. .	
5,272,016	12/1993	Ralph .	
5,272,236	12/1993	Lai et al. .	
5,278,272	1/1994	Lai et al. .	
5,350,807	9/1994	Pettijohn et al. .	
5,374,700	12/1994	Tsutsui et al. .	
5,376,439	12/1994	Hodgson et al. .	
5,395,471	3/1995	Obijeski et al. .	
5,395,810	3/1995	Shamshoum et al. .	
5,408,004	4/1995	Lai et al. .	
5,444,145	8/1995	Brant et al. .	
5,464,905	11/1995	Tsutsui et al. .	
5,519,091	5/1996	Tsutsui et al. .	
5,530,065	6/1996	Farley et al. .	
5,656,696	8/1997	Yamamoto et al. .	
5,663,236	9/1997	Takahashi et al. .	
5,677,383	10/1997	Chum et al.	525/240

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada .
0 374 695	6/1990	European Pat. Off. .

(List continued on next page.)

OTHER PUBLICATIONS

Modern Methods of Polymer Characterization, pp. 103–112, (1991) "Measurement of Long–Chain Branch Frequency in Synthetic Polymers", by Alfred Rudin.

(List continued on next page.)

Primary Examiner—David W. Wu
Assistant Examiner—R. Harlan

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

US006111023A

United States Patent [19]

Chum et al.

[11] **Patent Number: 6,111,023**

[45] **Date of Patent: *Aug. 29, 2000**

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**; **George W. Knight**, both of Lake Jackson; **Ronald P. Markovich**, Friendswood; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/927,393**

[22] Filed: **Aug. 27, 1997**

Related U.S. Application Data

[63] Continuation of application No. 08/544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of application No. 08/378,998, Jan. 27, 1995, abandoned, which is a continuation of application No. 08/054,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of application No. 07/776,130, Oct. 15, 1991, Pat. No. 5,272,236, which is a continuation-in-part of application No. 07/939,281, Sep. 2, 1992, Pat. No. 5,278,272.

[51] **Int. Cl.**[7] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320; 526/160, 161, 352

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,983,704	5/1961	Roedel .	
3,179,720	4/1965	Hillmer .	
3,231,636	1/1966	Synder et al. .	
3,340,328	9/1967	Brindell et al. .	
3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,914,342	10/1975	Mitchell .	
3,998,914	12/1976	Lillis et al. .	
4,205,021	5/1980	Morita et al. .	
4,230,831	10/1980	Sakurai et al. .	
4,263,422	4/1981	Lowery, Jr. et al. .	
4,320,088	3/1982	Nicco .	
4,330,639	5/1982	Matsuura et al. .	
4,346,834	8/1982	Mazumdar .	
4,374,227	2/1983	Michie, Jr. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al. .	
4,438,238	3/1984	Fukushima et al. .	
4,461,873	7/1984	Bailey et al. .	
4,469,752	9/1984	Yoshimura et al. .	
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,542,199	9/1985	Kaminsky et al. .	
4,659,685	4/1987	Coleman, III et al. .	
4,668,752	5/1987	Tominari et al. .	
4,701,432	10/1987	Welborn, Jr. .	
4,752,597	6/1988	Turner .	
4,770,912	9/1988	Furrer et al. .	
4,786,688	11/1988	Thiersault et al. .	
4,789,714	12/1988	Cozewith et al. .	
4,801,652	1/1989	Mizutani et al. .	
4,804,714	2/1989	Olivo .	
4,828,906	5/1989	Nishimura et al. .	
4,837,262	6/1989	Jeon et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,939,217	7/1990	Stricklen .	
4,981,760	1/1991	Naito et al. .	
4,987,212	1/1991	Morterol et al. .	
5,001,206	3/1991	Bashir et al. .	
5,026,798	6/1991	Canich .	
5,028,663	7/1991	Chung .	
5,032,651	7/1991	McDaniel et al. .	
5,041,501	8/1991	Shirodkar .	
5,047,468	9/1991	Lee et al. .	
5,055,438	10/1991	Canich .	
5,077,255	12/1991	Welborn .	
5,082,902	1/1992	Gurevitch et al. .	
5,084,540	1/1992	Albizzati et al. .	
5,091,228	2/1992	Fujii et al. .	
5,177,147	1/1993	Spenadel et al. .	
5,189,106	2/1993	Morimoto et al. .	
5,206,075	4/1993	Hodgson, Jr. .	
5,210,142	5/1993	Kale et al. .	
5,218,071	6/1993	Tsutsui et al. .	
5,266,392	11/1993	Land et al. .	
5,272,016	12/1993	Ralph .	
5,272,236	12/1993	Lai et al. .	
5,278,272	1/1994	Lai et al. .	
5,350,807	9/1994	Pettijohn et al. .	
5,374,700	12/1994	Tsutsui et al. .	
5,376,439	12/1994	Hodgson et al. .	
5,395,471	3/1995	Obijeski et al. .	
5,395,810	3/1995	Shamshoum et al. .	
5,408,004	4/1995	Lai et al. .	
5,444,145	8/1995	Brant et al. .	
5,464,905	11/1995	Tsutsui et al. .	
5,519,091	5/1996	Tsutsui et al. .	
5,530,065	6/1996	Farley et al. .	
5,656,696	8/1997	Yamamoto et al. .	
5,663,236	9/1997	Takahashi et al. .	
5,677,383	10/1997	Chum et al.	525/240

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada .
0 374 695	6/1990	European Pat. Off. .

(List continued on next page.)

OTHER PUBLICATIONS

Modern Methods of Polymer Characterization, pp. 103–112, (1991) "Measurement of Long–Chain Branch Frequency in Synthetic Polymers", by Alfred Rudin.

(List continued on next page.)

