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Clarke, Modet & Cº

COLOMBIA

**SEÑORES
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
E. S. D.**

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Rad: 06-117732- -00002-0000
Fee: 2007-02-02 17:17:52 Dep. 2020 NUECREACIONES
Tm. 11 PATENTEYI
Ivs: 378 FASENACIONALI
Net 444 RESPUESTAREQUE Folios: 208**

**REF: EXPEDIENTE No. 06117732
FECHA DE LA SOLICITUD: NOVIEMBRE 21, 2006
SOLICITANTE: CHEVRON PHILIPPS CHEMICAL COMPANY, LP
TITULO: SISTEMA DE CATALIZADORES PARA PRODUCIR
POLÍMEROS QUE TIENEN DISTRIBUCIONES DE AMPLIO PESO
MOLECULAR Y MÉTODOS PARA LA FABRICACIÓN DE LOS
MISMOS**

ASUNTO: CONTESTACIÓN A REQUERIMIENTO OFICIAL

**DILIA RODRIGUEZ D'ALEMAN, en mi condición de apoderada de la sociedad
solicitante, por el presente escrito doy respuesta a su auto notificado por
estado de Diciembre 11 de 2006, que vence Febrero 9 de 2007 y me
permite presentar los siguientes documentos:**

- **El documento de PODER otorgado a mi favor, junto con la prueba de
existencia y representación legal del solicitante, debidamente
legalizados.**
- **Su traducción oficial al Español debidamente avalada por el
Ministerio de Relaciones Exteriores.**
- **El documento en el que consta la CESIÓN del derecho a la patente
otorgado por los inventores al solicitante, debidamente legalizado.**
- **Su traducción oficial al Español debidamente avalada por el
Ministerio de Relaciones Exteriores.**

Adicionalmente presento los siguientes documentos:

1. **Notificación del reporte del examen preliminar Capítulo I**
2. **Notificación de la transmisión del reporte de búsqueda**
3. **Opinión escrita**
4. **PCT Solicitud**

Ruego a usted continuar con el presente trámite.

Señor Jefe,


DILIA RODRIGUEZ D'ALEMAN
TLR/sr
P. 856

P. 856 125
R

TRADUCCIÓN OFICIAL No. 00542 de un documento escrito en Inglés, el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Juan Pablo Piedrahíta Aguilera, Traductor e Intérprete Oficial debidamente reconocido de conformidad con el Certificado de Idoneidad Profesional No. 0045 expedido por la Universidad Nacional de Colombia, por el Ministerio de Relaciones Exteriores y autorizado por el Ministerio del Interior y de Justicia, por resolución número 718 de 2003.

(Se traduce un Poder, otorgado por la compañía CHEVRON PHILLIPS CHEMICAL CO LP., firmado por Michael E. Lee, con fecha Octubre 16, 2006, certificado notarial y Apostilla No. N-558217, escritos en Inglés.)

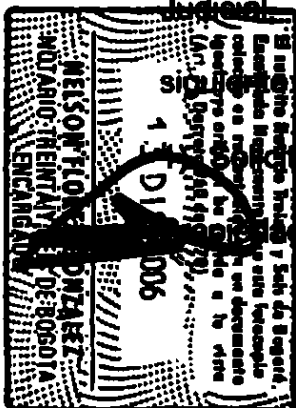
Clarke, Modet & Co.

COLOMBIA

(Dirección en español)

PODER

Yo (nosotros) Michael E. Lee., representante legal de CHEVRON PHILLIPS CHEMICAL CO LP, sociedad constituida y existente bajo las leyes de Delaware y en actual cumplimiento de su objeto social, con domicilio en 10001 Sux Pines Dr. The Woodlands, TX, por el presente por el presente confiero (conferimos) poder especial a favor de a DILIA MARÍA RODRÍGUEZ D'ALEMÁN, identificada con cédula de ciudadanía No. 41.654.882 de Bogotá y Tarjeta Profesional 20824 y CLAUDIA LUCIA CARO RAMIREZ, identificada con Tarjeta Profesional 36448 y cédula de ciudadanía No 40.017.374 de Tunja, con domicilio en Bogotá, Colombia, para que actuando en su orden en nombre de la otorgante la representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a la



clar, tramitar, obtener y/o registrar cualesquiera de las modalidades de Industrial, tales como: Patentes de Invención, Modelos de Utilidad;

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B

Diseños Industriales, variedades vegetales, Marcas, Lemas, Nombres y Enseñas Comerciales y Denominaciones de Origen; así como sus renovaciones, prórrogas, traspasos, cambios de nombre y/o domicilio, contratos y licencias.

2) Solicitar, tramitar, obtener, y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.

3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórrogas, cesiones, traspasos, cambios de nombre y/o domicilio, contratos y licencias.

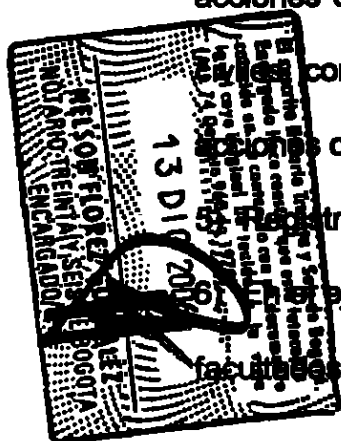
4) Ejercer acciones de oposición, observación, reclamos, reivindicaciones, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrán intervenir en juicios

comerciales, penales, contencioso-administrativos, tutelas y de policía; o juicios promovidos por el mandante o contra él.

Registrar nombres de dominio ante la entidad competente.

En el ejercicio de este mandato los mandatarios arriba mencionados quedan

facultados para: conciliar, cancelar, transigir, aceptar cláusulas



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compromisorias, desistir, recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistir derechos concedidos o en curso de concesión, admitir los hechos del proceso.

7) Ratificar o no la agencia oficiosa.

8) Así mismo facultamos a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieren.

Dado y firmado en (en blanco), hoy día 16 de Octubre, 2006.

Por: (Firmado) Michael E. Lee

Asesor Legal Asistente – IP

CERTIFICADO NOTARIAL (Cuando el solicitante es una SOCIEDAD)

(Poderes otorgados en El Salvador, México, Estados Unidos de América y Venezuela)

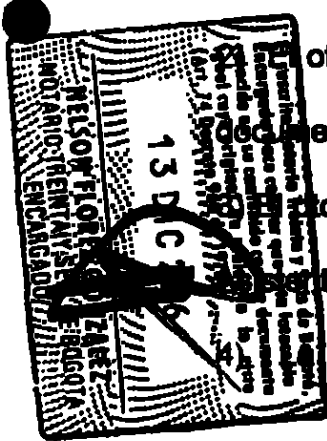
Expedido hoy día 16 de Octubre, 2006, el suscrito Notario CERTIFICA que:

1). Michael E. Lee, (nombre de quien firma el poder), mayor de edad y domiciliado en (ilegible) Texas, suscribió el anterior documento.

El otorgante le es conocido personalmente y tiene capacidad para firmar el documento.

El otorgante ha suscrito el anterior documento en su calidad de Asesor Legal Asistente de la persona jurídica CHEVRON PHILLIPS CHEMICAL CO LP.

La mencionada persona jurídica con domicilio comercial en 10001 Sux



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Pines Dr. The Woodlands, TX, está debidamente constituida, tiene actualmente existencia legal y el fin para el cual se otorga este poder se encuentra dentro de su objeto social.

5) El otorgante tiene en efecto la capacidad referida y su representación es legal y está autorizado para otorgar este poder.

6) Fundamento las certificaciones 3), 4) y 5) en los documentos auténticos que para tal fin me fueron exhibidos.

(Firmado) KIM GREGG, Notario Público

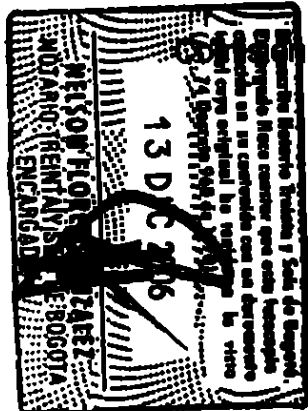
Nota: El Consulado de Colombia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Cónsul de Colombia o ante quien se otorgue, debe expedir una certificación dejando constancia de: 1) la existencia legal de la sociedad, 2) que cumple actualmente con su objeto social, y 3) que la persona o personas que otorgan este poder están facultadas para hacerlo. El Cónsul también certificará que los tuvo a la vista los documentos que prueban y acreditan tales circunstancias.

LEGALIZACIÓN POR EL CÓNSUL DE COLOMBIA A O POR APOSTILLA

(Sello Notarial a tinta: KIM GREGG, Notario Público, Estado de Texas, Mi

Vence Agosto 3, 2010)



(Sello Pre-impreso del Estado de Texas)

El Estado de Texas

Secretario de Estado

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TRADUCCION OFICIAL No. _____
JUAN PABLO MEDRAHITA AGL
TRADUCTOR E INTERPRETE OFC.
RES. 718 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUST.

1296

APOSTILLA

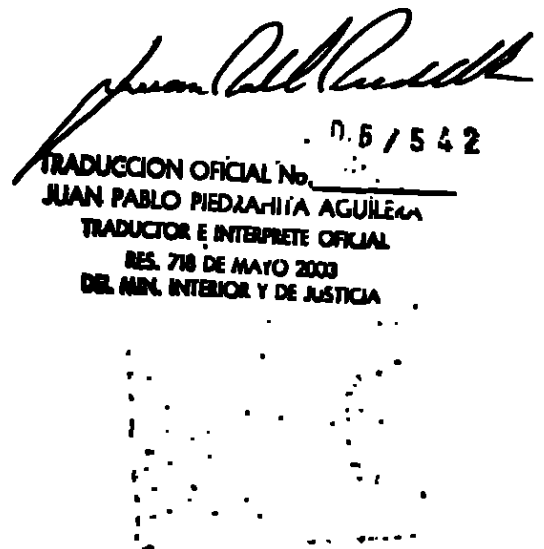
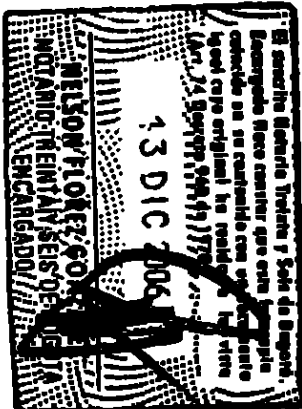
(Convención de la Haya de Octubre 5 de 1961)

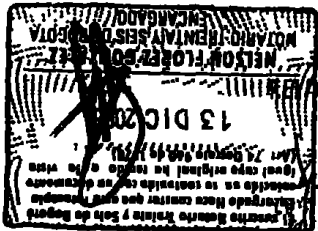
1. País: Estados Unidos de América
Este documento público
2. Ha sido firmado por KIM GREGG
3. Obrando en calidad de Notario Público, Estado de Texas
4. Lleva el sello/estampilla de KIM GREGG, Notario Público, Estado de Texas, Comisión vence 08-03-10

CERTIFICADA

5. En Austin, Texas
6. Hoy Noviembre 1, 2006
7. Por el Secretario de Estado de Texas
8. Certificado Número N-558217
9. (Sello) (Sello Pre-impreso del Estado de Texas)
10. (Firma) Firmado
(Firmado) Roger Williams, Secretario de Estado
ST/clk

ES TRADUCCIÓN FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su confrontación y a la cual me remito.
Bogotá, Diciembre 11, 2005.





MINISTERIO DE
INTERIORES

539780
Juan Piedrahita

FIRMA ADECUADA EN EL
DOCUMENTO DESEMPLEA
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2006 DIC 11 A 10:53

Jefe de Legalizaciones
BOGOTÁ D C



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The State of Texas

Secretary of State

APOSTILLE

(Convention de La Haye du 5 Octobre 1961)

1. Country: United States of America
2. This public document has been signed by KIM GREGG
3. acting in the capacity of Notary Public, State of Texas
4. and bears the seal/stamp of KIM GREGG, Notary Public, State of Texas,
Commission Expires: 08-03-10

CERTIFIED

5. at Austin, Texas
6. on November 1, 2006
7. by the Secretary of State of Texas

Certificate No. N-558217

10. Signature:



Roger Williams

Roger Williams
Secretary of State
TRADUCCION SE/DEL No. 0.8 / - - -
JUAN PABLO MED ARITA ALON
TRADUCTOR E INTERPRETE OFICIAL
RES. 718 DE MAYO 2006
Del MIN. INTERIOR Y DE JUSTI -

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COLOMBIA

Carrera 11 N° 86-53 Piso 6 Bogotá Colombia Tel: (57 1) 6181088 -Fax: (57 1) 6350824-E-mail: info@clarkeandson.com.co

PODER

Yo (nosotros), abajo firmante(s)

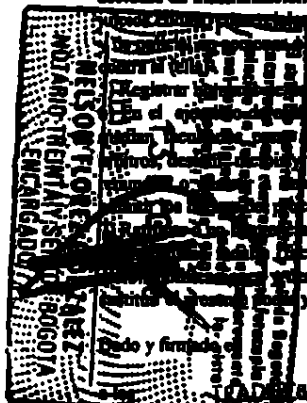
en mi (nuestro) carácter de representante(s) legales de

una sociedad organizada y existente de acuerdo con las leyes de

y en actual cumplimiento de su objeto social, con domicilio en

por el presente instrumento confiere (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN, con Cédula de Ciudadanía No. 41.654.882 de Bogotá, y tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, con Cédula de Ciudadanía No. 40.017.374 de Tunja, y tp. 36448, con domicilio en Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante le (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos:

- 1) Solicitar, transferir, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad, diseños industriales, variedades vegetales, marcas, lemas, nombres y emblemas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 2) Solicitar, transferir, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.
- 3) Solicitar, transferir, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia estatal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en procedimientos penales, contencioso-administrativos, tutelas, acciones de nulidad y recursos promovidos por el (la) mandante o en su nombre.
- 5) Registrar los asuntos antes mencionados ante la entidad competente.
- 6) En el ejercicio del presente mandato los mandatarios arriba mencionados podrán, negociar, transigir, cancelar, transferir, comprometer en litigio, desistirse de la cosa objeto de litigio y tomar posesión de la cosa objeto de litigio y demás acciones y recursos concedidos o en curso de concesión, en el orden judicial y extrajudicial.
- 7) Representar y defender los intereses de los mencionados apoderados para todo lo anterior y revocar las sustituciones que hicieren.



TRANSCRIPCION OFICIAL No. 001542
JUAN PABLO RIVERA AGUIRRE
TRADUCTOR E INTERPRETE OFICIAL
REC. 718 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUSTICIA

POWER OF ATTORNEY

I (we), the undersigned Michael E. Lee

legal representative(s) of Chevron Phillips Chemical Co.

an organization existing under the laws of Delaware

and in present execution of its business activity, domiciled at

10001 Six Pines Dr, The Woodlands, TX

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ D'ALEMAN, Identification card No. 41.654.882 of Bogotá, and tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ, tp. 36448, Identification card No. 40.017.374 of Tunja, residing in Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, specially before those Administrative, Administrative-Contentious, Judicial, arbitration courts, and/or any other, in all matters concerning the following:

- 1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models; Designs, plant varieties; Marks, Slogans, Trade Names and emblems and appellations of Origin; as well as their renewals, assignments, changes of name and/or domicile, agreements and licenses.
- 2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how.
- 3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses; as well as their renewals or assignments, changes of name and/or domicile, agreements and licenses.
- 4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of Licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtaining or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contentious-Administrative Trials; the actions for writ mandamus, police actions; in actions, lawsuits or litigations instituted by the grantor or against him.
- 5) To register domain names before the competent entity.
- 6) To the effect of this mandate the above-named proxy are empowered to: constitute, counsel, settle, submit to arbitration, withdraw and to receive and take possession of the litigation related object and waive or renounce the rights granted or in process of granting, admit the facts of the case.
- 7) To ratify or not the officious agency.
- 8) I (we) hereby appoint the afore mentioned attorneys with powers to receive notifications and to designate judicial and extrajudicial attorneys, substitute this Power of Attorney and to revoke such substitutions.

Granted and signed at

on this 16 day of October of 2006

Firma / signature

Michael E. Lee
Assistant General Counsel -- IP

TRADUCCION OFICIAL No. 06-5 / 2
JUAN PABLO PIEDRA ANITA A. JUAN
TRADUCTOR E INTERPRETE OFICIAL
DIA 16 DE MAYO 2006
DEL MUN. INTERIOR Y DE JUSTICIA

CERTIFICADO NOTARIAL

(Cuando el solicitante es SOCIEDAD)
(Powers of attorney granted in: El Salvador, Estados Unidos, México y Venezuela)

A los _____ días del mes de _____ de _____
el Notario que suscribe DA FE de que:

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____
firmó de su puño y letra el documento que antecede.

2. Conoce al (a la) otorgante y que este (a) está legalmente capacitado para el otorgamiento.

3. El otorgante ha firmado el referido documento en su carácter de _____
de la persona jurídica _____

4. La citada persona jurídica con sede en _____ está legalmente constituida, que tiene actualmente existencia legal y que el acto para el cual se ha otorgado este poder está comprendido entre los que constituyen su objeto social.

5. El otorgante tiene efectivamente la representación que ostenta, que esta es legítima y que está facultado para otorgar este poder.

6. Las anteriores certificaciones de los puntos 3, 4 y 5, me constan porque he tenido a la vista los documentos auténticos.

Notario Público

NOTA: A continuación de lo anterior, el Cónsul de Colombia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (Cuando el solicitante es INDIVIDUO)

A los _____ días del mes de _____ de _____
el Notario que suscribe DA FE de que:

(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____
firmó en su presencia

el documento que antecede, conoce al otorgante y que este está legalmente capacitado para el otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Cónsul de Colombia debe autenticar la firma del Notario Público.

Para legalizar la presente ante el Señor Cónsul de Colombia o ante el Señor Cónsul de Colombia, debe presentar una certificación dejando constancia 1) de la existencia legal de la sociedad, 2) de que esta ejerce actualmente su objeto social, y 3) de que la persona o personas que otorgan el poder están facultados para hacerlo, dejando constancia así mismo de que tuvo a la vista las pruebas que acreditan tales circunstancias.

LEGALIZACIÓN POR EL CONSUL DE COLOMBIA
O POR APOSTILLA

NOTARIAL CERTIFICATE

(When the applicant is a CORPORATION)
(Powers of attorney granted in: El Salvador, Mexico, U.S.A. and Venezuela)

This 16 day of October, 2006
the undersigned Notary CERTIFIES that:

1. Michael E. Lee
(name of the person who signs the power of attorney)

of legal age and domiciled in Central, Texas at his hand on the foregoing document.

2. The grantor is to him personally known and that he/she has legal capacity to execute the document.

3. The grantor has executed the foregoing document in his capacity of Assistant General Counsel - IP of the juridical person Chevron Phillips Chemical Co LP

4. The mentioned juridical person with place of business in 10001 Sue Rivers Dr The Woodlands TX is duly organized, has actual legal existence and that the purposes for which the power of attorney is granted are within the scope of its corporate purposes.

5. The grantor has in fact the referred quality and that his/her representation is legal and that he/she is empowered to grant this power of attorney.

6. I have based the above certifications 3, 4 and 5, on the documents which for such purpose were exhibited to me.

Notary Public

NOTA: Then the Colombian Consul must legalize the signature of the Notary Public.

NOTARIAL CERTIFICATE (When the applicant is an INDIVIDUALS)

On this _____ day of _____
the undersigned Notary CERTIFIES that:

1. _____
(name of the person who signs the Power of Attorney)

of legal age and domiciled at _____ signed in his presence the foregoing document, the grantor is to him personally known and that he/she has legal capacity to execute the document.

Notary Public

NOTA: Then the Colombian Consul must legalize the signature of the Notary Public.

For all other countries the Colombian Consul or before who it is granted must have a certification stating 1) the legal existence of the corporation, 2) that the corporate purposes are actually being accomplished, 3) that the person or persons who grant this Power of Attorney are empowered to do it. The Consul will certify also that the documents evidencing those circumstances were exhibited to him.

LEGALIZATION BY THE COLOMBIAN CONSUL OR - BY - APOSTILLE

P. 856 132

TRADUCCIÓN OFICIAL No. 07/040 de un documento escrito en inglés, el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Juan Pablo Piedrahíta Aguilera, Traductor e Intérprete Oficial debidamente reconocido por el Ministerio del Interior y de Justicia, por resolución número 718 de 2003 y autorizado por el Ministerio de relaciones Exteriores de Colombia.

(Se traduce un documento de registro de cesión de la solicitud de patente No. 10/829,550 a favor de la compañía CHEVRON PHILLIPS CHEMICAL COMPANY, ante la Oficina de Patentes y Marcas de los Estados Unidos de América y Apostilla No. 07009421-12, escritos en inglés.)

A 7039672

ESTADOS UNIDOS DE AMERICA

A TODOS A QUIENES ESTOS PRESENTES LLEGAREN:

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS

Noviembre 17, 2006

POR EL PRESENTE CERTIFICO QUE ADJUNTA SE ENCUENTRA UNA
COPIA FIEL DE LOS ARCHIVOS DE ESTA OFICINA DE UN DOCUMENTO
REGISTRADO EL 9 de Julio, 2004.

Por autoridad del

Por autoridad del

Bajo la Secretaría de Comercio para Propiedad Intelectual y el
Director de la Oficina de Patentes y Marcas de los Estados Unidos

(FIRMADO) H. L. JACKSON

Funcionario que Certifica

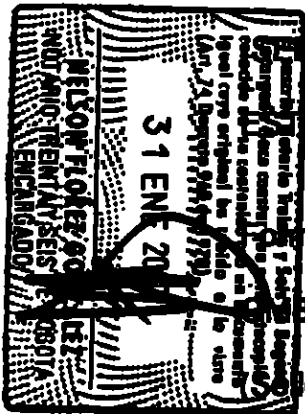
COPIA FIEL DE LOS ARCHIVOS DE ESTA OFICINA DE UN DOCUMENTO
REGISTRADO EL 9 de Julio, 2004.

Formulario PTO-1595, (Rev 10/02)

Formulario No. 0651-0027 (vence 6/30/2005)

Sello OIPE JC19, Julio 9, 2004, Oficina de Patentes y Marcas de los EE.UU.)

07-15-2004, Código de barras, 102791940



TRADUCCIÓN OFICIAL No. 07/040
JUAN PABLO PIEDRAHÍTA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
RECONOCIDO POR EL MINISTERIO
DEL MIN. INTERIOR Y DE JUSTICIA

133/10

Departamento de Comercio de los Estados Unidos, Oficina de Patentes y
Marcas Expediente 210481US00 (4081-05900)

CARÁTULA DEL FORMULARIO DE REGISTRO - SOLO PATENTES

Al Honorable Comisario de la Oficina de Patentes y Marcas de los EE.UU.:

Favor registrar los documentos adjuntos o sus copias.

1. Nombre de la(s) parte(s) que traspasa(n) / Fechas de suscripción:

Max P. McDaniel	05/20/2004	7-9-04
Elizabeth A. Benham	05/24/2004	
Steven J. Secora	05/20/2004	
Michael D. Jensen	05/20/2004	
Kathy S. Collins	05/14/2004	

Se adjuntan nombres o partes que traspasan adicionales? Si No
(en blanco) x

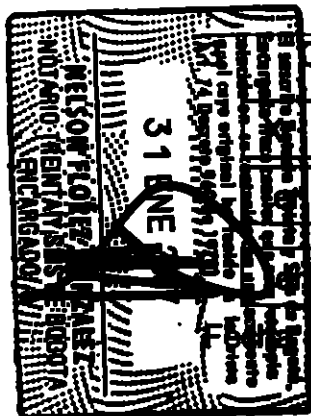
2. Nombre y Dirección de la parte que recibe:

Nombre: Chevron Phillips Chemical Company LP

Dirección: 10001 Six Pines Drive

Ciudad: The Woodlands Estado: TX Código Postal Zip 77380

Se adjuntan nombres o partes que traspasan adicionales ? Si No
(en blanco) x



Clase de Traspaso

(en blanco)	Cesión	(en blanco)	Fusión
(en blanco)	Contrato de Valores	(en blanco)	Cambio de Nombre
(en blanco)	Otra		

Fecha de suscripción: McDaniel (05/20/2004); Benham (05/24/2004); Secora

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(5/20/2004); Jensen (05/20/2004); Collins (6/14/2004);

4. Solicitud No(s). ó No(s) de Patente:

Si este documento se presenta junto con una nueva solicitud, la fecha de suscripción de la solicitud es: (en blanco)

A. No(s). de Solicitud(es) de Patente(s) 10/829,550 presentada Abril 22, 2004

B. (s). de Solicitud(es) de Patente(s) (en blanco)

Hay números adicionales adjuntos? (en blanco) Si ☒ No

5. Nombre y Dirección de la parte a quien se le debe dirigir la correspondencia concerniente al documento:

Rodney B. Carroll

CONLEY ROSE P.C.

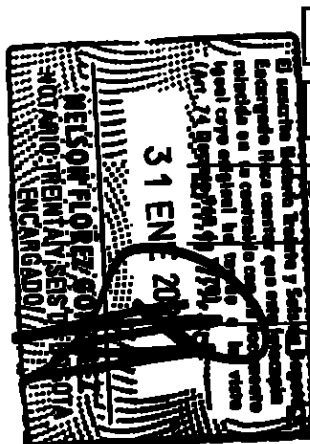
Granite Park Two

5700 Granite Parkway #330

Plano, Texas 75024

6. Número total de solicitudes de patentes involucradas: (en blanco)

7. Total Derechos (37 CFR §3.41) \$40.00



☒ Adjuntos
☐ (en Blanco) Autorización para cargo a cuenta de depósito

Cuenta de Depósito Número 50-1515

NO USE ESTE ESPACIO (en blanco)

Firma

Rodney B. Carroll

(Firmado) 7-6-04

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01 FC: 8021 40.00 OP)

RIEL: 015554 MARCO: 0427

CESION

UN CATALIZADOR DE CROMO Y UN COCATALIZADOR DE METAL DE N -
TRICICLÓN CLOPENTADIENIL (la "Invención"), y de la solicitud de patente
Estados Unidos que revela dicha invención, No. de Serie 10/829,550,
el 22 de Abril, 2004, también conocida por el expediente de la
número 210481US00 (4081-05900); y

FOR CUANTO, CHEVRON PHILLIPS CHEMICAL COMPANY ("CPCHEM"),

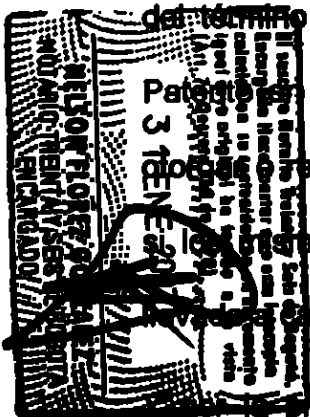
TRADUCCION OFICIAL No. 12
 JUAN PABLO P. CAHITA AGUILERA
 TRADUCTOR E INTERPRETE OFICIAL
 del 7.º de MARZO 2005
 DE LA CIUDAD DE GUAYAMA, P.R.

136

sociedad constituida bajo las leyes del Estado de Delaware, desea adquirir la totalidad de los derechos propiedad y participación en y sobre dicha invención, en todo el mundo,, y la totalidad de los derechos, propiedad y participación en, sobre y bajo todos y cualesquiera Títulos de Patente de los Estados Unidos y de los demás países extranjeros alrededor del mundo;

AHORA EN CONSECUENCIA, por una buena y valiosa contraprestación, recibo de la cual se reconoce en la presente, por la presente vendo, cado, transfiero y traspaso a CPCHEM, la totalidad de los derechos propiedad y participación sobre dicha invención alrededor del mundo, y de la solicitud de Título de Patente en los Estados Unidos, y todas y cualesquiera otras solicitudes de dicha invención, incluyendo las divisionales, de continuación, provisionales, no provisionales, comunes y solicitudes de reexpedición, y todos y cualesquiera Títulos de Patente en los Estados Unidos y en países extranjeros que sobre ella se otorguen, las mismas a ser tenidas y gozadas por CPCHEM para su propio uso y beneficio, y para uso y beneficio de sus sucesores, causahabientes y otros representantes legales, hasta la finalización

del término o términos para los cuales se puedan otorgar dichos Títulos de Patente en los Estados Unidos o que se hayan otorgado o se hayan podido reexpedir en países extranjeros sobre ella, tan completamente como los mismos hubieran sido tenido y gozados si esta cesión no se hubiera llevado a cabo.



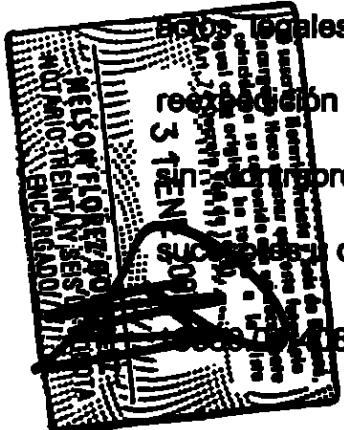
En la presente autorizo y le solicito al Comisario de Patentes y Marcas

137

expedir todas y cualesquiera Títulos de Patente de los Estados Unidos sobre dicha invención o que resulte de dicha solicitud y de todas las divisiones, continuaciones, y reexpediciones de la misma, a CPCHEM, como cesionario de la totalidad de mi participación, y por la presente convengo en que tengo el pleno derecho de traspasar la totalidad de la participación aquí cedida, y que no he firmado ni firmaré acuerdo alguno que pueda estar en conflicto con la presente.

Y además convengo y acuerdo que yo, en cualquier momento, a solicitud, firmaré y entregaré todos y cualesquiera documentos que sean necesarios o convenientes para perfeccionar la titularidad de dicha invención y de dichos Títulos de Patente que se puedan otorgar sobre ella, a favor de CPCHEM, sus sucesores, causahabientes y otros representantes legales, y si CPCHEM, sus sucesores, causahabientes y otros representantes legales desean presentar cualesquiera solicitudes divisionales, o de continuación o asegurar una reexpedición de tales Títulos de Patente, o de presentar una exclusión de la misma, a solicitud, firmaré todos los documentos, haré los juramentos de ley y

haré los juramentos legales que se requieran para la presentación de dicha solicitud de reexpedición y entrega de la misma, y para la presentación de dicha exclusión, y para la prestación adicional pero con cargo a dicho cesionario, sus sucesores, causahabientes y otros representantes legales.



081.05900

Página 1

PATENTE

138
15

RIEL: 015554 MARCO: 0428

Expediente No. 210481US (4081-05900)

(LOGO –CEVRON PHILLIPS)

Y además me comprometo y convengo que, en cualquier momento, a solicitud, le comunicaré a CPCHEM, a sus sucesores, causahabientes y otros representantes legales, todos los hechos referentes a dicha Invención y a dicho Título de Patente o la historia de archivo de la misma, en la forma en que sea conocida por nosotros, y daremos testimonio de la misma, en cualquier interferencia o litigio cuando se solicite hacerlo, sin contraprestación adicional, pero con cargo a dicho cesionario, a sus sucesores u otros representantes legales.

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Mayo 20, 2004

(Firmado) Max P. McDaniel

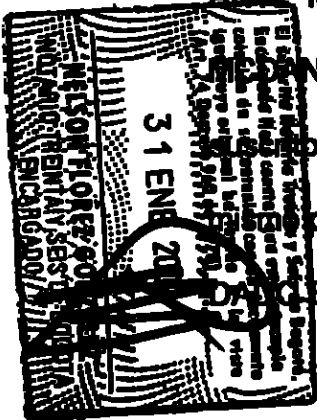
Max P. McDaniel

ESTADO DE OKLAHOMA §

CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día MAX P. McDANIEL, a quien conozco, y quien sé que es la persona cuyo nombre está en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

DADE BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.



7

TRADUCCION OFICIAL No. 162000
JUAN PABLO RUIZ MARTIN RODRIGUEZ
TRADUCTOR E INTERPRETE OFICIAL
REC. 113 DE MAYO 2004
DEL MIN. INTERIOR Y DE JUSTICIA

139
K

[SELLO] (Firmado) Sherry G. Woods

Notario Público, Estado de Oklahoma

Mi comisión vence, 2-18-06

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

16330.01/4081.05900

Página 2

PATENTE

RIEL: 015554 MARCO: 0429

Expediente No. 210481US (4081-05900)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Kingwood, Texas, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Mayo 24, 2004

(Firmado) Elizabeth A. Benham

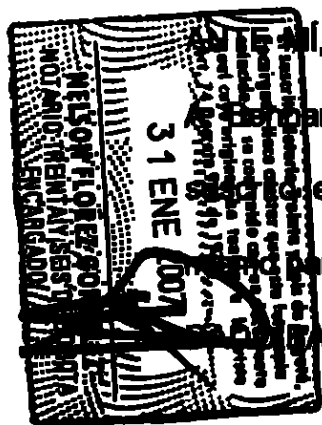
Elizabeth A. Benham

ESTADO TEXAS

§

CONDADO DE HARRIS

§



Yo, la autoridad suscrita, compareció personalmente hoy día Elizabeth Benham, a quien conozco, y quien sé que es la persona cuyo nombre está en el instrumento anterior, y quien reconoció ante mí que firmó el para los fines y por la contraprestación en él expresados.

BAJO MI FIRMA Y SELLO OFICIAL, hoy día 24 de Mayo, 2004.

8

TRANSMISION ORIGINAL No. 0273010
JUAN PABLO PEDRAZITA 4081-05900
TRADUCTOR E INTERPRETE OFICIAL
RES. 718 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUSTICIA

140
/

[SELLO] (Firmado) Dennis Charles Farinetti

Notario Público, Estado de Texas

Mi comisión vence, Noviembre 18, 2006

(Sello Notarial a tinta: Dennis Charles Farinetti, Notario Público Estado de Texas, Comisión vence Noviembre 18, 2006)

16330.01/4081.05900

Página 3

PATENTE
RIEL: 015554 MARCO: 0430

Expediente No. 210481US (4081-05900)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Mayo 20, 2004

(Firmado) Steven J. Secora

ESTADO DE OKLAHOMA §

CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Steven J.

Secora, a quien conozco, y quien sé que es la persona cuyo nombre está

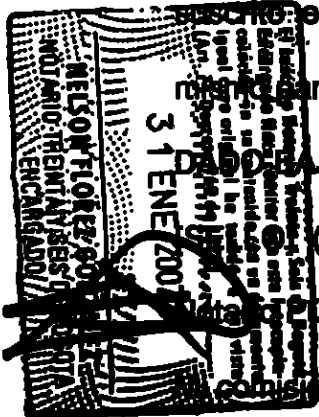
así escrito en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

DADO BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.

(Firmado) Sherry G. Woods

Notario Público, Estado de Oklahoma

comisión vence, 2-18-06



141
12

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

16330.01/4081.05900

Página 4

PATENTE
RIEL: 015554 MARCO: 0431

Expediente No. 210481US (4081-05900)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: 05-20-04

(Firmado) Michael D. Jensen

Michael D. Jensen

ESTADO DE OKLAHOMA §

CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Michael D. Jensen, a quien conozco, y quien sé que es la persona cuyo nombre está suscrito en el instrumento anterior, y quien reconoció ante mí que firmó el

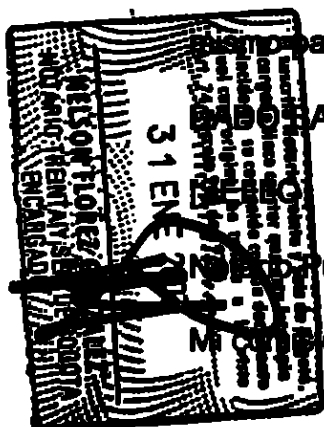
instrumento para los fines y por la contraprestación en él expresados.

BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.

(Firmado) Sherry G. Woods

Notario Público, Estado de Oklahoma

Mi comisión vence, 2-18-06



142

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

16330.01/4081.05900

Página 5

PATENTE
RIEL: 015554 MARCO: 0432

Expediente No. 210481US (4081-05900)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Junio 14, 2004

(Firmado) Kathy S. Collins

Kathy S. Collins

ESTADO DE OKLAHOMA §
CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Kathy S. Collins, a quien conozco, y quien sé que es la persona cuyo nombre está

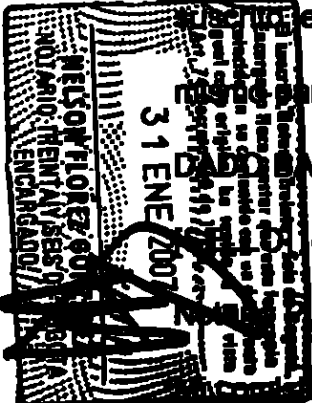
escrito en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

DAJO BAJO MI FIRMA Y SELLO OFICIAL, hoy día 14 de Junio, 2004.

(Firmado) Sherry G. Woods

Notario Público, Estado de Oklahoma

mi comisión vence, 2-18-06



TRADUCCION
JUAN PABLO RODRIGUEZ
TRADUCCION INGLÉS-ESPAÑOL
EL 14 DE MAYO 2004
DEL MIN. INTERIOR Y DE JUSTICIA

143
20

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario
Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero,
2006)

02001756

16330.01/4081.05900
REGISTRADA 07/09/2004

Página 6

PATENTE
RIEL: 015554 MARCO: 0433

APOSTILLA

(Convención de la Haya de Octubre 5 de 1961)

1. **País: *Estados Unidos de América***

Este documento público

2. **Ha sido firmado por H.L. JACKSON**

3. **Obrando en calidad de Funcionario que certifica**

4. **Lleva el sello/estampilla de Oficina de Patentes y Marcas**

CERTIFICADA

5. **En Washington D.C.**

6. **Hoy Ocho de Enero, 2007**

7. **Por el *Funcionario Asistente de Autenticaciones, Departamento de Estado de los Estados Unidos***

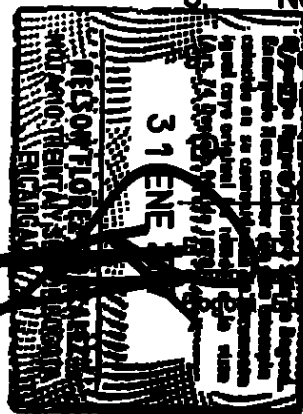
8. **No. 07009421-12**

Sello (Sello en Relieve del Departamento de Estado de los Estados Unidos)

Firma (Firmado)

Sonya N. Johnson

**COPIA FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su
conservación y a la cual me remito.
Ocho de Enero 20, 2007.**



Juan Pablo Piedra
TRADUCCION OFICIAL No. _____
JUAN PABLO PIEDRA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
RES. 718 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUSTICIA



MINISTERIO DE
ACIONES EXTERIORES

559467
Juan Piedrahita
SIGMA AFILCE EN EL
MENTO DESEMPEÑO
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2007 ENE 30 P 2 02

Cup
JEFE DE LEGALIZACIONES
BOGOTÁ D C

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by H. L. Jackson3. acting in the capacity of Certifying Officer4. bears the seal/stamp of Patent and Trademark Office

Certified

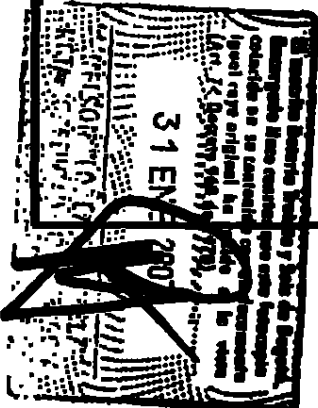
5. at Washington, D.C.

6. the eighth of January, 20077. by Assistant Authentication Officer, United States Department of State8. No. 07009421-12

9. Seal/Stamp:

10. Signature:

Sonya N. Johnson



TRADUCCION OFICIAL No. _____
BUREAU FEDERAL DE LA REGISTRATION
TRADUCCION OFICIAL
MINISTERIO DE JUSTICIA
DE LA NACION

145
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A 7039672

THE UNITED STATES OF AMERICA

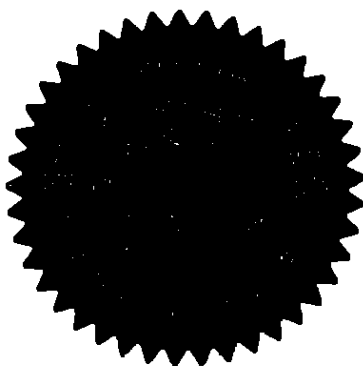
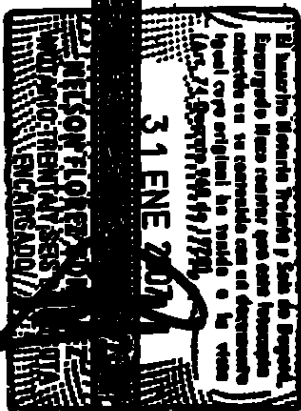
TO ALL TO WHOM THESE PRESENTS SHALL COME

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

November 17, 2006

THIS IS TO CERTIFY THAT ANNEXED IS A TRUE COPY FROM THE
RECORDS OF THIS OFFICE OF A DOCUMENT RECORDED ON
July 09, 2004

By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office



H. L. Jackson
H. L. JACKSON
Certifying Officer

TRANSLATION OFFICIAL No. 071040
DIRECTOR OF INTELLECTUAL PROPERTY
U.S. DEPARTMENT OF COMMERCE



07-15-2004

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Attorney Docket No. 210481US00 (4081-05900)

Form PTO-1385
(Rev. 10/02)
OMB No. 0651-0027 (Rev. 10/02/2005)



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SHEET

U. S. DEPARTMENT OF COMMERCE
Patent and Trademark Office

Y

To the Honorable Commissioner of Patents and Trademarks: Please record the attached original documents or copy thereof.

1. Name of conveying party(ies):

Execution Date

Max P. McDaniel
Elizabeth A. Berham
Steven J. Secora
Michael D. Jensen
Kathy S. Collins

05/20/2004
05/24/2004
05/20/2004
05/20/2004
08/14/2004

Additional name(s) of conveying party(ies) attached? ☐ Yes ☒ No

3. Nature of conveyance:

- ☒ Assignment ☐ Merger
☐ Security Agreement ☐ Change of Name
☐ Other

Execution Date: McDaniel (5/20/04); Berham (5/24/04);
Secora (5/20/04); Jensen (5/20/04); Collins (8/14/04)

2. Name and address of receiving party(ies):

Name: Chevron Phillips Chemical Company LP

Internal Address:

Street Address: 10001 Six Fines Drive

City: The Woodlands State: TX Zip: 77380

Additional name(s) & address(es) attached? ☐ Yes ☒ No

4. Application number(s) or patent number(s):

If this document is being filed together with a new application, the execution date of the application is: _____

A. Patent Application No.(s):

10/028,580 filed April 22, 2004

B. Patent No.(s):

Additional numbers attached? ☐ Yes ☒ No

5. Name and address of party to whom correspondence concerning document should be mailed:

Rodney B. Carroll
CONLEY ROSE, P.C.
Granite Park Two
5700 Granite Parkway, #330
Plano, Texas 75024

6. Total number of application and patents involved:

7. Total fee (37 CFR 3.41)\$ 40.00

- ☒ Enclosed
☐ Authorized to be charged to deposit account

8. Deposit account number: 50-1515

DO NOT USE THIS SPACE

9. Signature.

Rodney B. Carroll
Name of Person Signing

[Signature]
Signature

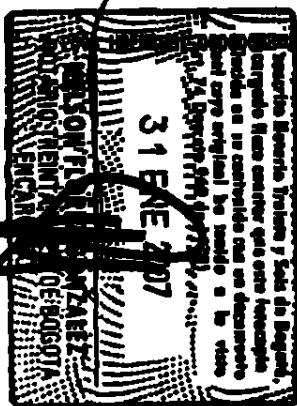
7-6-04
Date

Total number of pages including cover sheet, attachments, and documents 5/22/04

Mail documents to be recorded with required cover sheet information to:

Mail Stop Assignment Recordation Services,

Commissioner of US Patent & Trademark Office, P. O. Box 1450, Alexandria, VA, 22313-1450



40.00

PATENT
REEL: 015564 FRAME: 0427

TRADUCCION OFICIAL No. 071040

TRADUCTOR E INTERPRETE OFICIAL

ELABORADO POR: [Signature]

147
24

ASSIGNMENT

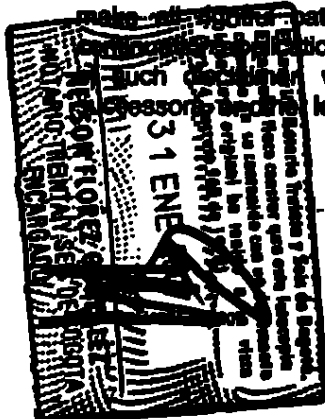
WHEREAS, I, among the following inventors, Max P. McDaniel, Elizabeth A. Benham, Steven J. Secora, Michael D. Jensen and Kathy S. Collins, am an inventor of **CATALYST SYSTEMS COMPRISING A CHROMIUM CATALYST AND A NON-TRANSITION METAL CYCLOPENTADIENYL COCATALYST** (the "Invention"), and of an application for United States Patent disclosing said invention, Serial No. 10/829,550, filed April 22, 2004, also known as company docket number 210481US00 (4081-05900); and

WHEREAS, CHEVRON PHILLIPS CHEMICAL COMPANY ("CPCHEM"), a corporation created and existing under and by virtue of the laws of the State of Delaware, is desirous of acquiring the entire right, title and interest in and to the aforesaid invention throughout the world, and all right, title and interest in, to and under any and all Letters Patent of the United States and all other countries throughout the world;

NOW, THEREFORE, for good and valuable consideration, the receipt of which is hereby acknowledged, I hereby sell, assign, transfer and set over to CPCHEM, all right, title and interest in and to the said invention throughout the world, and said application for U.S. Letters Patent, and any and all other applications for said invention, including divisional, continuation, provisional, non-provisional, regular, and reissue applications, and any and all Letters Patent of the United States and foreign countries which may be granted therefor, the same to be held and enjoyed by CPCHEM for its own use and benefit, and for the use and benefit of its successors, assigns, or other legal representatives, to the end of the term or terms for which said Letters Patent of the United States or foreign countries are or may be granted or reissued, as fully and entirely as the same would have been held and enjoyed if this assignment and sale had not been made.

And I hereby authorize and request the Commissioner of Patents and Trademarks to issue any and all Letters Patent of the United States on said invention or resulting from said application and from any and all divisions, continuations, and reissues thereof, to CPCHEM, as assignee of my entire interest, and hereby covenant that I have the full right to convey the entire interest herein assigned, and that I have not executed and will not execute any agreement in conflict herewith.

And I further hereby covenant and agree that I will, at any time, upon request, execute and deliver any and all papers that may be necessary or desirable to perfect the title of said invention and to such Letters Patent as may be granted therefor, to CPCHEM, its successors, assigns, or other legal representatives and that if CPCHEM, its successors, assigns or other legal representatives shall desire to file any divisional or continuation applications or to secure a reissue of such Letters Patent, or to file a disclaimer relating thereto, I will upon request, sign all papers, make all proper oaths and do all lawful acts requisite for the filing of such divisional or continuation applications, or such application for reissue and the procuring thereof, and for the filing of such disclaimer, without further compensation but at the expense of said assignee, its successors, assigns, or other legal representatives.



Page 1

PATENT
REEL: 016554 FRAME: 0428

TRADUCCION OFICIAL No. 071040
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
255, 718 DE MAYO 2003
32. MIN. INTERIOR Y DE JUSTICIA

148
25

And I do further covenant and agree that I will, at any time upon request, communicate to CPCHEM, its successors, assigns or other legal representatives, such facts relating to said invention and Letters Patent or the file history thereof as may be known to us, and testify as to the same in any interference or other litigation when requested so to do, without further compensation but at the expense of said assignee, its successors, or other legal representatives.

EXECUTED at Bartlesville, Oklahoma, on the date indicated below, opposite my signature.

ASSIGNOR:

Date: May 20 2004Max P. McDaniel
Max P. McDaniel

THE STATE OF OKLAHOMA §
 §
COUNTY OF WASHINGTON §

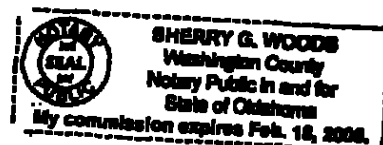
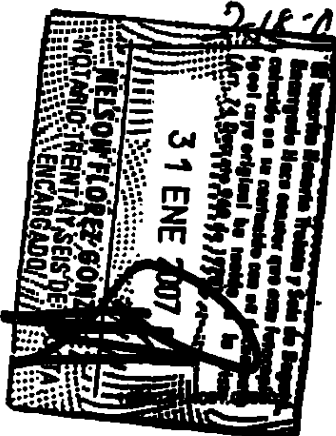
BEFORE ME, the undersigned authority, on this day personally appeared MAX P. MCDANIEL, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:



02001754

Page 2

PATENT
REEL: 016554 FRAME: 0429

TRADUCCION OFICIAL No. 671244
JUAN PABLO FLORES, Notario Publico
TRADUCTOR E INTERPRETE OFICIAL
MEXICO
DIRECCION GENERAL DE REGISTRO



Docket. No. 210481US (4081-05900)

149
26

EXECUTED at Kingwood, Texas, on the date indicated below, opposite my signature.

ASSIGNOR:

Date: May 24, 2004

Elizabeth A. Benham
Elizabeth A. Benham

THE STATE OF TEXAS §
COUNTY OF HARRIS §

BEFORE ME, the undersigned authority, on this day personally appeared ELIZABETH A. BENHAM, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

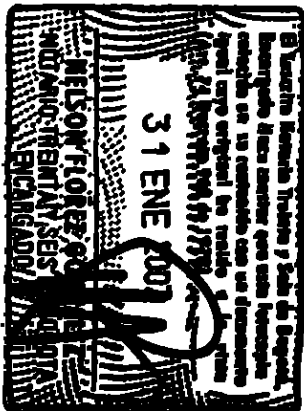
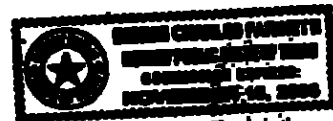
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 24 day of May, 2004.