Primary Examiner—David W. Wu
Assistant Examiner—R. Harlan

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

US0[illegible]7383A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,677,383

[45] Date of Patent: Oct. 14, 1997

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **544,497**

[22] Filed: **Oct. 18, 1995**

Related U.S. Application Data

[63] Continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,491,073	1/1970	Marinak .	
3,645,992	2/1972	Elston .	
3,998,914	12/1976	Lillis et al.	260/897
4,205,021	5/1980	Morita et al. .	
4,405,774	9/1983	Miwa et al. .	
4,429,079	1/1984	Shibata et al.	525/240
4,438,238	3/1984	Fukushima et al.	525/240
4,510,303	4/1985	Oda et al. .	
4,530,914	7/1985	Ewen et al. .	
4,668,752	5/1987	Tominari et al. .	
4,935,474	6/1990	Ewen et al. .	
4,937,299	6/1990	Ewen et al. .	
4,981,760	1/1991	Naito et al.	428/523
4,987,212	1/1991	Morterol et al. .	
5,026,798	6/1991	Canich .	
5,055,438	10/1991	Canich .	
5,084,540	1/1992	Albizzati et al. .	
5,189,106	2/1993	Morimoto et al.	525/240
5,206,075	4/1993	Hodgson, Jr.	428/216
5,218,071	6/1993	Tsutsui et al.	526/348
5,272,236	12/1993	Lai et al.	526/348.5
5,278,272	1/1994	Lai et al.	526/348.5
5,374,700	12/1994	Tsutsui et al.	526/348.3
5,395,471	3/1995	Obijeski et al.	156/244.11
5,395,810	3/1995	Shamshoum et al.	502/113
5,408,004	4/1995	Lai et al.	525/240
5,444,145	8/1995	Brant et al.	526/348.3

FOREIGN PATENT DOCUMENTS

2008315	7/1990	Canada	C08F 4/16
0416815A2	3/1991	European Pat. Off. .	
0 447 035 A3	9/1991	European Pat. Off.	C08F 297/08
9003414	4/1990	WIPO .	
WO 90/03414 A1	4/1990	WIPO	C08L 23/08
WO 93/03093 A1	2/1993	WIPO	C08L 23/04
WO 93/08221 A2	4/1993	WIPO	C08F 10/00
WO 93/13143 A1	7/1993	WIPO	C08F 10/02
WO 94/06857 A1	3/1994	WIPO	C08L 23/04
WO 94/12568 A1	6/1994	WIPO	C08L 23/08
WO 95/13321 A1	5/1995	WIPO	C08L 23/04

OTHER PUBLICATIONS

Journal of Polymer Science, Part A, vol. 1 (pp. 2869–2880 (1963)), "Long–Chain Branching Frequency in Polyethylene" by J. E. Guillet.

Polymer Preprints, Amer. Chem. Society, vol. 12, No. 1, pp. 277–281 (Mar. 1971), "Evidence of Long–Chain Branching in High Density Polyethylene" by E. E. Drott and R. A. Mendelson.

Journal of the American Chemical Society, 98:7, pp. 1729–1742 (Mar. 31, 1976) "Structure and Chemistry of Bis(cyclopentadienyl)–MLn Complexes" by Joseph W. Lauher and Roald Hoffman.

Polymer Engineering and Science, vol. 16, No. 12, pp. 811–816 (Dec. 1976), "Influence of Long–Chain Branching on the Viscoelastic Properties of Low–Density Polyethylenes" by L. Wild, R. Ranganath, and D. Knobeloch.

Angew. Chem. Int. Ed. Engl., pp. 630–632 (1976) vol. 15, No. 10, "Halogen–Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature" by Arne Andresen et al.

Advances in Organometallic Chemistry, pp. 99–148, vol. 18, (1980) "Ziegler–Natta Catalysis" by Hansjorg Sinn and Walter Kaminsky.

Angew. Chem. Int. Ed. Engl., pp. 390–393, vol. 19 No. 5 (1980) "Living Polymers' on Polymerization with Extremely Productive Ziegler Catalysts" by Hansjorg Sinn, Walter Kaminsky, Hans–Jurgen Vollmer, and Rudiger Woldt.

Polymer Bullentin, 9, pp. 464–469 (1983) "Halogen Free Soluble Ziegler Catalysts with Methylalumoxan as Catalyst" by Jens Herwig and Walter Kaminsky.

Makromol. Chem., Rapid Commun., 4, pp. 417–421 (1983) "Bis(cyclopentadienyl)zirkon–Verbingungen und Aluminoxan als Ziegler–Katalysatoren fur die Polymerisation und Copolymerisation von Olefinen" by Walter Kaminsky et al.

ANTEC Proceedings, pp. 306–309 (1983), "Analysis of Long Chain Branching in High Density Polyethylene" by J.K. Hughes.

(List continued on next page.)

Primary Examiner—David W. Wu

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

18 Claims, 2 Drawing Sheets

MAIL ROOM
JUL 13 1993
82
PAT. & TRADEMARK OFF.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum
Serial No.: 08/054379 Group Art Unit:
Filed: April 28, 1993 Examiner:
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, On July 7, 1993
DATE OF DEPOSIT
Margaret Greene
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE
Margaret Greene
SIGNATURE OF PERSON SIGNING CERTIFICATE
July 7, 1993
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

FILING OF DECLARATION

Filed herewith is the Declaration and Power of Attorney in the above-identified patent application. The filing date of the application is as noted above.

The $130.00 fee for the separate filing of this Declaration required under 37 CFR 1.16(e) may be charged to our Deposit Account No. 04-1512. Duplicate copies of this sheet are enclosed.

Respectfully submitted,

By L. Wayne White

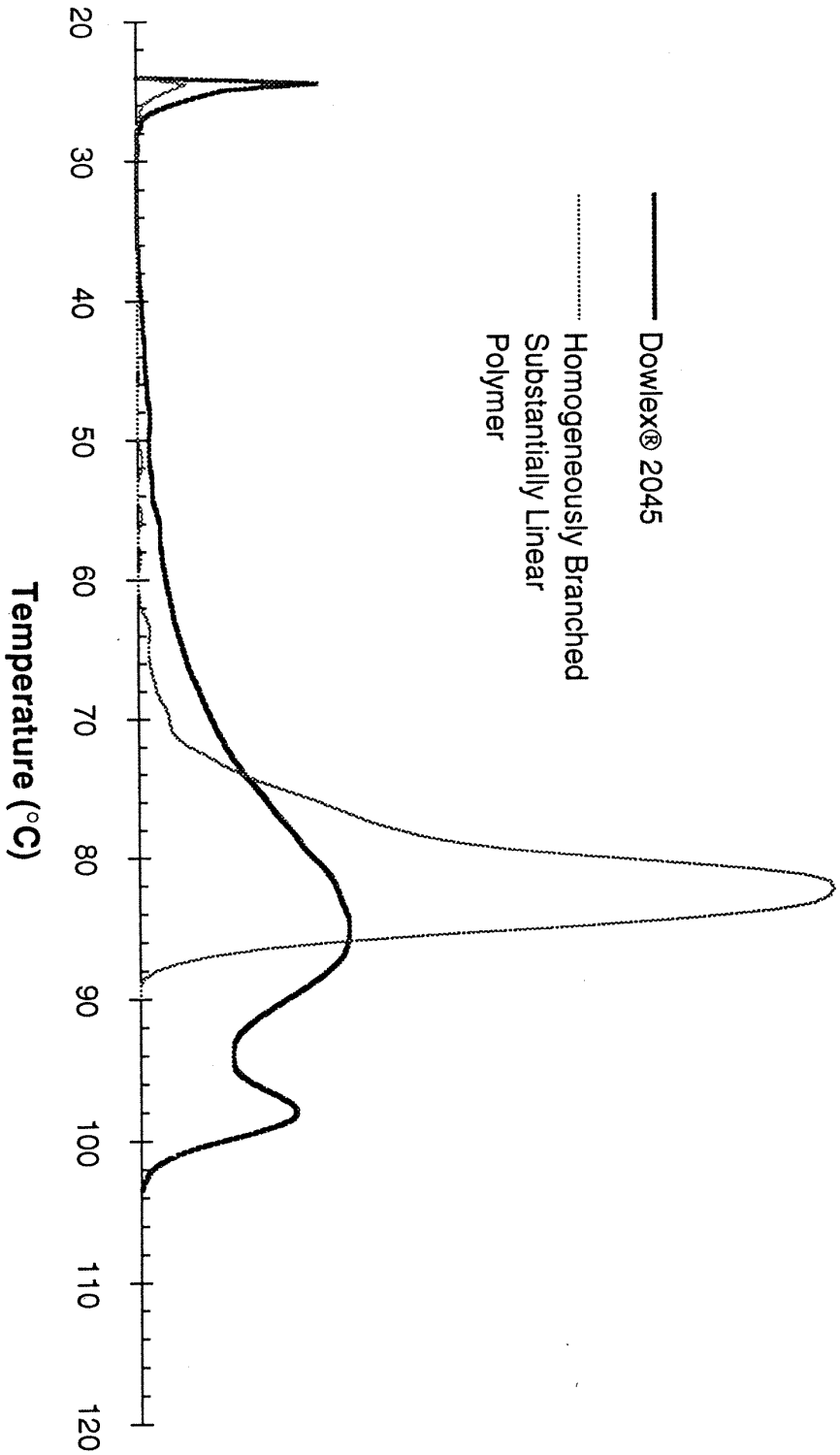
L. Wayne White
Registration No. 25,415
Phone: 409-238-2149

Freeport, Texas 77541
LWW/mfg

C-40,121-G -1-

08/054379

Figure 2

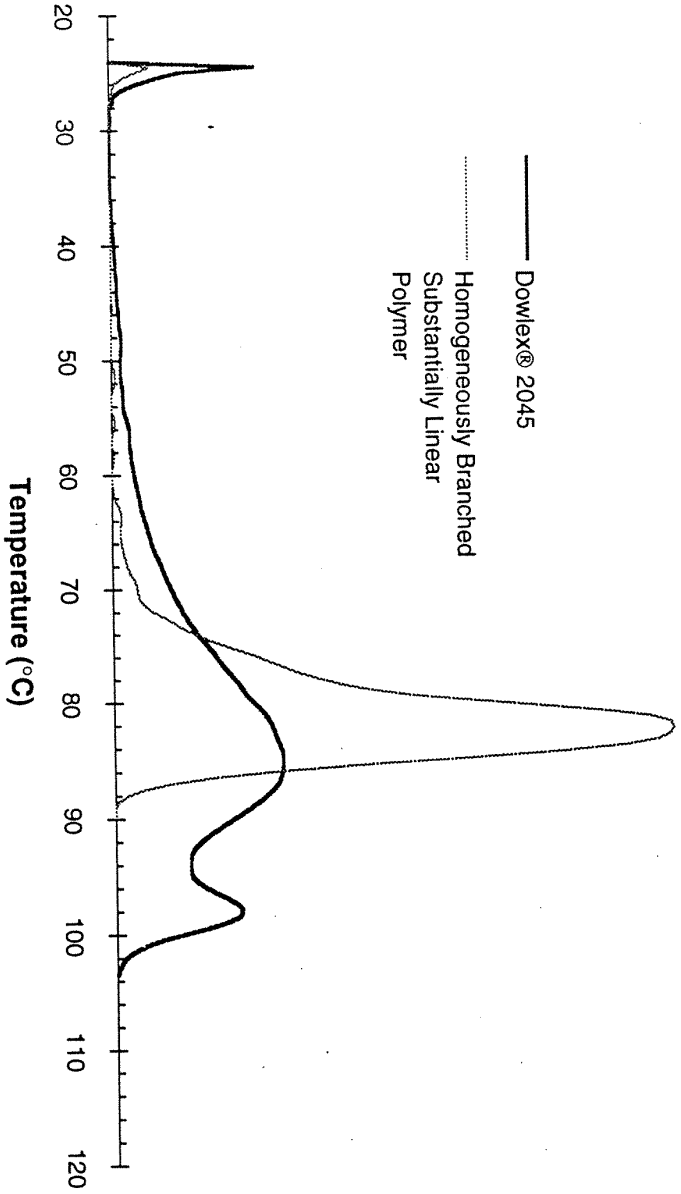




C-40,121-G
FABRICATED ARTICLES MADE FROM
ETHYLENE POLYMER BLENDS
Chum et al.
Sheet 2 of 2.