[SEAL]

James Charles Lamm
Notary Public, State of Texas

My Commission Expires:

November 18, 2006



Page 3

PATENT
REEL: 015554 FRAME: 0430.

TRADUCCION OFICIAL No. 210481US
TRADUCTOR E INTERPRETE OFICIAL
JAMES CHARLES LAMM
NOTARY PUBLIC, STATE OF TEXAS

150
27

EXECUTED at Bartlesville, Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: May 20, 2004

Steven J. Secora
Steven J. Secora

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared STEVEN J. SECORA, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

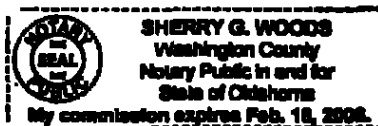
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

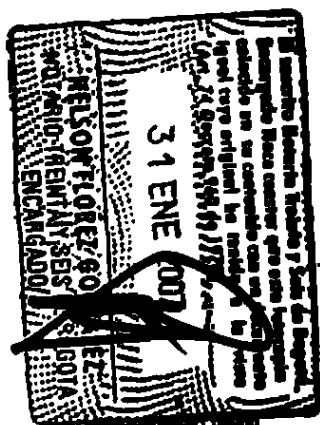
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-06



02001756



Page 4

PATENT
REEL: 015554 FRAME: 0431.

TRANSLATION OF ORIGINAL NO. 077040
TRANSLATED BY
TRANSLATOR E. INTL. PATENT OFFICE
1000 11th St. N.W.
WASHINGTON, D.C. 20540



Docket No. 210481US (4081-05900)

151
28

EXECUTED at Bartlesville Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: 05-20-04

Michael D. Jensen
Michael D. Jensen

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared MICHAEL D. JENSEN, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

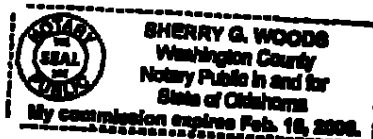
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

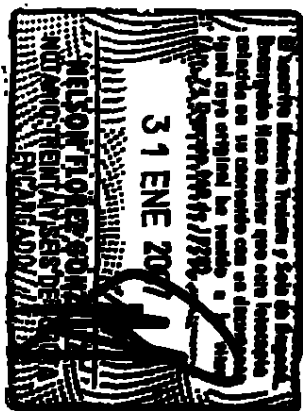
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-06



02001754



Page 5

PATENT

REEL: 016654 FRAME: 0432

TRADUCCION OFICIAL No. 7144

JUAN PABLO PIEDRITA ALONSO

TRADUCTOR E INTERPRETE OFICIAL

RES. 718 DE MAYO 2003

CC. MIN. INTERIOR Y DE JUSTICIA



Docket No. 210481US (4081-05900)

152
29

EXECUTED at Bartlesville, Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: June 14, 2004

Kathy S. Collins
Kathy S. Collins

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared KATHY S. COLLINS, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

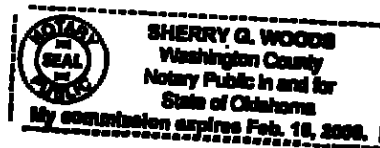
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 14 day of June, 2004.

[SEAL]

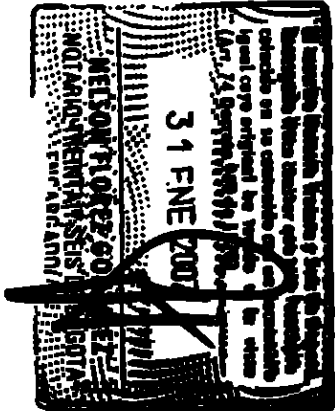
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-04



02001756



Page 6

REC RDED: 07/09/2004

PATENT
REEL: 015554 FRAME: 0433

TRADUCCION OFICIAL No. 127174
JUAN MANUEL PÉREZ ARCE
TRADUCTOR E INTERPRETE OFICIAL

P. 856.30
153
TRADUCCIÓN OFICIAL No. 07/039 de un documento escrito en inglés, el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Juan Pablo Piedrahita Aguilera, Traductor e Intérprete Oficial debidamente reconocido por el Ministerio del Interior y de Justicia, por resolución número 718 de 2003 y autorizado por el Ministerio de relaciones Exteriores de Colombia.

(Se traduce un documento de registro de cesión de la solicitud de patente No. 10/829,842 a favor de la compañía CHEVRON PHILLIPS CHEMICAL COMPANY, ante la Oficina de Patentes y Marcas de los Estados Unidos de América y Apostilla No. 07009421-11, escritos en inglés.)

A 1540297

ESTADOS UNIDOS DE AMERICA

A TODOS A QUIENES ESTOS PRESENTES LLEGAREN:

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS

Noviembre 9, 2006

POR EL PRESENTE CERTIFICO QUE ADJUNTA SE ENCUENTRA UNA
COPIA FIEL DE LOS ARCHIVOS DE ESTA OFICINA DE UN DOCUMENTO
REGISTRADO EL 9 de Julio, 2004.

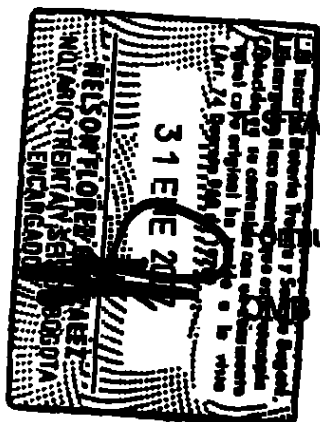
Por autoridad del

Por autoridad del

Bajo la Secretaría de Comercio para Propiedad Intelectual y el
Director de la Oficina de Patentes y Marcas de los Estados Unidos

(FIRMADO) T. LAWRENCE

Funcionario que Certifica



COPIA DE OBLEA DE LA OFICINA DE PATENTES Y MARCAS DE LOS
ESTADOS UNIDOS DE AMÉRICA)

Formulario PTO-1595, (Rev 10/02)

Form No. 0651-0027 (vence 6/30/2005)

07-15-2004, Código de barras, 102792015

7-9-04

Departamento de Comercio de los Estados Unidos, Oficina de Patentes y

3154

Marcas

Expediente 210481US01 (4081-05901)

CARÁTULA DEL FORMULARIO DE REGISTRO - SOLO PATENTES

Al Honorable Comisario de la Oficina de Patentes y Marcas de los EE.UU.:

Favor registrar los documentos adjuntos o sus copias.

1. Nombre de la(s) parte(s) que traspasa(n) / Fechas de suscripción:

Max P. McDaniel 05/20/2004

Elizabeth A. Benham 05/24/2004

Steven J. Secora 05/20/2004

Michael D. Jensen 05/20/2004

Kathy S. Collins 05/20/2004

(Sello OIPE JC19, Julio 9, 2004, Oficina de Patentes y Marcas de los EE.UU.)

Se adjuntan nombres o partes que traspasan adicionales? Si No

(en blanco)

x

2. Nombre y Dirección de la parte que recibe:

Nombre: Chevron Phillips Chemical Company LP

Dirección: 10001 Six Pines Drive

Ciudad: The Woodlands Estado: TX Código Postal Zip 77380

Se adjuntan nombres o partes que traspasan adicionales ? Si No

(en blanco)

x

Clase de Traspaso

(en blanco) Cesión

(en blanco)

Fusión

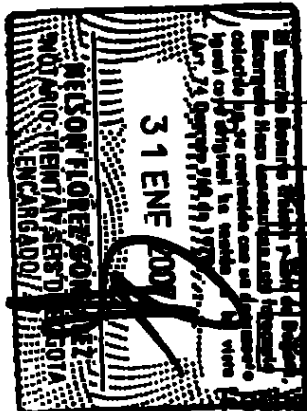
(en blanco) Contrato de Valores

(en blanco)

Cambio de Nombre

(en blanco) Otra

Fecha de suscripción: McDaniel (05/20/2004); Benham (05/24/2004); Secora (5/20/2004); Jensen (05/20/2004); Collins (05/20/2004);



32155

4. Solicitud No(s). ó No(s) de Patente:

Si este documento se presenta junto con una nueva solicitud, la fecha de suscripción de la solicitud es: (en blanco)

A. No(s). de Solicitud(es) de Patente(s) 10/829,842 presentada Abril 22, 2004

B. (s). de Solicitud(es) de Patente(s) (en blanco)

Hay números adicionales adjuntos? Si ☒ No

5. Nombre y Dirección de la parte a quien se le debe dirigir la correspondencia concerniente al documento:

Rodney B. Carroll

CONLEY ROSE P.C.

Granite Park Two

5700 Granite Parkway #330

Plano, Texas 75024

6. Número total de solicitudes de patentes involucradas: (en blanco)

7. Total Derechos (37 CFR §3.41) \$40.00

☒ Adjuntos
 Autorización para cargo a cuenta de depósito

Cuenta de Depósito Número 50-1515

NO USE ESTE ESPACIO (en blanco)

Firma

Rodney B. Carroll

(Firmado)

7-6-04

Nombre del Firmante

Firma

Fecha

33,56

Número Total de páginas, incluyendo la carátula, los anexos y documentos: 7

Envíe por correo los documentos a registrar con la información de la carátula requerida a: Casilla Cesiones, Servicios de Registro, Comisario de Patentes P.O. Box 1450, Alexandria VA 22313-1450

(Sello: 07/12/2004 HDEMESS1 0000061 10829842

01 FC: 8021 40.00 OP)

PATENTE

RIEL: 015554 MARCO: 0680

Expediente No. 210481US01 (4081-05901)

(LOGO –CEVRON PHILLIPS)

CESION

POR CUANTO, Yo, entre los siguientes inventores, Max P. McDaniel, Elizabeth A. Benham, Steven J. Secora, Michael D. Jensen y Kathy S. Collins, soy uno de los inventores de **POLÍMEROS QUE TIENEN DISTRIBUCIONES DE AMPLIO PESO MOLECULAR Y MÉTODOS PARA PREPARAR LA**

FABRICACIÓN DE LOS MISMOS (la "Invención"), y de la solicitud de patente

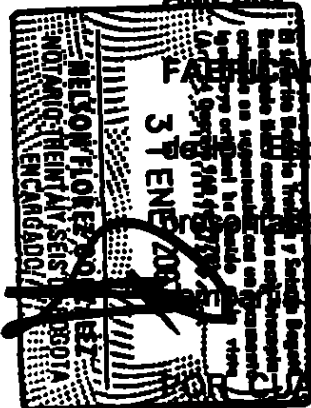
de los Estados Unidos que revela dicha invención, No. de Serie 10/829,842,

presentada el 22 de Abril, 2004, también conocida por el expediente de la

patente número 210481US01 (4081-05901); y

POR CUANTO, CHEVRON PHILLIPS CHEMICAL COMPANY ("CPCHEM"),

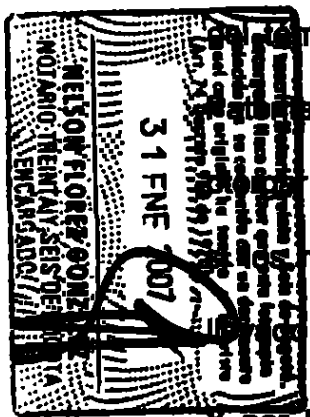
sociedad constituida bajo las leyes del Estado de Delaware, desea adquirir la



34
157

totalidad de los derechos propiedad y participación en y sobre dicha invención, en todo el mundo,, y la totalidad de los derechos, propiedad y participación en, sobre y bajo todos y cualesquiera Títulos de Patente de los Estados Unidos y de los demás países extranjeros alrededor del mundo;

AHORA EN CONSECUENCIA, por una buena y valiosa contraprestación, recibo de la cual se reconoce en la presente, por la presente vendo, cedo, transfiero y traspaso a CPCHEM, la totalidad de los derechos propiedad y participación sobre dicha invención alrededor del mundo, y de la solicitud de Título de Patente en los Estados Unidos, y todas y cualesquiera otras solicitudes de dicha invención, incluyendo las divisionales, de continuación, provisionales, no provisionales, comunes y solicitudes de reexpedición, y todos y cualesquiera Títulos de Patente en los Estados Unidos y en países extranjeros que sobre ella se otorguen, las mismas a ser tenidas y gozadas por CPCHEM para su propio uso y beneficio, y para uso y beneficio de sus sucesores, causahabientes y otros representantes legales, hasta la finalización



termino o términos para los cuales se puedan otorgar dichos Títulos de Patente en los Estados Unidos o que se hayan otorgado o se hayan podido otorgar o reexpedir en países extranjeros sobre ella, tan completamente como si los mismos hubieran sido tenido y gozados si esta cesión no se hubiera llevado a cabo.

Y por la presente autorizo y le solicito al Comisario de Patentes y Marcas expedir todas y cualesquiera Títulos de Patente de los Estados Unidos sobre

12/23/9
JUAN PABLO RIVERA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
DEL ESTADO DE CALIFORNIA

76
159

(LOGO -CEVRON PHILLIPS)

Y además me comprometo y convengo que, en cualquier momento, a solicitud, le comunicaré a CPCHEM, a sus sucesores, causahabientes y otros representantes legales, todos los hechos referentes a dicha Invención y a dicho Título de Patente o la historia de archivo de la misma, en la forma en que sea conocida por nosotros, y daremos testimonio de la misma, en cualquier interferencia o litigio cuando se solicite hacerlo, sin contraprestación adicional, pero con cargo a dicho cesionario, a sus sucesores u otros representantes legales.

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

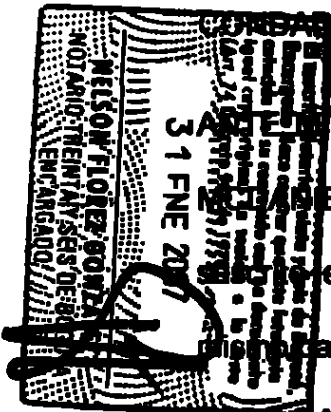
Fecha: Mayo 20, 2004

(Firmado) Max P. McDaniel

Max P. McDaniel

ESTADO DE OKLAHOMA §

CONDADO DE WASHINGTON §



Yo, la autoridad suscrita, compareció personalmente hoy día MAX P. McDaniel, a quien conozco, y quien sé que es la persona cuyo nombre está en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

DADO BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.

[SELLO] (Firmado) Sherry G. Woods

37
160

Notario Público, Estado de Oklahoma

Mi comisión vence, 2-18-06

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

17941.01/4081.05901

Página 2

PATENTE
RIEL: 015554 MARCO: 0682

Expediente No. 210481US01 (4081-05901)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Kingwood, Texas, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Mayo 24, 2004

(Firmado) Elizabeth A. Benham

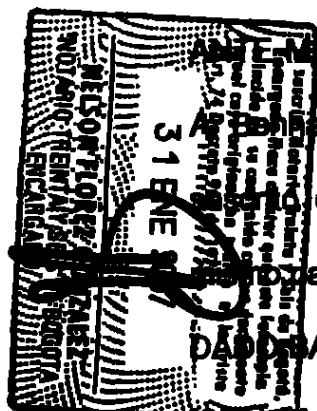
Elizabeth A. Benham

ESTADO TEXAS

§

CONDADO DE HARRIS

§



Yo, la autoridad suscrita, compareció personalmente hoy día Elizabeth A. Benham, a quien conozco, y quien sé que es la persona cuyo nombre está en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

DADO BAJO MI FIRMA Y SELLO OFICIAL, hoy día 24 de Mayo, 2004.

[SELEO] (Firmado) Dennis Charles Farinetti

~~38~~
(b)

(Sello Notarial a tinta: Dennis Charles Farinetti, Notario Público Estado de Texas, Comisión vence Noviembre 18, 2006)

Página 3

Expediente No. 210481US01 (4081-05901)

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

(Firmado) Steven J. Secora

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Steven J. Secora, a quien conozco, y quien sé que es la persona cuyo nombre está suscrito en el instrumento anterior, y quien reconoció ante mí que firmó el

NELSON FLORENCE INZABET
NOT A MORTUARY - INDEPENDENT
ENCLOSURE

[Signature] (Firmado) Sherry G. Woods

My condition vence, 2-18-06

Selle Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario

39
162

Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

17941.01/4081.05901

Página 4

PATENTE
RIEL: 015554 MARCO: 0684

Expediente No. 210481US01 (4081-05901)

(LOGO -CEVRON PHILLIPS)

FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: 05-20-04

(Firmado) Michael D. Jensen

Michael D. Jensen

ESTADO DE OKLAHOMA §

CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Michael D. Jensen, a quien conozco, y quien sé que es la persona cuyo nombre está suscrito en el instrumento anterior, y quien reconoció ante mí que firmó el mismo para los fines y por la contraprestación en él expresados.

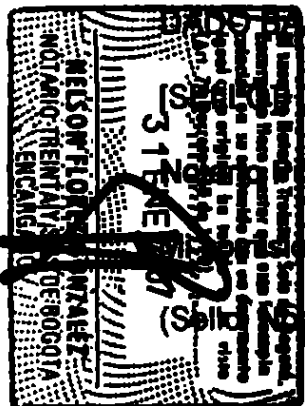
BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.

(Firmado) Sherry G. Woods

Notario Público, Estado de Oklahoma

Comisión vence, 2-18-06

(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario



40
163

Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

17941.01/4081.05901 **Página 5**
PATENTE
RIEL: 015554 MARCO: 0685
Expediente No. 210481US01 (4081-05901)

(LOGO -CEVRON PHILLIPS)
FIRMADO en Bartlesville, Oklahoma, en la fecha escrita a continuación, al frente de mi firma.

Fecha: Mayo 20, 2004 (Firmado) Kathy S. Collins

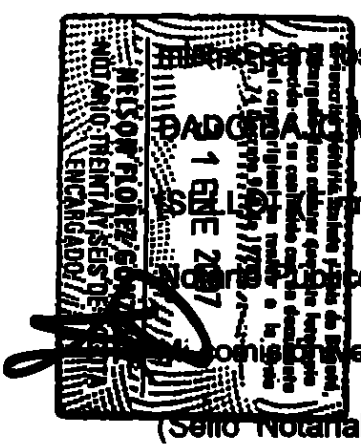
Kathy S. Collins

ESTADO DE OKLAHOMA §
CONDADO DE WASHINGTON §

ANTE MÍ, la autoridad suscrita, compareció personalmente hoy día Kathy S. Collins, a quien conozco, y quien sé que es la persona cuyo nombre está suscrito en el instrumento anterior, y quien reconoció ante mí que firmó el

instrumento para los fines y por la contraprestación en él expresados.
DADO BAJO MI FIRMA Y SELLO OFICIAL, hoy día 20 de Mayo, 2004.

(Firmado) Sherry G. Woods
Sherry G. Woods, Estado de Oklahoma
Comisión vence, 2-18-06



(Sello Notarial a tinta: Sherry G. Woods, Condado de Washington, Notario

TRADUCCION OFICIAL No. _____
JUAN PABLO J. GARCIA
TRADUCTOR E INTERPRETE OFICIAL
Lic. No. 0000000000
DEL MUN. AUTONOMO DE BOGOTA

Público en y para el Estado de Oklahoma, Mi comisión vence, el 18 de Febrero, 2006)

02001756

17941.01/4081.05901
REGISTRADA 07/0/2004

Página 6

PATENTE
RIEL: 015554 MARCO: 0686

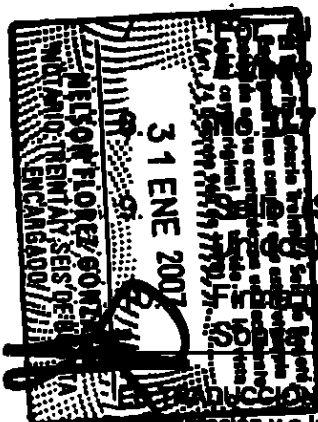
APOSTILLA

(Convención de la Haya de Octubre 5 de 1961)

1. País: *Estados Unidos de América*
Este documento público
2. Ha sido firmado por T. LAWRENCE
3. Obrando en calidad de Funcionario que certifica
4. Lleva el sello/estampilla de Oficina de Patentes y Marcas

CERTIFICADA

5. En Washington D.C.
6. Hoy Ocho de Enero, 2007



Funcionario Asistente de Autenticaciones, Departamento de
de los Estados Unidos

009421-11

Sello en Relieve del Departamento de Estado de los Estados

Firmado)

Stacy N. Johnson

TRANSLACIÓN FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su
comparación y a la cual me remito.
Bogotá, Enero 29, 2007.

TRANSLACION OFICIAL No. 12
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
RES. 718 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUSTICIA



MINISTERIO DE
RELACIONES EXTERIORES

559466
Juan Piedrahíta
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPEÑA
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2007 ENE 30 P 2 02
Juo
JEFE DE LEGALIZACIONES
BOGOTÁ D C

42
165

APOSTILLE
(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by T. Lawrence

3. acting in the capacity of Certifying Officer

4. bears the seal/stamp of Patent and Trademark Office

Certified

5. at Washington, D.C.

6. the eighth of January, 2007

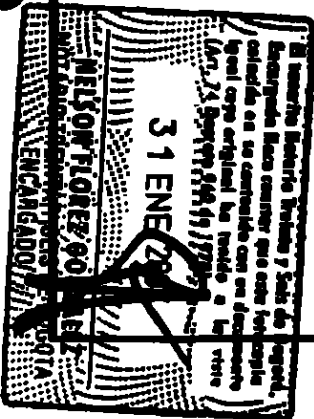
7. by Assistant Authentication Officer, United States Department of State

8. No. 07009421-11

9. Seal/Stamp:

10. Signature:

Sonya N. Johnson



TRADUCCION OFICIAL No. 1000
JUAN FRANCISCO AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
P. 218 DE MAYO 2003
DEL MIN. INTERIOR Y DE JUSTICIA

43
166

A 2840287

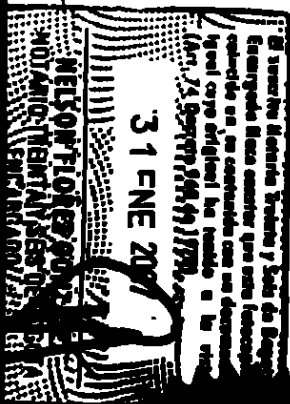
THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

November 09, 2006

THIS IS TO CERTIFY THAT ANNEXED IS A TRUE COPY FROM THE
RECORDS OF THIS OFFICE OF A DOCUMENT RECORDED ON
JULY 9, 2004.



By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office

T. Lawrence

T. LAWRENCE
Certifying Officer

TRADEMARK OFFICIAL No. **97074-939**
RECEIVED BY THE U.S. PATENT AND TRADEMARK OFFICE
TRADITIONAL INVENTOR'S OFFICE
U.S. PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. 20503

167
4/6

[illegible]

U. S. DEPARTMENT OF COMMERCE
Patent and Trademark Office

79.04 PATENTS ONLY

To the Honorable Commissioner of Patents and Trademarks: Please record the attached original documents or copy thereof.

1. Name of conveying parties: Max P. McDaniel Elizabeth A. Benham Steven J. Secora Michael D. Jensen Kathy S. Collins Execution Date 05/20/2004 05/24/2004 05/20/2004 05/20/2004 05/20/2004 Additional name(s) of conveying party(ies) attached? ☐ Yes ☒ No 3. Nature of conveyance: ☒ Assignment ☐ Merger ☐ Security Agreement ☐ Change of Name ☐ Other Execution Date: McDaniel (5/20/04); Benham (5/24/04); Secora (5/20/04); Jensen (5/20/04); Collins (5/20/04)		2. Name and address of receiving party(ies): Name: <u>Chevron Phillips Chemical Company LP</u> Internal Address: _____ Street Address: <u>10001 Six Pines Drive</u> City: <u>The Woodlands</u> State: <u>TX</u> Zip: <u>77380</u> Additional name(s) & address(es) attached? ☐ Yes ☒ No	
4. Application number(s) or patent number(s): If this document is being filed together with a new application, the execution date of the application is : _____ A. Patent Application No.(s). _____ <u>10529-942 filed April 22, 2004</u> Additional numbers attached? ☐ Yes ☒ No			
5. Name and address of party to whom correspondence concerning document should be mailed: Rodney B. Carroll CONLEY ROSE, P.C. Granite Park Two 5700 Granite Parkway, #330 Plano, Texas 75024		6. Total number of application and patents involved: _____ 7. Total fee (37 CFR 3.41) <u>\$ 40.00</u> ☒ Enclosed ☐ Authorized to be charged to deposit account 8. Deposit account number: <u>50-1518</u>	
DO NOT USE THIS SPACE			
Signature. <u>Rodney B. Carroll</u> Name of Person Signing		 Signature <u>7-6-04</u> Date	
Total number of pages including cover sheet, attachments, and documents <u>10/2/04</u>			

DO NOT USE THIS SPACE

Signature

Rodney B. Cantel
Name of Person Submitting

Signature

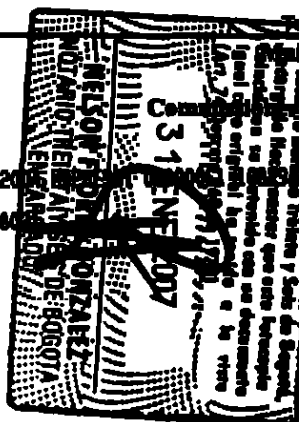
Date _____

Total number of pages including cover sheet, attachments, and documents: 175/200

Documents to be recorded with required cover sheet information is:

Mail Stop Assignment Recordation Services.

Office of US Patent & Trademark Office, P. O. Box 1450, Alexandria, VA, 22313-1450



REEL: 015654 FRAME: 0680

TRADUCCION OFICIAL No. 07 / 039



168
S/S

ASSIGNMENT.

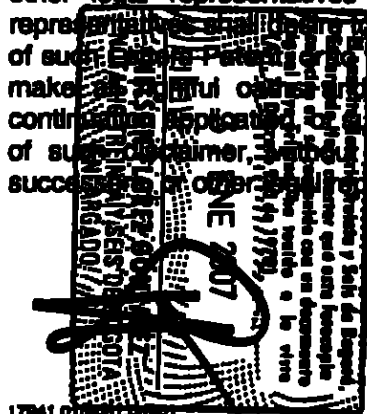
WHEREAS, I, among the following inventors, Max P. McDaniel, Elizabeth A. Benham, Steven J. Secora, Michael D. Jensen and Kathy S. Collins, am an inventor of **POLYMERS HAVING BROAD MOLECULAR WEIGHT DISTRIBUTIONS AND METHODS OF MAKING THE SAME** (the "Invention"), and of an application for United States Patent disclosing said invention, Serial No. 10/829,842, filed April 22, 2004, also known as company docket number 210481US01 (4081-05901); and

WHEREAS, CHEVRON PHILLIPS CHEMICAL COMPANY ("CPCHEM"), a corporation created and existing under and by virtue of the laws of the State of Delaware, is desirous of acquiring the entire right, title and interest in and to the aforesaid Invention throughout the world, and all right, title and interest in, to and under any and all Letters Patent of the United States and all other countries throughout the world;

NOW, THEREFORE, for good and valuable consideration, the receipt of which is hereby acknowledged, I hereby sell, assign, transfer and set over to CPCHEM, all right, title and interest in and to the said Invention throughout the world, and said application for U.S. Letters Patent, and any and all other applications for said Invention, including divisional, continuation, provisional, non-provisional, regular, and reissue applications, and any and all Letters Patent of the United States and foreign countries which may be granted therefor, the same to be held and enjoyed by CPCHEM for its own use and benefit, and for the use and benefit of its successors, assigns, or other legal representatives, to the end of the term or terms for which said Letters Patent of the United States or foreign countries are or may be granted or reissued, as fully and entirely as the same would have been held and enjoyed if this assignment and sale had not been made.

And I hereby authorize and request the Commissioner of Patents and Trademarks to issue any and all Letters Patent of the United States on said Invention or resulting from said application and from any and all divisions, continuations, and reissues thereof, to CPCHEM, as assignee of my entire interest, and hereby covenant that I have the full right to convey the entire interest herein assigned, and that I have not executed and will not execute any agreement in conflict herewith.

And I further hereby covenant and agree that I will, at any time, upon request, execute and deliver any and all papers that may be necessary or desirable to perfect the title of said Invention and to such Letters Patent as may be granted therefor, to CPCHEM, its successors, assigns, or other legal representatives and that if CPCHEM, its successors, assigns or other legal representatives shall desire to file any divisional or continuation applications or to secure a reissue of such Letters Patent or to file a disclaimer relating thereto, I will upon request, sign all papers, make all lawful oaths and do all lawful acts requisite for the filing of such divisional or continuation applications, or such application for reissue and the procuring thereof, and for the filing of such disclaimer, without further compensation but at the expense of said assignee, its successors, or other legal representatives.



PATENT
REEL: 015554 FRAME: 0681

TRADUCCION OFICIAL No. 07 / 039
JUAN R. GARCIA, D. U. L. T. A. G. U. I. L. L. A.



Docket No. 210481US01 (4081-05901)

~~169~~

And I do further covenant and agree that I will, at any time upon request, communicate to CPCHEM, its successors, assigns or other legal representatives, such facts relating to said invention and Letters Patent or the file history thereof as may be known to us, and testify as to the same in any interference or other litigation when requested so to do, without further compensation but at the expense of said assignee, its successors, or other legal representatives.

EXECUTED at Bartholomew Oklahoma, on the date indicated below, opposite my signature.

ASSIGNOR:

Date: May 20 2004

Max P McDaniel

Max P. McDaniel

THE STATE OF OKLAHOMA

§

COUNTY OF WASHINGTON

§

§

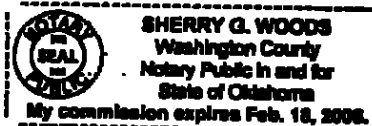
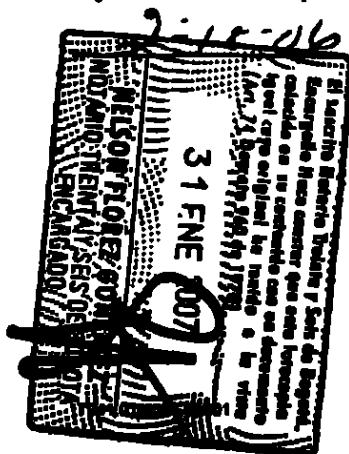
BEFORE ME, the undersigned authority, on this day personally appeared MAX P. MCDANIEL, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:



02001754

Page 2

PATENT
REEL: 015554 FRAME: 0682

TRADUCCION OFICIAL No. 02001754
JUAN PABLO PERAZA ALVARADO
TRADUCTOR E INTERPRETE OFICIAL
del 718 DE MAYO 2003
D.C. 14 - 1 - 2003



170
47

EXECUTED at Kingwood, Texas, on the date indicated below, opposite my signature.

ASSIGNOR:

Date: May 24, 2004

Elizabeth A. Benham
Elizabeth A. Benham

THE STATE OF TEXAS

§
§
§

COUNTY OF HARRIS

BEFORE ME, the undersigned authority, on this day personally appeared ELIZABETH A. BENHAM, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

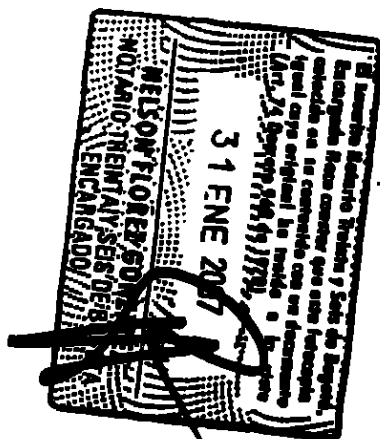
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 24 day of MAY, 2004.

[SEAL]

Dominic Charles Lamm
Notary Public, State of Texas

My Commission Expires:

November 18, 2006



17941.01/4081.05901

Page 3

PATENT
REEL: 015554 FRAME: 0683

TRADUCCION OFICIAL No. 17941.01/4081.05901
JUAN PABLO PIEDRAHITA AGUIRRA
TRADUCTOR E INTERPRETE OFICIAL
RES 718 DE MAYO 2003
C/1



Docket No. 210481US01 (4081-05901)

171
~~178~~

EXECUTED at Bartlesville Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: May 20, 2004

Steven J. Secora
Steven J. Secora

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared STEVEN J. SECORA, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

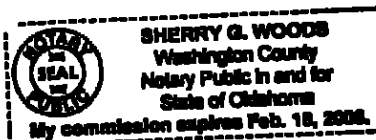
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

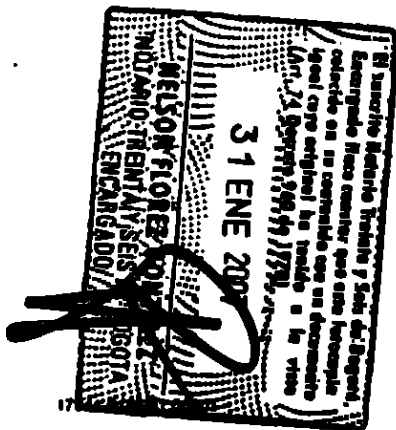
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-06



02001754



Page 4

PATENT
REEL: 015554 FRAME: 0684

TRANSLATION OF
PAULO HERNANDEZ AGUILERA
TRANSLATOR & INTERPRET OFFICIAL



49172

EXECUTED at Bathurst Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: 05-20-04

Michael D Jensen
Michael D. Jensen

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared MICHAEL D. JENSEN, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

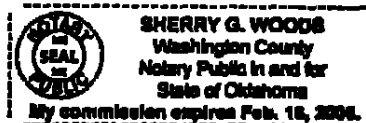
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

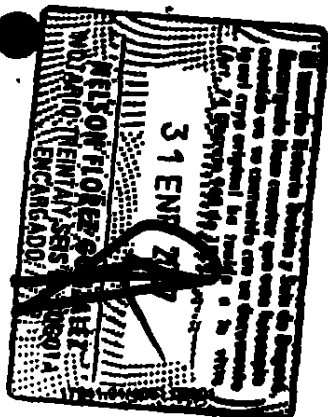
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-06



02001754



PATENT
REEL: 015554 FRAME: 0685

TRADUCCION OFICIAL No. _____
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
C. 173 DE MAYO 2003
DEL MIN. INTERIOR Y DE F. SIG.



Docket No. 210481US01 (4081-05901)

173
S

EXECUTED at Bartlesville Oklahoma, on the date indicated below,
opposite my signature.

ASSIGNOR:

Date: May 20, 2004

Kathy S. Collins
Kathy S. Collins

THE STATE OF OKLAHOMA §
COUNTY OF WASHINGTON §

BEFORE ME, the undersigned authority, on this day personally appeared KATHY S. COLLINS, known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he executed the same for the purposes and consideration therein expressed.

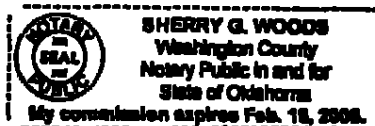
GIVEN UNDER MY HAND AND SEAL OF OFFICE, this the 20 day of May, 2004.

[SEAL]

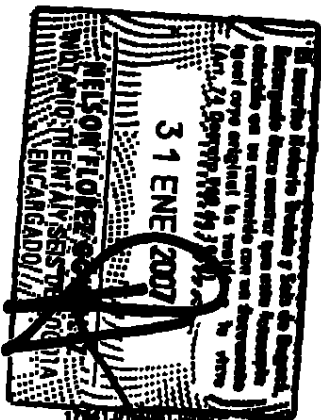
Sherry G. Woods
Notary Public, State of Oklahoma

My Commission Expires:

2-18-06



02001754



Page 6

RECORDED: 07/09/2004

PATENT
REEL: 015554 FRAME: 0686

TRADUCCION OFICIAL No. _____
JUAN P. J. P. D. AHITA AGUILERA
TRADUCCION E INTERPRETE OFICIAL
10 DE MAYO 2003
CEL. MIN. INTERIOR Y DE JUSTICIA

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING
TRANSMITTAL OF COPY OF INTERNATIONAL
PRELIMINARY REPORT ON PATENTABILITY
(CHAPTER I OF THE PATENT COOPERATION
TREATY)
(PCT Rule 44bis.1(c))

To:

BROWN, Kimberly, L.
Chevron Phillips Chemical Company LP
10001 Six Pines Drive
The Woodlands, TX 77380
ETATS-UNIS D'AMERIQUE

RECEIVED

NOV 10 2006

CPC - LEGAL DEPT.

Date of mailing (day/month/year)
02 November 2006 (02.11.2006)

Applicant's or agent's file reference
210481PCT

IMPORTANT NOTICE

International application No.
PCT/US2005/009869

International filing date (day/month/year)
24 March 2005 (24.03.2005)

Priority date (day/month/year)
22 April 2004 (22.04.2004)

Applicant

CHEVRON PHILLIPS CHEMICAL COMPANY LP et al

The International Bureau transmits herewith a copy of the international preliminary report on patentability (Chapter I of the Patent Cooperation Treaty)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Nora Lindner

Facsimile No. +41 22 338 82 70

e-mail: pat2@wipo.int

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44bis)

Applicant's or agent's file reference 210481PCT	FOR FURTHER ACTION	See item 4 below
International application No. PCT/US2005/009689	International filing date (day/month/year) 24 March 2005 (24.03.2005)	Priority date (day/month/year) 22 April 2004 (22.04.2004)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant CHEVRON PHILLIPS CHEMICAL COMPANY LP		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 bis.1(a).

2. This REPORT consists of a total of 10 sheets, including this cover sheet.

In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

- | | |
|--|---|
| ☒ Box No. I | Basis of the report |
| ☐ Box No. II | Priority |
| ☒ Box No. III | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| ☒ Box No. IV | Lack of unity of invention |
| ☒ Box No. V | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| ☐ Box No. VI | Certain documents cited |
| ☐ Box No. VII | Certain defects in the international application |
| ☒ Box No. VIII | Certain observations on the international application |

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44bis.3(c) and 93bis.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44bis .2).

	Date of issuance of this report 25 October 2006 (25.10.2006)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nora Lindner
Facsimile No. +41 22 338 82 70	e-mail: pct@wipo.int

Form PCT/IB/373 (January 2004)

PATENT COOPERATION TREATY

REC'D 31 JAN 2006
WIPO PCT

176
83

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/US2005/009889

International filing date (day/month/year)
24.03.2005

Priority date (day/month/year)
22.04.2004

International Patent Classification (IPC) or both national classification and IPC
C08F10/00, C08F4/22

Applicant
CHEVRON PHILLIPS CHEMICAL COMPANY LP

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of three months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office
D-80335 Munich
Tel. +49 89 2369 - 0 Tx: 523636 epmu d
Fax: +49 89 2369 - 4465

Authorized Officer

Balmer, J-P

Telephone No. +49 89 2369-8520



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

17781
International application No.
PCT/US2005/009669

Box No. 1 Basis of the opinion

1. With regard to the language, this opinion has been established on the basis of the International application in the language in which it was filed, unless otherwise indicated under this item.
☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).
2. With regard to any nucleotide and/or amino acid sequence disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
☐ a sequence listing
☐ table(s) related to the sequence listing
 - b. format of material:
☐ in written format
☐ in computer readable form
 - c. time of filing/furnishing:
☐ contained in the international application as filed.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

178 55
International application No.
PCT/US2005/009669

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 38-54,60-74,76

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for the whole application or for said claims Nos. 38-54,60-74,76

☐ the nucleotide and/or amino acid sequence listing does not comply with the standard provided for in Annex C of the Administrative Instructions in that:

the written form

☐ has not been furnished

☐ does not comply with the standard

the computer readable form

☐ has not been furnished

☐ does not comply with the standard

☐ the tables related to the nucleotide and/or amino acid sequence listing, if in computer readable form only, do not comply with the technical requirements provided for in Annex C-bis of the Administrative Instructions.

☐ See separate sheet for further details

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

17956
International application No.
PCT/US2005/009669

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has:
- ☒ paid additional fees.
 - ☐ paid additional fees under protest.
 - ☐ not paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is
- ☐ complied with
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
 - ☒ the parts relating to claims Nos. 1-34

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	1-37,55-59,75
Inventive step (IS)	Yes: Claims	
	No: Claims	1-37,55-59,75
Industrial applicability (IA)	Yes: Claims	1-37,55-59,75
	No: Claims	

2. Citations and explanations

see separate sheet

Box No. VII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

180 57
International application No.

PCT/US2005/009669

Re Item III.

According to point IV below, only claims 1-34, 55-59, 75 have been searched.
Therefore with regard to Rules 66.1(e) and 66.1 bis (a) PCT this written opinion will be drafted according to the searched claims, namely 1-34 of the present application.

Re Item IV.

The separate inventions or groups of inventions are:

Claims 1-34

A catalyst according to claim 1 and its use according to claim 10.

A method to prepare a supported catalyst according to claim 11.

A method of polymerizing an olefin with a chromium catalyst according to claim 25 and the polymer obtained therewith.

Claims 35-37, 55-59, 75

A polymer composition according to claim 35, its use and article made therewith.

Claims 38-39, 55-59, 75

A polymer composition according to claim 38 its use and article made therewith.

Claims 40-41, 55-59, 75

A polymer composition according to claim 40, its use and article made therewith.

Claims 42-54

A polymer composition according to claim 42

Claims 60-64, 75, 76

A copolymer of ethylene and hexene according to claim 60, its use and article made therewith.

Claims 65-69, 75, 76

A polymer according to claim 65, its use and article made therewith.

Claims 70

A polymer according to claim 70.

Claims 71-72, 75, 76

A polymer according to claim 71, its use and article made therewith.

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

181 58
International application No.

PCT/US2005/009889

Claims 73-76

A polymer according to claim 73, its use and article made therewith.

They are not so linked as to form a single general inventive concept (Rule 13.1 PCT) for the following reasons:

The present application is directed to a chromium based catalyst system using a specific type of cocatalyst, namely a non-transition metal Cp compound (CpLi and Cp2Mg are exemplified).

This in order to prepare polyolefins and in particular copolymers of ethylene and hexene, having a broad molecular weight distribution.

This aspect of the invention is clearly shown in the claims 1-34.

But in addition to the latter claims, the applicant filed a set of independent claims of polymers or polymer compositions (not even restricted to polyolefin as it should be according to the description), which are not related by a single inventive concept.

As example, claim 36 discloses a HLMI range from 1 to 10 g/10min, whereas claim 60 discloses a HLMI range from 15 to 50 g/10min.

These polymers disclosed in these different claims aim to different applications and are linked together simply by the fact that they are "polymers" (or "polymer compositions") which is not an inventive concept as such.

Therefore as the claims 35-76 are not clearly linked to the specific polymerization process using the specific chromium catalyst system as disclosed in the description, the present invention lacks non unity a priori according to the set of inventions disclosed above.

Remark

Novelty and Inventiveness of a product by process can be acknowledged when the product as such cannot be characterized otherwise than by the process to prepare it.

On the other side the claimed products according to claims 34-76 have to be novel and inventive as such, independently from the process to prepare them.

Re Item V.

1. Reference is made to the following documents:

- 182 89
- D1: US-A-3 071 493
D2: WO-A-96/23006
D3: US-A-5 418 200
D4: HEINEMANN, OLIVER ET AL: "Bis(indenyl) chromium is a Dimer"
ORGANOMETALLICS , 15(26), 5462-5483 CODEN: ORGND7; ISSN: 0276-
7333, 1996, XP002335284
D5: LIANG, YUANFENG ET AL: "Constrained Geometry Chromium Catalysts for
Olefin Polymerization" ORGANOMETALLICS , 15(25), 5284-5286 CODEN:
ORGND7; ISSN: 0276-7333, 1996, XP002335285
D6: US-A-2001/004663
D2: US-A-2002/013432
D3: US-A-2003/199648

2. The document D1 discloses a metal plating process using a bimetallic organometallic composition which, as in the examples XXIII and XXIV comprises an aluminum(Cp) part and a Cr(CO)₃ part.

These compounds corresponds to the ones as defined in the present claims 1,2, 7-9, 11.12.

Accordingly D1 is novelty destroying for the present claims 1,2, 7-9, 11.12 with regard to Article 33(2) PCT.

3. The present invention discloses a catalyst system comprising a chromium catalyst which is contacted to a cocatalyst as disclosed in present claim 1.

According to the description presumably the cocatalyst, which is considered as very reactive, will be combined to the chromium atom similarly to the preparation of a Cr(Cp) compound.

Therefore it is strongly assumed, unless the applicant can bring the evidence of the contrary, that the aim of present claim 1 and of the description is in fact the preparation, may be in situ, of a Cr(Cp) catalyst which is already known from the prior art, see D2-D4. In particular D2 discloses in the examples 2-5 such complexes of a chromium atom linked to Cp's and to a non-transition metal (i.e. Lithium).

Therefore, independently from the wording used by the applicant in its invention "cocatalyst" the documents D2-D5 disclose catalyst systems identical to the ones presently disclosed.

Therefore present claims 1-34 are not novel or do not involve an inventive step over D2-D5 with regard to Article 33(2 + 3) PCT.

4. The document D6 discloses in example 9 a copolymer of ethylene and hexene prepared with a chromium-based catalyst wherein both melt index MI and HLMI are within the scope of the ranges disclosed in present claims 35-37. The molecular weight Mw is not explicitly mentioned, only the heterogeneity index, i.e. the polydispersity which is rather high. The document D7 discloses in the examples 1,2,6 a copolymer of ethylene and hexene similarly to D6. The document D8 discloses similar copolymers as in D6 and D7, in particular the examples H-M wherein the Mw is above 600 000 and the HLMI is between 1 and 10 g/10min. The melt index is not mentioned, only the HLMI. Since the ratio HLMI/MI (i.e. MFR = melt flow ratio) in D6 and D7 and the ratio Mw/Mn (i.e. polydispersity) in D8 are very high it is strongly assumed that the Mw in D6, D7 and the MI in D8 will be within the scope of present claims 35-37. This is supported by the sole inventive example of the present application being within the scope of claims 35-37, namely run 16 of table 3, which shows a high polydispersity together with a high MFR. Accordingly unless the applicant can unambiguously demonstrate that D6-D8 are not within the scope of the present claims 35-37, the examining division will consider D6-D8 as novelty destroying of present claims 35-37, 55-59,75 with regard to Article 33(2) PCT.

Re Item VIII

1. In example 1, p.16,l.13 there is written "runs 2 and 3 were run using different amounts of the", this is not correct. Further on l.17-18 the effect of the absence of hydrogen is not demonstrated, according to table 1.
2. In table 2, runs 5 and 6 show a reduction of the PDI when hydrogen is introduced during the polymerization, this is strange. Explanation is requested. Further, run 12 does not show any analysis of the polymer, despite the fact that this is the sole run without the use of hydrogen....Why ????
3. On page 13 the Charpy measurement of energy is mentioned at 0°C, but in table 7 this is done at 23°C why ????. What is the standard?
4. On table 7 the measurement of the shear rate is somehow very high compared to the

prior art, nearly 5 times higher. There must be an error somewhere. Also the definition of this measurement is not clear for the skilled man to be reproduced correctly.

5. Example 6 relates to figure 2, but in example 6 $Mg(Cp)_2$ is used, contrary to what is disclosed in figure 2 (CpLi) ????
6. In table 6, runs 10 and 11 show a rather bad Charpy performance, why ???
Further the Charpy energy should be expressed with J/m² and not J/m Isn't it ???
7. According to the examples the chromium catalyst is always supported and with a reduced oxidation state, so should it be mentioned in the claims as well, as the applicant could not prove anything for his invention for other chromium type catalysts.....
8. Certain claims (see claims 35,36,57 in particular) recite only a polymer or a polymer composition as such, together with different parameter like MI or HLMI. Depending of the type of polymer meant the MI or HLMI method used will differ, for example in temperature or load.
Accordingly as matter of clarity the applicant should draft his claims in order to define clearly the method used to determine the characteristics in relation to the type of polymer covered by the said claim.
~~In all cases the polymer composition of claim 35 should be reduced at least to a polyolefin composition which is what was achieved in the description.~~
9. The units used in particular on page 23 and 25 should be in accordance with the International unit system.

PATENT COOPERATION TREATY

110.4.11

cat/26/RF
18562

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

CHEVRON PHILLIPS CHEMICAL
COMPANY LP
Attn. Brown, Kimberly L.
10001 Six Pines Drive
The Woodlands, Texas 77380
UNITED STATES OF AMERICA

FEB - 6 2006

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Date of mailing (day/month/year)	30/01/2006
Applicant's or agent's file reference	210481PCT
FOR FURTHER ACTION	See paragraphs 1 and 4 below
International application No.	PCT/US2005/009669
International filing date (day/month/year)	24/03/2005
Applicant	CHEVRON PHILLIPS CHEMICAL COMPANY LP
DOCKETED	PCT 210481PCT
DUE	4/30/06 US

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 18:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 48):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the International Search Report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 338.82.70

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.
3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.
- ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Reminders

Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within 18 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 30 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 18 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the PCT Applicant's Guide, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Corine Le Bolloch

NOTES TO FORM PCT/ISA/220

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These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the letter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume I/A, paragraph 296).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 48.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 48.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

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The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/PEA/401).

If a demand for international preliminary examination is made, the written opinion of the International Searching Authority will, except in certain cases where the International Preliminary Examining Authority did not act as International Searching Authority and where it has notified the International Bureau under Rule 68.1bis(b), be considered to be a written opinion of the International Preliminary Examining Authority. If a demand is made, the applicant may submit to the International Preliminary Examining Authority a reply to the written opinion together, where appropriate, with amendments before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later (Rule 43bis.1(c)).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicant's Guide*, Volume II.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 210481PCT	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, Item 5 below.	
International application No. PCT/US2005/009669	International filing date (day/month/year) 24/03/2005	(Earliest) Priority Date (day/month/year) 22/04/2004
Applicant CHEVRON PHILLIPS CHEMICAL COMPANY LP		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 7 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ Certain claims were found unsearchable (See Box II).