PRINT OF DRAWINGS
AS ORIGINALLY FILED

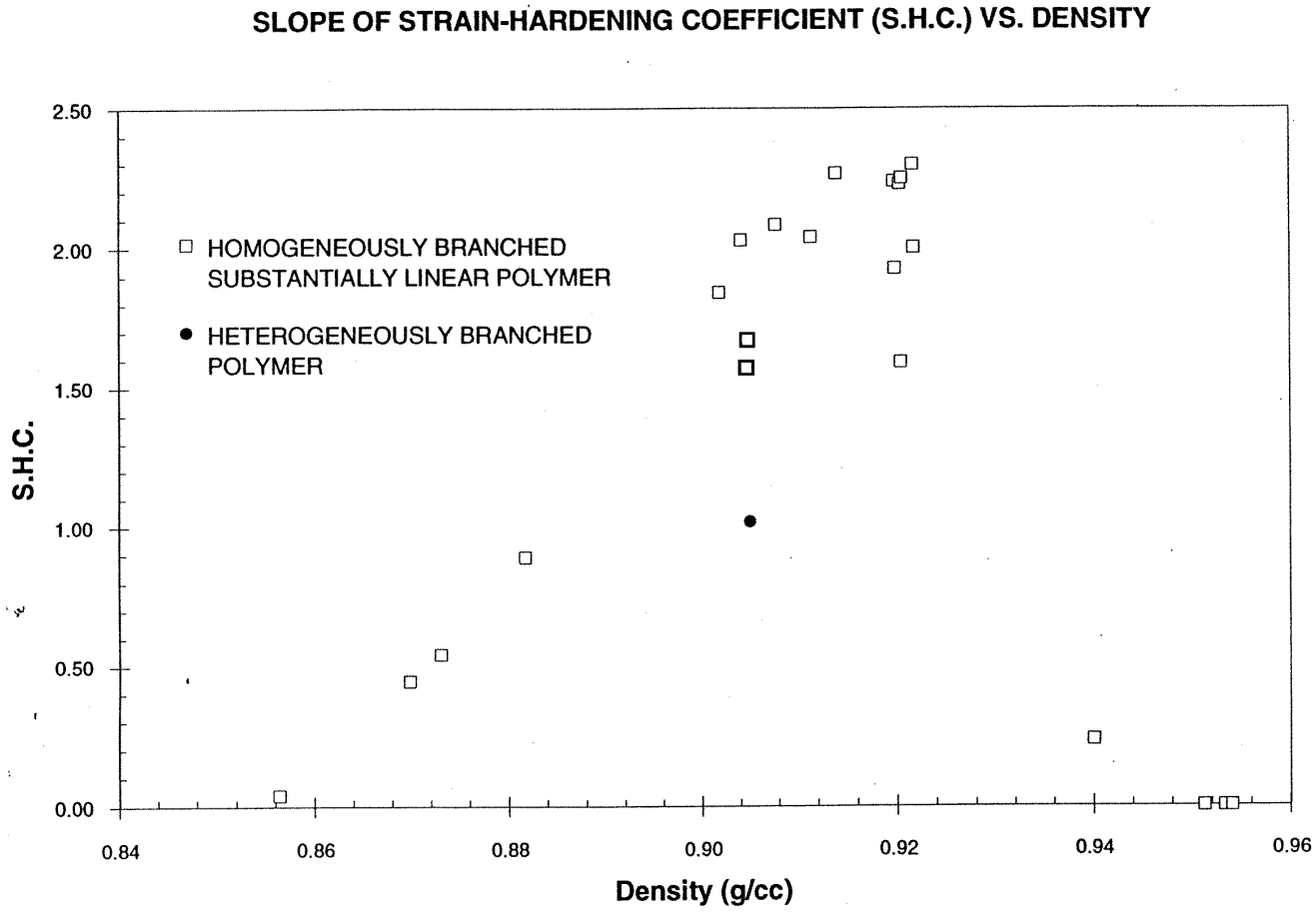
08/054379



Analytical Temperature Rising Elution Fractionation (ATREF)
Comparison of SCBD

Figure 2

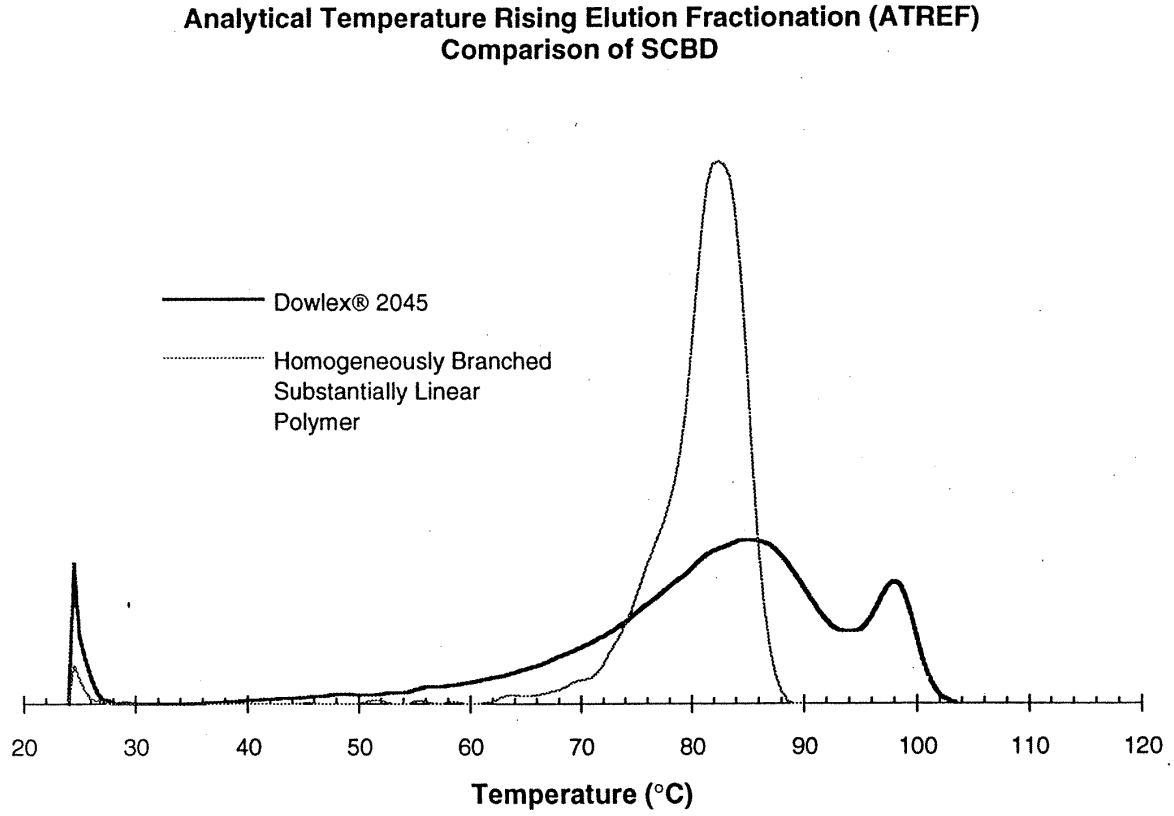
FIGURE 1



08/054379
PRINT OF DRAWINGS AS ORIGINALLY FILED

08/054379

Figure 2



PRINT OF DRAWINGS
AS ORIGINALLY FILED

08/054379

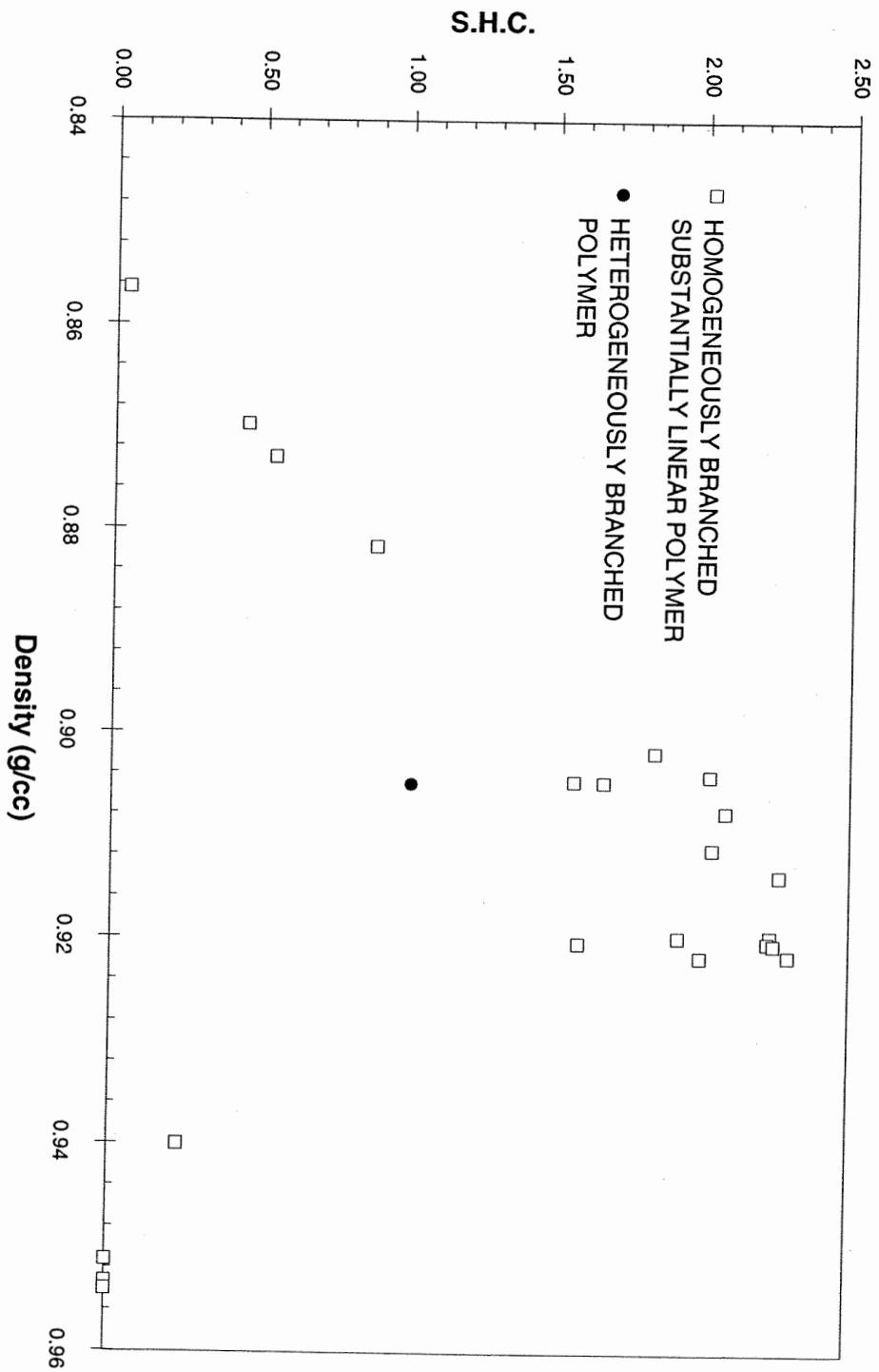


FIGURE 1

SLOPE OF STRAIN-HARDENING COEFFICIENT (S.H.C.) VS. DENSITY



C-40,121-G
FABRICATED ARTICLES MADE FROM
ETHYLENE POLYMER BLENDS
Chum et al.
Sheet 1 of 2.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.
Serial No.: 08/378,998 Group Art Unit: 1505
Filed: January 27, 1995 Examiner: David Wu
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 21 1995
GP 1500

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

Transmitted herewith is an amendment requiring an additional fee in the above-identified application.

The fee has been estimated as shown below.

CLAIMS AS AMENDED

(1)	(2) Claims remaining after amendment	(3)	(4) Highest number previously paid for	(5) Present Extra	(6) Rate	(7) Add'l Fee
Total Claims	* 17	Minus	** 20	0	$22	$0
Independent Claims	* 4	Minus	*** 3	1	$76	$76
First Presentation of Multiple Dependent Claims					$240	$0
			Total additional fee for this amendment:			$76

*If the entry in Column 2 is less than the entry in Column 4, write "0" in Column 5.
**If the "Highest Number Previously Paid For" in this space is less than 20, write "20" in this space.
***If the "Highest Number Previously Paid For" in this space is less than 3, write "3" in this space.

Please charge the above fee to our Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Three copies of this sheet are enclosed.

Respectfully submitted,

Osborne K. McKinney
Registration No. P-40,084
Phone: (409) 238-7889

Dated: September 20, 1995

OKM/mfg

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.
Serial No.: 08/378,998 Group Art Unit: 1505
Filed: January 27, 1995 Examiner: David Wu
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 21 1995
GP 1500

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

Transmitted herewith is an amendment requiring an additional fee in the above-identified application.

The fee has been estimated as shown below.

CLAIMS AS AMENDED

(1)	(2) Claims remaining after amendment	(3)	(4) Highest number previously paid for	(5) Present Extra	(6) Rate	(7) Add'l Fee
Total Claims	* 17	Minus	** 20	0	$22	$0
Independent Claims	* 4	Minus	*** 3	1	$76	$76
First Presentation of Multiple Dependent Claims					$240	$0
			Total additional fee for this amendment:			$76

*If the entry in Column 2 is less than the entry in Column 4, write "0" in Column 5.
**If the "Highest Number Previously Paid For" in this space is less than 20, write "20" in this space.
***If the "Highest Number Previously Paid For" in this space is less than 3, write "3" in this space.