3. ☒ Unity of invention is lacking (see Box III).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

CHROMIUM BASED POLYMERIZATION CATALYST, THE METHOD TO PREPARE IT AND POLYMERS PREPARED THEREWITH

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

- a. the figure of the drawings to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☒ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/009669

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A. CLASSIFICATION OF SUBJECT MATTER
C08F10/00 C08F4/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 071 493 A (WHALEY THOMAS P ET AL) 1 January 1963 (1963-01-01) ✓ the whole document	1-24
X	WO 96/23006 A (CHEVRON CHEMICAL COMPANY) 1 August 1996 (1996-08-01) ✓ the whole document	1-34
X	US 5 418 200 A (CARNEY ET AL) 23 May 1995 (1995-05-23) ✓ the whole document	1-34
X	HEINEMANN, OLIVER ET AL: "B1s(1ndeny1) chromium Is a Dimer" ORGANOMETALLICS, 15(26), 5462-5463 CODEN: ORGN7; ISSN: 0276-7333, 1996, XP002335284 the whole document	1-34
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"A" document member of the same patent family

Date of the actual completion of the international search

18 January 2006

Date of mailing of the international search report

30.01.2006

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentkan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-3040, Tx. 31 681 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Balmer, J-P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/009669

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIANG, YUANFENG ET AL: "Constrained Geometry Chromium Catalysts for Olefin Polymerization" ORGANOMETALLICS , 15(25), 5284-5286 CODEN: ORGND7; ISSN: 0276-7333, 1996, XP002335285 the whole document	1-34
X	US 2001/004663 A1 (BERGMEISTER JOSEPH J ET AL) 21 June 2001 (2001-06-21) example 9	35-37, 55-59,75
X	US 2002/013432 A1 (MCDANIEL MAX P ET AL) 31 January 2002 (2002-01-31) examples 1,2,6	35-37, 55-59,75
X	US 2003/199648 A1 (MCDANIEL MAX P ET AL) 23 October 2003 (2003-10-23) examples H-M	35-37, 55-59,75

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/009669

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3071493	A	01-01-1963	NONE	
WO 9623006	A	01-08-1996	AU 4860896 A	14-08-1996
US 5418200	A	23-05-1995	CA 2063090 A1 MX 9201390 A1	30-09-1992 01-10-1992
US 2001004663	A1	21-06-2001	AU 2031400 A CA 2349834 A1 EP 1192188 A1 WO 0032640 A1 US 6201077 B1	19-06-2000 08-06-2000 03-04-2002 08-06-2000 13-03-2001
US 2002013432	A1	31-01-2002	AU 2923301 A CA 2390617 A1 CN 1402738 A EP 1240208 A1 HU 0203866 A2 NO 20022250 A WO 0134661 A1	06-06-2001 17-05-2001 12-03-2003 18-09-2002 28-04-2003 09-07-2002 17-05-2001
US 2003199648	A1	23-10-2003	WO 2004076499 A1 US 2003236366 A1 US 6525148 B1	10-09-2004 25-12-2003 25-02-2003

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2005/009669

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Box II Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 8.4(a).

Box III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
1-37, 55-59, 75
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-34

A catalyst according to claim 1 and its use according to claim 10.

A method to prepare a supported catalyst according to claim 11.

A method of polymerizing an olefin with a chromium catalyst according to claim 25 and the polymer obtained therewith.

2. claims: 35-37, 55-59, 75

A polymer composition according to claim 35, its use and article made therewith.

3. claims: 38-39, 55-59, 75

A polymer composition according to claim 38 its use and article made therewith.

4. claims: 40-41, 55-59, 75

A polymer composition according to claim 40, its use and article made therewith.

5. claims: 42-54

A polymer composition according to claim 42

6. claims: 60-64, 75, 76

A copolymer of ethylene and hexene according to claim 60, its use and article made therewith.

7. claims: 65-69, 75,76

A polymer according to claim 65, its use and article made therewith.

8. claim: 70

A polymer according to claim 70.

9. claims: 71-72,75,76

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

A polymer according to claim 71, its use and article made therewith.

10. claims: 73-76

A polymer according to claim 73, its use and article made therewith.

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1. The present communication is an Annex to the Invitation to pay additional fees (Form PCT/ISA/206). It shows the results of the international search established on the parts of the international application which relate to the invention first mentioned in claims Nos.:

see 'Invitation to pay additional fees'
2. This communication is not the international search report which will be established according to Article 18 and Rule 43.

3. If the applicant does not pay any additional search fee, the information appearing in this communication will be considered as the result of the international search and will be included as such in the international search report.

4. If the applicant pays additional fees, the international search report will contain both the information appearing in this communication and the results of the international search on other parts of the international application for which such fees will have been paid.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 071 493 A (WHALEY THOMAS P ET AL) 1 January 1963 (1963-01-01) the whole document	1-24
X	WO 96/23006 A (CHEVRON CHEMICAL COMPANY) 1 August 1996 (1996-08-01) the whole document	1-34
X	US 5 418 200 A (CARNEY ET AL) 23 May 1995 (1995-05-23) the whole document	1-34
X	HEINEMANN, OLIVER ET AL: "Bis(indenyl) chromium Is a Dimer" ORGANOMETALLICS, 15(26), 5462-5463 CODEN: ORGND7; ISSN: 0276-7333, 1996, XP002335284 the whole document	1-34
X	LIANG, YUANFENG ET AL: "Constrained Geometry Chromium Catalysts for Olefin Polymerization" ORGANOMETALLICS, 15(25), 5284-5286 CODEN: ORGND7; ISSN: 0276-7333, 1996, XP002335285 the whole document	1-34

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

146 21

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-34

A catalyst according to claim 1 and its use according to claim 10.

A method to prepare a supported catalyst according to claim 11.

A method of polymerizing an olefin with a chromium catalyst according to claim 25 and the polymer obtained therewith.

2. claims: 35-37, 55-59, 75

A polymer composition according to claim 35, its use and article made therewith.

3. claims: 38-39, 55-59, 75

A polymer composition according to claim 38 its use and article made therewith.

4. claims: 40-41, 55-59, 75

A polymer composition according to claim 40, its use and article made therewith.

5. claims: 42-54

A polymer composition according to claim 42

6. claims: 60-64, 75, 76

A copolymer of ethylene and hexene according to claim 60, its use and article made therewith.

7. claims: 65-69, 75, 76

A polymer according to claim 65, its use and article made therewith.

8. claim: 70

A polymer according to claim 70.

9. claims: 71-72, 75, 76

A polymer according to claim 71, its use and article made therewith.

10. claims: 73-76

A polymer according to claim 73, its use and article made therewith.

The present application is directed to a chromium based catalyst system using a specific type of cocatalyst, namely a non-transition metal Cp compound (CpLi and Cp2Mg are exemplified).

This in order to prepare polyolefins and in particular copolymers of ethylene and hexene, having a broad molecular weight distribution. This aspect of the invention is clearly shown in the claims 1-34. But in addition to the latter claims, the applicant filed a set of independent claims of polymers or polymer compositions (not even restricted to polyolefin as it should be according to the description), which are not related by a single inventive concept.

As example, claim 36 discloses a HLMI range from 1 to 10 g/10min, whereas claim 60 discloses a HLMI range from 15 to 50 g/10min.

These polymers disclosed in these different claims aim to different applications and are linked together simply by the fact that they are "polymers" (or "polymer compositions") which is not an inventive concept as such.

Therefore as the claims 35-76 are not clearly linked to the specific polymerization process using the specific chromium catalyst system as disclosed in the description, the present invention lacks non unity a priori according to the set of inventions disclosed above.

Remark

Novelty and inventiveness of a product by process can be acknowledged when the product as such cannot be characterized otherwise than by the process to prepare it.

On the other side the claimed products according to claims 34-76 have to be novel and inventive as such, independently from the process to prepare them.

Patent Family Annex

Information on patent family members

International Application No

PCT/US2005/009669

198 2/3

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3071493	A	01-01-1963	NONE
WO 9623006	A	01-08-1996	AU 4860896 A WO 9623006 A1
US 5418200	A	23-05-1995	AT 168700 T CA 2108860 A1 DE 69319837 D1 DE 69319837 T2 EP 0595182 A1 US 5684100 A CA 2063090 A1 MX 9201390 A1 AT 153034 T DE 69219668 D1 DE 69219668 T2 EP 0509294 A2 ES 2101765 T3 JP 2759016 B2 JP 6145233 A
			15-08-1998 21-04-1994 27-08-1998 03-12-1998 04-05-1994 04-11-1997 30-09-1992 01-10-1992 15-05-1997 19-06-1997 11-09-1997 21-10-1992 16-07-1997 28-05-1998 24-05-1994

Important Information

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General

- The **claims cannot be changed** at this point in the procedure, the transmitted report is **not** the international search report (see Art. 19 PCT).
- Any payment has to be made **directly** to this ISA, payments to other entities will not be accepted.
- In case of a **total of more than 2 inventions** found: when paying please **specify exactly** which claims should be searched.
- An **extension of the set time limit** cannot be granted.

Payment by cheque:

- The **date to be considered as the date on which the payment is made** is the **date of receipt of the cheque at the EPO**, provided that the cheque is met.
- Copies of cheques sent by fax or by post are not considered to be a valid payment.
- The fees shall be paid in euro, no equivalents in other currencies.

Payment or transfer to a bank account:

- The **date to be considered as the date on which the payment is made** is the date on which the amount of the payment or the transfer is **actually entered** in a bank account or Giro account held by the EPO.
- The fees shall be paid in euro, no equivalents in other currencies.

Payment by deposit account:

- The **date to be considered as the date on which the payment is made** is the date that the **authorisation to deduct fees from the deposit account is received at the EPO**.

Note: If you don't have a deposit account with the EPO yourself you might want to consider using the account of an associate as a safe and quick way of paying.

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- Payments by **credit card** are **not possible**.

Payments under protest according to Rule 40 PCT:

- The protest will **not be accepted without a payment** of additional fees.
- The protest has to be **accompanied by a technical reasoning**.

200 75

Important Information

Rule 40 PCT has been amended as of 1 April 2005. For general information on the protest procedure under the PCT please refer to OJ EPO 3/2005, pages 226/227.

1. As in the past the payment of any additional fee may be made under protest i.e. accompanied by a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fees is excessive according to amended Rule 40.2(c) PCT.
2. Although no longer obligatory, prior to examination of the protest by the Board of Appeal the EPO will subject the invitation to pay additional fees to an internal review which is free of charge. The result of this review will be communicated to the applicant.
3. The fee for examination of the protest (Rule 40.2(e) PCT) is payable within one month of the date of the invitation to pay additional fees (Rule 40.1(III) PCT), however, in order to allow the applicant to consider the result of the internal review, the applicant may pay the protest fee within one month from the date of notification of the result of the review.
4. Should the applicant wish to maintain his protest in light of the review he must pay the protest fee within one month from the date of notification of the result of the internal review, in which case the protest will be referred to the Board of Appeal. Should the Board of Appeal find that the protest was entirely justified, the protest fee shall be refunded.
5. In the event of the applicant already having paid the protest fee before notification of the result of the review, the protest will be referred to the Board of Appeal unless the result of the internal review was that the protest was entirely justified or the applicant indicates within one month from the date of notification of the result of the review that he does not wish to continue the protest, in both cases the protest fee will be refunded.

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(54) OLEFIN POLYMERS, METHOD OF MAKING, AND USE THEREOF

(57) ABSTRACT

(76) Inventors: Max P. McDaniel, Bartlesville, OK (US); Elizabeth A. Benham, Spring, TX (US); Al R. Wolfe, Bartlesville, OK (US); Paul J. DeLauriers, Bartlesville, OK (US); Pamela L. Menger, Bartlesville, OK (US); William R. Constant, Bartlesville, OK (US); David C. Rohlfing, Bartlesville, OK (US); Steven J. Secora, Bartlesville, OK (US)

Correspondence Address:

JOHN S. PRATT
KILPATRICK STOCKTON LLP (CHEVRON)
1100 PEACHTREE STREET
SUITE 2800
ATLANTA, GA 30309 (US)

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Related U.S. Application Data

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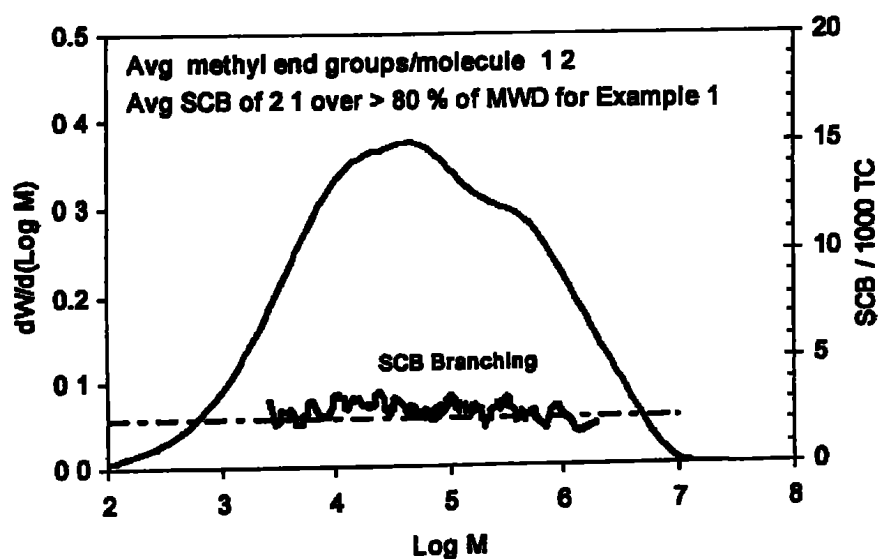
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526/348.6

The present invention is directed to homo-polymers and copolymers of mono-1-olefins, a method of making such polymers, and uses of such polymers. Polymers of the present invention are formed by contacting, at least one mono-1-olefin having from 2 to about 20 carbon atoms per molecule and at least one mono-1-olefin co-monomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. The catalyst system of the present invention comprises a chromium source on an aluminophosphate support which has a phosphorous to aluminum mole ratio of less than about 0.3. Further, the catalyst system is treated with less than about 7 weight percent fluorides based on the weight of the support and is calcined. Cocatalysts are selected from trialkylboron compounds, triarylboron compounds, alkylaluminum compounds, and combinations thereof.

In another aspect of the present invention, ethylene copolymers are employed to produce PE-100 pipe. These copolymers are formed by contacting ethylene with at least one mono-1-olefin comonomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. Additionally, the comonomers may be selected from mono-1-olefins having 4 to 10 carbon atoms, such as, 1-hexene, 1-butene, 4-methyl-1-pentene, 1-octene, and 1-decene. Further, these ethylene copolymers may be employed to produce PE-100 pipe having both small diameters and diameters in excess of 42 inches substantially without sagging or other gravitational deformation. Copolymers of ethylene and 1-hexene are disclosed which are used to produce PE-100 pipe.

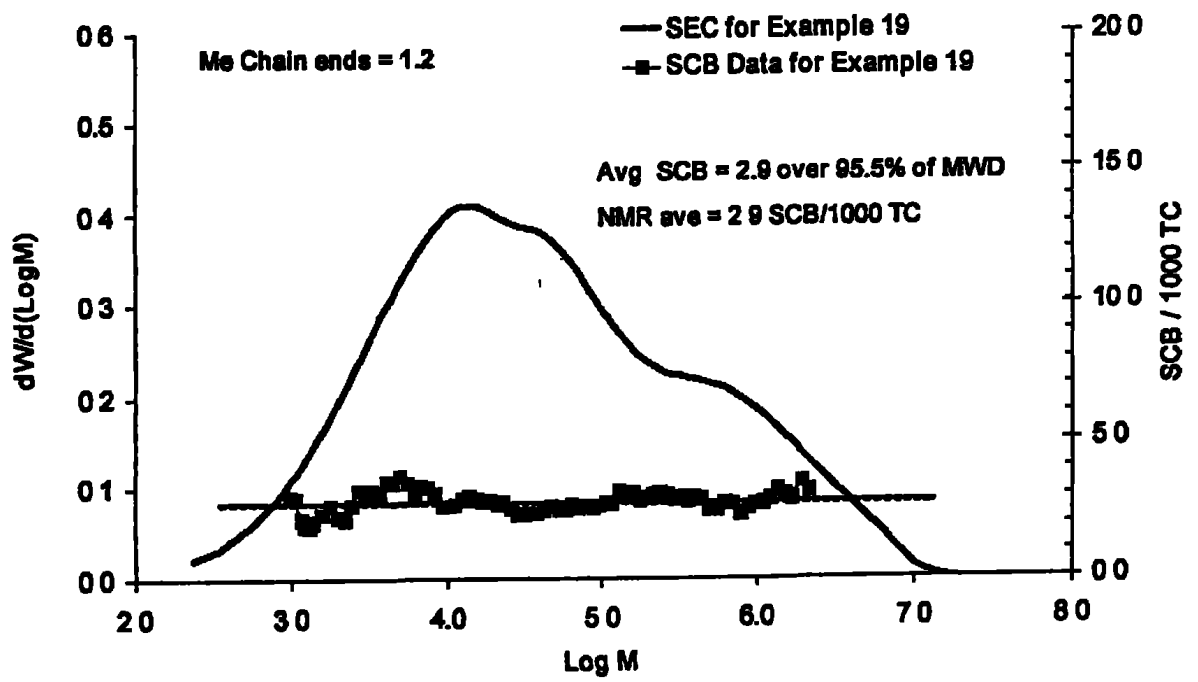
Figure 1



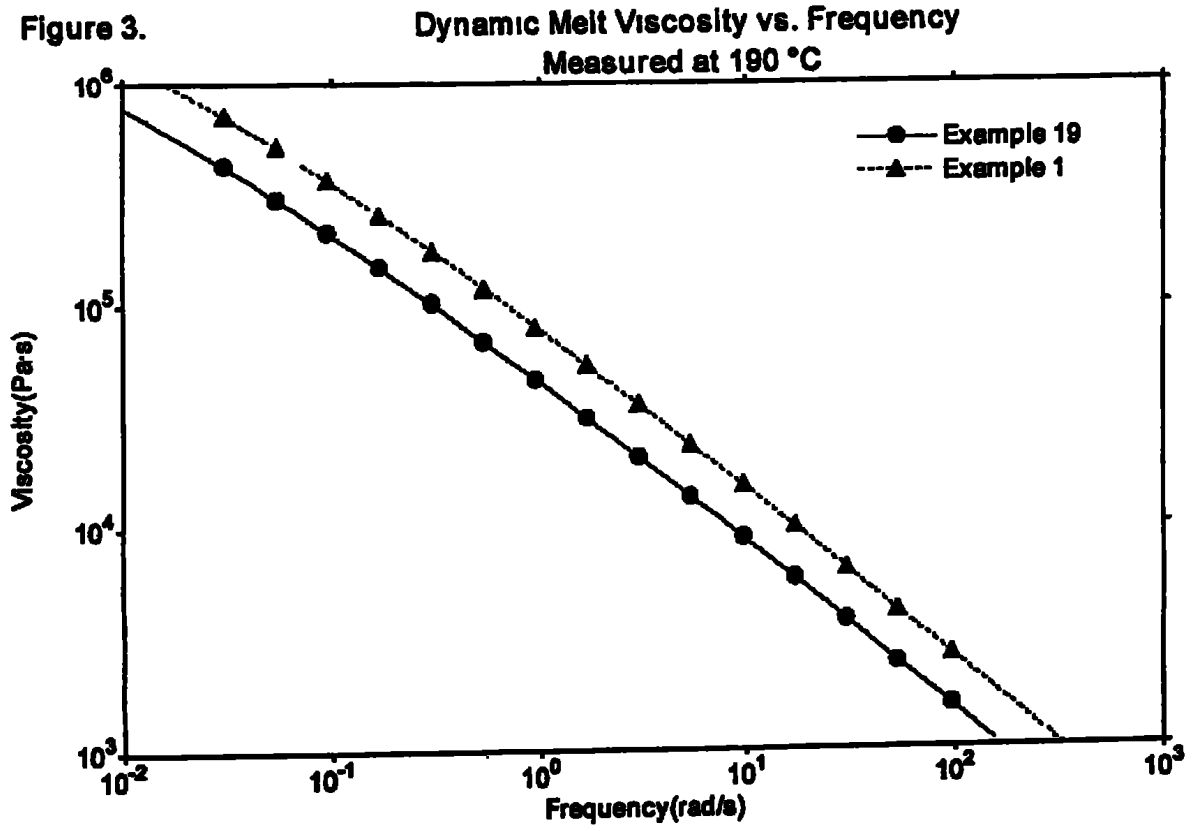
SEC-FTIR

Mw (g/mol)	Mn (g/mol)	Mz (g/mol)	PDI
410,000	7,200	2,800,000	57

Figure 2.



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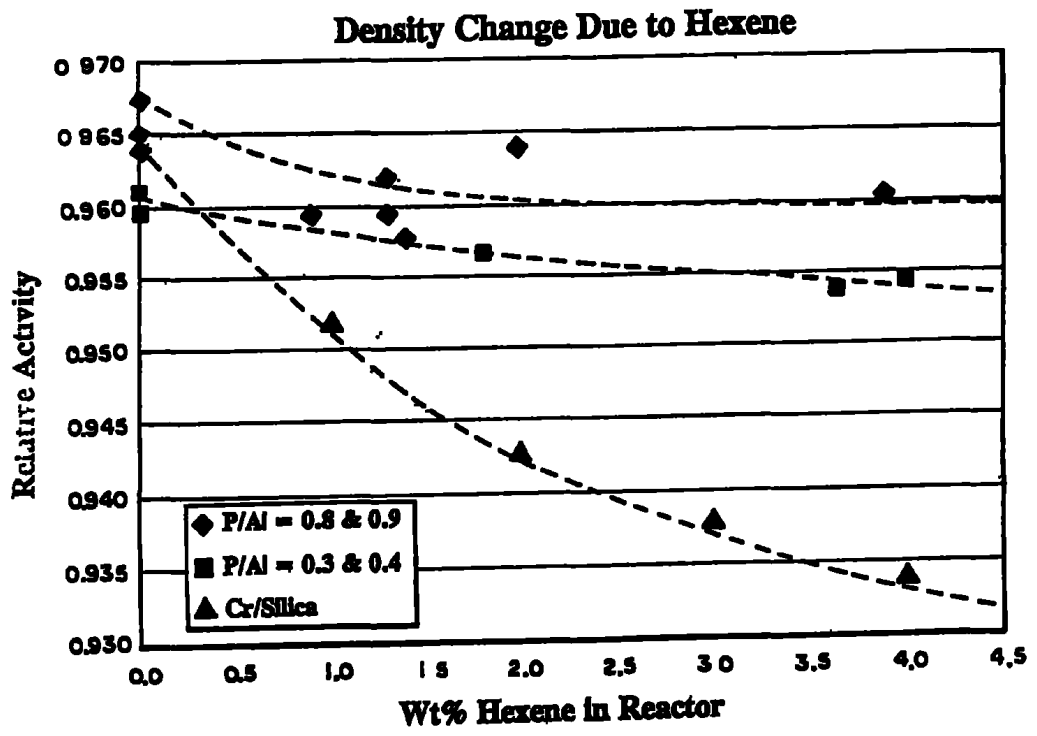


Figure 4

88

86

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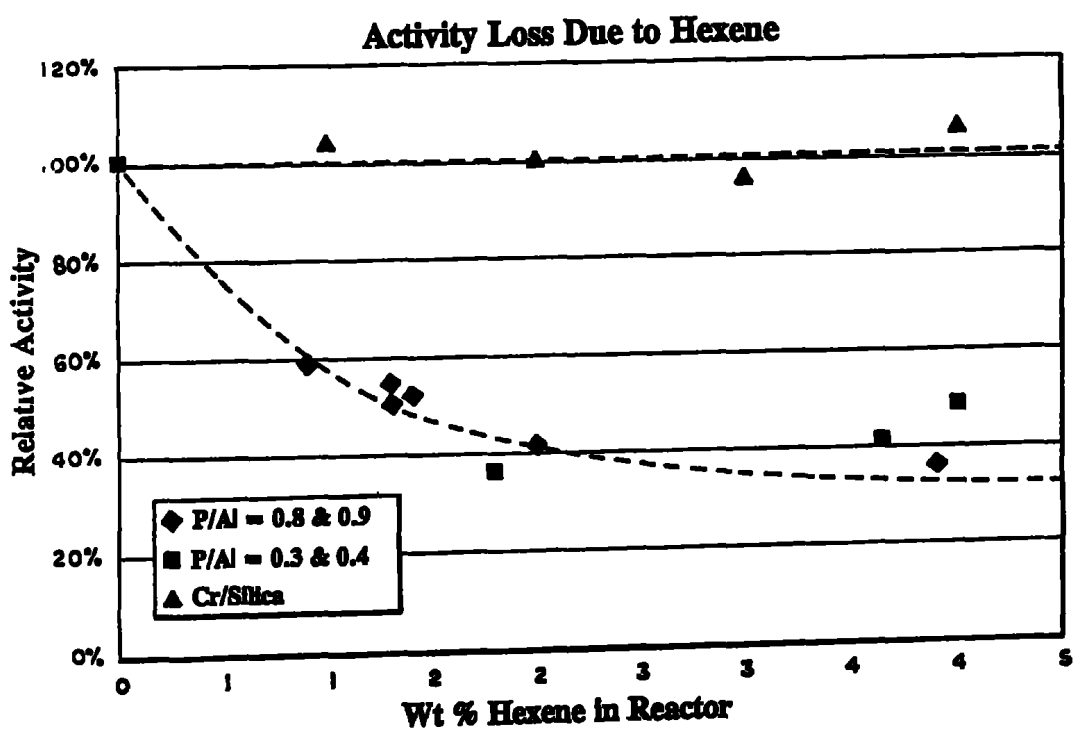


Fig. 5

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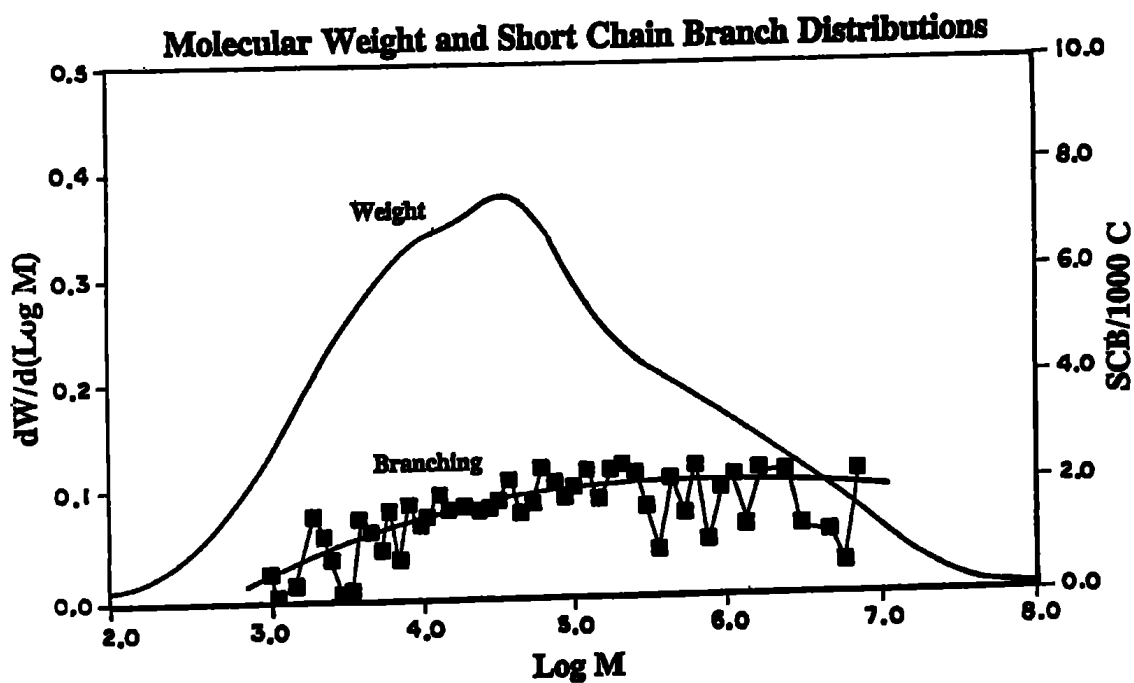


Fig. 6

OLEFIN POLYMERS, METHOD OF MAKING, AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of co-pending U.S. patent application Ser. No. 09/640,868 filed Aug. 18, 2000.

FIELD OF THE INVENTION

[0002] The present invention relates to polyolefin compositions, methods for producing polyolefin compositions, articles of manufacture using polyolefin compositions, and processes for producing articles of manufacture using polyolefin compositions. More particularly, the present invention relates to mono-1-olefin homo- and copolymer compositions, methods for producing such compositions, articles of manufacture using such compositions, and processes for producing articles of manufacture using such compositions.

BACKGROUND OF THE INVENTION

[0003] Presently, various resins are used to produce numerous types and styles of pipe. For example, polyethylene resins have long been used to produce high stiffness pipe used in water, gas, and other fluid transport applications. Polyethylene pipe classified as PE-100, MRS 10, or ASTM D3350 typical cell classification 345566C is especially desirable for use under conditions requiring higher pressure ratings. The higher pressure ratings are due in part to the pipe's higher stiffness. To obtain a PE-100 classification, PE-100 pipe is required to meet certain standards specifying stiffness, resistance to chemical attack, and brittleness, as expressed as rapid crack propagation under cold temperature environments or applications. Further, such pipe must meet a deformation standard which is determined under pressure at elevated temperatures.

[0004] Although certain PE-100 classified polyethylene resins are commercially available, these polyethylene resins are the "bimodal" type. Bimodal polyethylene resins are made in reactor systems involving two or more reaction zones or by blending two or more distinct polymers. Unfortunately, despite the excellent toughness of these resins, bimodal resins are found to be deficient when pipe is formed by extrusion under certain conditions. Typically, bimodal resins perform adequately in the production of standard, small diameter pipe, that is, pipe having diameters between 1-12 inches. However, when forming large diameter and/or thick-walled pipe, the bimodal resins begin to "sag" or "slump" as the newly formed pipe emerges from the extrusion die. Apparently, the still semi-molten polymer does not have sufficient melt strength during the short time before the pipe cools and hardens to resist deformation due to gravitational force. This phenomenon causes an inconsistency in the pipe which results in the lower portion of the pipe to be thicker and heavier than the upper portion. A pipe manufacturer can compensate to some degree by adjusting the die to form pipe that is "out of round" as it exits the die, so that it subsequently sags back into a better balance. However, such adjustments are complicated, and the degree to which the pipe manufacturer can compensate for "sag" is limited. As a result, currently available PE-100 classified resins are typically used only to produce small diameter pipe. Accord-

ingly, there is a need for a PE-100 classified resin which can be employed to produce both small and large diameter PE-100 pipe.

[0005] During the production of high density olefin polymers or resins, such as high density polyethylene, conventional supported chromium catalyst systems may be employed. However, as originally commercialized, use of these conventional supported chromium catalyst systems are limited. Typically, the conventional supported chromium catalyst systems are used in solution polymerization processes. A more economical route to produce many grades of commercial olefin polymers employs a slurry process. In the slurry process, the polymerization reaction employs one or more monomers in the presence of a diluent and the catalyst system. Beneficially, the polymerization reaction occurs in the slurry process at a temperature which is sufficiently low to permit the resulting polymer to be largely insoluble in the diluent. However, as explained below, conventional supported chromium catalyst systems are undesirable for use in a slurry process to produce a PE-100 classified resin. Accordingly, there is a need for a supported chromium catalyst system which may be employed in a slurry process to produce a PE-100 classified resin.

[0006] Currently, mono-1-olefins, such as ethylene, are polymerized with catalyst systems employing transition metals such as titanium, vanadium, chromium, or other metals, either unsupported or on a support, such as alumina, silica, aluminophosphate, titania, zirconia, magnesia, and other refractory metals. Such catalyst systems are used to form homopolymers of ethylene. Additionally, comonomers such as propylene, 1-butene, 1-hexene, or other higher mono-1-olefins may be copolymerized with ethylene to provide resins tailored to specific end uses.

[0007] Polymers having broad molecular weight distributions and improved physical properties, such as environmental stress crack resistance (ESCR), slow crack growth resistance (PENT), and impact resistance, can be formed by employing chromium catalyst systems containing aluminophosphate supports, to include alumina (Al_2O_3). For example, polymers having a molecular weight distribution (M_w/M_n) of up to 30 can be obtained with aluminophosphate supported catalyst systems. Aluminophosphate supports are characterized by the amount of phosphate in the support, or more precisely, by the phosphorus to aluminum molar ratio (P/Al) of the composition. The P/Al molar ratio can vary from 0, e.g. alumina, to 1 for stoichiometric aluminum phosphate ($AlPO_4$). At a P/Al molar ratio of 1, a crystalline solid of very little surface area and minimal pore volume is obtained. As a result, the activity of catalyst systems employing an aluminophosphate support having a P/Al ratio of 1 is minimal. Additionally, catalyst systems employing chromium supported on alumina also have a very low activity. Therefore, in practice, the commercially preferred P/Al molar ratio of phosphorus to aluminum in chromium/aluminophosphate catalyst systems is 0.7 to 0.9. See *The Structure of Coprecipitated Aluminophosphate Catalyst Supports*; T. T. P. Cheung, K. W. Wilcox, M. P. McDaniel, and M. M. Johnson; *Journal of Catalysis*, Vol. 102, p. 10-20 (1986).

[0008] Below a P/Al molar ratio of 0.3, the activity is considered too low to be practical. Yet, catalyst systems employing aluminophosphate supports having such lower

P/Al molar ratios produce polymers which desirably have the broadest molecular weight distributions, and thus, the highest ESCR and impact resistance values. Another disadvantage of conventional chromium/aluminophosphate catalyst systems is that they incorporate certain comonomers, such as 1-hexene, very poorly. In conventional processes, 1-hexene can kill the activity of chromium/aluminophosphate catalyst systems. Thus, while conventional chromium/aluminophosphate catalyst systems are excellent for producing very high density blow molding resins, such catalyst systems have not gained acceptance for the commercial production of lower density copolymers which are used to produce film and pipe.

[0009] Despite existing catalyst systems, methods, and resins, a need exists for improved catalyst systems, methods, and resins for producing PE-100 pipe. It is to the provision of catalyst systems, methods, and resins that meet these needs that the invention is primarily directed.

[0010] This invention also relates to polyolefin compositions, methods for producing polyolefin compositions, and to processes for using polyolefin compositions for producing pipe. More specifically this invention relates to the production of PE-100 classification polyethylene pipe and the resin used to make that pipe.

[0011] This invention relates to the polymerization and copolymerization of a mono-1-olefin, such as ethylene, with a higher alpha-olefin comonomer, such as 1-hexene.

[0012] This invention further relates to producing cost-effective ethylene polymers and copolymers of exceptional toughness, which can be processed into large diameter pipe without the distortion caused by the commonly observed "sag" or "slumping" phenomenon during extrusion.

[0013] The present invention describes a new type of PE-100 polyethylene resin which does not exhibit the slumping behavior, and which can, for the first time, be used to produce very large diameter pipe without problem. The present invention also describes the unique catalyst system that is used to produce this polymer in a single reaction zone, which means that the resin can be manufactured more efficiently than the common "bimodal" type resins.

SUMMARY OF THE INVENTION

[0014] The present invention is directed to homo-polymers and copolymers of mono-1-olefins, a method of making such polymers, and uses of such polymers. Polymers of the present invention are formed by contacting at least one mono-1-olefin having from 2 to about 20 carbon atoms per molecule and at least one mono-1-olefin co-monomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. The catalyst system of the present invention comprises a chromium source on an aluminophosphate support which has a phosphorous to aluminum mole ratio of less than about 0.3. Further, the catalyst system is treated with less than about 7 weight percent fluoride based on the weight of the support and is calcined. Cocatalysts are selected from trialkylboron compounds, triarylboron compounds, alkylaluminum compounds, and combinations thereof.

[0015] In another aspect of the present invention, ethylene copolymers are employed to produce PE-100 pipe. These

copolymers are formed by contacting ethylene with at least one mono-1-olefin comonomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. Additionally, the comonomers may be selected from mono-1-olefins having 4 to 10 carbon atoms, such as, 1-hexene, 1-butene, 4-methyl-1-pentene, 1-octene, and 1-decene. Such inventive ethylene copolymers have a molecular weight distribution (M_w/M_n) greater than about 50 and a substantially constant branch distribution profile at molecular weights greater than about 1×10^4 . Further, these ethylene copolymers may be employed to produce PE-100 pipe having both small diameters and diameters in excess of 42 inches substantially without sagging or other gravitational deformation. The ethylene copolymers of the present invention have a high load melt index (HLMI) within a range of about 0.5 to about 10 g/10 minutes, a density within a range of about 0.945 to about 0.955 g/cc, a molecular weight distribution (M_w/M_n) greater than about 50, a PENT slow crack growth resistance value of greater than about 1000 hours, and a branch profile of greater than about 1 branch/1000 carbons at 1 million molecular weight.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The following is a brief description of the Figures.

[0017] FIG. 1 is a graph illustrating the substantially constant short chain branch distribution across the molecular weight distribution of the PE-100 polyethylene copolymer made in accordance with the present invention in Example 1.

[0018] FIG. 2 is a graph further illustrating the substantially constant short chain branch distribution across the molecular weight distribution of the PE-100 polyethylene copolymer made in accordance with the present invention in Example 19, even though the molecular weight profile is considerably different from that shown for Example 1.

[0019] FIG. 3 is a graph showing typical rheology curves at 190° C. of the inventive polyethylene copolymers as demonstrated by Examples 1 and 19.

[0020] FIG. 4 is a graph of polymer density (g/cc) vs. weight percent 1-hexene in the reactor.

[0021] FIG. 5 is a graph of the relative activity of the catalyst system (g/g/h) vs. weight percent 1-hexene in the reactor.

[0022] FIG. 6 is a graph of short chain branch distributions (SCB/1000 total carbons) of a polymer given in Example VII vs. molecular weight (Log M).

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention is directed to homo-polymers and copolymers of mono-1-olefins, a method of making such polymers, and uses of such polymers. Polymers of the present invention are formed by contacting at least one mono-1-olefin having from 2 to about 20 carbon atoms per molecule and at least one mono-1-olefin comonomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. The

catalyst system of the present invention comprises a chromium source on an aluminophosphate support which has a phosphorous to aluminum mole ratio of less than about 0.3. Further, the catalyst system is treated with less than about 7 weight percent fluoride based on the weight of the support and is calcined. Cocatalyst are selected from trialkylboron compounds, triarylboron compounds, alkylaluminum compounds, and combinations thereof.

[0024] In another aspect of the present invention, ethylene copolymers are employed to produce PE-100 pipe. These copolymers are formed by contacting ethylene with at least one mono-1-olefin comonomer having from 2 to about 10 carbon atoms per molecule in a reaction zone under polymerization conditions in the presence of a hydrocarbon diluent, a catalyst system, and a cocatalyst. Additionally, the comonomers may be selected from mono-1-olefins having 4 to 10 carbon atoms, such as, 1-hexene, 1-butene, 4-methyl-1-pentene, 1-octene, and 1-decene. Such inventive ethylene copolymers have a molecular weight distribution (M_w/M_n) greater than about 50 and a substantially constant branch distribution profile at molecular weights greater than about 1×10^6 . Further, these ethylene copolymers may be employed to produce PE-100 pipe having both small diameters and diameters in excess of 42 inches substantially without sagging or other gravitational deformation. The ethylene copolymers of the present invention have a high load melt index (HLMI) within a range of about 0.5 to about 10 g/10 minutes, a density within a range of about 0.945 to about 0.955 g/cc, a molecular weight distribution (M_w/M_n) greater than about 50, a PENT slow crack growth resistance value of greater than about 1000 hours, and a branch profile of greater than about 1 branch/1000 carbons at 1 million molecular weight.

[0025] In accordance with yet another embodiment of this invention, herein is provided a composition comprising a copolymer of ethylene and 1-hexene, wherein said copolymer has a high load melt index (HLMI) within a range of about 0.5 to about 10 g/10 minutes, a density within a range of about 0.947 to about 0.953 g/cc, a molecular weight distribution (M_w/M_n) of greater than about 80, a PENT slow crack growth resistance value of greater than about 1000 hours, and a branch profile of greater than about 1 branch/1000 carbons at 1 million molecular weight. Further, in another aspect of the present invention, the inventive ethylene copolymers have a high load melt index (HLMI) within a range of about 0.5 to about 10 g/10 minutes, a density within a range of about 0.945 to about 0.955 g/cc, a molecular weight distribution (M_w/M_n) greater than about 40, a PENT slow crack growth resistance value of greater than about 1000 hours, and a branch profile of greater than about 1 branch/1000 carbons at 1 million molecular weight.

[0026] Polymers of the present invention may be formed or extruded into articles of manufacture, including pipe, by any method known in the art. Typically, pipe is formed by extruding polymers of the present invention in a molten state through a die to form the pipe, and the pipe is subsequently cooled to fix the shape of the pipe. Additionally, pipe extrusion is discussed in U.S. Pat. No. 5,028,376, which is incorporated herein by reference.

[0027] Catalyst Systems

[0028] As used in this disclosure, the term "support" refers to a carrier for one or more catalytic components. In

accordance with the present invention, the support may comprise materials and compositions which are inert with respect to polymerization reactions. Further, the support may comprise materials or compositions which contribute to catalytic activity and selectivity of polymerization reactions. In addition, other materials or components which do not adversely affect the catalyst system and/or the polymerization reaction of the present invention or are present to produce some unrelated results or polymer properties may be present in the support as well.

[0029] Generally, the aluminophosphate support of the present invention can be prepared by any method known to one skilled in the art, such as, for example, use of a cogel. Examples of preparations which may be employed in the present invention are described in U.S. Pat. Nos. 4,364,842; 4,444,965; 4,364,855; 4,504,638; 4,364,854; 4,444,964; 4,444,962; 4,444,966; and 4,397,765, all of which are incorporated herein their entirety by reference. When the aluminophosphate support is prepared by cogellation, a hydrogel can be produced by contacting an aluminum compound and phosphorus compound as an aqueous solution. To assist in forming the solution of the aluminum and phosphorus compounds, the mixture can be warmed to a temperature sufficient to dissolve the compounds, for example, to at least about 40° C. (104° F.). Base is added to bring the solution to near neutral pH, causing precipitation of the aluminophosphate. By varying the amounts of aluminum and phosphorus added, the desired P/Al molar ratio can be achieved. Also, alcoholic or other organic solutions may be employed, such as for example, hydrolyzing aluminum alkoxides by adding aqueous phosphate solutions.

[0030] Further, the aluminophosphate support employed in the present invention may be formed by contacting alumina with an inorganic or organic phosphate compound in an aqueous or organic solution. Thus, the phosphate, such as phosphoric acid, can be impregnated onto a preformed alumina of high porosity. Optionally thereafter, the impregnated alumina is dried. Aluminophosphate supports prepared according to this method are called "phosphated aluminas".

[0031] When a phosphated alumina is employed as the support, the alumina optionally may be calcined prior to treatment with phosphate. Sometimes alumina takes the form of $Al(OH)_3$, such as boehmite or other hydrates. Calcining the alumina converts the hydrated alumina support either partially or in total into aluminum oxide, such as gamma-alumina, Al_2O_3 . The alumina may be calcined in an atmosphere of an inert gas, such as air or nitrogen, or in a vacuum. Calcining may be conducted at temperatures between about 100° C. to about 800° C. In one aspect of the present invention, the alumina is calcined before the phosphate treatment at temperatures between about 500° C. to about 700° C.

[0032] Aluminophosphate supports having a P/Al molar ratio below about 0.7 are employed in the present invention. Further, aluminophosphate supports employed in the present invention may have a P/Al molar ratio below about 0.3, and generally, the P/Al molar ratio is within a range from about 0.03 to about 0.28. In another aspect of the present invention, the P/Al molar ratio of the aluminophosphate support is within a range from about 0.05 to about 0.28. Yet, in another aspect of the present invention, the P/Al molar ratio of the aluminophosphate support is within a range from

about 0.04 to about 0.20. Still, in another aspect of the present invention, favorable catalyst system activity, resin properties, and pipe properties can be achieved with a P/Al molar ratio of the aluminophosphate support within a range from about 0.05 to about 0.15.

[0033] Although not required, the aluminophosphate can be calcined as well prior to use or inclusion in the catalyst system of the present invention. The aluminophosphate can be calcined at a temperature within a range from about 200° C. (392° F.) to about 900° C., although temperatures up to about 1000° C. (1832° F.) may be employed. In another aspect of the present invention, the aluminophosphate can be calcined at a temperature within a range from about 400° C. to about 800° C. (1472° F.). Yet, in another aspect of the present invention, the aluminophosphate can be calcined at a temperature within a range from about 550° C. to about 700° C. (1292° F.) for 3 to 4 hours.

[0034] The chromium component of the catalyst system can be combined with the support component in any manner known in the art, such as by cogellation as described above, or by post-impregnation in which a chromium compound such as chromium (VI) trionide, chromium (III) acetate, chromium (III) nitrate, and mixtures thereof can be dissolved into aqueous or alcoholic or other organic solvents. Other chromium compounds known in the art also can be employed. The chromium solution then is impregnated into or onto the aluminophosphate support and evaporated to dryness. The chromium component of the catalyst system comprises from about 0.1 to about 5 weight percent chromium based on the weight of the support. In another aspect of the present invention, the chromium component comprises from about 0.8 to about 3 weight percent based on the weight of the support. Yet, in another aspect of the present invention, the chromium component comprises about 0.8 to about 1.5 weight percent chromium based on the weight of the support. Still, in another aspect of the present invention, the chromium component comprises about 1 to about 2.5 weight percent chromium based on the weight of the support.

[0035] Additionally, a fluoriding agent is employed in the catalyst system of the present invention. Any organic or inorganic fluoriding agent which can form a surface fluoride with a support can be used in the invention. Suitable fluoriding agents include, but are not limited to, hydrofluoric acid (HF), ammonium fluoride (NH₄F), ammonium bifluoride (NH₄HF₂), ammonium fluoroborate (NH₄BF₄), ammonium silicofluoride ((NH₄)₂SiF₆), ammonium fluorophosphate ((NH₄)₂PF₆), ammonium hexafluoroantimonate ((NH₄)₂TiF₆), ammonium hexafluorozirconate ((NH₄)₂ZrF₆), and combinations thereof. Due to ease of use and availability, ammonium bifluoride may be employed as the fluoriding agent. The amount of fluoride deposited into or onto the support is generally within a range from about 0.3 to about 7 weight percent based on the weight of the support. In another aspect of the present invention, the amount of fluoride present in the catalyst system of the present invention is from about 0.7 to about 4 weight percent based on the weight of the support. Yet, in another aspect of the present invention, the amount of fluoride present in the catalyst system of the present invention is from about 1.3 to about 3.5 weight percent based on the weight of the support.

[0036] Generally, the fluoriding agent can be added to the support by forming a slurry of the support in a solution of the

fluoriding agent and a suitable solvent, such as alcohol or water. Examples of solvents which may be employed in the present invention include, but are not limited to, alcohols containing from about one to about three carbon atom molecules due to their volatility and low surface tension. A suitable amount of the solution can be utilized to provide the desired concentration of fluoride on or in the support after drying. Drying can be effected by any method known in the art. For example, drying can be completed by suction filtration followed by evaporation; drying under a vacuum, by spray drying, flash drying, and the like. Optionally, the support may be treated with the fluoriding agent during calcination. Any fluoriding agent capable of contacting the support during calcination can be used. In addition to the fluoriding agents as described above, organic fluoriding agents with high volatility may be employed. Examples of organic fluoriding agents with high volatility include, but are not limited to, freons, perfluorobutane, perfluorobenzene, fluoromethane, trifluoroethanol, and mixtures thereof. Further, such high volatility fluoriding agents may be employed in any combination with the fluoriding agents described above. Gaseous hydrogen fluoride or fluorine itself may be employed as well. One convenient method of contacting the support is to vaporize the fluoriding agent into a gas stream which can be used to fluidize the support during calcination.

[0037] The catalyst system, either before, during, or after the fluoriding treatment, is activated by calcination by any method(s) known to one in the art to produce a calcined catalyst system. In accordance with the present invention, the catalyst system may be calcined in an oxygen-containing ambient in any manner conventionally used in the art. For example, the catalyst system can be calcined in any dry oxidizing gas, such as oxygen, nitrous oxide, air, mixtures of oxygen other inert gas or gases, and the like. Because of economy, air or dry air may be employed as the oxygen-containing ambient. The calcination temperature generally employed is within a range from about 400° C. (752° F.) to about 800° C. In another aspect of the present invention, the calcination temperature is within a range from about 500° C. (932° F.) to about 700° C. (1292° F.). Yet, in another aspect of the present invention, the calcination temperature is within a range from about 550° C. (1022° F.) to about 650° C. (1202° F.).

[0038] The time period for conducting the calcination of the fluoridized catalyst system is generally within a range from about 1 minute to about 100 hours. In another aspect of the present invention, calcination of the fluoridized catalyst system is conducted from about 1 hour to about 30 hours. Yet, in another aspect of the present invention, calcination of the fluoridized catalyst system is conducted from about 3 hours to about 10 hours. Under these calcination conditions, at least a substantial portion of any chromium in a lower valence state is converted to a hexavalent form.

[0039] After calcination, the catalyst system optionally can be cooled and subjected to at least a partial reduction of hexavalent chromium which may be present to a lower valence state. In one aspect of the present invention, a substantial portion of the chromium is in the divalent state (Cr(II)) after the reduction process.

[0040] Any compound capable of reducing chromium(VI) to a lower valence state may be employed as a reducing

agent. For example, carbon monoxide may be employed as the reducing agent due to its ready availability, ease of use, safety, and lack of hydrogen, which can produce moisture as a by-product. Reducing agents can be employed at temperatures within a range from about 150° C. (752° F.) to about 600° C. (1112° F.). In another aspect of the present invention, the temperature is within a range from about 200° C. (392° F.) to about 500° C. (932° F.). Yet, in another aspect of the present invention, the temperature is within a range from about 300° C. (572° F.) to about 400° C. (752° F.). The partial pressure of the reducing gas in the reduction process can be varied from sub-atmospheric pressures to relatively high pressures, but the simplest reducing process is to utilize a dilute solution of a pure reducing agent at about atmospheric pressure. Usually, a solution of about 10% by volume of carbon monoxide in an inert ambient, such as, for example, nitrogen and/or argon, can be used.