Please charge the above fee to our Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Three copies of this sheet are enclosed.

Respectfully submitted,

Osborne K. McKinney
Registration No. P-40,084
Phone: (409) 238-7889

Dated: September 20, 1995

OKM/mfg

BAR CODE LABEL

U.S. PATENT APPLICATION

SERIAL NUMBER	FILING DATE	CLASS	GROUP ART UNIT
08/378,998	01/27/95	526	1505

APPLICANT

PAK-WING STEVE CHUM, LAKE JACKSON, TX; GEORGE W. KNIGHT, LAKE JACKSON, TX; RONALD P. MARKOVICH, FRIENDSWOOD, TX; SHIH-YAW LAI, SUGAR LAND, TX.

CONTINUING DATA********
VERIFIED THIS APPLN IS A CON OF 08/054,379 04/28/93
WHICH IS A CON OF 07/776,130 10/15/91 PAT 5,272,236

FOREIGN/PCT APPLICATIONS********
VERIFIED

STATE OR COUNTRY	SHEETS DRAWING	TOTAL CLAIMS	INDEPENDENT CLAIMS	FILING FEE RECEIVED	ATTORNEY DOCKET NO.
TX	2	15	2	$730.00	C-40.121-AB

ADDRESS

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

TITLE

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

This is to certify that annexed hereto is a true copy from the records of the United States Patent and Trademark Office of the application which is identified above.

By authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

Date Certifying Officer

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.

Serial No.: 08/378,998 Group Art Unit: 1505

Filed: January 27, 1995 Examiner: David Wu

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 2 1 1995
GROUP 1500

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

EXTENSION OF TIME

Applicant(s) hereby request(s) that the shortened statutory period for response now set to expire July 18, 1995 in this application be extended for a period of three (3) month(s), the extended period then expiring on October 18, 1995. This is a first request for an extension of time.

Please charge $870 to our Deposit Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Two duplicate copies of this sheet are enclosed.

Respectfully submitted,

By _____
Osborne K. McKinney
Registration No. P-40,084
Phone: (409) 238-7889

Freeport, Texas 77541

OKM/mfg
C-40,121-AB

MAIL ROOM
MAY
16
1994
PAT. & TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RECEIVED
JUN 0 1 1994
GROUP 150

Applicant(s): Pak-Wing Steve Chum et al.

Serial No.: 08/054,379 Group Art Unit: 1505

Filed: April 28, 1993 Examiner: D. WU

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, On May 13, 1994

DATE OF DEPOSIT

Jan Alverson

PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Jan Alverson

SIGNATURE OF PERSON SIGNING CERTIFICATE

5-13-94

DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

EXTENSION OF TIME

Applicant(s) hereby request(s) that the shortened statutory period for response now set to expire February 15, 1994 in this application be extended for a period of three (3) months, the extended period then expiring on May 15, 1994. This is a first request for an extension of time.

Please charge $840 to our Deposit Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Two duplicate copies of this sheet are enclosed.

Respectfully submitted,

By Noreen D Warrick
Noreen D. Warrick
Registration No. 34,573
Phone: 409-238-4510

May 11, 1994
Freeport, Texas 77541

LWW/mfg
C-40,121-G



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum, et al.

Serial No.: 08/054,379 Group Art Unit: 1505

Filed: April 28, 1993 Examiner: D. Wu

RECEIVED
FEB 27 1995
GROUP 1500

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

"Express Mail" mailing label number TB 184 380 515
Date of Deposit January 27, 1995
I hereby certify that this paper or fee is being deposited with the United States Postal Service, with sufficient postage "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231
Jan Alverson
(Typed or printed name of person mailing paper or fee)
Jan Alverson
(Signature of person mailing paper or fee)

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

EXTENSION OF TIME

Applicant(s) hereby request(s) that the shortened statutory period for response now set to expire October 27, 1994 in this application be extended for a period of three (3) month(s), the extended period then expiring on January 27, 1995. This is a second request for an extension of time.

Please charge $870.00 to our Deposit Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Two duplicate copies of this sheet are enclosed.

Respectfully submitted,

By L Wayne White

L. Wayne White
Registration No. 25,415
Address: Bldg. B-1211
Freeport, Texas 77541
Phone: 409-238-2149

LWW/jka
C-40,121-G

HE UNITED STATES PATENT AND TRADE RK OFFICE

Applicant(s): Pak-Wing Steve Chum, et al.
Serial No.: 08/054,379
Filed: April 28, 1993
Group Art Unit: 1505
Examiner: D. Wu
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS



BOX FWC
The Commissioner of Patents and Trademarks
Washington D.C. 20231

"Express Mail" mailing label number TB 184 380 515
Date of Deposit January 27, 1995
I hereby certify that this paper or fee is being deposited with the United States Postal Service, with sufficient postage "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231
Jan Alverson
(Typed or printed name of person mailing paper or fee)
Jan Alverson
(Signature of person mailing paper or fee)

Sir:

This is a request for filing a ☒ continuation ☐ divisional ☐ continuation-in-part) application under) 37 C.F.R. 1.62.

1. The following information is provided in accordance with 37 C.F.R. 1.62(h) (if different from originally filed or that stated in the Declaration and Power of Attorney presently of record) :
   (a) Title:
   (b) Names and addresses of Applicant(s):
2. Priority claim ☐ has ☒ has not been made pursuant to 35 USC 119, and if so, is identified as follows:
3. ☐ Cancel in this application claims _____ of the prior application before calculating the filing fee.
4. ☐ A Preliminary Amendment is enclosed.
5. ☒ The filing fee is calculated below.