[0041] The reduction time can vary from a few minutes to several hours or more. The extent of reduction can be followed by visual inspection of the catalyst system color. The color of the initial oxidizing gas activated catalyst system is generally orange, indicating the presence of hexavalent chromium. The color of the reduced catalyst system is typically blue, indicating that all, or substantially all, of the initial hexavalent chromium has been reduced to lower oxidation states, generally to the divalent state.

[0042] After reduction, the catalyst system can be cooled to about room temperature, e.g., about 25° C. (77° F.), in an inert atmosphere, such as argon or nitrogen, to flush out the reducing agent. After the flushing treatment, the catalyst system is kept away from contact with either a reducing agent or an oxidizing agent.

[0043] In order to achieve the desired resultant effects on the resin product, or polymer, it is beneficial for the catalyst system to have relatively high pore volume. For example, after calcination, the catalyst system should have a pore volume of at least about 0.5 cc/g, as measured by nitrogen sorption. In another aspect of the present invention, the pore volume of the catalyst system is at least about 1.0 cc/g. Yet, in another aspect of the present invention, the pore volume of the catalyst system is at least about 1.2 cc/g. Additionally, the catalyst system after calcination should have a high surface area, as measured by the BET method, usually within a range of from about 150 m²/g to about 1000 m²/g. In another aspect of the present invention, the surface area of the catalyst system is within a range from about 200 m²/g to about 500 m²/g. Yet, in another aspect of the present invention, the surface area of the catalyst system is within a range from about 250 m²/g to about 450 m²/g.

[0044] Cocatalysts

[0045] As indicated above, a cocatalyst is employed with the supported chromium catalyst system of the present invention. Examples of cocatalysts useful in the present invention include, but are not limited to, one or more trialkylboron compounds, one or more triarylboron compounds, one or more alkylaluminum compounds, and combinations thereof.

[0046] Trialkylboron compounds are effective agents to improve polymer properties and increase catalyst activity during polymerization. Examples of suitable trialkylboron compounds include those containing from 1 to about 12

carbon atoms per alkyl group. Another aspect of the present invention employs trialkylboron compounds containing from about 2 to 5 carbon atoms per alkyl group. Trialkylboron compounds which may be employed in the present invention include, but are not limited to, trimethylborane, triethylborane (TEB), tri-*n*-butyl borane, tributylborane, tripropylborane, and combinations thereof.

[0047] Triarylboron compounds also may be employed as a cocatalyst in the present invention. Examples of suitable triarylboron compounds include, but are not limited to, triphenylborane and tribenzylborane.

[0048] Examples of suitable alkylaluminum compounds include, but are not limited to, those with the general formula (I):



[0049] In formula (I), X is a hydride, alkoxide, siloxane, or halide; R' is a hydrocarbyl radical having from about 1 to 12 carbon atoms per radical group; and n is an integer from 1 to 3. Such aluminum compounds include, but are not limited to, trimethylaluminum, triethylaluminum (TEA), diethylaluminum chloride (DEAC), diethylaluminum ethoxide (DEALE), tributylaluminum, and combinations thereof. In one aspect of the present invention, the trialkylaluminum compounds employed are trimethylaluminum, triethylaluminum, tributylaluminum, and combinations thereof. Aluminosiloxanes are alkylaluminum compounds which may also be employed as cocatalysts in the present invention. Examples of aluminosiloxanes include, but are not limited to, methylaluminosiloxane, propylaluminosiloxane, *n*-butylaluminosiloxane, and isobutylaluminosiloxane.

[0050] Also, as indicated above, alkylsiloxylaluminum compounds are identified as alkylaluminum compounds which may be employed as a cocatalyst in the present invention. In addition to the alkylsiloxylaluminum compounds included within the scope of formula (I) above, other suitable alkylsiloxylaluminum compounds include, but are not limited to, those with the general formula (II):



[0051] In formula (II), the R groups can be the same or different and have in the range of from about 1 to 12 carbon atoms per alkyl group. Alkylsiloxylaluminum compounds include, but are not limited to, triethylsiloxylaluminum diethyl, trimethylsiloxylaluminum diethyl, tripropylsiloxylaluminum dimethyl, and combinations thereof. Presently preferred trialkylsiloxylaluminum compounds include, but are not limited to, triethylsiloxylaluminum diethyl.

[0052] The total amount of boron and/or aluminum cocatalyst compound(s) used is generally within a range between about 0.1 to about 100 parts by weight per 1000 parts by weight of the calcined catalyst system fed to the polymerization reactor. In a continuous particle form process using a single loop reactor, for example, it is convenient to introduce the cocatalyst as a separate stream into the reactor, either continuously or in pulses, as a dilute solution in an inert hydrocarbon, for example 0.1 weight percent in isobutane. The concentration of the cocatalyst also can be expressed in parts per million (ppm) based on the diluent used in the polymerization reactor. The concentration of the cocatalyst compound(s) usually is within a range between about 0.1 ppm to about 20 ppm, based on the amount of diluent charged or weight of the diluent. In one aspect, the

concentration of cocatalyst compound(s) is within a range between about 0.5 ppm to about 15 ppm. In another aspect, the concentration of cocatalyst compound is within a range between about 0.5 ppm to about 10 ppm. Yet, in another aspect, the concentration of cocatalyst compound is within a range between about 0.5 ppm to about 7 ppm. Still, in another aspect, the concentration of cocatalyst compound is within a range between about 2 ppm to about 12 ppm.

[0053] Reactants

[0054] Catalyst systems of the present invention can be used to polymerize at least one mono-1-olefin containing from about 2 to about 20 carbon atoms per molecule. Suitable mono-1-olefins include, but are not limited to, ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and mixtures thereof. When the desired polymerization product is a homopolymer, ethylene or propylene should be employed as the monomer. If the reaction product is a copolymer, at least one mono-1-olefin is polymerized with a different mono-1-olefin comonomer. In one aspect of the present invention, the comonomer comprises from about 3 to about 10 carbon atoms per molecule. In another aspect of the present invention, the comonomer comprises from about 3 to about 8 carbon atoms per molecule.

[0055] In a further aspect of the present invention, catalyst systems of the present invention are particularly beneficial when employed to polymerize ethylene with one or more mono-1-olefin comonomers containing from about 2 to about 20 carbon atoms per molecule. Suitable mono-1-olefin comonomers include, but are not limited to, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and mixtures thereof. Polymer product toughness can be maximized by employing 1-hexene as the comonomer.

[0056] Generally, a comonomer can be added to the polymerization reactor, or reactor zone, in an amount within a range from about 1 to about 20 weight percent based on the weight of the monomer. In another aspect of the invention, the comonomer generally can be added within a range from about 7 to about 18 weight percent based on the weight of the monomer. Yet, in another aspect of the invention, the comonomer generally is present in the reaction zone within a range from about 10 to about 16 weight percent based on the weight of the monomer. The amount of comonomer may be tailored to produce a copolymer having the most desired physical properties.

[0057] When ethylene polymers are desired, the comonomer can be added to the polymerization reactor, or reactor zone, in an amount within a range of from about 0.1 to about 20 weight percent of the hydrocarbon diluent in order to produce a polymer having the most desired physical properties. Alternatively, the comonomer can be added within a range from about 0.3 to about 10 weight percent based on the weight of the diluent. Yet, the comonomer present in the reaction zone may be within a range from about 0.7 to about 5.0 weight percent based on the weight of the diluent. By varying the ethylene to comonomer ratio in the reactor, the density of the polymer can be controlled. Also, the molecular weight of the polymer can be controlled by various means known in the art, such as, for example, adjusting the

temperature, introducing or varying the amount of hydrogen present, or varying the catalyst system compounds.

[0058] Polymerization

[0059] Polymerization can be carried out in any manner known to one skilled in the art, such as gas phase, solution, multi-reactor, or slurry polymerization conditions, to effect polymerization. A stirred reactor can be utilized for a batch process, or the reaction can be carried out continuously in a loop reactor, such as a single loop reactor, or in a continuous stirred reactor. A polymerization technique readily employable in the present invention is that which is referred to as particle-form, or slurry, polymerization conditions using a loop reactor. Under such conditions, the temperature is kept below the temperature at which a polymer swells or goes into solution. Slurry polymerization processes can be much easier to operate and maintain than other polymerization processes, in that a polymer product produced by a slurry process can be recovered much more easily. Such polymerization techniques are well-known in the art and are disclosed, for instance, in Norwood, U.S. Pat. No. 3,248,179, which is incorporated herein by reference. For example, two polymerization techniques which may be employed in the present invention for the slurry process are those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel, or combinations thereof wherein the reaction conditions can be different in the different reactors.

[0060] The slurry process generally is carried out in an inert diluent (medium), such as, for example, a paraffin, cycloparaffin, and/or aromatic hydrocarbon. An inert diluent which may be employed in the present invention is an alkane having less than about 12 carbon atoms per molecule, for optimal reactor operation and polymer product. Exemplary diluents include, but are not limited to, propane, n-butane, isobutane, n-pentane, 2-methylbutane (isopentane), and mixtures thereof. Isobutane is an economically efficient diluent due to low cost and ease of use. Examples of the use of isobutane as a diluent in slurry polymerization processes can be found in U.S. Pat. Nos. 4,421,341; 4,501,885; 4,613,484; 4,737,280; and 5,597,892, all of which are incorporated herein in their entirety by reference. These techniques provide efficient polymerization of ethylene, for example, ethylene and a different mono-1-olefin, such as an alpha-1-olefin, or propylene.

[0061] The temperature of the polymerization reactor, or reaction zone, is usually within a range from about 80° C. to about 110° C. (212° F.), although higher or lower temperatures can be used. In another aspect of the present invention, the temperature is within a range from about 90° C. (194° F.) to about 107° C. (225° F.). Yet, in another aspect of the present invention, the temperature is within a range from about 95° C. (203° F.) to about 105° C. (221° F.).

[0062] Pressures in the slurry process can vary from about 100 psia to about 1000 psia (0.76-7.6 MPa). In another aspect of the present invention, the pressures can vary in a range from about 200 psia to about 700 psia. Yet, in another aspect of the present invention, the reaction zone is maintained at a pressure within a range from about 300 psia to about 600 psia for optimal reactor operating parameters and resultant polymer product.

[0063] The catalyst system is kept in suspension and is contacted with the monomer and comonomer(s) at a suffi-

cient pressure to maintain the medium and at least a portion of the monomer and comonomer(s) in the liquid phase. The medium and temperature are thus selected so that the polymer or copolymer is produced as solid particles and is recovered in that form. Catalyst system concentrations in the reactor can be such that the catalyst system content ranges from about 0.0005 to about 1 weight percent based on the weight of the reactor contents. During the production of ethylene polymers, catalyst system concentrations in the reactor can be such that the catalyst system content ranges from about 0.0005 to about 0.05 weight percent based on the weight of the reactor contents.

[0064] Polymer Description

[0065] Polymers produced in accordance with the present invention can be homopolymers of at least one mono-1-olefin and copolymers of mono-1-olefins. For example, such polymers include copolymers of ethylene and at least one mono-1-olefin of 4-10 carbons, such as 1-hexene, 1-butene, 4-methyl-1-pentene, 1-octene, and 1-decene. Further, polymers produced according to the present invention are much more easily processed than polymers produced in conventional polymerization processes. Additionally, the polymers produced according to the present invention can have extremely broad molecular weight distributions and can have excellent characteristics for high stiffness pipe applications.

[0066] The high load melt index (HLMI) of polymers produced in accordance with the present invention usually is within a range of from about 2 g/10 minutes to about 20 g/10 minutes. Additionally, polymers produced in accordance with the present invention can have a HLMI within a range from about 3 g/10 minutes to about 15 g/10 minutes. Further, the HLMI of the polymer product is within a range from about 5 g/10 minutes to about 10 g/10 minutes. With respect to ethylene polymers made in accordance with the present invention, the HLMI usually is within a range from about 0.1 g/10 minutes to about 20 g/10 minutes. Still, the ethylene polymers can have a HLMI within a range from about 1 g/10 minutes to about 10 g/10 minutes. Even further, the HLMI of the ethylene polymer product is within a range from about 1.5 g/10 minutes to about 7 g/10 minutes.

[0067] The polymers of this invention have a broad molecular weight distribution as evidenced by polydispersity, or weight average molecular weight divided by number average molecular weight (M_w/M_n). Generally, the M_w/M_n ratio for polymers produced in accordance with the present invention is at least about 50. In another aspect of the present invention, the M_w/M_n ratio for the inventive polymers is greater than about 80. Yet, in another aspect of the present invention, the M_w/M_n ratio for the inventive polymers is greater than about 100. Still, in another aspect of the present invention, the M_w/M_n ratio for the inventive polymers is greater than about 140 with an upper limit of about 500. The polymers of this invention also have a very narrow density range, usually within a range of from about 0.945 g/cc to about 0.955 g/cc. Additionally, polymers of the present invention may be produced having a density within a range from about 0.947 g/cc to about 0.953 g/cc. Further, polymers of the present invention may be produced having a density within a range from about 0.948 g/cc to about 0.952 g/cc.

[0068] Specifically, for ethylene copolymers produced in accordance with the present invention, usually the M_w/M_n

ratio is at least about 40. The ethylene copolymers produced in accordance with the present invention may have a M_w/M_n ratio greater than about 50. Further, the ethylene copolymers produced in accordance with the present invention may have a M_w/M_n ratio greater than about 60.

[0069] Polymers produced in accordance with the present invention also have high PENT slow crack growth resistance values. Generally, the polymer has a PENT value of greater than about 750 hours. However, polymers produced in accordance with the present invention can also have PENT values greater than about 1000 hours, greater than about 1500 hours, greater than about 1800 hours, and greater than about 2000 hours.

[0070] Polymers produced in accordance with this invention have a unique branch distribution. Until now, polymers produced from process which employ conventional chromium catalysts have a branch content, or amount of comonomer incorporated, that decreases with increasing molecular weight of the polymer. In contrast, polymers of the present invention have a branch content that does not decrease with increasing molecular weight. Further, the polymers of the present invention have a short chain branch content that is substantially constant with the molecular weight of the polymer from a molecular weight of about 10^4 and higher, at least up to 10^7 . In general, these inventive polymers are characterized by having a high concentration of branching in the molecular weight range of greater than one million. The polymer product generally has greater than about 0.5 short chain branches per thousand carbons (SCB/1000C) at one million molecular weight (MW). Further, the polymer may have greater than about 1 SCB/1000C at one million molecular weight (MW). Still further, the polymer product may have greater than about 1.5 SCB/1000C at one million molecular weight (MW).

[0071] The inventive polymer also may be characterized by having a high concentration of branching in the molecular weight range of greater than ten million. The polymer product generally has greater than about 0.5 short chain branches per thousand carbons (SCB/1000C) at ten million molecular weight (MW). Further, the polymer may have greater than about 1 SCB/1000C at ten million molecular weight (MW). Still further, the polymer product may have greater than about 1.5 SCB/1000C at ten million molecular weight (MW).

[0072] The polymers of the present invention are additionally characterized by having a relatively high molecular weight. Generally, these inventive polymers have a weight average molecular weight (M_w) in a range from about 300,000 g/mol to about 1 million g/mol. Further, polymers of the present invention can have a M_w in a range from about 350,000 g/mol to about 750,000 g/mol. Yet further, polymers of the present invention can have a M_w in a range from about 400,000 g/mol to about 600,000 g/mol. Still further, polymers of the present invention can have a M_w in a range from about 450,000 g/mol to about 550,000 g/mol.

[0073] Despite the high molecular weight, the polymers of the present invention are unique in having a relatively low melt viscosity at low shear rates, compared to polymers derived from conventional chromium based catalysts. While not wishing to be unduly bound by theory, it is thought that this unique combinations of high molecular weight and low melt viscosity is due to the polymer having little or no long

chain branching as compared to conventional chromium derived polymers. One measure of this characteristic is the zero shear melt viscosity, which is extrapolated from a the rheology curve at 190° C. Sometimes called $\eta(0)$, the zero shear viscosity can be obtained by fitting the Carreau-Yasuda equation to the experimental viscosity derived at 190° C. as a function of shear rate. See R. Byron Bird, Robert C. Armstrong, and Ole Hassager, *Dynamics of Polymeric Liquids, Volume 1, Fluid Mechanics*, (John Wiley & Sons, New York, 1987). Sometimes, during the extrusion of various types of pipe, it is desired for the low shear viscosity not be too large. Otherwise certain fusion and other molding problems can result. In this regard polymers of the present invention have an $\eta(0)$ of less than about 5×10^7 pa-sec. In another aspect of the present invention, the polymers have an $\eta(0)$ less than 2.5×10^7 pa-sec. Yet, in another aspect of the present invention, the polymers have an $\eta(0)$ less than 1.5×10^7 pa-sec. Still, in another aspect of the present invention, the polymers have an $\eta(0)$ less than about 1×10^7 pa-sec.

[0074] Alternatively, in other applications, high melt viscosities at low shear rates are desired. This is particularly true of large diameter pipe applications where the pipe can "slump" or deform from the effect of gravity during the slow cool-down period. For these applications, the higher the zero shear viscosity, the more resistant the molten polymer is toward this so-called "slumping" deformation. For applications which require slump resistance, polymers of the present invention generally have an $\eta(0)$ greater than about 1×10^8 pa-sec. In another aspect of the invention, polymers of the present invention have an $\eta(0)$ greater than about 5×10^8 pa-sec. Yet, in another aspect of the invention, polymers of the present invention have an $\eta(0)$ greater than about 1×10^9 pa-sec. Still, in another aspect of the invention, polymers of the present invention have an $\eta(0)$ greater than about 2×10^9 pa-sec.

[0075] Despite the high molecular weight of these polymers, and the sometimes high low-shear melt viscosity, the polymers of the present invention are also characterized by having a relatively low melt viscosity at high shear rates. Since the extrusion into pipe is done at relatively high shear rates, a low high-shear melt viscosity is desirable because molten polymer flows easily during the molding operations. Generally, the polymers of the present invention have a melt viscosity of less than 6×10^3 pa-sec at 100/sec shear rate, called $\eta(100)$. In another aspect of the present invention, the polymers of the present invention have an $\eta(100)$ of less than 3×10^3 pa-sec. Yet, in another aspect of the present invention, the polymers of the present invention have an $\eta(100)$ of less than 2×10^3 pa-sec.

[0076] Another distinguishing feature of these unique inventive polymers is the narrow relaxation time distribution. The breadth of the relaxation time distribution, sometimes called the CY-a parameter, can also be derived from the Carreau-Yasuda equation cited above, when applied to melt viscosity data obtained at 190° C. as a function of shear rate. CY-a is usually higher than polymers of similar molecular weight derived from conventional chromium catalysts. Generally, the CY-a of these inventive polymers is greater than about 0.2. In another aspect of the present invention, the polymers have a CY-a is greater than about 0.25. Yet, in another aspect of the present invention, the polymers have a CY-a is greater than about 0.3.

[0077] A further distinguishing feature of these inventive polymers is that they can be extruded into pipe that meets the rigorous standards of the PE-100, MRS 10, or ASTM D3350 typical cell classification 345566C. This includes hoop stress testing and rapid crack propagation, or S4, testing (see ISO/TC 138/SC 4 Parts 1 & 2 Dated Jan. 1, 2008).

EXAMPLES

[0078] The following examples are presented to further illustrate the invention and are not to be construed as unduly limiting the scope of the invention. These examples illustrate the various aspects of the present invention, including a description of catalyst system preparation, catalyst system use in a polymerization process to produce the desired resin, the physical properties of that resin, and its use to make a PE-100 classified, large diameter pipe.

[0079] Chromium/Aluminophosphate Catalyst Preparation

[0080] The aluminophosphate catalyst system was prepared from a commercial alumina manufactured by W. R. Grace under the name "Alumina A". This material is substantially all alumina after calcination at about 600° C., having a pore volume of about 1.5 cc/g and a surface area of about 300 m²/g. In the preparation of a typical batch of catalyst, about 300 pounds (lbs) of Alumina A was calcined by passing it through a rotary calciner set at about 750° C. in a counter-current nitrogen flow. In a mix tank equipped with mechanical stirrer, about 900 lbs of anhydrous methanol was added, followed by about 9.0 lbs of ammonium bifluoride and 46 lbs of 85% phosphoric acid. This mixture was stirred until it made a homogeneous solution. After being calcined, the alumina was placed in a mechanical blender to which the above methanolic solution was also added. The resultant slurry was stirred for about two hours, after which 39 lbs of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added. This mixture was stirred for about another two hours, after which heat was applied to boil off the methanol solvent. Gentle stirring was continued until most of had been removed. The resultant powder was then transferred into a vacuum oven where it was heated at about 60° C. for about 12 hours to remove almost all of the residual methanol. Thereafter, the catalyst was passed through a 30 mesh screen to remove any large agglomerates.

[0081] Measurement of Resin Properties

[0082] Analysis of the resultant polymers were conducted according to the following procedures. Polymer density was determined in grams per cubic centimeter (g/cc) on a compression molded sample, cooled at about 15° C. per hour, and conditioned at room temperature, about 25° C., for about 40 hours in accordance with ASTM D1505-68 and ASTM D1928, condition C.

[0083] High load melt index (HLMI) was determined in grams of polymer per 10 minutes (g/10 min) in accordance with ASTM D1238, Condition 190/21.6, at 190° C. with a 21,600 gram weight.

[0084] Melt Index (MI) was determined in grams of polymer per ten minutes in accordance with ASTM D1238, condition 190/2.16, at 190° C. with a 2,160 gram weight.

[0085] PENT slow crack growth resistance values were obtained at 80° C. (176° F) according to ASTM F1473 (2001).

[0086] Molecular weights and molecular weight distributions were obtained using a PL 220 SEC high temperature chromatography unit (Polymer Laboratories) with trichlorobenzene (TCB) as the solvent, with a flow rate of 1 mL/minute at a temperature of about 145° C. BHT (2,6-di-tert-butyl-4-methylphenol) at a concentration of 0.5 g/L was used as a stabilizer in the TCB. An injection volume of 200 μ L was used with a nominal polymer concentration of 1.5 mg/mL. Dissolution of the sample in stabilized TCB was carried out by heating at about 150° C. for about 5 hours with occasional, gentle agitation. Subsequently, the sample was kept at about 130° C. for approximately 18 hours (over night) after which it was reheated to about 150° C. for about 2 hours prior to injection. The columns used were three PLgel Mixed A LS columns (7.8 $\times$ 300 mm) and were calibrated with a broad linear polyethylene standard (Phillips Marlex® BHB 5003) for which the molecular weight had been determined.

[0087] Molecular weight distributions and branch profiles were obtained through size exclusion chromatography using an FTIR detector. Chromatographic conditions are those described above, and the sample injection volume was 500 μ L. Samples were introduced to the FTIR detector via a heated transfer line and flow cell (KBr windows, 1 mm optical path, and ca. 70 μ L cell volume). The temperatures of the transfer line and flow cell were kept at 143 $\pm$ 1° C. and 140 $\pm$ 1° C., respectively. Perkin Elmer FTIR spectrophotometer (PE 2000) equipped with a narrow band mercury cadmium telluride (MCT) detector was used in these studies.

[0088] All spectra were acquired using Perkin Elmer Timebase software. Background spectra of the TCB solvent were obtained prior to each run. All IR spectra were measured at 8 cm^{-1} resolution (16 scans). Chromatograms were generated using the root mean square absorbance over the 3000-2700 cm^{-1} spectral region (i.e., FTIR serves as a concentration detector). Molecular weight calculations were made as previously described using a broad molecular weight polyethylene (PE) standard. See Jordens K, Wilkes G L, Janzen J, Rohlfing D C, Welch M B. *Polymer* 2000;41:7175. Spectra from individual time slices of the chromatogram are subsequently analyzed for comonomer branch levels using chemometric techniques. All calibration spectra were taken at sample concentrations which far exceeded that needed for good signal to noise (i.e., >0.08 mg/mL at the detector).

[0089] Branching determination was made as follows. Calibration and verification studies were conducted with solvent gradient fractions having a narrow molecular weight distribution (M_w/M_n ~1.1 to 1.3). These fractions were composed of polyethylene homopolymers or ethylene copolymers of 1-butene or 1-hexene and low molecular weight alkanes. The total methyl content of these samples ranged from 1.4 to 82.7 methyls per 1000 total carbons. Methyl content of samples was calculated from M_n or measured using C-13 NMR spectroscopy. C-13 NMR spectra were obtained on 15 wt. % samples in TCB using a 500 MHz Varian Unity Spectrometer run at 125° C. as previous described. See Randall J C, Hsieh E T, *NMR and Macromolecules: Sequence, Dynamic, and Domain Structure*, ACS Symposium Series 247, J. C. Randall, Ed., American Chemical Society, Washington D.C., 1984. Methyl content per 1000 carbons by NMR was obtained by multiplying ($\times$ 1000) the ratio of total methyl signals to total signal intensity.

[0090] A partial least squares (PLS) calibration curve was generated using Pirouette chemometric software (Infometrix) to correlate changes in the FTIR absorption spectra with calculated or NMR measured values for methyls/1000 total carbons for the 25 samples. The FTIR absorption spectra used in the calibration model were made from co-added spectra collected across the whole sample. Only a portion of the spectral region (2996 and 2836 cm^{-1}) was used in the calibration step in order to minimize the effects of residual solvent absorption. Preprocessing of spectral data included area normalization, taking the first derivative of the spectra and mean centering all data. A three-component calibration model was calculated and optimized using the process of cross validation (RSQ=0.999, SEV=0.5). Outlier detection for individual measurements was generated from probability values obtained through the Pirouette chemometric software. Samples having probabilities >0.99 were considered outliers.

[0091] Short chain branching levels were calculated by subtracting out methyl chain end contributions. The number of methyl chain ends (N_e) was calculated using the equation

$$N_e = (1 - V_{CH}) / (2 - V_{CH}) M$$

[0092] In this equation, V_{CH} is the number of vinyl terminated chain ends and M is the molecular weight calculated for a particular slice of the MWD. Typically, chain termination in chromium catalyzed resins results in the formation of a vinyl moiety. See Witt, D R. *Reactivity, Mechanism and Structure in Polymer Chemistry*. Jenkins A D, Ledwith A. Eds. Ch 13. John Wiley and Sons. New York. 1974. Conversely, methyl chain ends are formed in the chain termination step of Ziegler-Natta catalyzed resins. See Lenz, R W. *Organic Chemistry of Synthetic High Polymers*. Ch 15. John Wiley and Sons. New York. 1967. Therefore, in the above equation V_{CH} is assigned 1 for chromium catalyzed resins and 0 for Ziegler-Natta catalyzed resins. Also, the assumption is made that end group types (i.e., methyl or vinyl) remain fixed through out the molecular weight distribution. Negative values for methyls/1000 total carbons that may result from over correction for methyl chain ends at low branching levels are given values of zero. Further details of the procedure can be found in *Polymer* 2002;43:159, by DeLaurs P J, Rohlfing D C, and Hsieh E T.

[0093] Rheology measurements were obtained as follows: Samples for viscosity measurements were compression molded at 182° C. for a total of three minutes. The samples were allowed to melt at a relatively low pressure for one minute and then subjected to a high molding pressure for an additional two minutes. The molded samples were then quenched in a cold (room temperature) press. 2 mm $\times$ 25.4 mm diameter disks were stamped out of the molded slabs for rheological characterization. Fluff samples were stabilized with 0.1 wt % BHT dispersed in acetone and then vacuum dried before molding.

[0094] Small-strain oscillatory shear measurements were performed on a Rheometrics Inc. RMS-800 or ARRS rheometer using parallel-plate geometry over an angular frequency range of 0.03-100 rad/s. The test chamber of the rheometer was blanketed in nitrogen in order to minimize polymer degradation. The rheometer was preheated to the initial temperature of the study. Upon sample loading and after oven thermal equilibration, the specimens were

squeezed between the plates to a 1.6 mm thickness and the excess was trimmed. A total of about 8 minutes elapsed between the time the sample was inserted between the plates and the time the frequency sweep was started.

[0095] Strains were generally maintained at a single value throughout a frequency sweep, but larger strain values were used for low viscosity samples to maintain a measurable torque. Smaller strain values were used for high viscosity samples to avoid overloading the torque transducer and to keep within the linear viscoelastic limits of the sample. The instrument automatically reduces the strain at high frequencies if necessary to keep from overloading the torque transducer.

[0096] These data were fit to the Carreau-Yasuda equation to determine zero shear viscosity (η_0), relaxation time (τ), and a measure of the breadth of the relaxation time distribution (CY-a). See R. Byron Bird, Robert C. Armstrong, and Ole Hassager, *Dynamics of Polymeric Liquids, Volume 1, Fluid Mechanics*, (John Wiley & Sons, New York, 1987).

[0097] Pipe Extrusion

[0098] Pipe extrusion in the simplest terms is performed by making, conveying polyethylene pellets into a particular shape (generally a annular shape), and solidifying that shape during a cooling process. There are numerous steps to pipe extrusion including the following:

[0099] Feedstock (Assumes Pigmented Pipe)

[0100] Feedstock can either be a pre-pigmented polyethylene resin or it can be a mixture of natural polyethylene and color concentrates (referred to as "Salt and Pepper blends"). In North America, the most common feedstock for pipe extrusion is "Salt and Pepper blends". In Europe and other areas of the world, the most common feedstock for pipe extrusion is pre-pigmented polyethylene resin.

[0101] Feedstock is rigidly controlled to obtain the proper finished product (pipe) and ultimate consumer specifications.

[0102] Extruder

[0103] The most common extruder system for pipe production is a single-screw extruder.

[0104] The purpose of the extruder is to melt, convey and homogenize the polyethylene pellets.

[0105] Extrusion temperatures typically range from 178° C. to 232° C. depending upon the extruder screw design and flow properties of the polyethylene.

[0106] Die

[0107] The purpose of the die is to distribute the homogeneous polyethylene polymer melt around a solid mandrel, which forms it into an annular shape.

[0108] Adjustments can be made at the die exit to try to compensate for polymer sag through the rest of the process.

[0109] Pipe Sizing

[0110] In order for the pipe to meet the proper dimensional parameters, pipe sizing is the next step in the process.

[0111] There are two methods for sizing—vacuum or pressure. Both employ different techniques and different equipment.

[0112] Cooling

[0113] The next steps in the process are to cool the pipe and "freeze in" the desired dimensions.

[0114] Cooling is accomplished by the use of several water tanks where the outside pipe is either submerged or water is sprayed on the pipe exterior.

[0115] The pipe is cooled from the outside surface to the inside surface. The interior wall and inside surfaces of the pipe can stay very hot for a long period of time, as polyethylene is a poor conductor of heat.

[0116] Printing, Coiling or Cutting

[0117] The final steps in the extrusion process for pipe are to print, and either coil or cut-to-length the pipe.

Example 1

[0118] Catalyst Activation

[0119] The above-described catalyst was activated by calcination in dry air at 600° C. In a typical activation batch, about 500 lbs of the catalyst was added to commercial activator consisting of a porous plate inside 42 inch diameter inconel cylinder about 20 feet in height. The catalyst rested on the porous plate, through which dry air was passed at the rate of about 0.2 feet/second (ft/sec) in order to fluidize the bed. The temperature was gradually raised to about 600° C. over a period of about 8-10 hours. Once at 600° C., the activator was allowed to remain at that temperature, while fluidizing, for about another 10 hours. The activated catalyst was then cooled down to about 300° C., at which temperature the activated catalyst was removed from the activator. During the last 2-3 hours of the cool-down period, the fluidization air was replaced by dry nitrogen. After removal from the activator, the catalyst was stored under nitrogen in an air-tight container until its use in the polymerization reactor.

[0120] Polymerization

[0121] The activated catalyst described above was used to catalyze the copolymerization of ethylene and 1-hexene to make the novel polymers of the present invention. The reactor system used was a 24 inch diameter 3-legged loop reactor containing about 27,000 gallons of polymer slurry. The diluent used was prepolymerized isobutane, and the reactor contents were controlled so that they were typically about 38% by weight solid polymer and 62% by weight of liquid reactants and diluent. Catalyst, ethylene, 1-hexene, isobutane, triethylboron solution, and hydrogen were all added continuously to the reactor. The reactor temperature was set at about 101° C. Polymer and liquid were removed continuously through flashing, in which a small increment of the reactor contents were vented into a large collection tank. The liquid components then vaporized instantly, leaving the dry polymer powder. The production rate was about 30,000 lbs of polymer produced per hour. Ethylene was supplied on demand to maintain this rate and a dissolved ethylene concentration in the diluent of about 3 to 4 percent by weight of the liquid reactor contents. Hydrogen was supplied continuously to maintain a polymer high load melt index (HLMI) of from 2.0 to 3.5, which resulted in a reactor concentration of about 1.0 to 1.5 mole percent of the liquid contents. 1-Hexene comonomer was supplied on demand in order to maintain a polymer density of about 0.950, which

resulted in a concentration of 0.4 to 1.0 percent by weight of the reactor liquid contents. Triethylboron was continuously added to the reactor to maintain a concentration of about 10 parts per million by weight of the reactor liquid contents. The productivity of the catalyst was about 1300 lbs polymer per pound of catalyst.

[0122] After the polymer exited the reactor it was purged with nitrogen at about 50° C. to about 70° C. for about two hours to remove the last traces of hydrocarbon reaction mixture. It was then pelletized in a commercial Warner-Pfleider ZSK continuous extruder with appropriate small amount of antioxidants. The final high load melt index was about 2.3 and the final density was found to be about 0.950.

[0123] A study was conducted of the inventive polymer of Example 1 and four commercially available PE-100 bimodal polyethylene resins to compare various properties of the respective resins. The results are reported below in Table 1.

[0124] Another study was conducted to compare various properties of pipe formed from the inventive polymer of Example 1 and a non-PE-100 resin having commercially acceptable slump characteristics. The results are reported below in Table 2. The comparisons in Table 2 for pipe extrusion show the versatility of the inventive resin. Pipes as large as 42 inches in diameter with a wall thickness of 2.5 inches and as small as 2 inches in diameter with a wall thickness of 0.18 inch have been successfully produced. The inventive resin is compared to typical PE3408 resins that perform well in those pipe sizes. The PE3408 resins were Chevron Phillips Chemical Company's HD 943 ethylene/1-hexene copolymer which were made with a conventional chromium catalyst. Initially, the PE3408 resins were extruded into pipe and thereafter, the inventive resin was extruded through the same die initially at the same die setting. As indicated in note (3) of Table 2, the die for the 42" diameter pipe had been adjusted to be out of round to accommodate slumping of the PE3408 resins. Upon extrusion of the inventive resin of Example 1 through the die, the die was adjusted to substantially true round, indicating that the inventive resin had no or substantially no slump. Other PE-100 type resins, which are bimodal polyethylene resins, either cannot be successfully extruded into 42" IPS DR 11 pipe or suffer a severe penalty for pipe extrusion rate due to excessive heat generation and subsequent pipe sag or slumping. Although the inventive resin of Example 1 produced pipe which can be classified as PE-100 pipe, as discussed above, the conventional PE-100 resins are not employed to produce 42" diameter PE-100 pipe due to their excessive slumping characteristics.

[0125] Per D2513 "Standard Specification for Thermoplastic Gas Pressure Pipe, Tubing, and Fittings", the maximum wall thickness eccentricity is 12% and the maximum ovality is 5%. The data in Table 2 show the inventive resin to fall within those ranges for both the 42" and the 2" pipes.

Examples 2-19

[0126] Catalyst Preparation:

[0127] Several runs were made at a pilot plant scale employing the catalyst system of the present invention. The procedure used in Example 1 to prepare the catalyst was also used in these examples, except that the amount of phosphoric acid added to the preparation was adjusted to vary the P/Al molar ratio of the resultant catalyst. Other steps were identical. Catalyst activation was similarly carried out in a fluidized bed in air at about 600° C. in all cases. 1.5 lbs of

catalyst was charged to a six-inch diameter cylinder with distributor plate for fluidization. Dry air was used to fluidize the catalyst as the temperature was raised to about 600° C. This process required about eight hours, and the catalyst was allowed to remain fluidizing in dry air at about 600° C. for about another six hours. The catalyst was flushed with dry nitrogen during cool-down and then stored under nitrogen until ready for use.

[0128] Polymerization

[0129] Ethylene polymers were prepared in Examples 2-19 in a continuous particle form process (also known as a slurry process) by contacting the catalyst with ethylene and 1-hexene comonomer. Ethylene which had been dried over activated alumina was used as the monomer. Isobutane which had been degassed by fractionation and dried over alumina was used as the diluent.

[0130] The reactor was a liquid full 15.2 cm diameter pipe loop having a volume of 23 gallons (87 liters). Liquid isobutane was used as the diluent, and occasionally some hydrogen was added to regulate the molecular weight of the polymer product. The reactor pressure was about 4 Mpa (about 580 psi). The reactor temperature was varied over a range of about 90° C. to about 105° C. as indicated in each experiment. The reactor was operated to have a residence time of 1.25 hours. Catalyst was added through a 0.35 cc circulating ball-check feeder. At steady state conditions the isobutane feed rate was about 46 liters per hour, the ethylene feed rate was about 30 lbs/hr, and the 1-hexene feed rate was varied to control the density of the polymer product. Ethylene concentration in the diluent was 8-12-mole percent, as indicated in each experiment. Polymer was removed from the reactor at the rate of about 23 lbs per hour and recovered in a flash chamber. A Vulcan dryer was used to dry the polymer under nitrogen at about 60° C. to about 80° C.

[0131] Cocatalysts were used, including triethylaluminum (TEA), triethylboron (TEB), and a mixture of 3 parts by weight TEB and 1 part by weight TEA. The concentration of total cocatalyst was varied from about 2 ppm to up to about 14 ppm, as indicated in each example, expressed with reference to the isobutane diluent. To prevent static buildup in the reactor, a small amount (<5 ppm of diluent) of a commercial antistatic agent, sold as Statix 450, was usually also added.

[0132] Resin Testing

[0133] Polymer molecular weights, branch profiles, and rheology were determined as described above. Pipe was made at about two inches in diameter on a 2.5 inch extruder at 210° C.

[0134] Discussion of Results

[0135] Tables 3 and 4 show the results of resin and pipe testing of 12 different experimental resins made in the pilot plant from the inventive catalyst. As indicated in Tables 3 and 4, cocatalyst type and amount, reactor temperature and other reaction variables, and the catalyst P/Al molar ratio were all varied. The hoop stress testing is shown for three different temperatures, along the ISO corresponding requirements needed for PE-100 certification. As reported in Tables 3 and 4, many cases values in considerable excess of the PE-100 qualification values were obtained. Some extremely high PENT tests were also obtained and are reported in Tables 3 and 4.

[0136] Table 5 shows another series of experimental resins which were made from the same catalyst system. In these

runs the catalyst had a P/Al molar ratio of about 0.08 and was activated at about 600° C. The reactor temperature was about 213° F., the cocatalyst was TEB, and ethylene was added to maintain 10 mol % in the reactor. 1-Hexene was added to the reactor at about 0.8 to 1 lbs/hr, and ethylene at about 22.5 lbs/hr. Although these resins were not extruded into pipe, physical properties were obtained, and Table 5 is presented to demonstrate the high CY-a parameters which can rise from the catalyst system of the present invention. As discussed above CY-a varies inversely with the rheological breadth, or the breadth of the relaxation time distribution. Low CY-a indicates greater breadth. Conventional chromium catalysts generally produce resins having CY-a between 0.1 and 0.2, and occasionally CY-a values as high as 0.22 are obtained. However, as reported in Tables 3 and 5, and especially in Table 5, the catalyst system of the present invention yields extraordinarily high CY-a values for a chromium catalyst. In general CY-a decreases as the molecular weight is raised and as the chromatographic breadth (M_w/M_n) is broadened. This makes the CY-a values in Tables 3, 4, and 5 all the more remarkable, because the resins of the present invention encompass chromatographic breadth (M_w/M_n) previously unobtainable and were made at extremely high molecular weight. Nevertheless, it is believed that the resins of the present invention yield high CY-a values that are superior to resins produced from conventional chromium based catalysts. This seemingly contradictory data, that is, extreme chromatographic breadth combined with extreme rheological narrowness, is again interpreted as evidence that these resins are devoid of long chain branching to an unprecedented extent.

[0137] Referring to FIGS. 1 and 2, number average molecular weights (M_n/M_w) at various polymer molecular weights were determined for the inventive polymers of Examples 1 and 19. Further, short chain branches per 1000 carbons (SCB/1000C) were determined for these polymers at various polymer molecular weights. As shown in FIGS. 1 and 2, M_n/M_w and SCB/1000C, indicated as SCB/1000TC, for the inventive polymers of Examples 1 and 19, respectively, were plotted with respect to polymer molecular weight. Both figures indicate that the polymers of the present invention have a flat or substantially flat short chain branching profile across a broad molecular weight profile. This indicates that short chain branching of the polymers of the present invention remains substantially constant across a broad range of molecular weights.

[0138] With reference to FIG. 3, melt viscosities and shear rates were determined and examined for the inventive polymers of Examples 1 and 19. As shown in the figure, melt viscosity was plotted with respect to shear rate to produce the respective curves. As indicated in FIG. 3, each inventive polymer has a high shear rate at low melt viscosity and, in contrast, a low shear rate at high melt viscosity. As an extrudable polymer, it is desirable for the polymer to have a high shear rate at low melt viscosity due to the ease of passing the polymer through the die. However, to assist in the prevention or reduction of slumping after the polymer passes through the extruder, it is desirable for the polymer to have a high shear rate at high melt viscosity. FIG. 3 illustrates that the polymers of the present invention have both desirable properties for the production of PE-100 pipe.

TABLE 1

Commercial Pipe Formulas For PE-100 Resins					
Property	Marlex® HD168	Inventive Resin of Example 1	Dow DODA- 2400	Alkathene® XS-108	BP Solvay Elmag® TUB121
MI, g/10 min.	0.08	0.0	0.07	0.07	0.07
HLMI, g/10 min.	7.1	2.1	7.0	10.1	8.8
Density, g/cc	0.962	0.960	0.960	0.960	0.960
Density, g/cc (actual calculated)	0.952			0.951	0.950
Carbon Black Content, wt %	2.4	0	0	2.4	2.2
Rheology Data					
Eta 0/sec	2.07E+05	1.82E+07	2.08E+05	3.31E+05	2.34E+05
Eta at 0.1/sec	7.23E+04	3.57E+05	8.10E+04	8.18E+04	8.42E+04
Eta at 100/sec	2.46E+03	2.56E+03	1.76E+03	2.11E+03	2.24E+03
Zero Eta	1.2	432	5.4	2.8	2.0
Tensile Properties					
Tensile at Yield, psi	3,840	3,760	3,800	3,890	3,720
Tensile at Break, psi	5,220	4,300	5,110	4,700	5,200
Elongation at Break, %	720	670	700	700	740
Flexural Modulus, 2%	135,700	122,700	128,300	132,300	126,900
Seam, psi					
Typical SEC Data for actual resins					
Mn (g/mol)	16,000	7,500			
Mw (g/mol)	280,000	490,000			
Mn (g/mol)	1,600,000	3,900,000			
Mw/Mn	18	65			
PENT, km	>1100	>1000	3360	>2180	>2300

[0139]

TABLE 2

Commercial Pipe Extrusion Processing Data		
Extrusion Properties	Inventive Runs of Example 1	Commercial Gas Plasma PE3408 Process Rated Runs
Production Rate, lb/hr	1725	1700
Pipe Size	42" IPS DR 17	42" IPS DR 17
% Ovality (1)	2.3	2.2
Wall Thickness Eccentricity, % (2)	9.9	5.6
Pipe Extruder Size	6"	6"
Extruder L/D	30:1	30:1
Comments	(3)	

TABLE 2-continued

Commercial Pipe Extrusion Processing Data		
Extrusion Properties	Inventive Runs of Example 1	Commercial PP PE3408 Process Rated Runs
Production Rate, lb/hr	780	800
Pipe Size	2" IPS DR 11	2" IPS DR 11
% Ovality (1)	0.54	0.51
Wall Thickness Eccentricity, % (2)	3.5	2.2
Pipe Extruder Size	4.5"	4.5"
Extruder L/D	30:1	30:1

(1) % Ovality in ASTM D2513 is $[(\text{Maximum OD} - \text{Minimum OD}) / (\text{Minimum OD} + \text{Maximum OD})] \times 100$
 (2) Wall thickness eccentricity (E) defined in ASTM D2513 is $[(A - B)/A] \times 100$ where A is maximum wall thickness and B is minimum wall thickness
 (3) Sharp between the die face and the sliding sleeve was noticeably less and required a die adjustment to substantially true round indicating no or substantially no slump.

[0140]

TABLE 3

Example	2	3	4	5	6	7
F/AI Mol Ratio	0.09	0.12	0.12	0.12	0.12	0.08
Reaction Temp. (deg F)	212.3	214.8	214.8	214.9	214.9	190.4
Rhylene Conc. (mol %)	8.91	6.61	6.61	11.21	7.32	9.96
EI Conc. (mol %)	1.87	0.79	0.79	1.23	0.23	2.29
1-Hexene Conc. (mol %)	0.62	0.30	0.30	0.54	0.41	1.29
Catalyst Type	TEB	3-ITEB/TEA	3-ITEB/TEA	3-ITEB/TEA	3-ITEB/TEA	3-ITEB/TEA
Catalyst Conc. (ppm)	10.2	2.6	2.6	3.9	11.7	3.0
Hexene, lb/hr	0.8	0.9	0.9	1.63	1.2	1.9
Rhylene, lb/hr	23.3	21.5	21.5	22.74	21.9	25.5
HLMI (g/10 min)	5.1	4.7	4.7	5.7	5.8	2.23
Density (g/cc)	0.9301	0.9406	0.9482	0.9489	0.9489	0.9488
Catalyst Productivity "Lb/Lb)	1851.85	1541	1541	2370	1388	2899
SEC Mw/1000	7.5	7.5	8.2	5.3	5.2	6
Mw/1000	368	410	442	394	441	405
Mn/1000	3053	3133	3420	3491	4932	3127
Mw/Mn	49.4	54.3	53.7	73.9	85.1	67.8
Rheology Ea(J)	6.73E+06	8.70E+06	1.07E+07	1.02E+07	1.90E+07	1.32E+07
CV _{0.01s}	0.2661	0.2855	0.2802	0.2903	0.2618	0.2943
PERT, lbs (2.4 MPa)	3375	>1411	>1411	>1680	>1657	>4822
Pipe Extrusion						
Output pounds/inch	1.76	1.7	1.73	1.67	1.79	
Head Pressure, psi	2970	2950	2250	2220	2590	
Die Pressure, psi	1300	1200	860	750	1120	
Melt Temp, F	428	430	407	404	405	
Pressure Testing (ISO requirement)	Passed	Passed	Passed	Passed	Failed	Passed
20 C., 1800 psi, hrs (>100 hrs)	261, 277, 307	642, 535, 417	585, 608, 441	472, 654, 600	183, 146, 183	263, 424, 280
80 C., 770 psi, hrs (>165 hrs)	720, 864, 1109	618, 968, 935	916, >1048, >1048	367, >1066, 408	26, 20, 38	>1121, 972, 692
80 C., 725 psi, hrs (>1000 hrs)	1429, 1740, 2002	>1026, >1026, >1026	>1007, >1026, >1026	>1026, >1026, >1026	210, 189, 245	>1049, >1049, >1049

[0141]

TABLE 4

Example	8	9	10	11	12	13
P/Al Mol Ratio	0.08	0.08	0.08	0.12	0.12	0.12
Reaction Temp. (deg F)	213.8	213.8	213.6	214.9	214.9	215.0
Ethylene Conc. (mol %)	10.14	9.95	10.00	6.20	6.20	10.28
H ₂ Conc. (mol %)	1.62	1.49	1.36	2.61	2.61	1.07
1-Hexene Conc. (mol %)	0.29	1.26	1.06	0.11	0.11	0.27
Catalyst Type	3:1TEB:TEA	3:1TEB:TEA	3:1TEB:TEA	TEA	TEA	TEA
Catalyst Conc. (ppm)	3.1	12.0	12.3	1.04	1.04	5.02
Hexane, lb/hr	0.7	0.6	0.5	0.4	0.4	0.2
Ethylene, lb/hr	25.5	25.2	25.1	23.3	23.3	21.7
HLMI (g/10 min)	1.23	3.5	3.0	2.0	2.1	3.3
Density (g/cc)	0.9495	0.9493	0.9497	0.9497	0.9496	0.9498
Catalyst Productivity (Lb/Lb)	2944	1818	1794	1053	1053	1531
SBC Mw/1000	7	6	5.1	8.2	8.04	4.2
Mw/1000	487	452	490	410	426	427
Mn/1000	3235	3810	3994	3108	3192	3826
Mw/Mn	70.8	78.3	88.6	49.9	53.9	101.1
Rheology Ea(0)	1.04E+07	5.52E+06	7.04E+06	8.84E+06	8.29E+06	1.33E+07
CY-a _{0.5}	0.3610	0.3361	0.3319	0.2853	0.2723	0.249
PENT, km (2.4 MPa)	>4822	>1747	>1774	>1411	>1367	>1963
Pipe Extrusion						
Output pounds/hr/in	1.55	1.79	1.81	1.75	1.71	2.17
Head Pressure, psi	3350	2500	2710	2980	2950	2270
Die Pressure, psi	1480	1100	940	1450		930
Melt Temp, F	410	408	409	409	408	405
Pressure Testing (ISO requirement)	Passed	Failed	Passed	Passed	Passed	Failed
20 C., 1800 psi, km (>100 km)	>1031, >1031, 627	167, 240, 194	354, 473, 372	213, 297, 315	272, 272, 284	144, 81, 102
80 C., 770 psi, km (>165 km)	>1121, >1119, >1121	51, 38, 66	>1145, >1145, >1141	>716, >716, >716	>716, >716, >716	105, 123, 87
80 C., 725 psi, km (>1000 km)	>1031, >1031, >1031	>498, >498, >498	>1145, >1145, >1145	>716, >716, >716	>716, >716, >716	>433, >433, >433

[0142]

TABLE 5

Example	14	15	16	17	18	19
H ₂ Conc. (mol %)	1.008	0.503	0.969	1.472	0.957	1.3
1-Hexene Conc. (mol %)	0.339	0.389	0.376	0.377	0.476	2.33
Concentration of TEB (ppm)	3.19	3.17	10.55	10.66	5.28	(3:1 TEA/TEB)
Catalyst Productivity (Lb/Lb)	2500		1923	2326	2703	1613
HLMI (g/10 min)	1.53	0.93	1.76	2.75	1.09	9.4
Density (g/cc)	0.9492	0.9476	0.9488	0.9486	0.9484	0.9533
SBC Data						
Mw/100	6.86	6.68	6.34	5.94	6.36	4.94
Mw/1000	483.5	513.9	490.1	459.5	498.7	324.0
Mn/1000	2823.5	2881	2873.1	2808.5	2806.1	2824.8
Mw/Mn	70.6	77.2	77.5	77.7	80.3	67.0
Rheology Data-Dynamic						
Ea(0)	1.00E+07	1.35E+07	8.07E+06	6.94E+06	1.20E+07	2.16E+07
CY-a _{0.5}	0.3486	0.3738	0.3811	0.3613	0.3723	0.2690

[0143] In the following examples, data are included in the examples about catalyst system preparation, polymerization conditions, as well as the resultant polymer. All chemical handling, including reactions, preparations and storage, was performed under a dry, inert atmosphere (usually nitrogen), unless otherwise indicated.