For	Number Filed		Number Extra		Rate	Basic Fee $730.00
Total Claims	15	- 20 =	0	x	$ 22.00 =	0
Independent Claims	2	- 3 =	0	x	$ 76.00 =	0
Multiple Dependent Claims Presented					$240.00 =	0
Total Filing Fee ----------					=	$ 730

6. ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment, to Account No. 04-1512. This sheet is enclosed in triplicate.
7. ☒ Amend the specification by inserting after Title of the Invention: -- Cross-Reference to Related Application. This is a ☒ continuation ☐ divisional ☐ continuation-in-part of application Serial No. 08/054,379, filed April 28, 1993. --
8. ☐ A new declaration or oath is attached pursuant to 37 C.F.R. 1.62(c).
9. ☐ New drawings are enclosed.
10. ☒ The inventorship of this application is the same as that of the prior copending U.S. application.
    ☐ Fewer inventors are to be named in this application than in the prior copending U.S. application. Delete _____ as inventor(s) in this application.
    ☐ The inclusion of additional claimed subject matter in this application requires that additional inventor(s) be named. The additional inventor(s) are identified in No. 1 above and a new oath or declaration is enclosed.
11. ☐ Enter the amendment previously filed on _____, but unentered, in the prior application.
12. ☐ A new Disclosure Statement is enclosed.
    ☒ Applicant(s)' Disclosure Statement is as filed with the parent application.
13. ☒ The Power of Attorney in the prior application is to STEPHEN P. KRUPP, Reg. No. 34,366; L. Wayne White, Reg. No. 25,415; Glenn H. Korfhage, Reg. No. 27,204; Richard G. Waterman, Reg. No. 20,128.
    Please address all communications to The Dow Chemical Company, Patent Department, B-1211, 2301 N. Brazosport Blvd., Freeport, Texas 77541.
    a. ☒ The power appears in the original papers in the prior application.
    b. ☐ The power does not appear in the original papers. A copy of the power in the prior application is enclosed.
    c. ☒ Recognize as Associate Attorney Noreen D. Warrick whose Registration No. is 34,573 and whose phone number is 409-238-4510.

1/27/95
(Date)

L. Wayne White
Registration No. 25,415
Phone: 409-238-2149

C-40,121-AB
NDW/jka

POLYOLEFIN COMPOSITIONS EXHIBITING HEAT RESISTIVITY, LOW HEXANE-EXTRACTIVES AND CONTROLLED MODULUS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation of application Ser. No. 08/327,156, filed Oct. 21, 1994, abandoned, which is related to the following pending applications: U.S. patent application Ser. No. 08/054,379, filed on Apr. 28, 1993; U.S. patent application Ser. No. 08/010,958, filed on Jan. 29, 1993; U.S. patent application Ser. No. 08/239,495, filed on May 9, 1994; and U.S. patent application Ser. No. 08/239,496, filed on May 9, 1994, the disclosures of all of which are incorporated herein by reference.

FIELD OF THE INVENTION

This invention pertains to a polyolefin composition comprising at least two polymer material components. Particular embodiments of this invention, such a composition, or a film, coating or molding fabricated from such a composition, will be characterized as having a high heat resistivity, high percent residual crystallinity, low level of hexane extractives, low heat seal and hot tack initiation temperatures, high hot tack strength and controlled modulus.

BACKGROUND OF THE INVENTION

Although polyolefin resins have long found utility in food packaging and food storage container applications, a polyolefin resin with the desired balance of properties in the form of a film, coating and molding has not been available to fabricators and packagers. An optimum polyolefin resin for packaging and storage applications would possess a number of key performance properties. In particular, an optimum resin would be characterized by a high percent residual crystallinity and/or high Vicat softening point (indicating high heat resistivity which is important, for example, for microwavable food container and in hot-fill film packaging applications); a controllably high or low modulus (indicating good dimensional stability which is important for efficient product loading and bag-making operations or indicating good openability of refrigerated food containers, respectively); a low heat seal and hot tack temperature (indicating the ability to readily convert films and coatings into packages); high tear, dart impact resistance and puncture resistance (indicating greater package or container integrity under abuse); and a low level of hexane extractives (indicating a lower tendency for low molecular weight impurities or polymer fractions to migrate into sensitive packaged goods such as foodstuffs in food contact applications).

Traditionally, enhancement of one particular resin property has required some sacrifice with respect to another important resin property. For instance, low modulus, low heat seal and hot tack initiation temperatures, high tear strength, high dart impact resistance and high puncture resistance are typically achieved by increasing the comonomer content of the resin. In contrast, high crystallinity, high Vicat softening points, high modulus and low levels of n-hexane extractives are typically achieved by decreasing the comonomer content of the resin. Accordingly, improving the resin with respect to one class of properties has been historically achieved to the detriment of other properties.

One particular problem which has confronted industry is that the Vicat softening point of a resin and the heat seal initiation or hot tack initiation temperatures of a film layer fabricated from such a resin have been historically viewed as directly related. That is, while preferred resins will have a high Vicat softening point to promote heat resistivity, such improved heat resistivity traditionally comes at the cost of increased heat seal initiation and hot tack temperatures, which imposes decreased packaging line speeds and increased energy costs upon the package fabricator. Also, conventional resins typically have heat seal and hot tack initiation temperatures that either approximate their respective Vicat softening points or, more undesirably, are higher than their respective Vicat softening points. Thus, it is presently desirable to maximize the difference between the Vicat softening point of a resin and the heat seal and/or hot tack initiation temperature of a film layer fabricated from that resin as well as to provide polymer compositions that are characterized as having initiation temperatures more than 6° C. lower than their respective Vicat softening points such that packages having high heat resistivity and high ultimate hot strength may be more economically prepared.

Another particular problem which has confronted industry is that while ethylene alpha-olefin polymers having a higher comonomer content, (i.e., a density less than about 0.900 g/cc) yield films and coatings that exhibit good performance in terms of low heat seal and hot tack initiation temperatures, tear strength, dart impact resistance and puncture resistance, such polymers either exhibit excessive n-hexane extractives or are substantially soluble in n-hexane. In contrast to simple extraction, which pertains to the solubilizing of low molecular weight impurities, polymer fractions or degradation products which represent only small portions of the total polymer, substantially complete solubility in n-hexane is attributable to higher degrees of polymer amorphosity, i.e., a lower degree of crystallinity characteristic of interpolymers having a higher comonomer content.