[0144] Polymerization Processes

[0145] Polymerization runs for the following examples were conducted using both a bench scale reactor and a loop reactor. Bench scale polymerizations were carried out in a 2.2 liter, stirred autoclave reactor equipped with a steel jacket for precise temperature control. Unless otherwise stated, a small amount (usually 0.01 to about 0.10 grams) of solid chromium containing catalyst was first charged under nitrogen to the dry reactor. Next, 1.2 liters of isobutane liquid was charged and the reactor was heated up to the specified temperature, usually around 95° C. (203° F.). When a cocatalyst was used, such as triethylboron (TEB) or triethylaluminum (TEA), a small amount (usually 1-2 mL) of a solution containing 1 weight percent of the cocatalyst diluted in heptane was added midway during the isobutane addition. Finally, ethylene was added to the reactor to bring the total reactor pressure to 550 pounds per square inch gauge (psig), which was maintained during the polymerization run. Stirring was continued for a specified time, usually around 1 hour, with the catalyst system activity being noted by recording the amount of ethylene flowing into the reactor required to maintain the set pressure. After the specified time, ethylene flow was discontinued and the reactor was allowed to depressurize and subsequently was opened to recover a granular polymer powder. In all cases, the reactor was clean with no indication of any wall scale, coating, or other forms of fouling. The polymer powder was removed and weighed. Activity was specified as grams of polymer produced per gram of solid catalyst charged per hour.

[0146] Polymerization runs were also carried out under continuous particle form process conditions in a loop reactor (also known as a slurry process) by contacting a chromium containing solid catalyst system with ethylene and sometimes 1-hexene as indicated. Ethylene used was polymerization grade ethylene (obtained from Union Carbide Corporation) which was purified through a column of alumina and activated at 250° C. (482° F.) in nitrogen. 1-Hexene, when used, was polymerization grade 1-hexene (obtained from Chevron Chemicals Company) which was purified by nitrogen purging and storage over 13x molecular sieve activated at 250° C. (482° F.) in nitrogen. The loop reactor was a liquid full, 15.2 cm diameter, loop reactor, having a volume of 23 gallons (87 liters). Liquid isobutane was used as the diluent, and occasionally some hydrogen was added to regulate the molecular weight of the polymer product. The isobutane was polymerization grade isobutane (obtained from Phillips Petroleum Company, Borger, Tex.) which was further purified by distillation and subsequently passed through a column of alumina and activated at 250° C. (482° F.) in nitrogen.

[0147] Reactor conditions included a pressure around 580 psi (4 MPa), and a temperature that was varied from about 65° C. (149° F.) to about 110° C. (230° F.) as indicated in the examples below. Also, the reactor was operated to have a residence time of 1.25 hours. The catalyst systems were added through a 0.35 cc circulating ball-check feeder. Cata-

lyst system concentrations in the reactor were within a range of from about 0.001 to about 1 weight percent based on the weight of the total reactor contents. Polymer was removed from the reactor at the rate of about 25 lbs per hour and recovered in a flash chamber. A Vulcan dryer was used to dry the polymer under nitrogen at about 60-80° C. (140-176° F.).

[0148] Cocatalysts such as triethylaluminum (TEA) and triethylboron (TEB) (obtained from Akzo Corporation) were also used. These cocatalysts were obtained as one molar solutions in heptane, but were further diluted to 1 weight percent. The cocatalysts were added as indicated in a concentration in a range of from about 1 to about 30 parts per million of the diluent in the polymerization reactor(s). To prevent static buildup of the reactor, a small amount (less than 5 ppm, by weight, of diluent) of a commercial antistatic agent sold as "Stadis 450" was usually added.

Example 20

[0149] This example illustrates the preparation of various catalyst systems used in the following Examples.

[0150] Chromium/Aluminophosphate Catalyst Systems

[0151] Aluminophosphate catalyst systems were prepared from a concentrated syrup containing aluminum nitrate nonahydrate, ammonium phosphate monobasic, and chromium nitrate. A small amount of water was added, usually about the same amount as the aluminum nitrate, and was warmed to about 40° C. (104° F.) to dissolve the mixture. The aluminum nitrate and ammonium phosphate monobasic were added in an amount needed to yield the desired phosphorus to aluminum mole ratio (P/Al). For example, to achieve a phosphorus to aluminum mole ratio (P/Al) of 0.2 in the final catalyst system, 0.2 moles of ammonium phosphate monobasic were added for each mole of aluminum nitrate nonahydrate. Chromium nitrate was added in an amount needed to yield 1 weight percent chromium on the final product. To this syrup then was added, with rapid and vigorous stirring, concentrated ammonium hydroxide to form a gel with a pH around 5-7. This gel was broken up and slurried in water to which more ammonium hydroxide was added to adjust the pH to about 8-9. At this pH, the slurry was heated to 60° C. (140° F.)-80° C. (176° F.) for about 1 hour, where it was aged. The slurry was then filtered, washed in about five times its volume in water, and filtered again. This process was repeated three times. The filtrate was given a final wash in n-propanol, filtered again, and dried at 110° C. (230° F.) under half an atmosphere of vacuum for 12 hours. The dried catalyst system was then pushed through a 35 mesh screen containing a 0.50 mm opening.

[0152] Some catalyst systems also were treated with fluoride by dissolving the desired amount of ammonium bifluoride in methanol. This solution was adjusted so that the resulting impregnated catalyst systems would come to the point of incipient wetness, and the solution then was impregnated onto or into the catalyst systems. The resultant damp powder then was dried again under half an atmosphere of vacuum at 110° C. (230° F.) for 12 hours.

[0153] Other Catalyst Systems

[0154] Other polymerization catalyst systems were used in the following examples and were loaded with about 1 weight percent chromium, unless otherwise indicated. 963 Magnapore®, 965 Sykopore®, and 969 MS are three polymer-

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ization catalyst systems that were used and are commercially available from Davison Chemical Company, a division of W. R. Grace & Co. 963 Magnapore®, a high porosity silica-titania catalyst system, was prepared in accordance with U.S. Pat. No. 3,887,494, the entirety of which is incorporated herein by reference. 963 Magnapore® contained 2.5 weight percent titanium, possessed a surface area of about 550 m²/g, and a pore volume of about 2.2 to about 2.5 cc/g. 965 Sylopor®, a lower porosity silica-titania catalyst system, was prepared in accordance with U.S. Pat. No. 4,981,83, the entirety of which is incorporated herein by reference. 965 Sylopor® contained 2.5 weight percent titanium, possessed a surface area of about 380 m²/g, and a pore volume of about 0.9 cc/g. 969MS, a silica supported catalyst system possessed a surface area of about 300 m²/g and a pore volume of 1.6 cc/g.

[0155] Activation of Catalyst Systems

[0156] On the bench scale reactor, described above, catalyst systems were activated by placing about 10 grams of the catalyst system in a 1.75 inch quartz tube fitted with a sintered quartz disk at the bottom. While catalyst systems were supported on the disk, dry air was blown up through the disk at the linear rate of about 1.6 to 1.8 standard cubic feet per hour. An electric furnace around the quartz tube was then turned on and the temperature was increased at the rate of 400° C. (752° F.) per hour to the desired temperature, such as, for example, 600° C. (1112° F.). The catalyst system was then collected and stored under dry nitrogen, where it was protected from the atmosphere until tested.

[0157] For the 23 gallon loop reactor, larger quantities of catalyst systems similarly were activated. The catalyst systems were activated by charging 1.5 pounds of catalyst system into a six inch diameter stainless steel furnace which was itself heated by electric coils surrounding the furnace. Dry air was allowed to rise up through a centered metal grid plate at the rate of about 0.12 to about 0.20 linear feet per second to fluid out of the catalyst system. The catalyst system then was heated up to the desired temperature over a period of about 5 hours. It was held at that specified temperature for another 6 hours, and cooled down to room temperature and stored under dry nitrogen until tested. About 65 to 85 percent of the catalyst system weight charged was recovered, the lost weight being water and very fine material.

[0158] In some cases, catalyst systems were treated with carbon monoxide before being discharged from the reactor and stored under nitrogen. This was done in order to reduce at least some of the hexavalent chromium to a divalent state, which can increase 1-hexene incorporation efficiency, as described in *Polymer Engineering and Science* (SPE), Vol. 28, No. 22, pp. 1469-1472 (1988). This was accomplished by fluidizing the catalyst systems in carbon monoxide at about 350° C. (700° F.) for about 2 hours after the calcination step. The carbon monoxide can be used pure or diluted with up to 90 percent nitrogen. Bench scale activations usually used pure carbon monoxide for convenience, while the 23 gallon loop reactor used 10 percent carbon monoxide. After carbon monoxide treatment, catalyst systems were flushed clean with nitrogen for about 1 hour, cooled in nitrogen, and then stored. The color of reduced catalyst systems was usually blue or green, indicating that all, or

substantially all, of the initial hexavalent chromium had been reduced to a lower oxidation state, generally the divalent state.

[0159] Analysis of the resultant polymers were conducted according to the following procedures.

[0160] Polymer density was determined in grams per cubic centimeter (g/cc) on a compression molded sample, cooled at about 15° C. (59° F.) per hour, and conditioned at room temperature for about 40 hours in accordance with ASTM D1505-68 and ASTM D1928, condition C.

[0161] High load melt index (HLMI) was determined in grams of polymer per 10 minutes (g/10 min) in accordance with ASTM D1238, Condition 190/2.16, at 190° C. (374° F.) with a 21,600 gram weight.

[0162] Melt Index (MI) was determined in grams of polymer per ten minutes in accordance with ASTM D1238, condition 190/2, at 190° C. (374° F.) with a 2,160 gram weight.

[0163] Typical molecular weights and molecular weight distributions were obtained using a Waters 150 CV size exclusion chromatograph (SEC) with trichlorobenzene (TCB) as the solvent, with a flow rate of 1 mL/minute at a temperature of 140° C. (284° F.). BHT (2,6-di-tert-butyl-4-methylphenol) at a concentration of 1.0 g/L was used as a stabilizer in the TCB. An injection volume of 220 L was used with a polymer concentration of 1.4 mg/L (at room temperature). Dissolution of the sample in stabilized TCB was carried out by heating at 160-170° C. (320-338° F.) for 4 hours with occasional, gentle agitation. The column was two Waters HPLW-6E columns (7.8x300 mm) and were calibrated with a broad linear polyethylene standard (Phillips Marlex® BHB 5003) for which the molecular weight had been determined. As a measure of volatile oligomeric components, or smoke, the amount of material found in the range of molecular weights from 100 to 1000 were listed.

[0164] A "Quantachrome Autosorb-6 Nitrogen Pore Size Distribution Instrument" was used to determine the surface area and pore volume of the supports. This instrument was acquired from the Quantachrome Corporation, Syosset, N.Y.

[0165] Environmental Stress Crack Resistance (ESCR, hrs) was determined according to ASTM D1693, Condition A.

[0166] PENT environmental stress crack resistance values were obtained at 80° C. (176° F.) according to ASTM F1473 (1997).

[0167] SEC-FTIR Branch Determination as a function of the molecular weight distribution was obtained as follows. For molecular weight determinations, a Polymer Laboratories model, 210 GPC equipped with two Styragel HT 6E columns (Waters), was used. Resin samples were dissolved in trichlorobenzene (TCB) containing 0.034 weight percent butylatedhydroxytoluene (BHT) by heating the mixture for 1 hour at 155° C. (311° F.) in a Blue M air convection oven. Resin samples of about 1.8 mg/mL were chromatographed at 1 mL/min using TCB as the mobile, at a sample injection volume of 500 µL. The samples were introduced to a Perkin Elmer Model 2000 FTIR spectrophotometer equipped with a narrow band mercury cadmium telluride (MCT) detector via a heated transfer line and flow cell (KBr windows, 1 mm optical path, and about 70 µL cell volume). The temperatures

of the transfer line and flow cell were kept at 143+/-1° C. (290+/-1° F.) and 140+/-1° C. (284+/-1° F.), respectively. Background spectra were obtained on the polymer free, solvent filled cell. All of the IR spectra were measured at 8 cm⁻¹ resolutions (16 scans).

[0168] Chromatograms were generated using the root mean square (rms) absorbance over the 3000-2700 cm⁻¹ spectral region and molecular weight calculations were made using a broad molecular weight PE standard. Spectra from individual time slices of the chromatogram were subsequently analyzed for co-monomer branch levels using the Chemometric techniques described below.

[0169] Narrow molecular weight distribution samples (M_w/M_n) of about 1.1 to about 1.3, solvent gradient fractions of ethylene 1-butene, ethylene 1-hexene, ethylene 1-octene copolymers, and polyethylene homopolymers were used in calibration and verification studies. Low molecular weight alkanes were also used. The total methyl content of these samples contained from about 1.4 to about 83.3 methyl groups per 1000 total carbon molecules. The methyl content of the samples was calculated from M_n (number average molecular weight) or was measured using C-13 NMR spectroscopy. C-13 NMR spectra were obtained on 15 weight percent samples in TCB using a 500 MHz Varian Unity Spectrometer at 125° C. (257° F.) as described in J. C. Randall and E. T. Hsieh; *NMR and Macromolecules; Sequence, Dynamic, and Domain Structure*, ACS Symposium Series 247, J. C. Randall, Ed., American Chemical Society, Washington D.C., 1984. Methyl content per 1000 carbon molecules by NMR was obtained by multiplying the ratio of branching signals to total signal intensity by 1000.

[0170] A calibration curve was generated using Pirovetti Chemometric software to correlate changes in the FTIR absorption spectra with calculated or NMR measured values for number of methyl groups per 1000 carbon molecules for the samples. The calibration results were obtained for the spectral region of 3000 cm⁻¹ and 2700 cm⁻¹ to avoid the solvent interference in quantitative results for prediction of the measured sample spectrum. Preprocessing of the spectral data included smoothing of 9 data points, baseline correction, and normalization. Further preprocessing of the spectral data entailed taking the first derivative of the spectra and mean centering all the data. A four component calibration model was calculated and optimized using the process of cross validation (RSQ=0.999, SEV=0.7). The calibration model was verified using 13 additional samples. The predicted versus actual values for the validation data showed excellent correlation (RSQ=0.987) and exhibited a root mean square error of prediction equal to +/-0.4 methyl groups per 1000 total carbon molecules.

[0171] Short chain branching levels were calculated by subtracting out methyl chain end contributions. The amount of methyl chain ends were calculated using the equation $Me_{en} = C(2 - V_{en})/M$, where Me_{en} is the number of methyl chain ends per 1000 total carbon molecules, C is a constant equal to 14000, V_{en} is the number of vinyl terminated chain ends (1 for chromium catalyzed resins), and M is the molecular weight calculated for a particular slice of the molecular weight distribution.

[0172] This example illustrates the traditional difficulties experienced in the art in using chromium/aluminophosphate catalyst systems. Table 6 compares the activity response of

the chromium/aluminophosphate catalyst systems when the phosphorus to aluminum (P/Al) mole ratio and activation temperature were varied. The chromium/aluminophosphate catalyst systems were obtained from a bench reactor operating at 95° C. (203° F.) with 4 ppm triethylboron (TEB) and 550 psig ethylene.

TABLE 6

Activity response of various chromium/aluminophosphate catalyst systems (g poly cat/hr) to various P/Al molar ratios and activation temperatures

P/Al molar ratio	Catalyst System Activity at Different Activation Temperatures		
	300° C.	300° C.	700° C.
0.0	0	535	1340
0.2	1085	1683	2295
0.4	2000	4790	5400
0.6	1970	6395	6300
0.8	2910	4444	4235
0.95	2500	3545	3770
1.0	0	0	700

[0173] As shown in Table 6, the highest activity catalyst systems were achieved with both high P/Al molar ratios and high activation temperatures. Catalyst systems run at low P/Al molar ratios and low activation temperatures generally yielded poor or unacceptable activity. However, it is at these low P/Al molar ratios and low activation temperatures where the broadest molecular weight distributions (MWD) are found and thus more desirable polymer properties.

Example 21

[0174] This example compares the environmental stress crack resistance (ESCR) values of polymers obtained from the loop reactor using chromium/aluminophosphate catalyst systems of varying P/Al molar ratios. The polymers (homopolymers) of this example were obtained from a 23 gallon loop reactor operating between about 93° C. (200° F.) to about 99° C. (210° F.) with 0.5 to 1 ppm triethylboron. The catalyst systems were activated at 600° C. (1112° F.) and the polymers obtained had melt index (MI) values of 0.15 to 0.35 g/10 minutes. As shown in Table 7, the highest ESCR values are obtained at low P/Al molar ratios.

TABLE 7

Environmental Stress Crack Resistance (ESCR) values of polymers versus P/Al molar ratios

P/Al									
0	0.2	0.3	0.37	0.4	0.5	0.55	0.6	0.8	0.9
ESCR, (hr)									
>100	>100	325	300	240	190	95	100	24	0

Example 22

[0175] This example illustrates another problem associated with chromium/aluminophosphate catalyst systems and the response to 1-hexene or other comonomers. Usually, commercial chromium catalyst systems (chromium/silica) incorporate 1-hexene well to easily produce ethylene/1-

225/100

benzene copolymers. The addition of 1-hexene in an amount equal to about 4 percent of the liquid diluent is usually sufficient to cover the entire copolymer range, from densities of 0.970 g/cc to densities as low as 0.920 g/cc for some catalyst systems. As 1-hexene is incorporated, the melt index potential of the catalyst system remains essentially unchanged due to the counter-balancing effect of an increase in melt index when 1-hexene is added and a decrease in melt index when the reactor temperature is lowered to prevent swelling.

[0176] However, chromium/aluminophosphate catalyst systems respond in a completely different manner. Even though 1-hexene can be added in large amounts, 1-hexene can be incorporated into the polymer only very sparingly. As a result, 1-hexene can have a poisoning effect on chromium/aluminophosphate catalyst systems which can decrease catalyst system activity and cause the melt index to rise excessively, often out of control. These effects are demonstrated in Table 8, below, and FIGS. 4 and 5. This data was obtained from the 23 gallon loop reactor under the conditions described above.

TABLE 8

Effect of 1-hexene on chromium/aluminophosphate catalyst systems compared to chromium/bifluoride catalyst systems			
Catalyst System	% Diluent of 1-hexene	Density of Polymer, g/cc	% Relative Activity of Catalyst System
Chromium/Aluminophosphate			
P/Al = 0.8	0.00	0.9369	100
P/Al = 0.8	0.90	0.9393	99
P/Al = 0.8	1.30	0.9395	95
P/Al = 0.8	1.40	0.9378	92
P/Al = 0.8	0.00	0.9672	100
P/Al = 0.8	1.30	0.9621	92
P/Al = 0.9	0.00	0.9630	100
P/Al = 0.9	2.00	0.9640	41
P/Al = 0.9	3.90	0.9605	36
P/Al = 0.3	0.00	0.9397	100
P/Al = 0.3	1.80	0.9367	96
P/Al = 0.3	3.65	0.9338	42
P/Al = 0.4	0.00	0.9610	100
P/Al = 0.4	4.00	0.9544	49
Chromium/Bifluoride			
	0.00	0.965	100
	1.00	0.952	104
	2.00	0.943	100
	3.00	0.938	96
	4.00	0.934	106

[0177] As Table 8, and FIGS. 4 and 5 illustrate, the decrease in density of the chromium/aluminophosphate catalyst systems is insignificant as 1-hexene is added, which is illustrative of the poor catalyst system activity. Even at large amounts of 1-hexene, i.e., up to 4 percent of the diluent, the density drop is still minimal. As Table 8 and FIGS. 4 and 5 represent, producing copolymers using typical chromium/aluminophosphate catalyst systems is problematic at best and certainly cannot produce copolymers with densities of about 0.955 g/cc and below.

INVENTIVE EXAMPLES A-M

[0178] The following examples illustrate the procedures of this invention and its effectiveness on the polymerization process and the resultant polymer.

[0179] Examples A-M demonstrate the effectiveness of the procedures of this invention. These examples, listed in Table 9, were prepared in the 23 gallon loop reactor described above using chromium/aluminophosphate catalyst systems (designated as AlPO₄ in the table) having a P/Al molar ratio of 0.2, which were further impregnated with 2% and 2.64% fluoride, as indicated (present in an effective amount of ammonium bifluoride). The catalyst systems were activated at a temperature of 1000° F. (538° C.) and 1100° F. (594° C.) as indicated, and run with 0 to about 2 ppm TEB cocatalyst, as indicated in the table.

[0180] As shown in Table 9, examples A-M have HLMI values at desired processing ranges of 5 to 10 g/10 minutes, densities ranging from 0.943-0.951 g/cc, and PENT ESCR values ranging from greater than 1950 hours to greater than 2091 hours. In all cases the PENT ESCR tests were stopped as the time approached 2000 hours; not because of sample failures, but in order to free the testing station for other work. The high PENT ESCR values associated with examples A-M was accomplished without excessively low HLMI values and at rather high densities, in one case at a density of 0.9516 g/cc. In addition, as shown in Table 9, examples H-M have weight average molecular weight distributions (M_w/M_n) ranging from 98 to 106, well above the comparative examples.

[0181] Carbon monoxide reduction can optionally be used in accordance with the procedures of this invention to improve 1-hexene incorporation. It can be seen in examples F and G the effects that carbon monoxide reduction can have on the resultant polymer. Although HLMI values of examples F and G are below the desired range, as shown in Table 9, copolymers were produced in accordance with this invention, even in the absence of carbon monoxide reduction.

TABLE 9

PENT ESCR values for selected pipe units											
Run	Catalyst System	Fluoride Level (wt % F)	Activation Temperature (° F)	CO reduction (700° F)	Cocatalyst (Conc ppm)	HLMI (g/10 min)	Density (g/cc)	ESCR (2.54 MPa)	M _w (<1000)	M _w (<1000)	M _w /M _n
A	Cr/ALPO ₄ = 0.2	2%	1000° F	No	TEB (2.05)	7.53	0.9505	>1950	—	—	—
B	Cr/ALPO ₄ = 0.2	2%	1000° F	No	TEB (1.32)	7.77	0.9491	>1957	—	—	—
C	Cr/ALPO ₄ = 0.2	2%	1000° F	No	TEB (1.16)	4.14	0.9484	>1966	—	—	—
D	Cr/ALPO ₄ = 0.2	2%	1100° F	No	TEB (1.5)	10.82	0.9496	>2095	—	—	—

TABLE 9-continued

PENT ESCR values for selected silica resins											
Run	Catalyst System	Fluoride Level (wt % F)	Activation Temperature (° F)	CO reduction (700° F)	Cocatalyst (Cmcs ppm)	HLMI (g/10 min)	Density (g/cc)	ESCR (2.54 MPa)	M _w (<1000)	M _w (>1000)	M _w /M _n
E	Cr/ALPO ₄ = 0.2	2%	1100° F.	No	TEB (1.77)	9.13	0.9453	>2091	—	—	—
F	Cr/ALPO ₄ = 0.2	2%	1100° F.	Yes	—	4.57	0.9481	>1562	—	—	—
G	Cr/ALPO ₄ = 0.2	2%	1300° F.	Yes	—	2.88	0.9456	>2006	—	—	—
H	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	4.8	0.9494	>2000	718	6900	104
I	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	6.0	0.9496	>2000	679	6900	98
J	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	7.9	0.9512	>2000	714	6900	105
K	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	5.3	0.9492	>2000	740	6900	107
L	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	6.2	0.9507	>2000	702	6900	108
M	Cr/ALPO ₄ = 0.2	2.64%	1100° F.	No	TEB (1)	7.5	0.9516	>2000	724	6900	108
C10	963 Magnapore	—	1200° F.	No	—	10.31	0.9443	64	173.45	17.85	9.72
C11	964 Magnapore	—	1200° F.	No	TEB (2.05)	11.28	0.9457	194	234.95	10.25	22.92
C12	963 Magnapore	—	1000° F.	Yes	TEB (3.12)	5.21	0.9493	113	—	—	—
C13	963 Magnapore	—	1200° F.	Yes	TEB (0.8)	10.32	0.9436	51	—	—	—
C14	963 Magnapore	—	1000° F.	No	TEB (6)	8.4	0.9511	230	554	8200	68
C15	963 Magnapore	—	1000° F.	No	TEB (6)	4.7	0.9504	374	564	8300	69
C16	963 Magnapore	—	1000° F.	No	TEB (6)	4.3	0.9507	281	571	7700	74
C17	963 Sytapore	—	1100° F.	No	TEB (1.75)	3.91	0.9486	52	—	—	—
C18	969 MS	—	1100° F.	No	TEB (2.15)	12.57	0.9435	356	254.94	12.81	19.9
C19	Cr/AlPO ₄ = 0.3	—	1100° F.	Yes	TEB (1)	21.44	0.9463	17	257.14	8.99	28.59
C20	Cr/AlPO ₄ = 0.3	—	1100° F.	Yes	TEB (1)	15.54	0.9507	37	—	—	—
C21	Cr/AlPO ₄ = 0.6	—	1100° F.	Yes	—	13.25	0.9432	143	259.02	11.03	23.48
C22	Cr/AlPO ₄ = 0.6	—	1100° F.	Yes	—	12.57	0.9440	166	170.6	9.5	17.95

*Weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity (M_w/M_n) was determined by SEC method (not coupled with FID).

COMPARATIVE EXAMPLES C10-C18

[0182] Also shown in Table 9 are similar pipe resins made under similar conditions, but using conventional catalyst systems. Notice that example C10, made from a Magnapore chromium/silica-titania catalyst system yielded a density much lower than desired and the PENT ESCR value was excessively low compared to the inventive examples described above. Although example C10 did not employ a triethylboron cocatalyst, known to broaden the molecular weight distribution of chromium/silica-titania catalyst systems, examples C11-C16 did employ a triethylboron cocatalyst. However, even with the addition TEB, it can be seen from Table 9 that the PENT ESCR value did improve, but the results were still inferior compared to the inventive examples. Also, in examples C12, and C14-C16 it can be seen the benefits that can be gained by using a lower activation temperature, in this case 1000° F. instead of 1200° F. Although examples C12, C14-C16 yielded high densities, the PENT ESCR values were poor in comparison to the inventive examples.

[0183] Also, example C17 used a triethylboron cocatalyst with a lower porosity chromium/silica-titania catalyst system, but again the PENT ESCR value was very low, even at the excessively low HLMI of 3.9 g/10 minutes. Even when a chromium/silica catalyst system was used instead of chromium/silica-titania catalyst system as shown in example 18, the benefits were minimal. Although the PENT ESCR value for the chromium/silica catalyst system was greater than the other chromium/silica-titania catalyst systems, it was still very low compared to the inventive examples.

COMPARATIVE EXAMPLES C19-C22

[0184] The low PENT ESCR values in examples C19-C22 show that not any chromium/aluminumphosphate catalyst system can be used, only those described in accordance with this invention. In these examples, chromium/aluminumphosphate catalyst systems were made as described above, and were run according to the same conditions used in inventive examples A-M, but the P/Al molar ratio was varied. In examples C19 and C20, the P/Al molar ratio was raised to 0.3, only slightly above the 0.2 molar ratio used in examples A-M. As shown in examples C21 and C22, the P/Al molar ratio was increased to 0.6, but again this resulted in low PENT ESCR values, even at the unacceptable low density obtained. As the data in Table 9 demonstrate, the PENT ESCR value suffered considerably when the P/Al molar ratio was increased much above 0.2. However, lower levels of P/Al molar ratios also can be unacceptable, since the catalyst system activity decreases substantially.

Example 23

[0185] This example illustrates the effect of fluoride on the catalyst systems used in accordance with this invention. It is generally known that fluoride improves activity for catalyst systems containing alumina, but its effects on density have not been previously known. In this example, chromium/aluminumphosphate catalyst systems were made as described above, but impregnated with different amounts of fluoride. Two P/Al molar ratios were chosen, one high (P/Al=0.6), and one low (P/Al=0.2) to illustrate fluoriding effects on density. Catalyst systems were activated at 1200° F. (649° C.) and polymers were produced in the 23 gallon loop reactor as described above using about 1 ppm triethylboron (TEB) cocatalyst. The results are described in Table 10 below.

TABLE 10

Effect of fluoride on polymer as indicated by density of polymer at P/Al molar ratios of 0.2 and 0.6		
Percent Fluoride added	Density of Polymer	
	P/Al = 0.2	P/Al = 0.6
0.00%	0.9382	0.9647
0.34%	0.9373	na
0.67%	0.9365	0.9625
1.34%	0.9347	0.9605
2.01%	0.9338	0.9600
2.68%	0.9339	na

[0186] As the data in Table 10 demonstrate, as fluoride was added to the catalyst systems, it was observed that the natural density of the polymers decreased. As shown in Table 10, most of the effect on density occurred by about 2 percent NH_4HF_2 addition (1.34% F), but small decreases in density were visible at increased fluoride percentages, both at P/Al molar ratios of 0.2 and 0.6. Natural lowering of density is very helpful for Chromium/aluminumophosphate catalyst systems because, as stated above, chromium aluminumophosphate catalyst systems have a tendency to be poisoned by 1-hexene comonomer which would ordinarily be used to lower density.

[0187] However, as shown in Table 11 below, adding too much fluoride can be detrimental.

TABLE 11

Effect of Fluoride on catalyst system activity				
% F	Grams of Catalyst system charged (g cat)	Grams of polymer obtained (g pol)	Time (min)	Activity (g pol/g cat/h)
0.00%	0.06	138.3	60.0	2305
2.68%	0.0487	122.3	53.3	3063
4.00%	0.0376	73.0	61.2	1903
4.00%	0.0350	213.0	62.5	2152
4.00%	0.0385	132	60.5	1908

[0188] The data in Table 11 were obtained from polymers made using the bench reactor with 8 ppm TEB cocatalyst, under conditions described above. Chromium/aluminumophosphate catalyst systems were made as described above at a P/Al molar ratio of 0.2 and at an activation temperature of 1100° F. (593° C.), except that the level of ammonium bifluoride was varied. As the data in Table 11 indicate, although initially fluoride enhanced the catalyst system activity, 6 percent NH_4HF_2 (4% F) appeared to impair catalyst system activity. Although the precise optimum level of fluoride will vary somewhat with activation temperature, surface area, and other factors, etc., it would appear that the optimum level would be in the general range of about 2 to about 4 percent NH_4HF_2 (1.34-2.68% F) or the equivalent thereto of some other fluoride source.

Example 24

[0189] This example illustrates the preferred use of cocatalyst(s) in the present invention. Since low P/Al molar ratios and low activation temperatures are preferred in chromium/aluminumophosphate catalyst systems for improved

polymer properties, the catalyst systems naturally exhibit low activity, especially if 1-hexene is added to make copolymers. Thus, the use of cocatalyst(s) to improve catalyst system activity is particularly effective for chromium/aluminumophosphate catalyst systems. Preferably, in accordance with the procedures of this invention, a cocatalyst(s) is present in the reactor in a concentration in the range of from about 0.3 to 10 ppm. In this example, aluminumophosphate catalyst systems were prepared according to the procedure described above at a temperature of 1200° F. (649° C.) and used with various cocatalysts as indicated in Table 12 below. The cocatalyst effect on catalyst system activity is noted.

TABLE 12

Cocatalyst Effect		
Cocatalyst	Concentration (ppm)	Activity (g pol/g cat/h)
None		1725
EtEt ₂	4	3920
EtEt ₂	8	4400
EtEt ₂	16	1930
EtEt ₂	4	5590
EtEt ₂	8	6264
EtEt ₂	16	5725
EtEt ₂	24	1033
EtPh ₂	8	1290
AlEt ₃	4	1885
AlEt ₃	8	1720
AlEt ₃ + EtEt ₂	4 & 4	6835
ZnEt ₂	8	1945
AlEt ₂ Cl	4	1790
AlEt ₂ Cl	8	1430
AlEt ₂ Cl	8	1065
MgEt ₂	8	1670
LiEt ₃	4	1540
LiEt ₃	8	1280
AlEt ₂ OEt	8	1230
EtEt ₂ Cl ₂	8	505
NaEtPh ₄	4	830
NaEtPh ₄	8	2130
NaEtPh ₄	32	260
LiEtEt ₂	4	1957
EtEt ₂	16	685
EtPh ₂	16	1730
EtZnEt	15	2060
EtEtOAlEt ₂	8	3125
GeEt ₄	16	0
Ph ₃ SiOEtEt ₂	16	0

Et = Ethyl
Et₂ = Diethyl
Ph = Phenyl

[0190] As the data in Table 12 demonstrate, trialkylboron compounds as cocatalyst was effective in its effect on catalyst system activity as well as trialkylaluminum compounds. Combinations of triethylboron and triethylaluminum compounds were also effective on catalyst system activity. In some cases, the combination of triethylboron and triethylaluminum compounds as cocatalyst(s) exhibited higher catalyst system activity than either compound alone.

Example 25

[0191] This example illustrates the molecular weight distribution of polymers produced in accordance with this invention. To obtain this distribution, a chromium/aluminumophosphate catalyst system with a P/Al molar ratio of 0.2 and 4 weight percent ammonium bifluoride was prepared by the method described above and activated at 1100° F. (649° C.). Triethylboron was used as cocatalyst at 2.1 ppm. The

resultant polymer was produced in the 23 gallon loop reactor as described above and had a HLMI of 6.75 g/10 minutes and a density of 0.9485 g/cc. A branch profile analysis of this polymer displaying the branching and molecular weight distribution is shown in FIG. 6.

[0192] Ordinarily, chromium based catalyst systems tend to incorporate comonomers into the low molecular weight portion of the distribution. This can be undesirable since desirable properties can be found in distributions containing branching in the largest chains, since these can serve as tie molecules between crystallites. FIG. 6, as well as FIGS. 1 and 2, demonstrates that the catalyst systems of this invention produce polymers where the branching tends to be weighted toward the high molecular weight end, which is where the superior PENT ESCR values can be found. Also, FIG. 6, as well as FIGS. 1 and 2, demonstrates the extremely broad molecular weight distribution of polymers produced in accordance with this invention. The weight average molecular weight (M_w) was 759,000 while the number average molecular weight (M_n) was 4310, giving a polydispersity breadth (M_w/M_n) of 176.3, as determined by SEC-FTIR Branch Determination method.

[0193] Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

What is claimed is:

1. A composition comprising a PE-100 copolymer of ethylene and 1-hexene having an average molecular weight greater than at least about 300,000 g/mol and a substantially constant branch distribution profile at molecular weights greater than about 1×10^4 .
2. The composition according to claim 1, wherein the average molecular weight is greater than at least about 350,000 g/mol.
3. The composition according to claim 1, wherein the average molecular weight is greater than at least about 400,000 g/mol.
4. The composition according to claim 1, wherein the average molecular weight is greater than at least about 450,000 g/mol.
5. The composition according to claim 1, wherein the branch distribution profile is substantially constant between molecular weights of about 1×10^4 to about 1×10^7 .

6. A PE-100 pipe comprising the composition according to claim 1.

7. A method of making a PE-100 pipe comprising extruding the composition according to claim 1 in a molten state through a die to form the PE-100 pipe and cooling the pipe.

8. A composition comprising a PE-100 copolymer of ethylene and 1-hexene having an $E_{tr}(0)$ greater than about 1×10^4 pa-sec and a substantially constant branch distribution profile at molecular weights greater than about 1×10^4 .

9. The composition according to claim 8, wherein the $E_{tr}(0)$ greater than about 5×10^4 pa-sec.

10. The composition according to claim 8, wherein the $E_{tr}(0)$ greater than about 1×10^7 pa-sec.

11. The composition according to claim 8, wherein the $E_{tr}(0)$ greater than about 2×10^7 pa-sec.

12. The composition according to claim 8, wherein the branch distribution profile is substantially constant between molecular weights of about 1×10^4 to about 1×10^7 .

13. A PE-100 pipe comprising the composition according to claim 8.

14. A method of making a PE-100 pipe comprising extruding the composition according to claim 8 in a molten state through a die to form the PE-100 pipe and cooling the pipe.

15. A composition comprising a PE-100 copolymer of ethylene and 1-hexene having an $E_{tr}(0)$ less than about 5×10^4 pa-sec and a substantially constant branch distribution profile at molecular weights greater than about 1×10^4 .

16. The composition according to claim 15, wherein the $E_{tr}(0)$ greater than about 2.5×10^4 pa-sec.

17. The composition according to claim 15, wherein the $E_{tr}(0)$ greater than about 1.5×10^4 pa-sec.

18. The composition according to claim 15, wherein the $E_{tr}(0)$ greater than about 1×10^7 pa-sec.

19. The composition according to claim 15, wherein the branch distribution profile is substantially constant between molecular weights of about 1×10^4 to about 1×10^7 .

20. A PE-100 pipe comprising the composition according to claim 15.

21. A method of making a PE-100 pipe comprising extruding the composition according to claim 15 in a molten state through a die to form the PE-100 pipe and cooling the pipe.

• • • • •

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United States Patent Office

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3,071,493
METAL PLATING PROCESS

Thomas F. Whaley, Baton Rouge, La., and Vello Nor-
mann, Chapel Hill, N.C., assignors to Ethyl Corpora-
tion, New York, N.Y., a corporation of Delaware
No Drawing: Filed Nov. 15, 1961, Ser. No. 152,453
7 Claims. (Cl. 117-197)

This invention relates to the plating of appropriate
substrates using polymetallic organometallic compounds.
More particularly this invention relates to the plating of
alloys on appropriate substrates by the decomposition of
bimetallic organometallic compounds. This invention is
a continuation-in-part of our copending application, Serial
No. 831,077, filed August 3, 1959, now Patent No. 3,018,
194.

Hitherto, in order to deposit alloys by the decompo-
sition of organometallic compounds, it has been neces-
sary to employ two different mono metal containing com-
pounds. For example, molybdenum-tungsten alloys have
been prepared by pyrolysis of the mixed carbonyl vapors,
i.e., a mixture of molybdenum carbonyl and tungsten
carbonyl. Furthermore, alloys have been produced by
hydrogen reduction of the mixed chloride vapors. Thus,
titanium-tantalum alloys have been obtained by co-depo-
sition from the respective bromides utilizing hydrogen
reduction. However, in attempting alloy plating from
two different chemical compounds it often happens that
a marked difference exists in the chemical affinities of the
two alloying constituents. In such cases deposition of
only one constituent will usually occur to the entire ex-
clusion of the other constituent. Thus, it becomes neces-
sary to, as nearly as possible, equalize rates of deposition
by proper choice of deposition temperature. In other
words, it becomes necessary to choose chemically com-
patible compounds as plating agents. Because of this,
the choice of available compounds for producing alloy
plates from two different mono metal containing com-
pounds becomes considerably narrowed. Consequently,
the types of feasible alloys also are decreased. Accord-
ing to the present invention, these inherent disadvantages
in the prior art processes for plating alloys by decompo-
sition or reduction of different metal compounds are over-
come by employing bimetallic organometallic compounds
in the plating process. By virtue of this plating process,
vastly improved alloy plates are provided on a wide range
of substrates.

Thus, among the objects of this invention is that of
providing a process for plating alloys on substrates using
bimetallic organometallic compounds. Another object is
to provide a decomposition process for plating substrates
using these bimetallic organometallic compounds. A
further object of this invention is to provide a thermal
process for plating substrates by thermal decomposition
of bimetallic organometallic compounds. Still another
object of this invention is to provide novel and highly
useful alloy plated articles made according to these pro-
cesses. Other important objects of this invention will be
apparent from the ensuing description.

According to this invention there is provided a process
for alloy plating a substrate by the decomposition of a
polymetallic organometallic compound in contact with
the substrate. In their broadest aspect the bimetallic
organometallic compounds of this invention contain at
least two different metals. Within the scope of this in-
vention is a process for plating a substrate comprising
heating the object to be plated to a temperature above
the decomposition temperature of a bimetallic organo-
metallic compound and contacting said compound with
said heated substrate. Those bimetallic organometallic
compounds which contain as the exclusive constituents of

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the molecule, two different metals and unsubstituted hy-
drocarbon radicals are especially useful in vapor phase
alloy plating operations. In carrying out these vapor
phase techniques the substrate to be alloy plated is heated
to a temperature above about 200° C. while maintained
under an inert atmosphere such as nitrogen, the rare
gases (e.g., neon, argon, krypton, xenon), etc.

Bimetallic organometallic compounds used in this in-
vention and comprising one embodiment thereof can be
represented by the general formula



wherein M is a metal selected from the group consisting
of groups I, II, III-B, IV-B, V-B, VI-B, VII-B, VIII
of the periodic chart of the elements and tin and alumi-
num; M' is a different metal selected from the group
consisting of group III-A of the periodic chart of the
elements and zinc and cadmium; R is a monovalent
anion—i.e., group or radical; x is an integer correspond-
ing to the valence of the metal M'; y is an integer corre-
sponding to the valence of the metal M. It is especially
preferred that the monovalent anion R be a substituent
which upon the decomposition of the bimetallic organo-
metallic plating agent forms decomposition by-products
which are devoid of free hydrogen. Hydrogen by-pro-
duct is particularly undesirable in those cases wherein the
alloys to be plated and the substrate are susceptible to
hydrogen embrittlement.

Bimetallic organometallic compounds which comprise
another embodiment of the present invention may be rep-
resented by the general formula



wherein M^(a) is a metal selected from the group consist-
ing of the group IV-A metals (silicon, germanium, tin
and lead) and aluminum; M^(b) is a different metal se-
lected from the groups consisting of IV-B, V-B, VI-B,
VII-B and VIII of the periodic chart of the elements. R
is an electron donating moiety individually selected from
the group consisting of hydrocarbon and hydrogen, and
w is an integer equaling the number of R groups bonded
to the metal M^(b). The following table gives the value
for x and z where the metal M^(b) contains odd and even
numbers of d orbital electrons.

	w=1	w=2	w=3
M ^(b) is a metal having an odd number of d orbital electrons.	x=2, z=3	x=1, z=3	x=2, z=1
M ^(b) is a metal having an even number of d orbital electrons.	x=1, z=3	x=1, z=1	x=2, z=1

y is calculated from the formula

$$y = \frac{G - m - N}{3}$$

where G is the atomic number of the next rare gas of the
metal M^(a); m is an integer equaling 1 when the number
of d orbital electrons of the metal M^(a) is odd and 2
when the number of d orbital electrons of said metal is
even. N equals the atomic number of the metal M^(b).
It is preferred that the radical R be a substituent upon
which the decomposition of the bimetallic organometallic
plating agent forms decomposition by-products which are
devoid of free hydrogen.

Other bimetallic organometallic compounds which
form another embodiment of the present invention can
be represented by the general formula



wherein M^(a) is a metal selected from the groups II-A,
II-B, III-A, IV-A and V-A of the periodic chart of ele-

ments, Fisher Scientific Company, 1955; $M^{(a)}$ is a metal selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of elements. R is an electron donating moiety individually selected from the group consisting of hydrocarbon and hydrogen, and R' is an unsaturated organo group containing up to about 20 carbon atoms. w is an integer having a value of from 0 up to the valence of the metal $M^{(a)}$ minus 1, and z is an integer having a value of 1, 2 or 3 and is dependent on the valence of the metal $M^{(a)}$ minus the value of the integer w. y is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(a)}$ in accordance with the equation

$$y = \frac{G_1 - n - (\beta_1 + 1)}{2}$$

wherein G_1 is an integer representing the number of electrons in the next inert gas after the metal $M^{(a)}$, and n is an integer equaling the atomic number of the metal $M^{(a)}$, while β_1 is an integer equaling the number of pi electrons of the unsaturated organo group R'.

Bimetallic organometallic compounds which form a further embodiment of the present invention can be represented by the general formula



wherein M^a is a metal selected from the group consisting of boron, aluminum, gallium, indium and thallium, and M^b is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin and lead. The groups R represent electron donating moieties individually selected from the groups consisting of hydrocarbon and hydrogen. a and b are integers having a value of from 0 to the valence of the respective metals, M^a and M^b , minus 1. x is an integer having a value of from 1 to the valence of the metal M^b minus the value of the integer a.

A further embodiment of the present invention is the bimetallic organometallic compounds which can be represented by the general formula



wherein $M^{(a)}$ is a metal selected from the group consisting of groups IV-B, V-B, VI-B, VII-B and VIII, and $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements. x is an integer having a value of 1 to 5, inclusive, in accordance with

$$y = \frac{G - m - N}{2}$$

the equation in which G is the atomic number of the next rare gas of the metal $M^{(a)}$. m is an integer having a value of 1 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is odd and 2 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is even, and N is the atomic number of the metal $M^{(a)}$.

y is an integer having a value of 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(a)}$, and m is an integer equaling 1 where the number of d orbital electrons in the metal $M^{(a)}$ is odd and 2 where the number of d orbital electrons in the metal $M^{(a)}$ is even. N is equal to the atomic number of the metal $M^{(a)}$.

z is an integer having the value of 1 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is odd and a value of 2 when the number of d orbital electrons in the metals is even.

A further embodiment of the present invention is the

bimetallic organometallic compounds which can be represented by the general formula



wherein $M^{(a)}$ is a transitional metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII; and $M^{(b)}$ is a different transitional metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII; and R' and R'' are unsaturated organo groups containing up to about 25 carbon atoms. R' and R'' may be the same or different; x is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(a)}$ and is calculated by the following formula

$$x = \frac{G_2 - n_2 - (\beta_2 + 1)}{2}$$

wherein G_2 represents the number of electrons in the next inert gas after the metal $M^{(a)}$; n_2 equals the atomic number of the metal $M^{(a)}$; and β_2 equals the number of pi electrons in R'.

y is an integer, having a value of from 1 to 5, inclusive, equaling the number of carbonyl groups bonded to the metal $M^{(b)}$ and is derived by using the following formula

$$y = \frac{G_2 - n_2 - (\beta_2 + 1)}{2}$$

wherein G_2 represents the number of electrons in the next inert gas after the metal $M^{(b)}$; n_2 equals the atomic number of the metal $M^{(b)}$; β_2 equals the number of pi electrons in R''.

A still further embodiment of the present invention is the bimetallic organometallic compounds having the general formula



wherein $M^{(a)}$ is a metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements. $M^{(b)}$ is a different transitional metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII. R is an unsaturated organo group containing up to about 25 carbon atoms. x is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(a)}$ and is defined by the following formula

$$x = \frac{G_3 - N_3 - (\beta_3 + 1)}{2}$$

wherein G_3 is the number of electrons in the next inert gas after $M^{(a)}$; N_3 is the atomic number of the metal $M^{(a)}$; and β_3 is equal to the number of pi electrons in R.

y is an integer, having a value of from 1 to 5, inclusive, equaling the number of carbonyl groups bonded to the metal $M^{(b)}$ and is defined by the formula

$$y = \frac{G_3 - m_3 - N}{2}$$

wherein G_3 equals the atomic number of the next rare gas of the metal $M^{(a)}$; m_3 is an integer having the value of 1 where the number of d orbital electrons in the metal $M^{(a)}$ is odd and a value of 2 where the number of d orbital electrons in the metal $M^{(a)}$ is even. N is an integer equaling the atomic number of the metal $M^{(b)}$.

z is an integer having a value of 1 when the number of d orbital electrons of the metal $M^{(b)}$ is odd and a value of 2 where the number of d orbital electrons in said metal is even.

A still further embodiment of the present invention is the bimetallic organometallic compounds having the general formula



wherein $M^{(a)}$ is a group III-A metal (boron, aluminum, gallium, indium and thallium); and $M^{(b)}$ is a metal selected from the group consisting of phosphorus, arsenic,

antimony and bismuth; R represents an electron donating moiety consisting of hydrogen and hydrocarbon, said hydrocarbon containing up to 20 carbon atoms.

The process of this invention presents a significant advance over the prior art in that for the first time it is possible to produce alloy plates from bimetallic organometallic compounds in a simple, safe, economical process. A further advantage of this invention is that through the employment of this process it becomes possible to produce alloy plates having exceptional purity and excellent adherence to the substrate on which the alloy is plated. Furthermore, the process of this invention provides easy control of the proportionate metallic content of the respective metal of the alloy. That is, because of the ready availability of bimetallic organometallic compounds having wide variation in the percent weight ratio of the different metals contained therein, it is, as a result of this invention, now simply a matter of choosing the compound having a metal content "tailor made" to producing the desired alloy. Thus, it becomes unnecessary to hunt for compounds having suitable mutual chemical affinity such as compatible decomposition temperatures, decomposition rates, etc., which heretofore has been such a limiting factor in applying organometallic decomposition technology to the production of alloys. Also, the process of this invention provides easy control of the alloy plate thickness. On the one hand, a micro molecular alloy film can be plated on the substrate and in other cases, if so desired, thicker alloy plates can be obtained. A particular advantage of using bimetallic organometallic compounds which upon decomposition yield by-products which are exclusive of free hydrogen and oxidizing materials is that the alloy plates are thereby obtained free of undesirable oxide impurities and are not deteriorated through hydrogen embrittlement.

In general, any prior art technique for metal plating an object by thermal decomposition of the metal containing compound can be employed in the plating process of this invention as long as a bimetallic organometallic compound is employed as the plating agent (i.e., the metallic source of the metal plate). Thus, for example, any technique heretofore known for the thermal decomposition and subsequent plating of group VI-B metals from the bisacarbonyl derivatives of those metals can be so employed. Illustrative are those techniques described by Lander and Germer, American Institute of Mining and Metallurgical Engineers, Tech. Publication No. 2259 (1957). Usually the technique to be employed comprises heating the object to be plated to a temperature above the decomposition temperature of the metal containing compound and thereafter contacting the metal containing compound with the heated object. The following examples are more fully illustrative of the process of this invention and in these and other working examples all parts and percentages are by weight.

The process employed in these examples is as follows: Into a conventional heating chamber provided with means for high frequency induction heating and gas inlet and outlet means is placed the object to be plated. The bimetallic organometallic compound is placed in a standard vaporization chamber provided with heating means, said vaporization chamber being connected through an outlet port to the aforesaid combustion chamber inlet means.

For the plating operation the substrate is heated to a temperature above the decomposition temperature of the bimetallic organometallic plating agent, the system is evacuated and the organometallic compound is heated to an appropriate temperature where it possesses vapor pressure of up to about 10 millimeters. In most instances the process is conducted at no lower than 0.01 millimeter pressure. The vapors of the bimetallic organometallic compound are pulled through the system as the evacuating means operates and they impinge on the heated object decomposing and forming alloy plates. No carrier

gas need be employed. However, in certain cases a carrier gas can be employed to increase the efficiency of the above disclosed plating system. In those cases where a carrier gas employed, a system such as described by Lander and Germer, American Institute of Mining and Metallurgical Engineers, Tech. Publication No. 2259 (1947) at page 7, can be utilized.

Example I

- 10 Compound ----- $\text{Sn}(\text{AlEt}_2)_2$ (tin bis- aluminum tetraethyl).
- Temp. of substrate --- 350°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.5 mm.
- 15 Compound temp. ----- $90-100^\circ \text{C}$.
- Time ----- 2 hours.
- Results ----- Dull, grey, metallic coating.

Example II

- 20 Compound ----- $\text{Li}(\text{AlCp})_2$ (lithium aluminum tetra cyclopentadienide).
- Temp. of substrate --- 350°C .
- Nature of substrate --- Mild steel.
- Pressure ----- 0.1 mm.
- 25 Compound temp. ----- 150°C .
- Time ----- 1 hour.
- Results ----- Dull metallic coating.

Example III

- 30 Compound ----- $\text{Li}(\text{Al indenide})_2$ (lithium aluminum tetraindenide).
- Temp. of substrate --- 300°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.5 mm.
- 35 Compound temp. ----- 130°C .
- Time ----- 1 hour.
- Results ----- Dull metallic.

Example IV

- 40 Compound ----- $\text{Li}(\text{AlEt}_2\text{H})_2$ (lithium aluminum triethyl hydride).
- Temp. of substrate --- 900°C .
- Nature of substrate --- Nickel.
- Pressure ----- 3-4 mm.
- 45 Compound temp. ----- 130°C .
- Time ----- 1 hour.
- Results ----- Dull metallic.

Example V

- 50 Compound ----- $\text{Cp}_2\text{TiCl}_2\text{AlEt}_2$ (dicyclopentadienyl titanium dichloride aluminum diethyl).
- Temp. of substrate --- 250°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.1 mm.
- 55 Compound temp. ----- 120°C .
- Time ----- 2 hours.
- Results ----- Dull metallic.

Example VI

- 60 Compound ----- $\text{Fe}(\text{CO})_5\text{SnEt}_2$ (iron tetracarbonyl tin diethyl).
- Temp. of substrate --- 450°C .
- Nature of substrate --- Graphite.
- Pressure ----- 5 mm.
- 65 Compound temp. ----- 75°C .
- Time ----- $2\frac{1}{2}$ hours.
- Results ----- Dark grey, dull coating.

Example VII

- 70 Compound ----- $\text{Fe}(\text{CO})_5\text{PbEt}_2$ (iron tetracarbonyl lead diethyl).
- Temp. of substrate --- 400°C .
- Nature of substrate --- Mild steel.
- Pressure ----- 2 mm.
- 75 Compound temp. ----- 80°C .

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Time _____ 1 hour.
Results _____ Dark grey, dull coating.

Example VIII

Compound _____ $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

Temp. of substrate _____ 250°C .
Nature of substrate _____ Glass.
Pressure _____ 2 mm.
Compound temp. _____ 125°C .
Time _____ 2 hours.
Results _____ Metallic grey coating.

Example IX

Compound _____ $(\text{C}_6\text{H}_5)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (diphenyl lead bis-manganese pentacarbonyl).

Temp. of substrate _____ 500°C .
Nature of substrate _____ Glass.
Pressure _____ 0.1 mm.
Compound temp. _____ 95°C .
Time _____ 45 minutes.
Results _____ Metallic grey coating.

Example X

Compound _____ $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ (triphenyl tin manganese tetracarbonyl triphenyl phosphite).

Temp. of substrate _____ 450°C .
Nature of substrate _____ Aluminum.
Pressure _____ 0.2 mm.
Compound temp. _____ 150°C .
Time _____ 30 minutes.
Results _____ Grey coating.

Example XI

Compound _____ $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate _____ 525°C .
Nature of substrate _____ Copper.
Pressure _____ 0.5 mm.
Compound temp. _____ 125°C .
Time _____ 4 hours.
Results _____ Black metallic coating.

Example XII

Compound _____ $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ (triphenyl tin manganese tetracarbonyl triphenyl phosphite).

Temp. of substrate _____ 400°C .
Nature of substrate _____ Glass.
Pressure _____ Atmospheric.
Compound temp. _____ 150°C .
Time _____ 30 minutes.
Results _____ Grey metallic coating.

Example XIII

Compound _____ $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

Temp. of substrate _____ $400\text{--}410^\circ\text{C}$.
Nature of substrate _____ Glass.
Pressure _____ 0.5 mm.
Compound temp. _____ 130°C .
Time _____ 2 hours.
Results _____ Dark grey metallic coating.

Example XIV

Compound _____ $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

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Temp. of substrate _____ 650°C .
Nature of substrate _____ Glass.
Pressure _____ 2 mm.
Compound temp. _____ 175°C .
Time _____ $2\frac{1}{4}$ hours.
Results _____ Grey, black metallic coating.

Example XV

10 Compound _____ $(\text{CH}_3)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (dimethyl lead bis-manganese pentacarbonyl).

Temp. of substrate _____ 250°C .
Nature of substrate _____ Glass.
Pressure _____ Atmospheric.
Compound temp. _____ 150°C .
Time _____ 3 hours.
Results _____ Dark grey metallic coating.

Example XVI

20 Compound _____ $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate _____ 250°C .
Nature of substrate _____ Iron.
Pressure _____ 0.1 mm.
Compound temp. _____ 95°C .
Time _____ 45 minutes.
Results _____ Grey metallic coating.

Example XVII

Compound _____ $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate _____ 400°C .
Nature of substrate _____ Steel.
Pressure _____ 0.1 mm.
Compound temp. _____ 150°C .
Time _____ 1 hour.
Results _____ Dark grey metallic coating.

Example XVIII

Compound _____ $(\text{CH}_3)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (dimethyl lead bis-manganese pentacarbonyl).

Temp. of substrate _____ 400°C .
Nature of substrate _____ Cobalt.
Pressure _____ 0.1 mm.
Compound temp. _____ 110°C .
Time _____ $2\frac{1}{4}$ hours.
Results _____ Dark grey metallic coating.

Example XIX

55 Compound _____ $(\text{C}_6\text{H}_5)_3\text{SiMo}(\text{CO})_5$ (diphenyl silicon molybdenum pentacarbonyl).

Temp. of substrate _____ 375°C .
Nature of substrate _____ Steel.
Pressure _____ 0.1 mm.
Compound temp. _____ 125°C .
Time _____ 2 hours.
Results _____ Grey metallic coating.

Example XX

65 Compound _____ $[(\text{CH}_3)_2\text{Al}]_2\text{Cr}(\text{CO})_5$ (bis(dimethyl aluminum) chromium pentacarbonyl).

Temp. of substrate _____ 350°C .
Nature of substrate _____ Molybdenum alloy.
Pressure _____ 0.1 mm.
Compound temp. _____ 145°C .
Time _____ $3\frac{1}{4}$ hours.
Results _____ Light grey metallic coating.

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Example XXI

Compound $(C_2H_5)_2GeNi(CO)_2$ (diethyl germanium nickel tricarbonyl).
 Temp. of substrate $500^\circ C$.
 Nature of substrate Ceramics.
 Pressure 10 mm.
 Compound temp. $175^\circ C$.
 Time 2 hours.
 Results Grey metallic coating.

Example XXII

Compound $(C_6H_5)_3Sn(C_6H_5)_2Mn(CO)_2$ (triphenyl-tin phenyl manganese dicarbonyl).
 Temp. of substrate $425^\circ C$.
 Nature of substrate Glass.
 Pressure 0.1 mm.
 Compound temp. $135^\circ C$.
 Time $2\frac{1}{4}$ hours.
 Results Grey metallic coating.

Example XXIII

Compound $(C_2H_5)_2AlCr(CO)_2$ (diethyl aluminum cyclopentadienyl chromium tricarbonyl).
 Temp. of substrate $295^\circ C$.
 Nature of substrate Steel alloy.
 Pressure 0.1 mm.
 Compound temp. $110^\circ C$.
 Time 3 hours.
 Results Light grey metallic coating.

Example XXIV

Compound $Al[Cr(CO)_2]_3$ (aluminum tris-cyclopentadienyl chromium tricarbonyl).
 Temp. of substrate $375^\circ C$.
 Nature of substrate Chromium.
 Pressure 0.1 mm.
 Compound temp. $98^\circ C$.
 Time 30 minutes.
 Results Dark grey coating.

Example XXV

Compound $(CH_3)_2Al(CH_3)_2Sn$ (dimethyl aluminum trimethyltin).
 Temp. of substrate $380^\circ C$.
 Nature of substrate Steel.
 Pressure 0.1 mm.
 Compound temp. $115^\circ C$.
 Time $1\frac{1}{4}$ hours.
 Results Grey metallic coating.

Example XXVI

Compound $(C_2H_5)_2B(C_6H_{11})_2Sn$ (diethyl boron triphenyl tin).
 Temp. of substrate $420^\circ C$.
 Nature of substrate Nickel alloy.
 Pressure 0.1 mm.
 Compound temp. $120^\circ C$.
 Time 12 hours.
 Results Grey black metallic coating.

Example XXVII

Compound $(C_2H_5)_2B(CH_3)_2Pb$ (diethyl boron dimethyl lead).
 Temp. of substrate $495^\circ C$.
 Nature of substrate Glass.
 Pressure 0.1 mm.
 Compound temp. $85^\circ C$.
 Time $2\frac{1}{4}$ hours.
 Results Grey black metallic coating.

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Example XXVIII

Compound $Co(CO)_4Mn(CO)_2$ (cobalt tetracarbonyl manganese pentacarbonyl).
 Temp. of substrate $450^\circ C$.
 Nature of substrate Graphite.
 Pressure 0.8 mm.
 Compound temp. $130^\circ C$.
 Time $6\frac{1}{4}$ hours.
 Results Grey metallic.

Example XXIX

Compound $[Co(CO)_4]_2Fe(CO)_4$ (bis-cobalt tetracarbonyl iron tetracarbonyl).
 Temp. of substrate $475^\circ C$.
 Nature of substrate Steel.
 Pressure 0.1 mm.
 Compound temp. $103^\circ C$.
 Time $2\frac{1}{4}$ hours.
 Results Light grey metallic.

Example XXX

Compound $[V(CO)_6]_2Ni(CO)_2$ (vanadium hexacarbonyl nickel tricarbonyl).
 Temp. of substrate $510^\circ C$.
 Nature of substrate Steel alloy.
 Pressure 0.3 mm.
 Compound temp. $95^\circ C$.
 Time 4 hours.
 Results Light grey metallic.

Example XXXI

Compound $(C_6H_5)_2Mn(CO)_2CpFe(CO)_2$ (benzene manganese dicarbonyl cyclopentadienyl iron dicarbonyl).
 Temp. of substrate $425^\circ C$.
 Nature of substrate Glass.
 Pressure 1 mm.
 Compound temp. $130^\circ C$.
 Time $3\frac{1}{4}$ hours.
 Results Metallic grey.

Example XXXII

Compound $(C_6H_5)_2Co(CO)_2MeCpNi(CO)$ (butadiene cobalt dicarbonyl methyl cyclopentadienyl nickel monocarbonyl).
 Temp. of substrate $475^\circ C$.
 Nature of substrate Steel.
 Pressure 0.1 mm.
 Compound temp. $110^\circ C$.
 Time $4\frac{1}{4}$ hours.
 Results Grey coating.

Example XXXIII

Compound $(C_6H_5)(CH_3)_2Co(CO)CpFe(CO)_2$ (cinnene cobalt monocarbonyl cyclopentadienyl iron dicarbonyl).
 Temp. of substrate $350^\circ C$.
 Nature of substrate Aluminum.
 Pressure 0.1 mm.
 Compound temp. $105^\circ C$.
 Time 2 hours.
 Results Grey coating.

Example XXXIV

Compound $[CpFe(CO)_2]_2Ni(CO)_2$ (bis-cyclopentadienyl iron dicarbonyl nickel tricarbonyl).
 Temp. of substrate $375^\circ C$.

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Nature of substrate — Molybdenum.
Pressure — 0.3 mm.
Compound temp. — 90° C.
Time — 10 hours.
Results — Dark grey metallic coating.

Example XXXV

Compound — $[\text{MeCyCr}(\text{CO})_2]_2\text{Ni}(\text{CO})_2$ (bis-methyl cyclopentadienyl chromium tricarbonyl nickel tricarbonyl).
Temp. of substrate — 425° C.
Nature of substrate — Cobalt alloy.
Pressure — 0.5 mm.
Compound temp. — 150° C.
Time — 8 hours.
Results — Dark grey metallic coating.

Example XXXVI

Compound — $\text{MeCyNi}(\text{CO})\text{Me}(\text{CO})_2$ (methyl cyclopentadienyl nickel monocarbonyl manganese pentacarbonyl).
Temp. of substrate — 480° C.
Nature of substrate — Steel.
Pressure — 0.1 mm.
Compound temp. — 125° C.
Time — 3 hours.
Results — Light grey metallic coating.

Example XXXVII

Compound — $(\text{C}_2\text{H}_5)_3\text{Al}(\text{C}_2\text{H}_5)_2\text{Sb}$ (triethyl aluminum trimethyl antimony).
Temp. of substrate — 290° C.
Nature of substrate — Steel.
Pressure — 0.1 mm.
Compound temp. — 105° C.
Time — 5 hours.
Results — Metallic grey coating.

Example XXXVIII

Compound — $(\text{CH}_3)_3\text{In}(\text{C}_6\text{H}_5)_2\text{Sb}$ (trimethyl indium triphenyl antimony).
Temp. of substrate — 375° C.
Nature of substrate — Ceramic.
Pressure — 0.5 mm.
Compound temp. — 95° C.
Time — 3 hours.
Results — Metallic grey coating.

Example XXXIX

Compound — $(\text{C}_6\text{H}_5)_3\text{Ti}(\text{C}_6\text{H}_5)_2\text{Bi}$ (triphenyl thallium triethyl bismuth).
Temp. of substrate — 395° C.
Nature of substrate — Glass.
Pressure — 1 mm.
Compound temp. — 115° C.
Time — 6 hours.
Results — Grey metallic coating.

Example XL

Compound — $(\text{C}_6\text{H}_5)_3\text{Pb}[\text{Te}(\text{CH}_3)_2]_2$ (diethyl lead bis-dimethyl telluride).
Temp. of substrate — 495° C.
Nature of substrate — Ceramic.
Pressure — 0.5 mm.
Compound temp. — 105° C.
Time — 5 1/2 hours.
Results — Grey black.

The process employed in Examples I and following is utilized with the exception that an ultrasonic generator is proximately positioned to the plating apparatus. The compound is heated to its decomposition threshold and thereafter the ultrasonic generator is utilized to effect final decomposition.

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Example XLI

Compound — $\text{Cu}(\text{AlEt}_2)_2$ (copper bis - aluminum tetraethyl).
Temp. of substrate — 200° C.
Nature of substrate — Glass wool.
Pressure — 0.1-0.2 mm.
Compound temp. — 110° C.
Time — 1 hour.
Results — Dull, metallic.
Method — Ultrasonic.

Example XLII

Compound — $\text{Cr}(\text{BEt}_2)_2$ (chromium tri-boron tetraethyl).
Temp. of substrate — 300° C.
Nature of substrate — —.
Pressure — 0.1 mm.
Compound temp. — 60° C.
Time — 4 hours.
Results — Powder—chromium boride or mixture.
Method — Ultrasonic.

As discussed hereinbefore the bimetallic organometallic plating agents of this invention can be represented by the general formula



wherein M is a metal selected from the group consisting of groups I, II, III-B, IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements and the metals tin and aluminum; M' is a metal selected from the group consisting of group III-A of the periodic chart of the elements and the metals zinc and cadmium; R represents a monovalent anion; x is an integer equal to the valence of M'; y is an integer equal to the valence of M.

The metals designated by M include lithium, sodium, potassium, rubidium, cesium, francium of group I-A. Within this group lithium is the especially preferred metal because of the desirable high temperature characteristics lithium imparts when alloyed with certain metals. The symbol M further designates the metals beryllium, magnesium, calcium, strontium, barium, radium within group II-A; scandium, indium, lanthanum, actinium (including the lanthanum and actinium series) within group III-B; titanium, zirconium, hafnium, within group IV-B; vanadium, niobium, tantalum within group V-B; chromium, molybdenum, tungsten within group VI-B; manganese, technetium, rhenium within group VII-B; and iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum of group VIII. Within the groups I-B and II-B, M designates the metals silver, copper, gold, zinc, cadmium and mercury. It of course should be recognized that because of the scarcity of certain of the above metals, their use would be reserved for those instances where their unique alloying properties are desired or needed.

The metal M' includes any of the elements of group III-A and thus includes boron, aluminum, thallium, indium and gallium. Of these aluminum is most preferred because of its wide availability and use in plating technology.

As noted above, R is a monovalent anion, preferably an unsubstituted hydrocarbon group. The hydrocarbon groups generally contain between about 1 and 20 carbon atoms each. A preferred class of bimetallic organometallic plating agent of this invention contains as one of the R groups at least one cyclopentadienyl group. By a cyclopentadienyl group is meant groups containing the five carbon atom ring found in cyclopentadiene itself. Examples are the cyclopentadienyl, indenyl and fluorenyl groups, and the corresponding groups substituted with one or more hydrocarbon radicals such as the methylcyclopentadienyl, methyl-tert-butylcyclopentadienyl, triethylindenyl, phenylcyclopentadienyl, and related groups.

R can also be other monovalent anions. These anions

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(gallium tetracyclopentadienide), barium bis(indium tetrafluoroborate), zinc bis(boron tetracyclopentadienide), zinc bis(aluminum tetracyclopentadienide), zinc bis(aluminum cyclopentadienide triethyl), cadmium bis(aluminum tetracyclopentadienide), mercury bis(boron cyclopentadienide trihydride), mercury bis(aluminum cyclopentadienide trihydride), mercury bis(aluminum cyclopentadienide trichloride), and mercury bis(gallium tetracyclopentadienide). In addition to the compounds above, similar compounds can be made containing other cyclopentadienyl groups including the isopropyl, diisopropyl, hexyl, tolyl, xylol, and other alkyl and aryl derivatives of cyclopentadienyl groups.

Another embodiment of the bimetallic organometallic plating agents is represented by the general formula



wherein R represents any alkyl or cycloalkyl group generally containing up to about 20 carbon atoms. The R groups which are bonded to the metal $M^{(a)}$ are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. The cycloalkyl groups which may be bonded to the metal may also be substituted alkyl groups. Thus, cyclohexane is a typical example of the cycloalkyl group which may be bonded to the metal, and ethyl cyclohexane is a typical example of a substituted cycloalkyl group.

The metal $M^{(a)}$ in the above formula may be any group IV-A metal, i.e., silicon, germanium, tin and lead, and aluminum found in group III-A. $M^{(b)}$ in the formula represents a different metal which may be selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements, Fisher Scientific Company, 1935. Thus, typical examples of the metal represented by $M^{(b)}$ are titanium, zirconium, hafnium, vanadium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, iron, rhodium, ruthenium, osmium, cobalt, iridium, nickel, platinum, palladium, and the like.

Typical examples of the compounds of the above formula are: diethyllead iron tetracarbonyl, dibutyllead iron tetracarbonyl, methylethyllead iron tetracarbonyl, di-2-ethylhexylgermanium iron tetracarbonyl, dimethylgermanium iron tetracarbonyl, diethylgermanium iron tetracarbonyl, dipropylgermanium iron tetracarbonyl, di-n-decylsilicon iron tetracarbonyl, diundecylsilicon iron tetracarbonyl, diethylsilicon iron tetracarbonyl, dimethyltin iron tetracarbonyl, diethyltin iron tetracarbonyl, hexyldodecyltin iron tetracarbonyl, dimethylaluminum manganese pentacarbonyl, diethylaluminum manganese pentacarbonyl, diisobutylaluminum manganese pentacarbonyl, bis(dimethyl)aluminum chromium pentacarbonyl, bis(diethyl)aluminum chromium pentacarbonyl, bis(di-n-hexyl)aluminum chromium pentacarbonyl, bis(diisobutyl)aluminum chromium pentacarbonyl, dihexadecyllead chromium pentacarbonyl, diheptyllead chromium pentacarbonyl, diethyllead chromium pentacarbonyl, dimethyllead chromium pentacarbonyl, methylethyllead chromium pentacarbonyl, diethylgermanium chromium pentacarbonyl, dioctadecylgermanium chromium pentacarbonyl, dipropylgermanium chromium pentacarbonyl, di-n-hexylgermanium chromium pentacarbonyl, dimethylsilicon chromium pentacarbonyl, dipropylsilicon chromium pentacarbonyl, diisobutylsilicon chromium pentacarbonyl, diethyltin chromium pentacarbonyl, dimethyltin chromium pentacarbonyl, dibutyltin chromium pentacarbonyl, diisobutyltin chromium pentacarbonyl, bis(dimethylaluminum)iron tetracarbonyl, bis(diisobutylaluminum)iron tetracarbonyl, bis(dipropylaluminum)iron tetracarbonyl, diisobutylaluminum cobalt tetracarbonyl, diethylaluminum cobalt tetracarbonyl, dimethylaluminum cobalt tetracarbonyl, dipropylaluminum cobalt tetracarbonyl,

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bonyl, bis(diethylaluminum)chromium pentacarbonyl, bis(dipropylaluminum)molybdenum pentacarbonyl, bis(diisobutylaluminum)molybdenum pentacarbonyl, bis(didodecylaluminum)molybdenum pentacarbonyl, bis(dimethylaluminum)tungsten pentacarbonyl, bis(diethylaluminum)tungsten pentacarbonyl, bis(diisobutylaluminum)tungsten pentacarbonyl, bis(diisopropylaluminum)tungsten pentacarbonyl, dimethyllead nickel tricarbonyl, diethyllead nickel tricarbonyl, dipropyllead nickel tricarbonyl, diisobutyllead nickel tricarbonyl, methylethyllead nickel tricarbonyl, dimethylgermanium nickel tricarbonyl, diethylgermanium nickel tricarbonyl, diisobutylgermanium nickel tricarbonyl, dipropylgermanium nickel tricarbonyl, dimethylsilicon nickel tricarbonyl, diethylsilicon nickel tricarbonyl, dipropylsilicon nickel tricarbonyl, diisobutylsilicon nickel tricarbonyl, diethyltin nickel tricarbonyl, diisobutyltin nickel tricarbonyl, dipropyltin nickel tricarbonyl, diisopropyltin nickel tricarbonyl, diisobutyltin nickel tricarbonyl, dioctadecyltin nickel tricarbonyl, bis(dimethylaluminum)nickel tricarbonyl, bis(diethylaluminum)nickel tricarbonyl, bis(dipropylaluminum)nickel tricarbonyl, bis(diisobutylaluminum)nickel tricarbonyl, bis(di-2-ethylhexylaluminum)nickel tricarbonyl, and the like.

A further embodiment of the bimetallic organometallic plating agents of this invention is represented by the general formula



wherein R represents any electron donating moiety bonded to the metal $M^{(a)}$. Typical of the electron donating moieties which are bonded to said metal are organic groups such as alkyl, aryl, cycloalkyl, alkaryl, and the like. Another electron donating moiety which may be bonded to the metal $M^{(a)}$ is hydrogen. Thus, typical examples of R in the above formula are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. Some examples of cycloalkyl groups which are sigma bonded to the metal are cyclohexane and cyclopentane. These cycloalkyl groups may also be substituted cycloalkyls. The metal $M^{(a)}$ may be any metal such as zinc, cadmium, mercury, beryllium, magnesium, strontium, barium, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and bismuth. R' is an unsaturated organic group pi bonded to the metal $M^{(b)}$. Thus, typical examples of unsaturated organic groups are the arenes, alkenes, cycloalkenes, alkynes, and the like. Typical examples of the unsaturated organic groups are cyclopentadiene, phenyl, butadiene, cyclohexadiene, methycyclopentadiene, toluene, xylene, cumene, and the like. $M^{(b)}$ can be any metal found in the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of elements which include titanium, vanadium, chromium, molybdenum, tungsten, manganese, technetium, rhodium, iron, ruthenium, osmium, cobalt, iridium, nickel, palladium, platinum, and the like. CO in the above formula represents carbonyl groups bonded to the metal $M^{(b)}$.

Typical examples of the compounds which correspond to the formula above are: triphenyltin cyclopentadienyl iron dicarbonyl, triphenyltin cyclopentadienyl nickel monocarbonyl, triphenyltin cyclopentadienyl chromium tricarbonyl, triphenyltin cyclopentadienyl molybdenum tricarbonyl, triphenyltin butadiene manganese tricarbonyl, triphenyltin phenyl cobalt monocarbonyl, triphenyltin butadiene cobalt dicarbonyl, triphenyltin phenyl manganese dicarbonyl, diethyl aluminum cyclopentadienyl iron dicarbonyl, diethyl aluminum cyclopentadienyl nickel monocarbonyl, diethyl aluminum cyclopentadienyl chromium tricarbonyl, diethyl aluminum butadiene manganese tricarbonyl, diethyl aluminum butadiene cobalt dicarbonyl, di-

ethyl aluminum phenyl manganese dicarbonyl, tri-n-propyl lead cyclopentadienyl iron dicarbonyl, triisopropyl cyclopentadienyl nickel monocarbonyl, triisopropyl lead cyclopentadienyl chromium tricarbonyl, triisopropyl lead cyclopentadienyl molybdenum tricarbonyl, tri-n-propyllead butadiene manganese tricarbonyl, tri-n-propyllead phenyl cobalt monocarbonyl, tri-n-propyllead butadiene cobalt dicarbonyl, tri-n-propyllead benzene manganese dicarbonyl, trixylyl germanium cyclopentadienyl iron dicarbonyl, trixylyl germanium cyclopentadienyl nickel monocarbonyl, trixylyl germanium cyclopentadienyl chromium tricarbonyl, trixylyl germanium cyclopentadienyl molybdenum tricarbonyl, trixylyl germanium cyclopentadienyl tungsten tricarbonyl, trixylyl germanium butadiene manganese tricarbonyl, trixylyl germanium phenyl cobalt monocarbonyl, trixylyl germanium butadiene cobalt dicarbonyl, trixylyl germanium phenyl manganese dicarbonyl, dimethyllead bis-cyclopentadienyl iron dicarbonyl, dimethyllead bis-cyclopentadienyl nickel monocarbonyl, dimethyllead bis-cyclopentadienyl chromium tricarbonyl, dimethyllead bis-cyclopentadienyl molybdenum tricarbonyl, dimethyllead bis-butadiene manganese tricarbonyl, dimethyllead bis-phenyl cobalt monocarbonyl, dimethyllead bis-butadiene cobalt dicarbonyl, dimethyllead bis-benzene manganese dicarbonyl, dibutyl germanium bis-cyclopentadienyl iron dicarbonyl, dibutyl germanium bis-cyclopentadienyl nickel monocarbonyl, dibutyl germanium bis-cyclopentadienyl chromium tricarbonyl, dibutyl germanium bis-cyclopentadienyl tungsten tricarbonyl, dibutyl germanium bis-methyl cyclopentadienyl molybdenum tricarbonyl, dibutyl germanium bis-2-ethyl butadiene manganese tricarbonyl, dibutyl germanium bis-phenyl cobalt monocarbonyl, dibutyl germanium bis-butadiene cobalt dicarbonyl, dibutyl germanium bis-phenyl manganese dicarbonyl, beryllium bis-cyclopentadienyl iron dicarbonyl, beryllium bis-cyclopentadienyl chromium tricarbonyl, beryllium bis-butadiene cobalt dicarbonyl, aluminum tris-cyclopentadienyl iron dicarbonyl, aluminum tris-cyclopentadienyl chromium tricarbonyl, aluminum tris-cyclopentadienyl molybdenum tricarbonyl, aluminum tris-methyl cyclopentadienyl tungsten tricarbonyl, aluminum tris-phenyl manganese dicarbonyl, phenyl silicon tris-cyclopentadienyl iron dicarbonyl, phenyl silicon tris-cyclopentadienyl chromium tricarbonyl, phenyl silicon tris-methyl cyclopentadienyl molybdenum tricarbonyl, phenyl silicon tris-ethyl cyclopentadienyl tungsten tricarbonyl, phenyl silicon tris-butadiene manganese tricarbonyl, phenyl silicon tris-phenyl cobalt monocarbonyl, phenyl silicon tris-butadiene cobalt dicarbonyl, phenyl silicon tris-phenyl manganese dicarbonyl, and the like.

A still further embodiment of the bimetallic organometallic plating agents of this invention is represented by the formula



wherein R represents an electron donating moiety which may be an alkyl, cycloalkyl group or hydrogen. The organic groups generally contain up to about 20 carbon atoms. Thus, typical examples of an alkyl group in the formula above would be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, eicosyl, nonadecyl, heptadecyl, hexadecyl, pentadecyl, and the like. The cycloalkyl groups represented by R in the above formula may be substituted cycloalkyl groups. Thus, a typical example of a cycloalkyl group is cyclohexane, while a typical example of an alkyl substituted cycloalkyl is 1-ethyl cyclohexane. Since there are three electron donating groups bonded to the metal, the electron donating groups in each instance may be the same or different.

M^a represents a metal selected from the group consisting of boron, gallium, indium and thallium, while M^b is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin, lead, and the like.

Typical examples of compounds which correspond to

the above formula are: diethyl boron trimethyl silicate, diethyl boron triethyl silicate, diethyl boron trimethyl silicate, aluminum hydride trimethyl silicate, dimethyl aluminum trimethyl silicate, diethyl aluminum trimethyl silicate, dipropyl aluminum triethyl silicate, diisobutyl aluminum triisopropyl silicate, diethyl gallium trimethyl silicate, dipropyl gallium trimethyl silicate, dipropyl gallium triethyl silicate, dimethyl indium triethyl silicate, diethyl indium triethyl silicate, diisobutyl indium trimethyl silicate, dimethyl thallium triethyl silicate, dimethyl thallium trimethyl silicate, dipropyl thallium trimethyl silicate, dipropyl thallium triethyl silicate, diisobutyl thallium trimethyl silicate, diundecyl thallium triundecyl silicate, diethyl boron trimethyl germanium, dipropyl boron triisobutyl germanium, dimethyl boron trimethyltin, diethyl boron triethyltin, dipropyl boron tripropyltin, diethyl boron triethyllead, dimethyl boron triethyllead, dibutyl boron ethyl dimethyllead, diethyl aluminum triethyl germanium, ethylpropyl aluminum, methylstyrylpropyl germanium, dibutyl aluminum trimethyl germanium, diisobutyl aluminum tributyl germanium, diethyl aluminum triethyltin, diethyl aluminum trimethyltin, methylstyryl aluminum dipropyl ethyltin, diisobutyl aluminum tributyltin, diethyl aluminum triethyllead, dimethyl aluminum triethyllead, diisobutyl aluminum methyl diethyllead, diisobutyl aluminum triethyllead, aluminum trihydride triethyllead, dimethyl gallium trimethyl germanium, dipropyl gallium trimethyl germanium, diundecyl gallium tripropyl germanium, dimethyl gallium trimethyltin, dipropyl gallium tripropyltin, diisobutyl gallium tributyltin, dimethyl gallium trimethyllead, dipropyl gallium triethyllead, dimethyl gallium ethyldimethyllead, dimethyl indium trimethyl germanium, dibutyl indium trimethyl germanium, dimethyl indium tributyltin, diethyl indium methyltriethyltin, diundecyl indium triethyltin, dimethyl tantalum trimethyllead, dimethyl tantalum triethyllead, diethyl tantalum methyltriethyllead, and the like.

Another embodiment of the bimetallic organometallic plating agents of this invention is represented by the formula



in which M^(a) and M^(b) represent different metals from the transitional metal series of the periodic chart of the elements, Fisher Scientific Company, 1955. Thus, typical examples of the metals represented in the above formula are titanium, zirconium, hafnium; vanadium, niobium; tantalum, chromium, molybdenum, tungsten; manganese, technetium, rhenium; iron; ruthenium, cadmium, cobalt, iridium; nickel, platinum, palladium, and the like. It should be noted that the compounds as described above have a unique metal to metal bond. In other words, the metals are bonded by free electrons; each metal having less than the adequate number of carbonyl groups on each to satisfy the electronic structure. Thus, the above formula does not represent a mere mixture of metal carbonyls but an actual metal to metal bond wherein each metal contains carbonyl groups bonded to it respectively.

Typical examples of organometallic compounds which represent the above formula are: cobalt tetracarbonyl manganese pentacarbonyl, vanadium hexacarbonyl manganese pentacarbonyl, vanadium hexacarbonyl cobalt tetracarbonyl, bis(cobalt tetracarbonyl)iron tetracarbonyl, bis(manganese pentacarbonyl)iron tetracarbonyl, vanadium hexacarbonyl iron tetracarbonyl, bis(cobalt tetracarbonyl)nickel tricarbonyl, bis(manganese pentacarbonyl)nickel tricarbonyl, vanadium hexacarbonyl nickel tricarbonyl, bis(cobalt tetracarbonyl)chromium pentacarbonyl, bis(manganese pentacarbonyl)chromium pentacarbonyl, vanadium hexacarbonyl chromium pentacarbonyl, bis(cobalt tetracarbonyl)molybdenum pentacarbonyl, bis(manganese pentacarbonyl)molybdenum pentacarbonyl, vanadium hexacarbonyl molybdenum pen-

tetracarbonyl, bis(cobalt tetracarbonyl)tungsten pentacarbonyl, bis(manganese pentacarbonyl)tungsten pentacarbonyl, vanadium hexacarbonyl tungsten pentacarbonyl, and the like.

A still further embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula



wherein R^* and R'' represent unsaturated organo groups containing up to about 25 carbon atoms. Typical examples of these groups are arenes, cycloalkanes, alkadienes, cycloalkadienes, and the like. In each instance, R^* and R'' may be the same or different. Typical examples of the organo groups which are bonded to the metals are butadiene, 2-methylbutadiene, benzene, naphthalene, toluene, xylene, cumene, cyclopentadienyl, methylcyclopentadienyl, p-isopropyl benzene, tertiary butyl benzene, fluorenyl, and the like. Other cyclopentadienyl groups which may be employed are the isopropyl, diisopropyl, tolyl and xylol derivatives of the cyclopentadienyl groups.

The metals represented by $M^{(a)}$ and $M^{(b)}$ are different transitional metals. The transitional metals include titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, ruthenium, iron, osmium, cobalt, iridium, nickel, and the like.

Typical examples of the compounds represented by the formula above are: butadiene manganese tricarbonyl cyclopentadiene iron dicarbonyl, benzene manganese dicarbonyl cyclopentadiene iron dicarbonyl, benzene manganese dicarbonyl cyclopentadiene nickel monocarbonyl, benzene manganese dicarbonyl cyclopentadiene chromium tricarbonyl, benzene manganese dicarbonyl cyclopentadiene tungsten tricarbonyl, benzene manganese dicarbonyl cyclopentadiene molybdenum tricarbonyl, butadiene manganese tricarbonyl cyclopentadiene nickel monocarbonyl, butadiene manganese tricarbonyl cyclopentadiene chromium tricarbonyl, butadiene manganese tricarbonyl cyclopentadiene molybdenum tricarbonyl, butadiene manganese tricarbonyl cyclopentadiene tungsten tricarbonyl, butadiene cobalt dicarbonyl cyclopentadiene iron dicarbonyl, butadiene cobalt dicarbonyl methyl cyclopentadiene iron dicarbonyl, butadiene cobalt dicarbonyl ethyl cyclopentadiene nickel monocarbonyl, butadiene cobalt dicarbonyl dimethyl cyclopentadiene chromium tricarbonyl, butadiene cobalt dicarbonyl cyclopentadiene molybdenum tricarbonyl, benzene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, toluene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, cumene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, mesitylene cobalt monocarbonyl cyclopentadiene nickel monocarbonyl, naphthalene cobalt monocarbonyl cyclopentadiene nickel monocarbonyl, cycloheptatriene cobalt monocarbonyl cyclopentadiene chromium tricarbonyl, cycloheptatriene cobalt monocarbonyl cyclopentadiene tungsten tricarbonyl, and the like.

Still another embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula



wherein R represents any unsaturated organo group containing up to about 25 carbon atoms. Thus, R may represent cyclopentadienyl groups, substituted aryl and alkyl cyclopentadienyl groups, aryl groups, alkyl substituted aryl groups, and the like. Typical examples of the unsaturated organo groups are cyclopentadienyl, methylcyclopentadienyl, fluorenyl, benzene, toluene, cumene, butadiene, naphthalene, acenaphthene, and the like. The metals $M^{(a)}$ and $M^{(b)}$ represent different transitional metals selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements, Fisher Scientific Company, 1955. These groups generally include the metals nickel, palladium, platinum, cobalt, iron, iridium, ruthenium, rhenium, osmium, manganese, chro-

mium, molybdenum, tantalum, vanadium, niobium, titanium, zirconium, hafnium, and the like.

Typical examples of the compounds represented by the above formula are:

- 5 bis(cyclopentadienyl iron dicarbonyl)nickel tricarbonyl, bis(cyclopentadienyl iron dicarbonyl)chromium pentacarbonyl, bis(cyclopentadienyl iron dicarbonyl)molybdenum pentacarbonyl,
- 10 bis(cyclopentadienyl iron dicarbonyl)tungsten pentacarbonyl, bis(cyclopentadienyl chromium tricarbonyl)nickel tricarbonyl,
- 15 bis(cyclopentadienyl chromium tricarbonyl)iron tetracarbonyl, bis(cyclopentadienyl molybdenum tricarbonyl)nickel tricarbonyl,
- 20 bis(cyclopentadienyl tungsten tricarbonyl)nickel tricarbonyl, bis(cyclopentadienyl molybdenum tricarbonyl)iron tetracarbonyl,
- 25 bis(cyclopentadienyl tungsten tricarbonyl)iron tetracarbonyl, bis(methylcyclopentadienyl chromium tricarbonyl)nickel tricarbonyl,
- 30 bis(ethylcyclopentadienyl molybdenum tricarbonyl)iron tetracarbonyl, bis(cyclopentadienyl nickel monocarbonyl)iron tetracarbonyl,
- 35 bis(cyclopentadienyl nickel monocarbonyl)chromium pentacarbonyl, bis(butylcyclopentadienyl nickel monocarbonyl)molybdenum pentacarbonyl,
- 40 bis(methylcyclopentadienyl nickel monocarbonyl)tungsten pentacarbonyl, methylcyclopentadienyl nickel monocarbonyl manganese pentacarbonyl,
- 45 cyclopentadienyl nickel monocarbonyl cobalt tetracarbonyl, cyclopentadienyl nickel monocarbonyl vanadium hexacarbonyl,
- 50 cyclopentadienyl iron dicarbonyl manganese pentacarbonyl, cyclopentadienyl iron dicarbonyl cobalt tetracarbonyl,
- 55 cyclopentadienyl iron dicarbonyl vanadium hexacarbonyl, cyclopentadienyl chromium tricarbonyl cobalt tetracarbonyl, methylcyclopentadienyl molybdenum tricarbonyl vanadium hexacarbonyl,
- 60 ethylcyclopentadienyl tungsten tricarbonyl manganese pentacarbonyl, bis(butadiene manganese tricarbonyl)iron tetracarbonyl, bis(butadiene cobalt dicarbonyl)iron tetracarbonyl,
- 65 bis(cycloheptadiene manganese tricarbonyl)iron tetracarbonyl, bis(cumene manganese dicarbonyl)chromium pentacarbonyl, bis(tolene manganese dicarbonyl)molybdenum pentacarbonyl,
- 70 bis(naphthalene manganese dicarbonyl)tungsten pentacarbonyl,

and the like.

A further embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula



- 70 wherein the R groups represent any organo group containing up to about 20 carbon atoms. These groups are generally the alkyl, aryl, cycloalkyl and aralkyl groups. Thus, typical examples of the organo groups in the above formula are methyl, ethyl, propyl, butyl, pentyl, hexyl,
- 75 heptyl, octyl, decyl, acetyl, undecyl, eicosyl, phenyl,

cumene, pseudocumene, naphthalene, cyclopentane, cyclohexane, and the like. $M^{(a)}$ in the formula above can be any metal such as boron, aluminum, gallium, indium, and thallium, while $M^{(b)}$ is a metal or metalloid representing phosphorus, arsenic, antimony, and bismuth.

Typical examples of compounds represented by the formula above are:

triethyl boron trimethyl arsenic,
tributyl boron trimethyl antimony,
triethyl boron tridecyl bismuth,
triethyl aluminum triphenyl arsenic,
triisobutyl aluminum tricumene arsenic,
tripropyl aluminum tricumene arsenic,
triethyl aluminum trimethyl antimony,
triisobutyl aluminum tripropyl antimony,
triisopropyl aluminum trimethyl bismuth,
triphenyl gallium trimethyl arsenic,
trimethyl gallium tributyl antimony,
tripropyl gallium triphenyl bismuth,
trimethyl indium trimethyl arsenic,
tripropyl indium tributyl arsenic,
triphenyl indium triisopropyl arsenic,
trimethyl indium trimethyl antimony,
tributyl indium triphenyl antimony,
triisopropyl indium trimethyl antimony,
tributyl indium tributyl bismuth,
triphenyl indium triphenyl bismuth,
triethyl thallium triethyl arsenic,
trimethyl thallium trimethyl arsenic,
triphenyl thallium triphenyl arsenic,
triisobutyl thallium trimethyl arsenic,
trimethyl thallium trimethyl antimony,
triethyl thallium triethyl antimony,
triphenyl thallium trimethyl antimony,
trimethyl thallium trimethyl bismuth,
triethyl thallium trimethyl bismuth,
triphenyl thallium tributyl bismuth,
tricumene thallium tributyl bismuth,

and the like.

When employing the bimetallic organometallic plating agents of this invention in the absence of a carrier gas, it is desirable to maintain enough vapor pressure below the decomposition temperature of the organometallic to enable the process to be conducted at an appreciable rate of plating. Too high vapor pressure results in poor substrate adherence. Thus, it is preferred to employ up to about 10 mm. pressure during the plating operation, preferably 0.01 to 10 mm. of pressure. When an inert carrier gas such as argon or other carrier gases such as hydrogen and carbon dioxide are employed in the process, it is desirable to employ a higher vapor pressure, e.g., between about 10 to 20 mm. of pressure. In this connection, however, it is to be noted that the partial pressure of the bimetallic organometallic is about 0.01 to about 10 mm. pressure during the plating operation.

Although temperatures above the decomposition temperature of the organometallic plating agent are generally employed (usually temperatures no higher than about 700° C. are used), a preferred temperature exists for each organometallic plating agent. When this temperature is employed, better plating results can be obtained. At these temperatures exceptionally brighter, better adhering coatings are obtained.

By the term alloy as employed herein is meant "a mixture of two or more metallic elements (or non-metals, such as—Te, P) which have a metallic appearance and which are either: (1) A molecular mixture, microscopically homogeneous; . . . (2) a colloidal mixture, microscopically heterogeneous"; . . . Hack's Chemical Dictionary, 3rd edition (1944), McGraw-Hill Book Co., Inc., page 34.

In some cases more uniform coating can be obtained through the employment of pack metalizing techniques. The plating agent when employed in such pack metalizing

technique is a solid such as chromium tris(aluminum tetraethyl). One of the advantages of employing such pack metalizing technique is that very uniform plating temperatures can be achieved because of the solid materials employed in this type of process. Pack metalizing involves packing the substrate to be plated into a metal or glass reaction vessel provided with a gas outlet means. (Usually a metal substrate is used.) With the plating agent is employed an inert filler material such as sand, refractory powders or any other material inert under the application conditions. Thus, the reaction vessel contains the object to be plated surrounded by the solid plating agent, the remaining space of the reaction vessel being filled with the aforesaid inert filler. The reaction container is thereafter placed in an induction heating furnace and the temperature of the furnace raised to a point above the decomposition temperature of the plating agent. The following example illustrates this technique more fully.

Example XLIII

Compound	Cr(AlEt) ₃ (chromium tris - aluminum tetraethyl).
Temp. of substrate	400° C.
Nature of substrate	Mild steel.
Pressure	0.1 mm.
Compound Temp.	—
Time	1½ hours.
Results	Dull, metallic.
Method	Pack metalizing.

In addition to the thermal and ultrasonic techniques discussed hereinabove, other methods for decomposition of the bimetallic organometallic plating agents of the instant invention can also be employed. These other methods encompass other techniques such as decomposition of the bimetallic organometallic plating agent with ultraviolet irradiation. In employing such a technique an apparatus substantially the same as employed in Example I is used, with the exception that in place of the high frequency induction heating means a source of ultraviolet irradiation is employed. This ultraviolet technique is particularly applicable to those bimetallic organometallic compounds of this invention having good volatility characteristics.

Another decomposition technique which can be employed in achieving alloy plates from the plating agents of this invention involves chemical decomposition. Illustrative of such chemical decomposition is the decomposition of copper tetraethylaluminum by treating with acid (50 percent HCl) to produce a colloidal alloy decomposition.

In general, any substrate which is stable to decomposition at the temperatures employed in the plating process utilized are suitable substrates for this invention. Exemplary of the wide diversity of substrates which can be employed in the instant invention are metallic substrates such as ferrous metal substrates (particularly steel), aluminum, copper, yttrium, molybdenum, beryllium, and the like. Alloy substrates can also be employed which result in the deposition of an alloy upon an alloy material. Glass substrates such as Pyrex can be used. Other substrates which can be employed are ceramics, cermets, refractories such as alumina, graphite, and the like; plastics such as "Teflon" (e.g., polyfluoro hydrocarbons), and a multitude of cellulose materials such as wood, cloth, paper, etc.

Other bimetallic organometallic plating agents can be employed in the above working examples to produce similar alloy plating on the substrate to be plated. Thus, when tin tetramethylboron, scandium, tetraethylboron, tin triethylzinc, titanium triethylzinc, potassium triethylboron chloride, sodium indium tetracyclopentadienide, beryllium bis(boron cyclopentadienide) triethyl, strontium bis(gallium tetracyclopentadienide), zinc bis(aluminum tetracyclopentadienide) are employed in the examples de-

scribed above, alloy plates of the corresponding metals contained in each of these compounds are deposited upon the substrate plated.

The decomposition techniques of this invention can be varied so that, in some instances, substrates can be plated with one or both of the metals from the bimetallic organometallic compound while concurrently depositing therefrom metal powders. By such techniques it is possible to produce two useful materials from one plating agent, i.e., the plated article of manufacture and the concurrently deposited metallic powders.

The alloy depositions produced from bimetallic organometallic compounds according to the processes of this invention have many applications in the metallurgical and related arts. In the following working example the application of the processes of this invention to plating aircraft landing gear fabrication materials is illustrated.

Example XLIV

A high performance steel aircraft landing gear structural member is placed in a conventional heating chamber provided with means for high frequency induction heating and gas inlet and outlet means. Lithium aluminum tetracyclopentadienide is placed in a standard vaporization chamber provided with heating means, said vaporization chamber being connected through an outlet port to the aforesaid combustion chamber inlet means. The member is heated to a temperature of approximately 350° C. and the system is evacuated. The lithium aluminum tetracyclopentadienide is heated to a temperature (about 150° C.) where it possesses vapor pressure of up to about 10 mm. The lithium aluminum tetracyclopentadienide vapors are pulled through the system by a vacuum pump and they impinge on the heated aircraft landing gear structural member decomposing and forming a well adherent lithium-aluminum alloy coating over the entire surface of the structural member. In such a manner the structural member is coated with a high performance corrosion resistant lithium-aluminum alloy coating having high tensile strength for application to the extreme requirements of modern age aircraft. The compounds above may be used to plate substrates such as ceramics in order to obtain semi-conductors of great value in the electronics industry.

Having thus described the process of this invention, it is not intended that it be limited except as set forth in the following claims.