Hexane-soluble materials and materials with high n-hexane extractives levels generally are not acceptable for use in direct food contact applications, such as sealant layers in multilayer film packages or injection molded food storage containers. Even where these materials are used for food packaging and storage in general, or for packaging and storing taste and odor sensitive goods, a substantial barrier material (such as, for example, aluminum foil) must be used between the material and the packaged or stored item. Accordingly, industry has historically been limited with respect to the utilization of lower density ethylene alpha-olefin resins having excellent heat seal and hot tack initiation performance and abuse properties in food contact applications as well as other applications involving taste or odor sensitive goods. Thus, it is also desirable to provide an ethylene alpha-olefin polymer composition having the beneficial performance attributes of ethylene alpha-olefin resins having densities less than 0.900 g/cc (e.g., attributes which indicate their utility as films and coatings having improved abuse properties and lower heat seal and hot tack initiation temperatures), but which are characterized by reduced levels of hexane extractives, making such polymer compositions suitable for use in food contact applications.

Still another problem that has plagued the plastic industry is the unavailability of optimum molding compositions for fabricating improved lids for freezer-to-microwave food containers. Such compositions should have good flexibility (i.e., a lower flexural modulus) to insure easy openability while the container is still at freezer or refrigerator temperatures, yet such compositions should also have good heat resistance to prevent undo melting, softening or distor-

BAR CODE LABEL

U.S. PATENT APPLICATION

SERIAL NUMBER	FILING DATE	CLASS	GROUP ART UNIT
08/054,379	04/28/93	528	1503

APPLICANT

PAK-WING STEVE CHUM, LAKE JACKSON, TX; GEORGE W. KNIGHT, LAKE JACKSON, TX; RONALD P. MARKOVICH, FRIENDSWOOD, TX; SHIH-YAW LAI, SUGAR LAND, TX.

CONTINUING DATA********
VERIFIED THIS APPLN IS A CIP OF 07/776,130 10/15/91

_____

FOREIGN/PCT APPLICATIONS********
VERIFIED

_____

FOREIGN FILING LICENSE GRANTED 08/26/93

STATE OR COUNTRY	SHEETS DRAWING	TOTAL CLAIMS	INDEPENDENT CLAIMS	FILING FEE RECEIVED	ATTORNEY DOCKET NO.
TX	2	30	4	$1,134.00	C40121G

ADDRESS

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
BLDG. B-1211
DALLAS, TX 77541

TITLE

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

This is to certify that annexed hereto is a true copy from the records of the United States Patent and Trademark Office of the application which is identified above.

By authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

Date Certifying Officer

[redacted]

SEARCHED

Class	Sub.	Date	Exmr.
525	240	4-14-95	WU

INTERFERENCE SEARCHED

Class	Sub.	Date	Exmr.

SEARCH NOTES

	Date	Exmr.

(RIGHT OUTSIDE)

Staple Issue Slip Here

POSITION		ID NO.	DATE
CLASSIFIER			
EXAMINER		401	2/23/95
TYPIST		357	2.24.95
VERIFIER			
CORPS CORR.			
SPEC. HAND			
FILE MAINT.			
DRAFTING			

INDEX OF CLAIMS

Claim Final	Claim Original	Date
	1	9/5
	2	4
	3	14
	4	
	5	
	6	
	7	
	8	✓
	9	
	10	
	11	
	12	
	13	
	14	
	15	
	16	
	17	✓
	18	
	19	
	20	
	21	
	22	
	23	✓
	24	
	25	
	26	
	27	
	28	
	29	
	30	
	31	
	32	
	33	
	34	
	35	
	36	
	37	
	38	
	39	
	40	
	41	
	42	
	43	
	44	
	45	
	46	
	47	
	48	
	49	
	50	

SYMBOLS

✓	Rejected
=	Allowed
- (Through numberal)	Canceled
+	Restricted
N	Non-elected
I	Interference
A	Appeal
O	Objected

Claim Final	Claim Original	Date
	51	
	52	
	53	
	54	
	55	
	56	
	57	
	58	
	59	
	60	
	61	
	62	
	63	
	64	
	65	
	66	
	67	
	68	
	69	
	70	
	71	
	72	
	73	
	74	
	75	
	76	
	77	
	78	
	79	
	80	
	81	
	82	
	83	
	84	
	85	
	86	
	87	
	88	
	89	
	90	
	91	
	92	
	93	
	94	
	95	
	96	
	97	
	98	
	99	
	100	

(LEFT INSIDE)

08/054379

[redacted]

APPROVED FOR LICENSE [b]

INITIALS _____

Date Entered or Coun ABANDONED

CONTENTS

Date Received or Mailed

	1.	Application _____ papers.	
	2.	LTR: Req. Signatures	6-19-93
	3.	Decl + Discharge	7-13-93
	4.	Req. (3 Mons.)	11-15-93 11/12
	5.	Ext of time (3 mos)	May 18, 1994 5/13
	6.	Draft Abandonment	May 18, 1994
	7.	2nd Req 3 mos.	7/27/94 7/27
	8.	Ext of time (3 mos)	Jan 27, 1995
	9.	Notice of abandonment	3/6/95 3/6
	10.		
	11.		
	12.		
	13.		
	14.		
	15.		
	16.		
	17.		
	18.		
	19.		
	20.		
	21.		
	22.		
	23.		
	24.		
	25.		
	26.		
	27.		
	28.		
	29.		
	30.		
	31.		
	32.		

(FRONT)

08/378998

PATENT APPLICATION

08378998

APPROVED FOR LICENSE ☐

INITIALS _____

Date Entered or Counted

ABANDONED

CONTENTS

Date Received or Mailed

RECEIVED
MAR U 9 1995
GROUP 1500

1. Application _____ papers.

10	Ltr Draft B	Jan 27, 1995
11.	F. Rejection	4/18/95 9/17
12.	Ext of time (3 mos)	Sept 21, 1995
13.	Draft C (NO) w/Decl	Sept 21, 1995
14.	Advisory Action	9-29-95 9/28
15.	Summary of Interview	10-5-95
16.	Draft D (NE) w/Decl	Oct 18 1995
17.	Draft E (NO)	Oct 23, 1995 10/25
18.	Advisory Action	10-26-95
19	Supp Ltr Ext	Oct 23, 1995
20	Abandoned	DEC 14 1995 12/11
21.	Request for access	June 18, 1998
22	Request for Access	10-2-98
23	Request for Access	12-7-98
24 16.	Request for access	1-22-04
25 17.	Request for Access	3-23-05
26 18.	Ltr of Con	10-26-05
27 19.	Request for Access	7-5-06
28 20.	Request for Access	7/12/06
29 21.	Request for access	11/22/06
	22.	
	23.	
	24.	
	25.	
	26.	
	27.	
	28.	
	29.	
	30.	
	31.	
	32.	

(FRONT)