We claim:

1. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bi-metallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the group consisting of the group IV-A metals and aluminum;
- (2) $M^{(b)}$ is a different metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- (3) R is an electron donating moiety individually selected from the group consisting of hydrocarbon and hydrogen;
- (4) w is an integer having a value of from 1 to 3, inclusive;
- (5) x and z are integers having a value from 1 to 2 and from 1 to 3, respectively, x and z being dependent

upon the identity of the metal $M^{(b)}$ in accordance with the following tabulated relationships:

	w=1	w=2	w=3
$M^{(a)}$ is a metal having an odd number of d orbital electrons.	x=2, z=3	x=1, z=2	x=2, z=1
$M^{(a)}$ is a metal having an even number of d orbital electrons.	x=1, z=3	x=1, z=1	x=2, z=1

and

- (6) y is an integer from 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

In which G is the atomic number of the next rare gas of the metal $M^{(a)}$; m is an integer from 1 to 2 and is 1 when $M^{(a)}$ is a metal having an odd number of d orbital electrons and is 2 when $M^{(a)}$ is a metal having an even number of d orbital electrons; N is the atomic number of the metal $M^{(b)}$.

2. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bi-metallic organometallic compound being further defined as having the formula



wherein

- (1) $M^{(a)}$ is a metal selected from the groups consisting of groups II-A, II-B, III-A, IV-A and V-A;
- (2) $M^{(b)}$ is a different metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII;
- (3) R is an electron donating moiety selected from the groups consisting of hydrocarbon and hydrogen;
- (4) R' is an unsaturated organo group containing up to 20 carbon atoms;
- (5) w is an integer having a value of from 0 to the valence of the metal $M^{(a)}$ minus 1;
- (6) z is an integer having a value of 1, 2 and 3 and is dependent on the valence of the metal $M^{(b)}$ minus the value of the integer w;
- (7) y is an integer having a value of from 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G_1 - u - (p_1 + 1)}{2}$$

In which G_1 is an integer representing the number of electrons in the next inert gas after the metal $M^{(a)}$; u is an integer representing the atomic number of the metal $M^{(b)}$; and p_1 is an integer representing the number of pi electrons of R'.

3. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) M^c is a metal selected from the group consisting of boron, aluminum, gallium, indium, and thallium;
- (2) M^d is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin and lead;
- (3) The groups R represent electron donating moieties individually selected from the groups consisting of hydrocarbon and hydrogen;
- (4) a and b are integers having a value of from 0 to the valence of the respective metal minus 1;
- (5) e is an integer having a value of from 1 to the

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valence of the metal M^a minus the value of the integer a .

4. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements;
- (3) x is an integer having a value of 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(a)}$; m is an integer having a value of 1 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is odd and 2 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is even; N is the atomic number of the metal $M^{(a)}$;

- (4) y is an integer having a value of 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(b)}$; m is an integer equaling 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and 2 where the number of d orbital electrons in the metal $M^{(b)}$ is even; N is equal to the atomic number of the metal $M^{(b)}$;

- (5) z is an integer having the value of 1 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is odd and a value of 2 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is even.

5. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a transition metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B, and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII;
- (3) R' and R'' are unsaturated organo groups containing up to about 25 carbon atoms;
- (4) x is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_a - n_a - (\beta_a + 1)}{2}$$

in which G_a represents the number of electrons in the next inert gas after the metal $M^{(a)}$; n_a equals the atomic number of the metal $M^{(a)}$; and β_a represents the number of pi electrons in R' ;

- (5) y is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_b - n_b - (\beta_b + 1)}{2}$$

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wherein G_b represents the number of electrons in the next inert gas after the metal $M^{(b)}$; n_b equals the atomic number of the metal $M^{(b)}$; and β_b represents the number of pi electrons in R'' .

6. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- (3) R is an unsaturated organo compound containing up to about 25 carbon atoms;
- (4) x is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_a - N_a - (\beta_a + 1)}{2}$$

in which G_a is the number of electrons in the next inert gas after the metal $M^{(a)}$; N_a is the atomic number of the metal $M^{(a)}$; and β_a is equal to the number of pi electrons in the group R ;

- (5) y is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_b - n_b - N}{2}$$

in which G_b represents the atomic number of the next rare gas of the metal $M^{(b)}$; n_b is an integer having the value of 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and a value of 2 where the number of d -orbital electrons of the metal $M^{(b)}$ is even; and N equals the atomic number of the metal $M^{(b)}$;

- (6) x is an integer having the value of 1 when the number of d orbital electrons of the metal $M^{(a)}$ is odd and 2 when the number of d orbital electrons in said metal is even.

7. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the group consisting of boron, aluminum, gallium, indium and thallium;
- (2) $M^{(b)}$ is a metal selected from the group consisting of phosphorus, arsenic, antimony and bismuth;
- (3) R is an electron donating moiety selected from the groups consisting of hydrogen and hydrocarbon.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,071,493

January 1, 1963

Thomas P. Whaley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 41, strike out "V-B," first occurrence; column 5, line 48, for "(1957)" read -- (1947) --; column 13, line 68, after "tetracyclohexylaluminum" insert a comma; line 70, strike out "boron, lithium tetrabutadienylboron; lithium ethyltributyl-" and insert instead -- lithium tetra-naphthylboron, lithium tetracyclohexenylboron, lithium tetrabutadienylboron; lithium ethyltributyl- --; column 25, line 14, after "V-B," insert -- VI-B, --; column 26, line 15, for "X (1)" read -- (1) --.

Signed and sealed this 3rd day of September 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

243 / 14

Constrained Geometry Chromium Catalysts for Olefin Polymerization

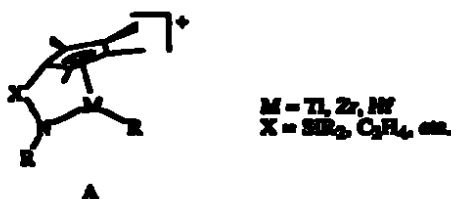
Yuanfeng Liang, Glenn P. A. Yap, Arnold L. Rheingold, and
Klaus H. Theopold^{*,†}

Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology,
University of Delaware, Newark, Delaware 19716

Received September 9, 1995[§]

Summary: Chromium(III) alkyls featuring an amido ligand tethered to a permethylcyclopentadienyl ring (i.e. [η^5 -Me₅C₅SiMe₂- η^1 -N^tBu]CrR) have been prepared and structurally characterized. They catalyze the polymerization of ethylene and the dimerization and isomerization of α -olefins.

Among the metallocene catalysts currently revolutionizing the field of Ziegler–Natta catalysis,¹ so-called constrained geometry molecules (see A)—i.e. metal



complexes containing an amide ligand tethered to a cyclopentadienyl group—play a special role as copolymerization catalysts.² The sterically unencumbered nature of the catalytic site is thought to facilitate incorporation of various α -olefins into growing polymer chains. Extension of this structural feature to chromium, one of the metals employed commercially in coordination polymerization,³ might thus be expected to generate a new family of Cr-based copolymerization catalysts. Herein we report the synthesis and characterization of the first constrained geometry chromium alkyls and an investigation of their reactivity with olefins.

Slow addition of Li₂(THF)₂[Me₅C₅SiMe₂N^tBu]⁴ to a suspension of CrCl₃(THF)₃ in THF at low temperature afforded dark green (Cp⁺SiNR)CrCl(THF) (1) in 65% yield. Alkylation of this starting material with various lithium alkyls yielded a new class of chromium(III) alkyls (see Scheme 1). Depending on the steric bulk of the alkyl group, the complexes either retained or lost the THF ligand; in the latter case (e.g. when R = CH₃-SiMe₂) a coordinatively unsaturated metal alkyl akin

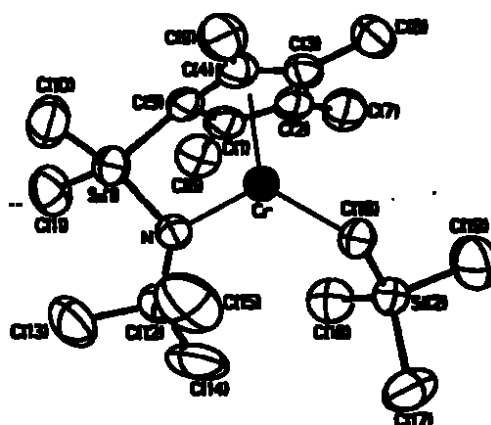


Figure 1. Molecular structure of (Cp⁺SiNR)CrCH₂SiMe₂ (4). Selected interatomic distances and angles: Cr–N, 1.920(4) Å; Cr–C(16), 2.092(5) Å; Cr–C_{cp}, 2.28 Å; N–Cr–C(16), 113.8(2)°; Cp_{centroid}–Cr–N, 115.9°; Cr–C(16)–Si(2), 119.6(3)°.

to A was isolated. Figure 1 shows the result of a crystal structure determination of (Cp⁺SiNR)CrCH₂SiMe₂ (4),⁵ a brown solid that is freely soluble in hydrocarbon solvent. The molecule has approximate mirror symmetry; the idealized mirror plane bisects the chelating ligand, and the alkyl carbon directly bonded to chromium deviates only very little from it (0.26 Å). The three-coordinate nitrogen is planar (sum of angles: 359.2°), and the Cr–N (1.92 Å) distance is considerably shorter than the Cr–C(16) bond (2.09 Å), the latter an entirely normal chromium(III)–carbon single-bond distance.⁶ Both observations are consistent with some degree of ligand-to-metal π -donation involving the amide ligand, albeit not sufficient for a full Cr=N double bond (ca 1.65 Å).⁷ The effective magnetic moment of the complex measured $\mu_{\text{eff}}(\text{RT}) = 4.0(1) \mu_{\text{B}}$, consistent with three unpaired electrons. Thus the π -acceptor orbital on the metal must be singly occupied, and the N–Cr π -bond is a three-electron interaction of attenuated strength. The Cp_{centroid}–Cr–N angle of 115.9° is an indication of the “openness” of the structure adjacent to the Cr–C bond, i.e. the anticipated site of catalytic activity. Despite its coordinative and electronic unsaturation, 4 exhibited no indication of an agostic interaction,⁸ e.g. with one of the methyl hydrogen atoms of the

[†] E-mail: theopold@udel.edu.

[§] Abstract published in *Advances in Catalysis*, November 15, 1996.

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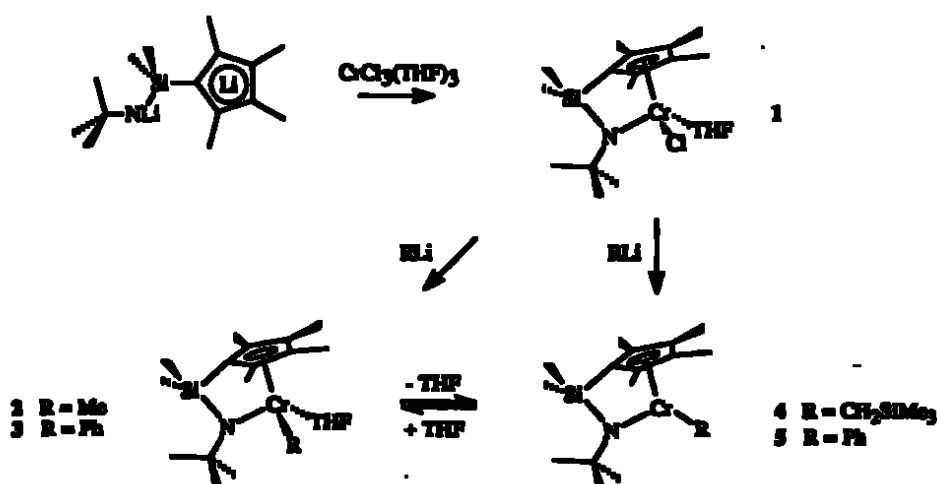
(5) 4: C₂₀H₂₄CrN₂, triclinic $P\bar{1}$, $a = 2.108(1) \text{ Å}$, $b = 2.078(1) \text{ Å}$, $c = 12.748(1) \text{ Å}$, $\alpha = 94.503(5)^\circ$, $\beta = 100.434(5)^\circ$, $\gamma = 102.06(1)^\circ$, $Z = 2$, $T = 297 \text{ K}$, $R = 5.30\%$, $R_w = 6.34\%$.

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Scheme 1



(trimethylsilyl)methyl ligand. Such interactions—at least in the ground state—would not appear to be important in chromium catalysis.⁹

We have previously established the minimum requirements for ethylene polymerization activity of organochromium catalysts, namely a chromium(III)–carbon σ -bond and coordinative unsaturation (i.e. pseudo-five-coordination in a cyclopentadienyl complex).¹⁰ Complex 4 fits this description, and accordingly it catalyzed the polymerization of ethylene. Exposure of a toluene solution (50 mL, 3.0 mM) at room temperature to ethylene (500 psi) for 3.5 h yielded 2.6 g of polyethylene. When the same polymerization reaction was carried out in a 1:1 mixture of toluene and 1-hexane, 2.1 g of polymer was formed.¹¹ By ¹³C NMR, this material showed no evidence for incorporation of the α -olefin! Despite the great concentration advantage of the hexane the catalyst selectively polymerized only ethylene. Attempts to polymerize propene, using 4 as a catalyst, were unsuccessful. However, when the reaction of 4 with propene at room temperature was monitored by ¹H NMR, complete conversion to 2-methyl-1-pentene was observed over the course of several hours (the product was identified by ¹H and ¹³C NMR). While "constrained geometry" chromium catalysts can apparently bind and insert α -olefins, the latter do not compete effectively with ethylene for incorporation into a growing polymer chain, and chain transfer by β -hydrogen elimination must be very facile for chromium alkyls featuring tertiary C–H bonds at the β -carbon atom.

Several observations are relevant to a consideration of the mechanism for the olefin dimerization reaction noted above. The isotropically shifted resonances of 4

remained constant during this transformation, and no new paramagnetic compounds were observed by ¹H NMR; furthermore, no organic compounds containing (trimethylsilyl)methyl groups were observed by NMR. Reaction of 1-hexene with 4 yielded not only the expected product of head-to-tail dimerization, i.e. 2-butyl-1-octene, but also a mixture of isomeric internal hexenes as well. Finally, both the dimerization and isomerization were accelerated by the addition of hydrogen (e.g. 300 Torr H₂). On the basis of these observations, we suggest that the actual catalyst may be the hydride [(Cp*SiNR)CrH]_n, small quantities of which may be formed by β -elimination from (Cp*SiNR)CrCH₂CH(R)CH₂SiMe₃, i.e. the product of insertion of an olefin in the chromium–carbon bond of 4. Indeed, prolonged exposure of 4 to H₂ yielded SiMe₄ and at least one new, and as yet unidentified, paramagnetic compound. Efforts to characterize this species fully are under way.

The catalytic regioselective head-to-tail dimerization of olefins may have applications in organic synthesis,¹² and we have tested a number of substrates to begin to delineate the scope of this transformation. Styrene or 3,3-dimethyl-1-butene did not react under these conditions. 1,5-Hexadiene yielded solely methylenecyclopentane, and 1,6-heptadiene gave methylenecyclohexane and 1-methyl-2-methylenecyclopentane in a 3:1 ratio. We are currently exploring the utility of 4 and its analogues for cyclizations of more complex organic substrates.

Our understanding of organochromium chemistry related to olefin polymerization has reached the stage where molecular design of catalysts is feasible. However, simple extrapolation of design principles from group 4 chemistry to the later metal fails, and a homogeneous chromium-based copolymerization catalyst remains elusive. The available evidence suggests that cyclopentadienylchromium(III) complexes feature

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(11) (a) Toluene: $M_n = 85730$, $M_w/M_n = 53$. (b) Toluene/1-hexane: $M_n = 102300$, $M_w/M_n = 37$. Note that these numbers reflect bimodal product distributions with most of the samples being of low molecular weight ($M_n = 1000$ – 10000). A possible explanation for this observation (suggested by a reviewer) is the presence of small amounts of a chromium alkyl resulting from cleavage of the Cp*–Si bond during the synthesis (i.e. a compound containing a $\text{C}_6\text{H}_5\text{Me}_2$ ligand); such fragmentation has been noted in group 4 chemistry, and low levels of contaminants would be hard to detect in paramagnetic Cr complexes.

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highly disparate rates of chain growth for ethylene and α -olefins.¹² Our results militate against a steric origin of this selectivity; the relevant electronic factors may influence both olefin binding and/or the migratory insertion step. That chromium is capable of copolymerization is demonstrated by the Phillips catalyst (inorganic CrSiO_2).³ Homogeneous complexes more closely related to its active site are reasonable synthetic targets in our quest for novel chromium catalysts.

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Supporting Information Available: Tables giving a summary of the crystal structure determination, positional and thermal parameters, and bond distances and angles of 4 and text providing syntheses and spectroscopic data for all complexes (10 pages). Ordering information is given on any current masthead page.

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Bis(indenyl)chromium Is a Dimer

Oliver Heinemann, Peter W. Jolly,* Carl Krüger, and Glenn P. J. Verhovnik¹

Max-Planck-Institut für Kohlenforschung, 45466 Mülheim an der Ruhr, Germany

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Summary: The reduction of chromium(III) chloride with sodium indenyl leads initially to chromium(II) chloride, which then gives the dimeric compounds (indenyl)₂Cr₂Cl (1) and (indenyl)₄Cr₂ (2), both of which have been shown to contain μ - η^3 -indenyl groups. 2 is catalytically active for the polymerization of ethylene and the hydrogenation of styrene to ethylbenzene.

Shortly after the discovery of chromocene,³ (indenyl)₂Cr formed the subject of a short, sharp polemic concerning the bonding situation,⁴ however, the compound was not actually isolated until 1976, when scientists at the Union Carbide Corp. reported its preparation by the reduction of CrCl₃ with 3 equiv of sodium indenyl⁵ and patented its use, supported on silica, as a catalyst for the polymerization of ethylene.⁶ We have had occasion to repeat the preparation and report here the true structure.

Initial experiments indicated that the reaction of Cr-(THF)₃Cl₃ with 1 equiv of sodium indenyl results solely in the reduction of the chromium salt to CrCl₂. Further reaction with sodium indenyl occurs in a stepwise manner: initially a brown compound is formed whose spectroscopic data indicate the formation of (indenyl)₂Cr₂Cl (1), and this reacts further to give a red-brown species having the composition (indenyl)₄Cr₂ (2) (Scheme 1).

Treatment of CrCl₃ with 1 equiv of sodium indenyl in THF at room temperature, followed by removal of the solvent under vacuum and crystallization from hot toluene, gave (indenyl)₂Cr₂Cl (1) as black crystals in 7% yield; mp 136 °C. Treatment of CrCl₃ with 3 equiv of sodium indenyl in the same manner as described above gave (indenyl)₄Cr₂ (2) as brown crystals in 59% yield, which decompose at 150 °C.⁷ 2 can also be obtained in 67% yield by reacting 1 with 1 equiv of sodium indenyl.

The molecular structures of both 1 and 2 have been determined by single-crystal X-ray diffraction analysis (Scheme 1)⁷ and show the compounds to be dinuclear and to contain both η^3 - and μ - η^3 -indenyl groups; the latter bonding arrangement is apparently unique among the indenyl-metal compounds. The structure is related to that of [η^3 -indenyl](μ - η^3 -C₉H₇)Cr]₂ (3), which we have

reported earlier.⁸ The ¹³C NMR spectra⁹ suggest that the structures of 1 and 2 in solution and in the crystal are similar: for example, the observation of two signals for C8/C9 confirms the nonsymmetric structure of 1, while the chemical shifts of the bridging allylic C atoms in 2 are similar to those observed for (η^3 -C₉H₇)₂Cr₂ (4).¹⁰

The structure of 2 should be contrasted to that of the permethylated indenyl compound (η^3 -C₉H₇Me)₂Cr¹¹ and to that of the 1-cyclo-C₉H₁₁CH₃-substituted species (η^3 -1-CyCH₂C₉H₉)₂Cr,¹² both of which have conventional metallocene structures, suggesting that steric factors play a role in the adoption of a dinuclear structure by 2.

Mechanistically interesting is the observation that a toluene solution of (indenyl)₄Cr₂ (2) is an active single-component catalyst for the polymerization of ethylene into linear polyethylene with a crystallinity of 77%¹³ at room temperature; in contrast, both of the related

(7) Crystal data for 1: C₂₀H₁₂CrCl₂, *M*_r = 484.9, black, crystal size 0.11 × 0.35 × 0.39 mm, *a* = 6.408(1) Å, *b* = 12.955(2) Å, *c* = 12.955(2) Å, *V* = 2109.6 Å³, *T* = 293 K, *D*_x = 1.48 g cm⁻³, μ = 11.12 cm⁻¹, *P*(000) = 982, *Z* = 4, orthorhombic, *P*2₁2₁2₁ (No. 19), Bruker-Nonius CAD4 diffractometer, λ = 0.710 89 Å, measuring method ω -2 θ , 4451 measured reflections ($\pm h, \pm k, \pm l$), [data $\sigma(2I)/I$ = 0.05 Å⁻¹], 4083 independent reflections, 3235 observed reflections (*I* ≥ 3 $\sigma(I)$) for 365 refined parameters, structure solved by heavy-atom methods, non-hydrogen atoms refined anisotropically, H atom positions were found and refined isotropically in the final refinement stage, $\Sigma w(F_o - F_c)^2$ minimized, *R* = 0.036, *R*_w = 0.039 ($w = 1/\sigma^2(F_o)$), maximum shift/error 0.44, final difference Fourier ρ = 0.66 e Å⁻³, selected bond distances (Å) and angles (deg) are as follows: Cr1-Cr2 = 2.817(1), Cr1-D1 = 1.94(1), Cr1-D3 = 2.14(8), Cr1-C1 = 2.235(1), C1-C2 = 1.436(7), C11-C12 = 1.399(2), C12-C14 = 1.351(2), Cr1-C1-Cr2 = 69.8(1), D1-Cr1-C1 = 122.8, D3-Cr1-C1 = 101.8, C1-C2-C3 = 119.8(4), C1-C2-C7 = 120.2(5), C10-C11-C12 = 109.2(5), C12-C17-C13 = 123.2(4). Crystal data for 2: C₂₀H₁₂Cr₂, *M*_r = 504.9, dark red-black, crystal size 0.25 × 0.67 × 0.11 mm, *a* = 21.140(4) Å, *b* = 7.577(1) Å, *c* = 23.602(3) Å, β = 92.89°, *V* = 5318.9 Å³, *T* = 293 K, *D*_x = 1.41 g cm⁻³, μ = 8.20 cm⁻¹, *P*(000) = 2238, *Z* = 8, monoclinic, *C*2_m (No. 15), Bruker-Nonius CAD4 diffractometer, λ = 0.710 89 Å, measuring method ω -2 θ , 5145 measured reflections ($\pm h, \pm k, \pm l$), [data $\sigma(2I)/I$ = 0.50 Å⁻¹], 4951 independent reflections, 3120 observed reflections (*I* ≥ 3 $\sigma(I)$) for 343 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions were calculated in the final refinement stage, $\Sigma w(F_o - F_c)^2$ minimized, *R* = 0.033, *R*_w = 0.057 ($w = 1/\sigma^2(F_o)$), max shift/error 0.02, final difference Fourier ρ = 0.73 e Å⁻³. Selected bond distances (Å) and angles (deg) are as follows: Cr1-Cr2 = 2.175(1), Cr1-D1 = 1.99(8), Cr1-D3 = 2.157, C1-C2 = 1.411(5), C1-C3 = 1.445(7), C11-C12 = 1.389(5), C12-C14 = 1.353(5), Cr1-C2-Cr2 = 56.2(1), D1-Cr1-D3 = 112.2, D1-Cr1-D5 = 121.4, C1-C2-C3 = 110.5(4), C1-C2-C7 = 120.5(5), C10-C11-C12 = 109.1(5), C12-C17-C13 = 123.2(5).

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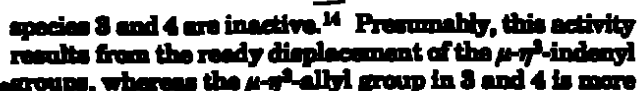
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firmly bonded. Styrene can be hydrogenated into ethylbenzene at room temperature and 40 bar of hydrogen in the presence of a solution of 2 in toluene.

ONDERDEEL

United States Patent [19]
Carney et al.

[11] Patent Number: **5,418,200**
[45] Date of Patent: **May 23, 1995**

US005418200A

[54] **CYCLOPENTADIENYL GROUP 6B METAL
 α -OLEFIN POLYMERIZATION CATALYSTS
AND PROCESS FOR POLYMERIZING
 α -OLEFINS**

[75] Inventors: **Michael J. Carney; David L. Beach,**
both of Kingwood, Tex.

[73] Assignee: **Chevron Chemical Company, Del.**

[21] Appl. No.: **963,531**

[22] Filed: **Oct. 20, 1992**

Related U.S. Application Data

[63] **Continuation-in-part of Ser. No. 841,673, Feb. 26, 1992,**
abandoned, which is a continuation-in-part of Ser. No.
677,725, Mar. 29, 1991, abandoned.

[51] **Int. Cl.⁶ B01J 31/00; B01J 31/34**

[52] **U.S. Cl. 502/117; 502/152;**
502/154; 502/155; 526/130; 526/154; 526/170

[58] **Field of Search 502/117, 152, 154, 155**

[56] **References Cited**

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Primary Examiner—Asok Pal

Attorney, Agent, or Firm—C. D. Holland

[57] **ABSTRACT**

Disclosed is a catalyst system for the homopolymeriza-
tion and copolymerization of alpha-olefins having 2-8
carbon atoms, said catalyst system comprising a cy-
clopentadienyl Group 6b metal hydrocarbyl compound
in which the metal has an oxidation state of +3, said
Group 6b metal compound being supported on an inor-
ganic support. The catalyst system may also contain a
Group 2 or Group 3 metal alkyl compound.

55 Claims, No Drawings

CYCLOPENTADIENYL GROUP 6B METAL α-OLEFIN POLYMERIZATION CATALYSTS AND PROCESS FOR POLYMERIZING α-OLEFINS

This application is a continuation-in-part of application Ser. No. 841,673, filed Feb. 26, 1992, which is a continuation-in-part of application Ser. No. 677,725, filed Mar. 29, 1991, now both abandoned.

FIELD OF THE INVENTION

The present invention relates to catalyst systems for polymerizing alpha-olefins and processes for polymerizing alpha-olefins using such catalysts.

BACKGROUND OF THE INVENTION

Chromium based catalysts are used in the commercial polymerization of small alpha-olefins such as ethylene and propylene. One such catalyst is prepared by depositing chromocene (bis(cyclopentadienyl) chromium (II)) on an inorganic metal oxide support, as disclosed in British Patent No. 1,253,063 to Karapinka. U.S. Pat. No. 4,015,099, issued Mar. 29, 1977 to Karol, describes the use of bis(indenyl)- and bis(fluorenyl)-chromium (II) compounds supported on activated inorganic oxide supports as catalysts for the polymerization of ethylene.

Recently, new synthetic methods have been described for preparing Cr⁺³ organometallic compounds. Theopold, *J. Am. Chem. Soc.* (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts", Theopold, *Acc. Chem. Res.* (1990), 23, 263 entitled "Organochromium (III) Chemistry: A Neglected Oxidation State" and Thomas et al., *J. Amer. Chem. Soc.*, 113 (1991), p. 893 et seq. disclose that certain pentamethylcyclopentadienyl chromium (III) alkyls can be prepared, and that they can be used for making polyethylene homogeneously in CH₂Cl₂. However, these homogeneous Cr (III) polymerization catalysts have several deficiencies. These include low polymer productivity, rapid deactivation, and the need to use polar, non-coordinating solvents. Additionally, since they are homogeneous catalysts, they are unsuitable for gas phase olefin polymerizations.

U.S. Pat. No. 4,530,914, issued Jul. 23, 1985 to Ewen et al., discloses a catalyst system for the polymerization of alpha-olefins which comprises two or more metallocenes, each having different propagation and termination rate constants, and aluminum compounds. The metallocenes are cyclopentadienyl derivatives of a transition metal of Group 4b, 5b, and 6b metals of the Periodic Table. They are described by the formulas $(C_5R'_m)_pR''_s(C_5R'_m)_pMeQ_p$ and $R''(C_5R'_m)_2MeQ$ where $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is hydrogen or a hydrocarbyl radical, R'' is an alkyl radical, a dialkyl-germanium or silicon or an alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical, Me is a Group 4b, 5b, or 6b metal, s is 0 or 1, p is 0, 1, or 2; when p=0, s=0; m is 4 when s is 1 and m is 5 when s is 0.

U.S. Pat. No. 4,939,217, issued Jul. 3, 1990 to Stricklen, also discloses a process for polymerizing olefins where the polymerization is conducted in the presence of hydrogen, and a catalyst system is used which contains aluminum compounds and at least two metallocenes, each having different olefin polymerization termination rate constants. The metallocenes disclosed are

similar to those described in aforementioned U.S. Pat. No. 4,530,914.

U.S. Pat. No. 4,975,403, issued Dec. 4, 1990 to Ewen, discloses a catalyst system for use in the polymerization of olefins. The catalyst system includes at least two different chiral, stereo-rigid metallocene catalysts of the formula $R''(C_5(R')_m)_2MeQ_p$ (where Me is a Group 4b, 5b or 6b metal and $(C_5(R')_m)$ is a cyclopentadienyl or substituted cyclopentadienyl ring) and an aluminum compound.

Canadian Patent Application No. 2,000,567, published Apr. 13, 1990, discloses a process for producing polyethylene using a composite catalyst made up of a solid catalyst component typified by a selected chromium compound, a modified aluminum compound typified by a trialkylaluminum, and an alkylaluminum alkoxide compound. The chromium compound may be chromium oxide, and the modified aluminum compound may be the reaction product of an organoaluminum compound and water.

It has now been discovered that when cyclopentadienyl Group 6b metal hydrocarbyl compounds, in which the Group 6b metal is in an oxidation state of +3, are supported on inorganic metal oxide or inorganic metal phosphate supports, high productivity alpha-olefin polymerization catalysts are produced, and that the use of a co-catalyst improves the productivity of many of these compounds.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a catalyst system for the homopolymerization and copolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation state of +3, said Group 6b metal compound being supported on an inorganic support.

There is also provided in accordance with the present invention a catalyst system for the homopolymerization and copolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation state of +3, said Group 6b metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

Further provided in accordance with the present invention is a process for the homopolymerization or copolymerization of alpha-olefins having 2-8 carbon atoms comprising polymerizing said alpha-olefin, or copolymerizing two or more alpha-olefins in the presence of a catalyst system comprising a cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation state of +3, said group 6b metal compound being supported on an inorganic support.

The present invention also provides a process for the homopolymerization or copolymerization of alpha-olefins comprising polymerizing said alpha-olefin, or copolymerizing two or more alpha-olefins in the presence of a catalyst system comprising a cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation state of +3, said group 6b metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

In the above catalyst systems and processes, chromium is a preferred Group 6b metal, silica, aluminum phosphate and alumina aluminum phosphate are pre-

ferred supports, and aluminoxanes and trialkylaluminum compounds are preferred Group 2 or 3 metal alkyl compounds.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides catalyst systems for use in the polymerization (either homopolymerization or copolymerization) of alpha-olefins, including ethylene, propylene, 1-butene, 1-hexene and 4-methyl-1-pentene.

It has quite surprisingly been found that, even though the productivity of many cyclopentadienyl Group 6b metal hydrocarbyl compounds is quite low when employed as catalyst in the homogeneous polymerization of alpha-olefins, when these compounds are supported on an inorganic metal oxide or inorganic phosphate solid support, their productivity increases dramatically, especially when co-catalysts are used. While the catalyst systems of the present invention can be used to polymerize a variety of alpha-olefins, they are especially useful in the polymerization of ethylene. These catalysts produce polyethylene in high yield, and the polymers produced have remarkably uniform particle size and highly desirable morphology (i.e., substantially spherical) that is suitable for gas phase polymerizations. The catalysts of the present invention allow the use of hydrogen during polymerization of polyethylene to reduce the molecular weight and to broaden the molecular weight distribution. In addition, the catalyst systems of this invention produce polyethylene with a variety of molecular weight distributions, depending on the support used.

A scanning electron micrograph (SEM) was produced at X10 magnification of a polyethylene sample produced by homogeneous polymerization using $[Cp^*Cr(THF)_2CH_3]^+[BPh_4]^-$ (where Cp^* represents pentamethylcyclopentadienyl, THF is tetrahydrofuran, and Ph is phenyl). This sample was characterized by very small, irregularly shaped particles. These particles were typically less than 20-30 μm (microns) in diameter. A SEM was taken at X10 magnification of a polyethylene sample produced by the method of the present invention using $Cp^*Cr(CH_3)_2(THF)$ on a silica support. This sample had particles of much larger size (about 1 μm in diameter) than the homogeneous polymerization sample. The particle size was quite suitable for gas phase polymerization applications. A third SEM was taken of a polyethylene sample produced by the method of this invention using $Cp^*Cr(CH_3)_2(THF)$ on an $Al_2O_3 \cdot 2AlPO_4$ support. The particles were quite uniform in size, and primarily spherical in nature. Again, the particle size and spherical nature of the polymer makes this system attractive for gas phase polymerization applications.

Activities for the catalyst systems of the present invention are greater than 3,000 grams of polymer per gram of chromium metal per hour ("g/g Cr/hr"), preferably greater than 30,000 g/g Cr/hr, and more preferably greater than 200,000 g/g Cr/hr.

The term molecular weight distribution ("MWD"), as used herein, is the weight average molecular weight (" M_w ") divided by the number average molecular weight (" M_n "), i.e., M_w/M_n . The polymers produced in accordance with the present invention using silica supported catalysts have a MWD greater than 10, preferably greater than 15, and more preferably greater than 20. These polymers, which have high MWD's, have

improved ease of processing, better melt behavior, and other desirable properties such as impact resistance and environmental stress crack resistance. Large blow molded products are superior when made with high MWD polymers. Additionally, film is more puncture resistant when made from polymer with a high MWD. The polymers made in accordance with this invention using alumina aluminum phosphate supported catalysts possess high molecular weight and a more narrow MWD, making them useful in such applications as injection molding. Typically, the MWD for polymers made with alumina aluminum phosphate supported catalysts is less than 3.

The catalyst systems of the present invention comprise at least one cyclopentadienyl Group 6b metal hydrocarbyl compound in which the Group 6b metal is in an oxidation state of +3, and which is catalytically active when deposited on an inorganic metal oxide or inorganic metal phosphate support. As used herein, the term "cyclopentadienyl" refers to unsubstituted cyclopentadienyl as well as substituted derivatives of cyclopentadienyl in which the cyclopentadienyl ring contains one or more substituents which do not interfere with the Group 6b metal compound's ability to function as an alpha-olefin polymerization catalyst. Examples of substituted cyclopentadienyl include pentamethylcyclopentadienyl, methylcyclopentadienyl, t-butylcyclopentadienyl, and pentaphenylcyclopentadienyl, as well as compounds where the substituent forms a multi-cyclic ring with the cyclopentadienyl ring. Examples of these multi-cyclic rings include indenyl and fluorenyl rings. For the sake of simplicity, the abbreviation "Cp" will be used herein to refer to unsubstituted cyclopentadienyl, and the abbreviation "Cp*" will be used to refer to pentamethylcyclopentadienyl. Cp* is a preferred cyclopentadienyl group as it stabilizes the organometallic compound of this invention.

The Group 6b metal compounds useful in the present invention include compounds wherein the metal is chromium, molybdenum or tungsten. Compounds in which the metal is chromium are preferred. The Group 6b metal atom in the compound has an oxidation state of +3.

These Group 6b metal compounds have, in addition to one cyclopentadienyl group, at least one hydrocarbyl group bonded to the metal atom. As used herein, the term "hydrocarbyl" refers to alkyl, alkenyl, aryl, aralkyl and alkaryl radicals and the like. Exemplary hydrocarbyl radicals include, but are not limited to, methyl, ethyl, propyl, butyl, amyl, isomyl, hexyl, neopentyl, isobutyl, heptyl, octyl, nonyl, decyl, undecyl, phenyl, benzyl and other similar groups. Additionally, organosilyl groups, such as trimethylsilyl methyl, i.e., $(CH_3)_3SiCH_2-$, and the like can be used. If more than one hydrocarbyl group is bonded to the metal atom, they can be independent or linked, i.e., they can form a 3-, 4-, 5-, 6-, or 7-membered metallocycle. Preferably, the hydrocarbyl group is sigma bonded to the Group 6b metal.

In addition to the cyclopentadienyl and hydrocarbyl groups, the Group 6b metal compounds of the present invention may also contain one or more sigma donor stabilizing ligands. These ligands contain an atom, such as oxygen, nitrogen, phosphorous or sulfur, which has a nonbonded electron pair. Examples of these ligands include, but are not limited to, ethers, amines, phosphines and thioethers. Ethers such as tetrahydrofuran (THF) and amines such as pyridine are preferred. Com-

pounds with pyridine are most preferred and give catalysts with high activity and stability.

Examples of the Group 6b metal compounds useful in this invention include, but are not limited to, compounds having the following general formulas:



wherein M is a Group 6b metal such as chromium, molybdenum and tungsten;

$(C_5(R')_2)_m$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

R' is at each independent occurrence hydrogen, a hydrocarbyl radical having 1-20 carbon atoms, or adjacent R' groups may together form one or more rings;

X is a hydrocarbyl radical having 1-20 carbon atoms (for example, a monovalent saturated aliphatic or allycyclic radical or a monovalent aromatic radical, or combinations thereof);

a=1 or 2, b=1 or 2 where a+b=3;

c=1 or 2 with the proviso that when c=2 then X is alkyl;

L is at each independent occurrence a sigma donor stabilizing ligand;

m=1 to 2 inclusive; and

A is an anion.

Examples of compounds having Formula (I) above include, but are not limited to, $Cp^*Cr(CH_3)_2(THF)$, $Cp^*Cr(Bayl)_2(THF)$, $Cp^*Cr(Bayl)_2(Pyr)$, $Cp^*Cr(CH_3)_2(Pyr)$, $Cp^*Cr(TMSM)_2(Pyr)$, $Cp^*Cr(TMSM)_2$, $Cp^*Cr(CH_3)_2(DMAP)$, $Cp^*Cr(CH_3)_2(PMe_2Ph)$, $Cp^*Cr(CH_3)_2(3,5\text{-Lutidine})$, and $Cp^*Cr(CH_3)_2(DMAP)$, where Bayl is benzyl, Pyr is pyridine, TMSM is trimethylsilylmethyl, DMAP is N,N-dimethylaminopyridine, and PMe_2Ph is dimethylphenylphosphine.

Further examples of the Group 6b compounds of this invention include monomeric Group 6b metal compounds, dimeric Group 6b metal compounds, and cationic Group 6b metal compounds. A preferred monomeric Group 6b metal compound is $Cp^*Cr(Bayl)_2(THF)$. $[Cp^*Cr(CH_3)_2]_2$ is a preferred dimeric compound, and a preferred cationic compound is $[Cp^*Cr(CH_3)_2(THF)_2]^+[BPh_4]^-$. Especially preferred compounds are $Cp^*Cr(CH_3)_2(Pyr)$, $Cp^*Cr(CH_3)_2(3,5\text{-Lutidine})$ and $Cp^*Cr(CH_3)_2(PMe_2Ph)$.

In part, the choice of Group 6b metal compound is based on the thermal stability of the compound and its ease of preparation. Of the Group 6b metal compounds useful in this invention, the organochromium compounds are preferred.

Theopold, *J. Am. Chem. Soc.* (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts", Theopold, *Acc. Chem. Res.* (1990), 23, 263 entitled "Organochromium (III) Chemistry: A Neglected Oxidation State", and Thomas et al., *J. Amer. Chem. Soc.*, 113 (1991), p. 893 et seq. (all of which are incorporated herein by reference) describe syntheses useful in making some of the Group 6b metal compounds of this invention. Similar procedures can be used to make related compounds.

In the catalyst systems of the present invention, the Group 6b metal compound is deposited on an inorganic support. Suitable inorganic metal oxide supports include silica, alumina, silica-alumina mixtures, thoria,

zirconia, magnesium oxide and similar oxides. Suitable inorganic metal phosphates include aluminum phosphate, zirconium phosphate, magnesium-containing alumina phosphate and alumina aluminum phosphate. Silica, aluminum phosphates and alumina aluminum phosphates are preferred. Suitable silica supports include Davison 952, Davison 955, Crossfield EP-10 and Crossfield EP17MS. Further examples of useful supports are the following: alumina aluminum phosphates with aluminum to phosphorus ratios of about 5:1 to 1:1 as disclosed in U.S. Pat. Nos. 4,080,311 and 4,219,444; magnesia-alumina-aluminum phosphates as described in U.S. Pat. No. 4,210,560; zinc oxide-cadmium oxide-alumina-aluminum phosphates such as those disclosed in U.S. Pat. No. 4,367,067; and the calcium, barium, and/or strontium oxide-alumina-aluminum phosphates described in U.S. Pat. Nos. 4,382,877 and 4,382,878. The acidity of these supports can be adjusted by judicious inclusion of basic metals such as alkali and alkaline earth metals (Ca, Be, Mg, K, Li) to counteract excessive acidity. Other useful supports include magnesium halides, particularly magnesium chloride, such as those described in "Transition Metals and Organometallics as Catalysts for Olefin Polymerization" (1988, Springer-Verlag) edited by W. Kaminsky and H. Sinn and "Transition Metal Catalyzed Polymerizations-Ziegler-Natta and Metathesis Polymerizations" (1988, Cambridge University Press) edited by R. Qohrt.

The supports useful in this invention should have a high surface area. In general, these supports should have the characteristics listed in the following table:

Property	Broad Range	Preferred Range
Surface area	25-800 m ² /g	100-370 m ² /g
Pore volume	0.25-4 cm ³ /g	0.7-3 cm ³ /g
Mean particle diameter	30-300 microns	60-140 microns

Preferably, the pore size distribution is broad, with a significant percentage of the pores in the macropore range (>500 Angstroms). Preferably, at least 50% of the pores are macropores. It is also desirable that the support be substantially anhydrous before the Group 6b metal compound is deposited on it. Thus, it is desirable to calcine the support prior to deposition of the Group 6b metal compound.

The supported catalysts of this invention are readily prepared by techniques well known in the art. For example, a solution of the Group 6b metal compound in aliphatic, aromatic or cycloaliphatic hydrocarbons, or ethers such as diethyl ether or tetrahydrofuran can be stirred with the support until the Group 6b metal compound is adsorbed on or reacted with the support. The amount of Group 6b metal compound relative to the amount of support will vary considerably depending upon such factors as the particle size of the support, its pore size and surface area, the solubility of the Group 6b metal compound in the solvent employed, and the amount of Group 6b metal compound which is to be deposited on the support. However, in general the amount of Group 6b metal compound used is adjusted so that the final metal content (calculated as the element), relative to the support, is in the range of from about 0.01 to about 10 weight percent. In most cases, the most desirable level is in the range of about 0.1 to about 5 weight percent.

It has been found that the activity of many of the supported Group 6b metal compounds of this invention is significantly increased when they are employed in conjunction with a co-catalyst. The co-catalysts useful in the practice of the present invention are Group 2 and Group 3 metal alkyls. As used herein, the term "Group 2 and Group 3 metal alkyls" refers to compounds containing a metal from Group 2 or Group 3 of the Periodic Table (such as Mg, Zn, B, or Al) to which is bonded at least one alkyl group, preferably a C₁ to C₄ alkyl group. Suitable Group 2 and Group 3 metal alkyls include dialkyl magnesium, dialkyl zinc, trialkylboranes, and aluminum alkyls. Suitable aluminum alkyls include trialkylaluminums (such as trimethylaluminum, triethylaluminum, triisobutylaluminum and trioctylaluminum). Trialkylaluminums with alkyl groups of four carbons or greater are preferred. Other aluminum alkyls useful in the practice of the present invention include alkylaluminum alkoxides (such as diethylaluminum ethoxide and ethylaluminum diethoxide), and alkylaluminum halides (such as diethylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide, diethylaluminum fluoride, ethyl aluminum dichloride, ethyl aluminum dibromide, ethyl aluminum diiodide, ethyl aluminum difluoride, and ethyl aluminum sesquichloride).

Other suitable aluminum alkyls are aluminosilanes, including those represented by the general formula (R-Al-O)_n for the cyclic form and R(R-Al-O)_n-AlR₂ for the linear form. In these formulas, R is, at each independent occurrence, an alkyl group (such as methyl, butyl, isobutyl and the like) preferably with more than two carbon atoms, more preferably with 3-5 carbon atoms, and n is an integer, preferably from 1 to about 20. Most preferably, R is an isobutyl group. Mixtures of linear and cyclic aluminosilanes may also be used. Examples of aluminosilanes useful in this invention include, but are not limited to, ethyl aluminosilane, isobutyl aluminosilane, and methyl aluminosilane. Aluminosilanes (also known as "aluminosilanes") suitable for use in this invention are described in Pasynkiewicz, "Aluminosilanes: Synthesis, Structure, Complexes and Reactions," Polyhedron 9, p. 429 (1990), which is incorporated by reference herein in its entirety.

The preferred Group 2 and Group 3 metal alkyls are the aluminosilanes and the trialkylaluminums.

When used, the Group 2 and Group 3 metal alkyls are used in a Group 2 or 3 metal alkyl to Group 6b metal compound mole ratio of from about 1:1 to about 1000:1. The preferred mole ratio is from about 10:1 to about 200:1.

The catalyst systems of the present invention may be used in either slurry or gas phase polymerization processes. After the catalysts have been formed, the polymerization reaction is conducted by contacting the monomer charge with a catalytic amount of the catalyst at a temperature and at a pressure sufficient to initiate the polymerization reaction. If desired, an organic solvent may be used as a diluent and to facilitate materials handling. The polymerization reaction is carried out at temperatures of from about 30° C. or less up to about 200° C. or more, depending to a great extent on the operating pressure, the pressure of the entire monomer charge, the particular catalyst being used, and its concentration. Preferably, the temperature is from about 30° C. to about 125° C. The pressure can be any pressure sufficient to initiate the polymerization of the monomer charge, and can be from atmospheric up to about 1000

psig. As a general rule, a pressure of about 20 to about 800 psig is preferred.

When the catalyst is used in a slurry-type process, an inert solvent medium is used. The solvent should be one which is inert to all other components and products of the reaction system, and be stable at the reaction conditions being used. It is not necessary, however, that the inert organic solvent medium also serve as a solvent for the polymer produced. The inert organic solvents which may be used include saturated aliphatic hydrocarbons (such as hexane, heptane, pentane, isopentane, isooctane, purified kerosene and the like), saturated cycloaliphatic hydrocarbons (such as cyclohexane, cyclopentane, dimethylcyclopentane, methylcyclopentane and the like), aromatic hydrocarbons (such as benzene, toluene, xylene and the like), and chlorinated hydrocarbons (such as chlorobenzene, tetrachloroethylene, o-dichlorobenzene and the like). Particularly preferred solvents are cyclohexane, pentane, isopentane, hexane and heptane.

When the catalyst is used in a gas phase process, it is suspended in a fluidized bed with, e.g., ethylene. Temperature, pressure and ethylene flow rates are adjusted so that to maintain acceptable fluidization of the catalyst particles and resultant polymer particles. Further descriptions of such a fluidized bed may be found in British Patent No. 1,253,063, to Karspinka, which is incorporated by reference herein.

The following examples are intended to further illustrate the present invention.

EXAMPLES

EXAMPLE 1

SUPPORTS

Silica supports were purchased from W. R. Grace & Co., and included Davison 932 and Davison 935 silicas. These silicas have the following properties:

Property	Davison 932	Davison 935
Surface area	340 m ² /g	300 m ² /g
Pore volume	1.68 cm ³ /g	1.60 cm ³ /g
Mean particle diameter	110 microns	40 microns

Other silica supports were purchased from Croscfield Catalysts. These included EP-10, EP-11 and EP-12 supports. Some properties of the EP-10 support are:

Property	Croscfield EP-10
Surface area	320 m ² /g
Pore volume	1.80 cm ³ /g
Mean particle diameter	105 microns

The AlPO₄ support was purchased from W.R. Grace & Co. The alumina aluminum phosphate supports used in the following examples were prepared by the procedure of Example 1 in U.S. Pat. No. 4,080,311, issued Mar. 21, 1978 to Kehl, which patent is incorporated by reference herein. The product had an Al₂O₃ to AlPO₄ ratio of 1:2.

CATALYST PREPARATIONS

In the preparation of the following catalysts, all manipulations were performed under argon using glove box or Schlenk techniques. All solvents were thor-

oughly dried over Na/benzophenone or calcium hydride and distilled prior to use.

EXAMPLE 2



The organochromium compound $[\text{Cp}^*\text{Cr}(\text{CH}_3)_2]_2$ was prepared by the procedure described in Theopold, *Acc. Chem. Res.*, 23 (1990), p. 264.

EXAMPLE 3

SUPPORTED $[\text{Cp}^*\text{Cr}(\text{CH}_3)_2]_2$

The organochromium compound $[\text{Cp}^*\text{Cr}(\text{CH}_3)_2]_2$ (0.040 g, 9.2×10^{-5} mole), prepared as described in Example 2, was dissolved in 10 ml of pentane, giving a dark brown solution to which was added Davison 952 silica (1.00 g). The resulting mixture was stirred for 15 minutes, giving a dark brown solid and a clear supernatant. The resulting solid catalyst was washed with pentane, and dried to a free-flowing powder.

EXAMPLE 4

SUPPORTED $\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{THF})$

$\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{THF})$ (0.040 g, 9.2×10^{-5} mole) was added to 20 ml of tetrahydrofuran ("THF") and stirred for 0.5 hour, generating a green colored solution containing $\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{THF})$. $\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$ (1.0 g) solid support was added all at once to this solution, and the resulting mixture was stirred for several minutes. All of the organochromium compound reacted with the solid support yielding a deep purple catalyst and a clear supernatant. The resulting catalyst slurry was filtered and the purple solid was washed twice with 10 ml of THF and dried under vacuum to a free flowing powder.

EXAMPLE 5



This compound was prepared by the method described in Thomas et al., *J. Amer. Chem. Soc.*, 113 (1990), p. 900. Preparation No. 13, method B was used to prepare compound number 14 in that paper, i.e., $[\text{Cp}^*\text{CrCH}_3(\text{THF})_2]^+[\text{BPh}_4]^-$.

EXAMPLE 6

SUPPORTED $[\text{Cp}^*\text{CrCH}_3(\text{THF})_2]^+[\text{BPh}_4]^-$

$[\text{Cp}^*\text{CrCH}_3(\text{THF})_2]^+[\text{BPh}_4]^-$ (0.075 g, 1.1×10^{-4} mole) was dissolved in 20 ml of THF and treated all at once with 1.00 g of $\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$. The resulting mixture was stirred for 15 minutes resulting in a dark blue solid and a clear supernatant. The solid was washed with THF, and dried to a free-flowing powder.

COMPARATIVE EXAMPLE A

ETHYLENE POLYMERIZATION USING AN UNSUPPORTED CATALYST

90.1 micromoles of $[\text{Cp}^*\text{CrCH}_3(\text{THF})_2]^+[\text{BPh}_4]^-$ was dissolved in 25 ml methylene chloride in a 50 ml Fischer-Porter bottle, and pressured to 50 psig with ethylene. The reactor was stirred at 25° C. for 1.0 hour. Initially, the ethylene uptake was rapid, but this rate

decreased rapidly over the first half hour. The reaction was stopped by venting the pressure. The polymer produced was washed with isopropanol and then with acetone. The polymer was then dried under vacuum. The results of this polymerization are indicated in Run 1 in Tables I and II.

COMPARATIVE EXAMPLE B

ETHYLENE POLYMERIZATION USING AN UNSUPPORTED CATALYST AND A CO-CATALYST

The procedure of Comparative Example A was repeated, except that 71 molar equivalents of isobutyl aluminumoxane (IBAO) was added to the reaction vessel prior to pressurization with ethylene. The results of this polymerization are indicated in Run 2 in Tables I and II.

EXAMPLE 7

ETHYLENE POLYMERIZATION

Polymerization runs were conducted in 1 or 2 liter autoclave reactors under particle form (slurry) conditions using between 300 and 500 ml heptane as diluent, and a weighed amount of catalyst (typically 0.030 to 0.250 g). Run times of 0.5 to 1.0 hour were normally employed. For example, in a typical run, 0.100 g of the catalyst prepared in Example 4 ($\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{THF})$ adsorbed on $\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$) was charged to a one-liter autoclave along with 300 ml of heptane. Polyisobutylaluminumoxane (0.5 ml of a 1.0M heptane solution, prepared by slow hydrolysis of triisobutylaluminum with 1.0 equivalents of H_2O as in Example 3 of U.S. Pat. No. 4,665,208, issued May 12, 1987 to Welborn et al., which patent is incorporated by reference herein) was added to the stirred reactor as co-catalyst. The reactor temperature and pressure were adjusted to 85° C. and 550 psi (with ethylene), respectively. The ethylene was supplied on demand from a pressurized reservoir. After 0.5 hour, the reaction was stopped by rapidly cooling the reactor and venting the pressure. The polymer produced was washed with isopropanol and acetone, and dried under vacuum to yield 82.9 g of white, granular solid. The results of this polymerization are indicated in Run 15 in Tables III and IV.

Polymerization runs similar to that described above were conducted using the catalysts and conditions shown in Tables I, III, and V below. Analytical data for the polyethylenes produced in these runs is shown in Tables II, IV and VI below. All molecular weights in these tables were determined by gel permeation chromatography.

EXAMPLE 8

GAS PHASE POLYMERIZATION

The procedure of Example 7 is repeated in a 2 liter, stirred autoclave using the supported Cr^{+3} catalysts described above, except that heptane is not added to the autoclave. The reactor temperature and pressure are adjusted to 85° C. and 550 psi (with ethylene), respectively. A white, granular polymer is produced.

TABLE I

Run	Support ^a	POLYMERIZATION DATA FOR $[\text{Cp}^*\text{CrCH}_3(\text{THF})_2]^+[\text{BPh}_4]^-$						Activity ^d	Activity ^e
		$\mu\text{mol Cr}$	Co-catalyst	Al:Cr ^b	C_2H_4 , psig	Temp. °C.			
1	none ^d	90.1	—	0	50	25	518	40	
2	none ^d	90.1	IBAO ^c	71:1	50	25	89	7	
3	Davison 952 Silica	28.2	IBAO	71:1	50	25	6,490 ^f	72	
4	Davison 952 Silica	21.6	—	0	550	80	0	0	

TABLE I-continued

POLYMERIZATION DATA FOR $[Cr^+CrMe_2(THF)_2] [BF_4]^-$								
Run	Support ^a	μ mol Cr	Co-catalyst	Al:Cr ^b	C_3H_6 , psig	Temp. °C	Activity ^c	Activity ^d
5	Davison 932 Silica	27.0	IBAO	110:1	530	80	48,400	523
6	Davison 932 Silica	27.0	IBAO	71:1	530	85	50,600	546
7	Davison 932 Silica	27.0	$Al(CH_3)_3$	71:1	530	85	3,700	40
8	$Al_2O_3 \cdot 2AlPO_4$	15.0	IBAO	33:1	530	85	233,000	2516

^aPreheated at 400° C. for 48 hours.^bMole ratio.^cg polymer/g Cr/hr.^dPerformed under homogeneous conditions in CH_2Cl_2 , catalyst rapidly deactivated.^eIBAO = isobutylalumoxane.^fPolymerization performed for two hours.^gg polymer/g catalyst/hr.

TABLE II

ANALYTICAL DATA FOR POLYETHYLENES
PREPARED WITH $[Cr^+CrMe_2(THF)_2] [BF_4]^-$

Run	Support ^a	T_m , °C	Density, g/cc	Mean Particle Diameter, Microns	$M_w^b \times 10^{-3}$	MWD
1	—	133.3	—	—	123	2.8
5	Davison 932 Silica	138.8	—	830	232	12.8
6	Davison 932 Silica	137.9	0.942	830	238	21.6
7	Davison 932 Silica	136.3	—	—	236	34.2
8	Al_2O_3	138.0	0.927	—	919	4.41

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TABLE IV

ANALYTICAL DATA FOR POLYETHYLENES
PREPARED WITH SUPPORTED $Cr^+CrMe_2(THF)_2$

Run	Support ^a	T_m , °C	Density, g/cc	$M_w^b \times 10^{-3}$	MWD
10	Davison 932 Silica	138.4	0.941	308	18.2
11	Davison 932 Silica	139.6	—	293	19.2
12	Davison 932 Silica	138.3	—	301	20.4
13	Davison 932 Silica	138.3	0.941	270	14.4
14	$Al_2O_3 \cdot 2AlPO_4$	133.1	—	805	2.68
15	$Al_2O_3 \cdot 2AlPO_4$	134.7	—	790	2.63
16	$Al_2O_3 \cdot 2AlPO_4$	136.6	0.927	1130	2.75
17	$Al_2O_3 \cdot 2AlPO_4$	138.0	0.924	917	4.13
18	$Al_2O_3 \cdot 2AlPO_4$	138.1	0.926	1134	3.61

^aCalculated at 400° C. for 48 hours.^bDetermined by GPC.

TABLE V

POLYMERIZATION DATA FOR SUPPORTED Cr^+CrMe_2

Run	Support ^a	μ mol Cr	Co-cat	Al:Cr ^b	C_3H_6 , psig	Temp. °C	Activity ^c	Activity ^d
19	Davison 932 Silica	76.7	—	0	530	85	15,200	164
20	Davison 932 Silica	76.8	—	0	530	85	16,000	173
21	$Al_2O_3 \cdot 2AlPO_4$	57.5	—	0	530	85	2,900	31

^aCalculated at 400° C. for 48 hours.^bMole ratio.^cg polymer/g Cr/hr.^dg polymer/g catalyst/hr. $2AlPO_4$ ^aPreheated at 400° C. for 48 hours.^bDetermined by GPC.^cPerformed under homogeneous conditions in CH_2Cl_2 .

TABLE VI

ANALYTICAL DATA FOR
POLYETHYLENES PREPARED
WITH SUPPORTED Cr^+CrMe_2

Run	Support ^a	T_m , °C	Density, g/cc	Mean Particle Diameter, Microns	$M_w^b \times 10^{-3}$	MWD
19	Davison 932 Silica	139.3	—	910	252	23.5

TABLE III

POLYMERIZATION DATA FOR SUPPORTED $Cr^+CrMe_2(THF)_2$

Run	Support ^a	μ mol Cr	Co-catalyst	Al:Cr ^b	C_3H_6 , psig	Temp. °C	Activity ^c	Activity ^d
9	Davison 932 Silica	46.0	—	0	530	80	0	0
10	Davison 932 Silica	46.0	IBAO ^e	44:1	530	80	15,200	164
11	Davison 932 Silica	46.0	IBAO ^e	44:1	530	85	33,000	356
12	Davison 932 Silica	46.0	IBAO	44:1	530	85	51,000	551
13	Davison 932 Silica	18.4	IBAO	54:1	530	85	33,900	604
14	$Al_2O_3 \cdot 2AlPO_4$	46.0	—	0	530	85	5,400	58
15	$Al_2O_3 \cdot 2AlPO_4$	18.4	IBAO	27:1	530	85	173,000	1868
16	$Al_2O_3 \cdot 2AlPO_4$	18.4	IBAO	54:1	530	85	272,000	2938
17	$Al_2O_3 \cdot 2AlPO_4$	18.4	IBAO	27:1	530	85	169,000	1825
18	$Al_2O_3 \cdot 2AlPO_4$	18.4	IBAO	27:1	530	85	240,000	2592

^aPreheated at 400° C. for 48 hours.^bMole ratio.^cg polymer/g Cr/hr.^dIBAO = isobutylalumoxane.^eIBAO = isobutylalumoxane.^fg polymer/g catalyst/hr.

TABLE VI-continued

ANALYTICAL DATA FOR POLYETHYLENES PREPARED WITH SUPPORTED $\text{Cp}^*\text{Cr}(\text{Mn})_2$						
Run	Support ^a	T_m °C	Density g/cc	Mean Particle Diameter, Microns	M_w^b $\times 10^{-3}$	MWD
20	Devcon 933 Silica	140.6	—	—	347	14.7
21	Al_2O_3 2AIPQ ₄	138.3	—	—	—	—

^aCalculated at 400° C. for 48 hours.^bDetermined by GPC.

Looking at Tables I and II, it can be seen that the polymerization using the homogeneous cationic Cr^{+3} compound has low activity (Run 1), and that adding triisobutyl-aluminosilane does not improve the activity, but rather reduces it (Run 2). These runs were performed at 25° C. so as to avoid decomposition of the thermally labile homogeneous catalyst.

In contrast, Run 3 shows an approximately ten-fold improvement in activity using a supported catalyst system of this invention.

Runs 4-8 show the need for a co-catalyst when using this cationic Cr^{+3} compound. The aluminosilane co-catalyst gives improved activity over the trimethylaluminum co-catalyst. Additionally, higher molecular weights (M_w) and higher molecular weight distributions ($MWD = M_w/M_n$) are obtained with the catalyst system of the present invention (see Table II). The activity of this catalyst system was highest when the support was an alumina aluminum phosphate support, and the polymer had higher molecular weight as well.

Looking at Tables III and IV, a co-catalyst appears to be necessary with the silica support and is advantageous with the alumina aluminum phosphate support. Using the aluminosilane with the longer alkyl groups (isobutyl vs. ethyl) gives higher activities. Also, the Davison 933 silica, which has a substantially smaller average particle size than the Davison 932 silica, gives higher activity (compare Runs 10 and 11 with Runs 12 and 13).

Table III also shows that the catalyst systems of this invention perform exceptionally well over the temperature range of 65°-85° C.

Looking at Tables V and VI, the catalyst system of this invention based on $[\text{Cp}^*\text{Cr}(\text{CH}_3)_2]_2$ dimer is also quite active, and gives polymers with very attractive high molecular weights and broad (high) MWD's.

EXAMPLE 9

 $\text{Cp}^*\text{Cr}(\text{TMSM})_2$

1.318 g of $\text{CrCl}_3(\text{THF})_3$ was placed in a 100 ml Schlenk flask along with a stirring bar and about 50-60 ml of THF. 0.500 g of Cp^*Li was added to the resulting slurry producing a blue solution ($[\text{Cp}^*\text{CrCl}_2]_2$). This solution was allowed to stir for at least three hours (preferably overnight). To the stirring solution was slowly added 2 equivalents of $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$. The solution changed from blue to purple.

The THF was then removed by rotoevaporation and the resulting solid was dissolved in pentane yielding a red brown solution which was filtered to remove LiCl . The pentane was removed by rotoevaporation and the solid was redissolved in a minimum amount of pentane and crystallized at -30° C. Yield 50-60%.

It is important to note that this compound is thermally unstable and decomposes at room temperature liberating tetramethylsilane.

EXAMPLE 10

SUPPORTED $\text{Cp}^*\text{Cr}(\text{TMSM})_2$

$\text{Cp}^*\text{Cr}(\text{TMSM})_2$ (0.075 g) was dissolved in 10 ml of pentane. $\text{Al}_2\text{O}_3 \cdot 2\text{AIPQ}_4$ (1.00 g) was added all at once to the stirred solution resulting in the formation of a purple solid and clear supernatant after 15 minutes. The solid was collected, washed twice with pentane, and dried in vacuo to a free-flowing powder.

EXAMPLE 11

The supported $\text{Cp}^*\text{Cr}(\text{TMSM})_2$ prepared in Example 10 was used to polymerize ethylene by a procedure similar to that described in Example 7, except that the polymerization was performed at 80° C.-85° C. and 550 psi total pressure (ethylene and hydrogen). The results of these polymerization runs are indicated in Table VII below, and analytical data for the polyethylenes produced are indicated in Table VIII below.

TABLE VII

POLYMERIZATION DATA FOR SUPPORTED $\text{Cp}^*\text{Cr}(\text{TMSM})_2$							
Run ¹	psi	Co	AlO^{2-}	H_2 (psi)	Temp °C	Activity ³	Activity ⁷
22	31	None	0	0	80	2,500	27
23	16	IBAO ⁴	16:1	0	80	250,000	2700
24	16	IBAO	32:1	0	80	341,000	3680
25	16	IBAO	32:1	0	80	372,000	4010
26	16	IBAO	19:1	0	80	248,000	2670
27	16	IBAO	19:1	0	80	230,000	2480
28	16	IBAO	32:1	10	80	294,000	3170
29	16	IBAO	32:1	25	80	340,000	3660
30	16	IBAO	32:1	25	80	227,000	2430
31	16	IBAO	32:1	30	80	227,000	2432
32	16	IBAO	32:1	50	80	249,000	2689
33	16	IBAO	32:1	100	80	194,000	2091
34	16	IBAO	32:1	200	80	124,000	1339
35	16	TEB ⁵	32:1 ⁶	0	80	—	0

¹Support deligated at 400° C. for 48 hours for all runs.²None note.³Reported as g polymer/g Cp^*Cr .⁴IBAO is isobutylaluminosilane.⁵TEB is triethylborane.⁶ Cp^*Cr molar ratio.⁷Reported as g polymer/g catalyst/hr.

All polymerizations performed at 550 psi total pressure (ethylene plus hydrogen).

TABLE VIII

ANALYTICAL DATA FOR POLYETHYLENES PREPARED WITH SUPPORTED $\text{Cp}^*\text{Cr}(\text{TMSM})_2$					
Run ¹⁰	T_m °C	MI ⁷	ELMI ⁸	$M_w^9 \times 10^{-3}$	MWD
23	139.1	0	0	1,124	2.02
24	139.4	0	0	891	7.61
25	136.3	—	—	1,073	2.72
26	138.1	—	—	901	2.71
27	137.6	—	—	834	2.43
28	138.9	0	0	—	—
29	139.9	0	2.27	330	9.29
30	144.9	0	2.03	276	8.52
31	139.7	0	6.50	228	9.62
32	138.8	0	11.9	203.6	9.40
33	138.0	2.12	12.7	116.3	8.37
34	133.0	High	High	33.3	10.50

¹⁰Melt Index (ASTM D-128, Condition B)⁷High load melt index (ASTM D-128, Condition F)⁸Determined by GPC.⁹Support deligated at 400° C. for 48 hours for all runs.

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EXAMPLE 12

 $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{THF})$

To a slurry of $\text{CrCl}_3(\text{THF})_3$ (2.00 g, 5.33 mmol) in 50 ml of THF was added LiCp^* (0.76 g, 5.34 mmol) slowly with stirring to yield a deep blue solution. This solution was stirred for two hours. Slow addition of benzyl magnesium chloride (5.3 ml of 2.0M solution) resulted in a deep purple solution after complete addition. Solvent was subsequently removed under vacuum to yield a sticky purple residue. Pentane (200 ml) was added and stirred overnight. The pentane solution slowly became green-brown during this time. The pentane solution was filtered to remove metal halides, concentrated to ca. 75 ml and stored at -40°C . overnight. The crystalline material that formed was collected, washed with cold pentane, and dried under vacuum, affording 680 mg (29%) of dark brown material.

COMPARATIVE EXAMPLE 13

HOMOGENEOUS POLYMERIZATION WITH

 $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{THF})$

Seventy-five milligrams of $\text{Cp}^*\text{Cr}(\text{CH}_2\text{Ph})_2(\text{THF})$ was dissolved in 50 ml of heptane and placed in a thick-walled glass vessel which was attached to a purified ethylene supply. Ethylene was added to 50 psi at ca. 20°C . A mild exotherm ensued with the generation of 0.70 g of beige polymer after one hour. The catalyst was essentially inactive after one hour as evidenced by the lack of ethylene uptake.

EXAMPLE 14

$\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{THF})$ was supported on $\text{Al}_2\text{O}_3\cdot 2\text{AlPO}_4$ (which had been dehydrated at 400°C . for 48 hours) and used to polymerize ethylene using the procedure described in Example 11. The results of these polymerization runs are indicated in Tables IX and X below.

TABLE IX

POLYMERIZATION DATA FOR $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{THF})$							
Run	mmol Cr	Co-catalyst	$\text{Al}:\text{Cr}^{10}$	C_2H_4 (psi)	Temp ($^\circ\text{C}$)	Activity ¹¹	Activity ¹³
36	12	IBAO	25:1	550	80	444,000	3900
37 ¹²	12	IBAO	25:1	550	80	235,000	1940
38 ¹²	12	IBAO	25:1	550	80	230,000	1920
39 ¹³	12	IBAO	25:1	550	80	613,000	5000
40 ^{12,13}	12	IBAO	25:1	300	80	234,000	1940
41	158	?	0	50	80	720	85 ¹⁴

¹⁰ Molar ratio.¹¹ Reported as g polymer/g Cr/hr.¹² Polymerization performed with argon/ethylene mixture (250 psi/200 psi).¹³ Reported as g polymer/g catalyst/hr.¹⁴ Data for unsupported catalyst per Example 13.¹⁵ Supported catalyst. $\text{Al}_2\text{O}_3\cdot 2\text{AlPO}_4$ dehydrated at 400°C . for 48 hours.

TABLE X

ANALYTICAL DATA FOR POLYETHYLENES PREPARED WITH $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{THF})$				
Run	T_m ($^\circ\text{C}$)	Density	$M_w \times 10^{-3}$	MWD
39	135.7	0.9288	1.243	1.75
40	134.4	0.9325	881	3.13
41	—	—	22.6	2.96

¹⁶ Determined by GPC.¹⁷ Data for homogeneous polymerization of unsupported catalyst per Example 13.

EXAMPLE 15

 $\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{Pyr})$

This compound was prepared following the general description contained in Noh, S. K.; Sendlinger, S. C.;

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Janiak, C.; Theopold, K. H. *J. Am. Chem. Soc.* (1989), 111, 9127. Lithium cyclopentadienide (0.380 g, 2.67 mmol) was added slowly to a slurry of 1.00 g (2.67 mmol) of $\text{CrCl}_3(\text{THF})_3$ in 50 mL of THF. The resulting blue solution was stirred for 2 hours. Pyridine (0.222 g, 2.80 mmol) was added resulting in the deposition of a light blue solid. Stirring was continued for 1 hour after which was added (dropwise) 2.0 equivalents (3.80 mL of 1.4M solution in Et_2O) of methylolithium. The dark green-brown solution was stirred an additional 0.5 hr and then taken to dryness under vacuum. The dark solid was extracted into pentane, filtered to remove metal halides, and taken dryness. The remaining solid was reextracted into pentane, filtered, and the solvent was reduced until microcrystals appeared. The dark brown solution was kept at -40°C . overnight resulting in the deposition of black crystals. The crystals were collected and dried under vacuum.

EXAMPLE 16

 $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{Pyr})$

This compound was prepared as in Example 15 except that two equivalents of benzylmagnesium bromide were substituted for methylolithium. A microcrystalline solid formed and was dried under vacuum. Anal. Calc. for $\text{C}_{29}\text{H}_{34}\text{N}_2\text{Cr}$: C, 77.65; H, 7.64; N, 3.12. Found: C, 77.03; H, 7.48; N, 2.80.

EXAMPLE 17

 $\text{Cp}^*\text{Cr}(\text{TMSM})_2(\text{Pyr})$

This compound was prepared as in Example 15 except that two equivalents of trimethylsilylmethylithium solution were added in place of methylolithium. Long, black needles formed after cooling to -40°C . overnight. These were collected and dried to yield 1.30 g (35%) of pure material. Anal. Calc. for $\text{C}_{23}\text{H}_{43}\text{NSi}_2\text{Cr}$: C, 62.67; H, 9.60; N, 3.17. Found: C, 62.36; H, 9.46; N, 2.84.

EXAMPLE 18

 $\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{DMAP})$

This compound was prepared as described in Example 15 except that 1.05 equivalents of N,N-dimethylaminopyridine (DMAP) were added instead of pyridine. Large, dark brown crystals were collected and dried under vacuum (710 mg, 78% yield). Anal. Calc. (Found) for $\text{C}_{19}\text{H}_{31}\text{N}_2\text{Cr}$: C, 67.22 (66.69); H, 9.20 (9.01); N, 8.25 (7.73).

EXAMPLE 19



This compound was prepared as described in Example 15 except that 1.0 equivalent of a 1.0M solution of sodium cyclopentadienide in the THF was added in place of lithium pentamethylcyclopentadienide. Dark brown microcrystals were obtained in 67% overall yield (485 mg). Anal. Calc. (Found) for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{Cr}$: C, 62.43 (62.12); H, 7.88 (7.87); N, 10.40 (10.42).

EXAMPLE 20



This compound was prepared as described in Example 15 except that 1.05 equivalents of dimethylphenylphosphine (PMe_2Ph) were added instead of pyridine. Large blue/purple crystals were obtained in 56% overall yield (530 mg). Anal. Calc. (Found) for $\text{C}_{20}\text{H}_{22}\text{PCr}$: C, 67.58 (67.14); H, 9.07 (8.96); N, 0.0 (0.12).

EXAMPLE 21



This material was prepared according to Example 20 except that 1.0 equivalents of sodium cyclopentadienide was added in place of lithium pentamethylcyclopentadienide. Long blue/purple needles were obtained in 59% yield (453 mg). Anal. Calc. (Found) for $\text{C}_{15}\text{H}_{22}\text{PCr}$: C, 63.15 (62.33); H, 7.77 (7.59); N, 0.0 (0.0).

added instead of lithium pentamethylcyclopentadienide.

EXAMPLE 24

SUPPORTED COMPLEXES

$\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{Pyr})$, $\text{Cp}^*\text{Cr}(\text{Bzyl})_2(\text{Pyr})$,
 $\text{Cp}^*\text{Cr}(\text{TMEM})_2(\text{Pyr})$, $\text{Cp}^*\text{CrMe}_2(\text{DMAP})$,
 $\text{Cp}^*\text{CrMe}_2(\text{DMAP})$, $\text{Cp}^*\text{CrMe}_2(\text{PMe}_2\text{Ph})$, $\text{Cp}^*\text{CrMe}_2(\text{PMe}_2\text{Ph})$, $\text{Cp}^*\text{CrMe}_2(3,5\text{-Lutidine})$, and $\text{Cp}^*\text{CrMe}_2(\text{Pyr})$ were individually supported on dehydrated (400° C.) supports as in Example 10 to give catalysts with ca 1.0 wt % chromium. The supports used are listed in the following tables.

EXAMPLE 25

The supported catalysts of Example 24 were each in turn used to polymerize ethylene by a procedure similar to that described in Example 11. The results of these polymerization runs are indicated in the following tables.

All molecular weight distributions were determined using liquid size exclusion (gel permeation) chromatography. The columns were Polymer Labs Inc. PLgel 20 μm Mixed-a columns. The solvent used was 1,2,4-trichlorobenzene at a temperature of 150° C.

All supports were dehydrated prior to use in order to provide increased polymerization activity. Specific dehydration temperatures and conditions are noted in the tables.

TABLE XI

Run #	Support ^a	Polymerization Data for $\text{Cp}^*\text{Cr}(\text{CH}_3)_2(\text{Pyr})^b$						Activity ^c	Activity ^d
		$\mu\text{mol Cr}$	Co-cat	AlCr ^e	Temp °C	$\text{P}(\text{C}_2\text{H}_4)$	$\text{P}(\text{H}_2)$		
42	$\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$	15.7	IBAO ^f	19	80	250	0	623,000	6700
43	$\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$	15.7	IBAO	19	80	250	0	237,000	2500
44	$\text{Al}_2\text{O}_3 \cdot 2\text{AlPO}_4$	8.4	IBAO	24	80	250	0	744,000	8230
45	AlPO_4	8.4	IBAO	24	80	250	0	1,488,000	16,070
46	AlPO_4	8.4	IBAO	24	80	250	0	1,600,000	17,280
47	AlPO_4	10.5	IBAO	29	80	200	0	437,000	4720
48	AlPO_4	10.5	IBAO	29	80	194	4	487,000	5280
49	AlPO_4	10.5	IBAO	29	80	188	12	515,000	5580
50	AlPO_4	10.5	IBAO	29	80	167	33	365,000	3940
51	AlPO_4	10.5	IBAO	29	80	280	20	735,000	7940
52	AlPO_4	10.5	IBAO	29	80	200	0	695,570	7510
53	AlPO_4	10.5	IBAO	29	80	200	0	361,111	3900
54	EP-10 ^g	16.7	IBAO	18	80	250	0	410,000	4428
55	EP-10 ^g	15.7	IBAO	19	80	250	0	256,000	2845
56	EP-10 ^g	10.5	IBAO	19	80	250	0	262,949	2840
57	EP-10 ^g	10.5	IBAO	29	80	250	0	355,536	3840
58	EP-10 ^g	10.5	IBAO	29	80	250	0	401,832	4340
59	EP-11 ^h	10.5	IBAO	29	80	250	0	322,222	3480
60	EP-12 ⁱ	10.5	IBAO	29	80	250	0	322,222	3480

^aSupports dehydrated at 400° C. for 24 hrs. for all runs unless indicated otherwise.

^bMolar ratio.

^cExpressed as g polymer/g Cr/hr.

^dPyr = pyridine.

^eIBAO = isobutyl aluminum.

^fPolymerization performed with 300 psi/250 psi ethylene/propylene ratio.

^gCrosslinked silica support (similar to Davison 682) dehydrated at 600° C. for 24 hrs.

^hDehydrated at 500° C. rather than 600° C. for 24 hrs.

ⁱExpressed as g polymer/g catalyst/hr.

EXAMPLE 22



Prepared as in Example 15 above except that 1.05 equivalents of 3,5-lutidine were added in place of pyridine. Dark microcrystals (510 mg, 59%) were collected and dried.

EXAMPLE 23



Prepared as described in Example 15 above except that 1.0 equivalent of sodium cyclopentadienide was

TABLE XII

ANALYTICAL DATA FOR POLYETHYLENES
PREPARED WITH SUPPORTED
 $\text{Cp}^*\text{CrMe}_2(\text{pyr})$ CATALYSTS OF TABLE X

Run #	T_m °C	MI ^a	HLMI ^b	Density g/cc	$M_w^c \times 10^{-3}$	MWD
42	137.0	0	0	0.9318	1036	2.52
43	138.8	0	0	0.9318	879	2.90
44	138.6	0	0	0.9284	886	2.13
45	139.3	0	0	0.9297	962	2.38
46	136.1	—	—	0.9306	844	2.13

TABLE XII-continued

Run #	T _m , °C	MP	HLMI ^b	Density g/cc	Mw ^c × 10 ⁻³	MWD
47	137.0	0	0	0.9297	840	2.73
48	—	0	1.46	—	340	6.01
49	—	0	14.08	—	274	5.33
50	—	1.61	High	—	129	7.44
51	—	0	7.84	0.9352	267	10.76
52	135.9	—	—	—	676	2.77
53	135.8	—	—	0.9307	796	2.61
54	137.1	0	0	0.9492	956	4.24
55	136.4	0	0	0.9387	606	39.9
56	136.5	—	—	0.9362	615	7.20
57	139.6	—	—	0.9423	722	5.99
58	137.3	—	—	0.9397	794	3.98
59	136.7	—	—	0.9398	810	4.24
60	136.9	—	—	0.9414	830	7.51

^aMelt Index (ASTM D-1228, Condition E).^bHigh Load Melt Index (ASTM D-1228, Condition F).^cDetermined by GPC.

nyl chromium hydrocarbyl compound in which the chromium has an oxidation state of +3, said chromium compound being supported on an inorganic support.

2. The catalyst system of claim 1 wherein the hydrocarbyl is sigma bonded to the chromium.

3. The catalyst system of claim 1 wherein the chromium compound has the formula:



wherein $(C_5(R')_2)_2$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

R' is at each independent occurrence hydrogen, a hydrocarbyl radical having 1-20 carbon atoms, or adjacent R' groups may together form one or more rings;

X is a hydrocarbyl radical having 1-20 carbon atoms; a=1 or 2, b=1 or 2 where a+b=3;

TABLE XIII

Run #	Support ^a	Cr Compound	mmol Cr	Co-catalyst	Al:Cr ^b	P(C ₃ H ₅) ₃	Temp °C	Activity ^c	Activity ^d
61	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(Benz) ₂ (Pyr) ^e	12.8	IBAO	24	350	80	750,000	8100
62	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(Benz) ₂ (Pyr) ^e	8.4	IBAO	36	350	80	794,000	6900
63	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(Benz) ₂ (Pyr) ^e	10.1	IBAO	20	350	80	370,000	3200
64	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(TMBA) ₂ (Pyr) ^e	12.8	IBAO	24	350	80	722,000	7798
65	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(TMBA) ₂ (Pyr) ^e	14.0	IBAO	22	350	80	722,000	6640
66	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	8.2	IBAO	24	350	80	317,000	3425
67	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.3	IBAO	29	350	80	401,800	4340
68	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.3	IBAO	29	200	80	168,500	1820
69	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.1	IBAO	30	350	80	1,229,000	13,270
70	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.1	IBAO	30	200	80	346,000	3740
71	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	9.6	IBAO	31	200	80	320,000	3460
72	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.5	IBAO	29	350	80	494,000	4900
73	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.8	IBAO	28	350	80	82,400	880
74	AlPO ₄	Cp*Cr(CH ₃) ₂ (DMAF) ^f	10.8	IBAO	28	200	80	39,400	426
75	Al ₂ O ₃ ·2AlPO ₄	Cp*Cr(CH ₃) ₂ (pyr) ^e	14.9	IBAO	20	350	80	194,000	2100

^aDehydrated under dry argon at 400° C. for 24 hrs.^bIBAO = isobutylalumoxane, mole ratio Al:Cr.^cThiophene in g/l.^dExpressed as g polymer/g Cr/hr.^ePyrl = benzyl Pyr = pyridine^fTMBA = trimethylsilylmethyl^gDMAF = N,N-dimethylaminopyridine^hPh₂Ph = dimethylphenylphosphineⁱExpressed as g polymer/g catalyst/hr.

TABLE XIV

Run	T _m , °C	MP	HLMI ^b	Density g/cc	Mw ^c × 10 ⁻³	MWD
61	139.6	0	0	0.9281	1,013	2.80
63	141.4	—	—	0.9280	1,414	1.72
64	137.6	0	0	0.9288	1,017	2.90
66	136.8	—	—	0.9288	921	2.15
67	136.7	—	—	0.9302	801	2.11
68	135.6	—	—	0.9280	847	3.04
69	137.2	—	—	—	830	3.20
70	137.6	—	—	—	934	3.14
71	135.5	—	—	0.9315	956	3.76
72	135.8	—	—	0.9301	882	2.83
73	137.5	—	—	0.9309	1,002	2.73
74	134.7	—	—	—	983	3.41
75	137.2	0	0	0.9294	740	2.82

^aMelt Index (ASTM D-1228, Condition E).^bHigh Load Melt Index (ASTM D-1228, Condition F).

What is claimed is:

1. A catalyst system for the homopolymerization or copolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a cyclopentadie-

c=1 or 2 with the proviso that when c=2 then X is alkyl;

L is at each independent occurrence a sigma donor stabilizing ligand;

m=1 to 2 inclusive; and

A is an anion.

4. The catalyst system of claim 3 wherein the chromium compound has the formula:



5. The catalyst system of claim 4 wherein $(C_5(R')_2)_2$ is pentamethylcyclopentadienyl.

6. The catalyst system of claim 4 wherein X is selected from the group consisting of methyl, benzyl and trimethylsilylmethyl, and L contains oxygen or nitrogen.

7. The catalyst system of claim 4 wherein L is tetrahydrofuran, pyridine, N,N-dimethylaminopyridine, dimethylphenylphosphine, or 3,5-lutidine.

8. The catalyst system of claim 3 wherein the chromium compound has the formula:



9. The catalyst system of claim 8 wherein $(C_5(R')_3)$ is pentamethylcyclopentadienyl.

10. The catalyst system of claim 8 wherein X is selected from the group consisting of methyl, benzyl and trimethylsilylmethyl.

11. The catalyst system of claim 8 wherein $c=2$.

12. The catalyst system of claim 3 wherein the chromium compound has the formula:



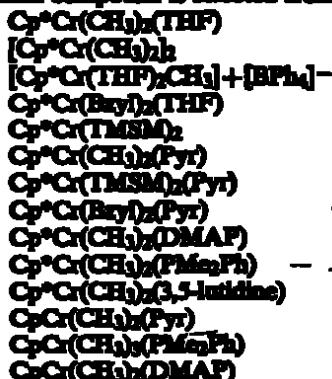
13. The catalyst system of claim 12 wherein $(C_5(R')_3)$ is pentamethylcyclopentadienyl.

14. The catalyst system of claim 12 wherein X is selected from methyl, benzyl and trimethylsilylmethyl.

15. The catalyst system of claim 12 wherein L contains oxygen or nitrogen.

16. The catalyst system of claim 15 wherein L is selected from tetrahydrofuran, pyridine, N,N-dimethylaminopyridine, dimethylphenylphosphine, or 3,5-lutidine.

17. The catalyst system of claim 3 wherein the chromium compound is selected from



where Cp^* is pentamethylcyclopentadienyl, THF is tetrahydrofuran, Ph is phenyl, Bz is benzyl, TMSM is trimethylsilylmethyl, Pyr is pyridine, DMAP is N,N-dimethylaminopyridine, PMe_2Ph is dimethylphenylphosphine, and Cp is unsubstituted cyclopentadienyl.

18. The catalyst system of claim 1 wherein the support is an inorganic metal oxide or inorganic metal phosphate.

19. The catalyst system of claim 18 wherein the support is selected from the group consisting of alumina, silica, silica-alumina, aluminum phosphate, zirconium phosphate, and alumina aluminum phosphate.

20. The catalyst system of claim 17 wherein the support is selected from silica, aluminum phosphate and alumina aluminum phosphate.

21. The catalyst system of claim 20 wherein the support is alumina aluminum phosphate.

22. The catalyst system of claim 17 wherein the support is selected from the group consisting of alumina, silica, silica-alumina, aluminum phosphate, zirconium phosphate, and alumina aluminum phosphate.

23. The catalyst system of claim 22 wherein the support is selected from silica, aluminum phosphate and alumina aluminum phosphate.

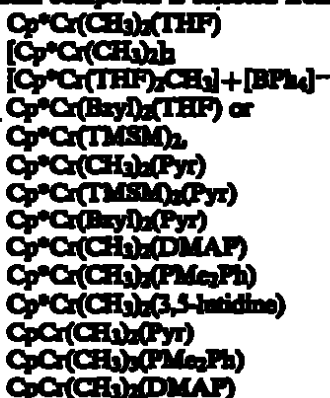
24. The catalyst system of claim 23 wherein the support is alumina aluminum phosphate.

25. A catalyst system for the homopolymerization or copolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a cyclopentadie-

nyl chromium hydrocarbyl compound in which the chromium has an oxidation state of +3, said chromium compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

26. The catalyst system of claim 25 wherein the hydrocarbyl is sigma bonded to the chromium.

27. The catalyst system of claim 25 wherein the chromium compound is selected from



the support is silica or alumina aluminum phosphate, and the alkylaluminum compound is an aluminumane or a trialkylaluminum compound.

28. The catalyst system of claim 27 wherein the support is alumina aluminum phosphate.

29. The catalyst system of claim 25 wherein the chromium compound has the formula:



(II) or



(III)

wherein $(C_5(R')_3)$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

R' is at each independent occurrence hydrogen, a hydrocarbyl radical having 1-20 carbon atoms, or adjacent R' groups may together form one or more rings;

X is a hydrocarbyl radical having 1-20 carbon atoms; $a=1$ or 2, $b=1$ or 2 where $a+b=3$;

$c=1$ or 2 with the proviso that when $c=2$ then X is alkyl;

L is at each independent occurrence a sigma donor stabilizing ligand;

$m=1$ to 2 inclusive; and

A is an anion.

30. The catalyst system of claim 29 wherein the chromium compound has the formula:



31. The catalyst system of claim 30 wherein $(C_5(R')_3)$ is pentamethylcyclopentadienyl.

32. The catalyst system of claim 30 wherein X is selected from the group consisting of methyl, benzyl and trimethylsilylmethyl, and L contains oxygen or nitrogen.

33. The catalyst system of claim 30 wherein L is tetrahydrofuran, pyridine, N,N-dimethylaminopyridine, dimethylphenylphosphine, or 3,5-lutidine.

34. The catalyst system of claim 29 wherein the chromium compound has the formula:

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35. The catalyst system of claim 34 wherein $(C_5(R')_2)$ is pentamethylcyclopentadienyl.

36. The catalyst system of claim 34 wherein X is selected from the group consisting of methyl, benzyl and trimethylsilylmethyl.

37. The catalyst system of claim 34 wherein $c=2$.

38. The catalyst system of claim 29 wherein the chromium compound has the formula:



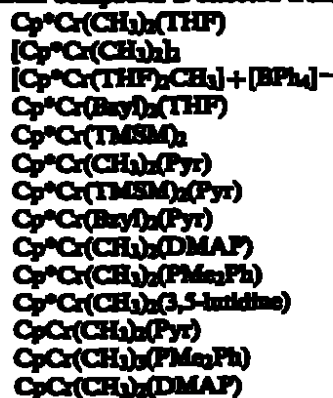
39. The catalyst system of claim 38 wherein $(C_5(R')_2)$ is pentamethylcyclopentadienyl.

40. The catalyst system of claim 38 wherein X is selected from methyl, benzyl and trimethylsilylmethyl.

41. The catalyst system of claim 38 wherein L contains oxygen or nitrogen.

42. The catalyst system of claim 41 wherein L is selected from tetrahydrofuran, pyridine, N,N-dimethylaminopyridine, dimethylphenylphosphine, or 3,5-lutidine.

43. The catalyst system of claim 29 wherein the chromium compound is selected from



where Cp^* is pentamethylcyclopentadienyl, THF is tetrahydrofuran, Ph is phenyl, Bzyl is benzyl, TMSM is trimethylsilylmethyl, Pyr is pyridine, DMAP is N,N-dimethylaminopyridine, PMe_2Ph is dimethylphenylphosphine, and Cp is unsubstituted cyclopentadienyl.

44. The catalyst system of claim 25 wherein the support is an inorganic metal oxide or inorganic metal phosphate.

45. The catalyst system of claim 44 wherein the support is selected from the group consisting of alumina,

silica, silica-alumina, aluminum phosphate, zirconium phosphate, and alumina aluminum phosphate.

46. The catalyst system of claim 45 wherein the support is selected from silica, aluminum phosphate and alumina aluminum phosphate.

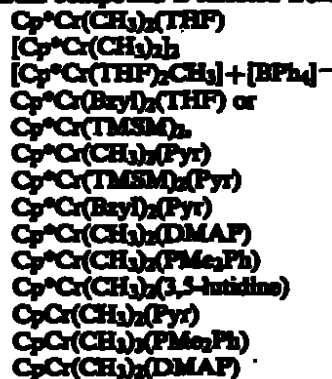
47. The catalyst system of claim 46 wherein the support is alumina aluminum phosphate.

48. The catalyst system of claim 25 wherein the Group 2 or Group 3 metal alkyl compound is an alkyl-aluminum compound.

49. The catalyst system of claim 48 wherein the alkyl-aluminum compound is selected from the group consisting of trialkylaluminum compounds, alkylaluminum alkoxides, alkylaluminum halides and aluminocenes.

50. The catalyst system of claim 49 wherein the alkyl-aluminum compound is an aluminocene or trialkylaluminum compound.

51. The catalyst system of claim 25 wherein the chromium compound is selected from



52. The catalyst system of claim 51 wherein the support is selected from the group consisting of alumina, silica, silica-alumina, aluminum phosphate, zirconium phosphate, and alumina aluminum phosphate, and the Group 2 or 3 metal alkyl compound is an alkylaluminum compound.

53. The catalyst system of claim 51 wherein the support is selected from silica, aluminum phosphate and alumina aluminum phosphate.

54. The catalyst system of claim 51 wherein the alkyl-aluminum compound is selected from the group consisting of trialkylaluminum compounds, alkylaluminum alkoxides, alkylaluminum halides and aluminocenes.

55. The catalyst system of claim 54 wherein the alkyl-aluminum compound is an aluminocene or trialkylaluminum compound.

* * * * *

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(21) International Application Number: PCT/US96/01224 (22) International Filing Date: 26 January 1996 (26.01.96) (30) Priority Data: 08/378,684 26 January 1995 (26.01.95) US (71) Applicant: CHEVRON CHEMICAL COMPANY (US/US); P.O. Box 3047, San Ramon, CA 94583-0947 (US). (72) Inventors: BEACH, David, L.; 5631 Sycamore Creek Drive, Kingwood, TX 77345 (US). CARNEY, Michael, J.; 6351 Georgetown Boulevard, Eldersburg, MD 21784 (US). MORA, Javier, M.; 130A Rebecca Street, Houston, TX 77022 (US). (74) Agents: MICHEL, Mariana, H.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US) et al.		(51) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GR, HU, IE, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MN, MW, MK, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG). European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BI, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TO). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: CYCLOPENTADIENYL GROUP 6B METAL-ALKALI METAL ALPHA-OLEFIN POLYMERIZATION CATALYSTS AND THEIR USE IN POLYMERIZATION PROCESSES (57) Abstract Disclosed is a catalyst system for the homopolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkyl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation such as lithium wherein the alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom such as oxygen, nitrogen, phosphorus or sulphur, said Group 6b metal-alkali metal compound being supported on an inorganic support. The catalyst system can contain, in addition, a Group 2 or Group 3 metal-alkyl compound.		

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**CYCLOPENTADIENYL GROUP 8B METAL-ALKALI METAL ALPHA-OLEFIN
POLYMERIZATION CATALYSTS AND THEIR USE IN POLYMERIZATION PROCESSES**

FIELD OF THE INVENTION

The present invention relates to catalyst systems for polymerizing alpha-olefins and processes for polymerizing alpha-olefins using such catalysts.

BACKGROUND OF THE INVENTION

Chromium based catalysts are used in the commercial polymerization of small alpha-olefins such as ethylene and propylene. One such catalyst is prepared by depositing chromocene (bis(cyclopentadienyl) chromium (II)) on an inorganic metal oxide support, as disclosed in British Patent No. 1,253,063 to Karapinka. U.S. Patent No. 4,015,059, issued March 29, 1977 to Karol, describes the use of bis(indenyl) - bis(fluorenyl) - chromium (II) compounds supported on activated inorganic oxide supports as catalysts for the polymerization of ethylene.

Recently, new synthetic methods have been described for preparing Cr³⁺ organometallic compounds. Theopold, J. Am. Chem. Soc. (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts," Theopold, Acc. Chem. Res. (1990), 23, 263

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1 entitled "Organochromium (III) Chemistry: A Neglected Oxidation State" and Thomas et al.,
2 J. Am. Chem. Soc., (1991), 113, p. 893 et seq. disclose that certain
3 pentamethylcyclopentadienyl chromium (III) alkyls can be prepared, and that they can be
4 used for making polyethylene homogeneously in CH_2Cl_2 . However, these homogeneous Cr
5 (III) polymerization catalysts have several deficiencies. These include low polymer
6 productivity, rapid deactivation, and the need to use polar, non-coordinating solvents.
7 Additionally, since they are homogeneous catalysts, they are unsuitable for gas phase olefin
8 polymerization.

9
10 U.S. Patent No. 4,530,914, issued July 23, 1985 to Ewen et al., discloses a catalyst system
11 for the polymerization of alpha-olefins which comprises two or more metallocenes, each
12 having different propagation and termination rate constants, and aluminorane. The
13 metallocenes are cyclopentadienyl derivatives of a transition metal of Group 4b, 5b, and 6b
14 metals of the Periodic Table. They are described by the formulas $(\text{C}_5\text{R}'_m)_p\text{R}''(\text{C}_5\text{R}'_m)\text{MeQ}_s$,
15 and $\text{R}''(\text{C}_5\text{R}'_m)_2\text{MeQ}'$ where $(\text{C}_5\text{R}'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl,
16 each R' is hydrogen or a hydrocarbyl radical, R'' is an alkylene radical, a dialkyl germanium
17 or silicon or an alkyl phosphine or amine radical bridging two $(\text{C}_5\text{R}'_m)$ rings, Q is a
18 hydrocarbon radical, ME is a Group 4b, 5b, or 6b metal, s is 0 or 1, p is 0, 1, or 2; when
19 $p=0$, $s=0$; m is 4 when s is 1 and m is 5 when s is 0.

20
21 U.S. Patent No. 4,939,217, issued July 3, 1990 to Stricklen, also discloses a process for
22 polymerizing olefins where the polymerization is conducted in the presence of hydrogen, and

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1 a catalyst system is used which contains aluminoxane and at least two metallocenes, each
2 having different olefin polymerization termination rate constants. The metallocenes disclosed
3 are similar to those described in aforementioned U.S. Patent No. 4,530,914.

4
5 U.S. Patent No. 4,975,403, issued December 4, 1990 to Ewen, discloses a catalyst system
6 for use in the polymerization of olefins. The catalyst system includes at least two different
7 chiral, stereo-rigid metallocene catalysts of the formula $R''(C_5(R'))_2MeQ$, (where Me is a
8 Group 4b, 5b, or 6b metal and $(C_5(R'))_2$ is a cyclopentadienyl or substituted cyclopentadienyl
9 ring) and an aluminum compound.

10
11
12 Canadian Patent Application No. 2,000,567, published April 13, 1990, discloses a process
13 for producing polyethylene using a composite catalyst made up of a solid catalyst component
14 typified by a selected chromium compound, a modified aluminum compound typified by a
15 trialkylaluminum, and an alkylaluminum alkoxide compound. The chromium compound may
16 be chromium oxide, and the modified aluminum compound may be the reaction product of an
17 organoaluminum compound and water.

18
19 European Patent Application 0,509,294 A2, published on October 21, 1992, relates to a
20 cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation
21 state of +3 and which compound is supported on an inorganic support as a catalyst for the
22 homopolymerization or copolymerization of alpha-olefins having from 2 to 8 carbon atoms.

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1 The catalyst system can also contain a Group 2 or Group 3 metal-alkyl compound such as an
2 aluminum trialkyl.

3
4 **SUMMARY OF THE INVENTION**

5
6 In accordance with the present invention, there is provided a catalyst system for the
7 homopolymerization of alpha-olefins, having from 2 to 8 carbon atoms, said catalyst system
8 comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a
9 cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has
10 an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation
11 selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is,
12 optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a
13 heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b metal-
14 alkali metal compound being supported on an inorganic support.

15
16 There is also provided in accordance with the present invention, a catalyst system as
17 described above which contains in addition a Group 2 or Group 3 metal-alkyl compound.

18
19 In the above catalyst systems and processes, chromium is a preferred Group 6b metal; silica,
20 aluminum phosphate and alumina aluminum phosphate are preferred supports, and
21 aluminoxanes and trialkylaluminum compounds are preferred Group 2 or 3 metal-alkyl
22 compounds.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides catalyst systems for use in the homopolymerization of alpha-olefins, including ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.

It has quite surprisingly been found that, even though the productivity of many cyclopentadienyl Group 6b metal hydrocarbyl compounds is quite low when employed as catalysts in the homogeneous polymerization of alpha-olefins, when these compounds are supported on an inorganic metal oxide or inorganic phosphate solid support, their productivity increases dramatically, especially when co-catalysts are used. While the catalyst systems of the present invention can be used to polymerize a variety of alpha-olefins, they are especially useful in the polymerization of ethylene. These catalysts produce polyethylene in high yield. When the supports have a proper morphology, the resulting polymers have a highly desirable morphology, i.e., substantially spherical which is especially useful for gas phase polymerization. The catalysts of the present invention are unusually sensitive to the use of hydrogen during polymerization of polyethylene to reduce the molecular weight. In addition, the catalyst system of this invention produces polyethylene with a variety of molecular weight distributions, depending on the support used.

Activities for the catalyst systems of the present invention are greater than 3,000 grams of polymer per gram of chromium metal per hour ("g/g Cr/hr"), preferably greater than 30,000 g/g Cr/hr, and more preferably greater than 200,000 g/g Cr/hr.

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1 The term molecular weight distribution ("MWD"), as used herein, is the weight average
2 molecular weight (" M_w ") divided by the number average molecular weight (" M_n "), i.e.,
3 M_w/M_n . The polymers produced in accordance with the present invention using silica
4 supported catalysts have a MWD greater than 8, preferably greater than 9, and more
5 preferably greater than 12. These polymers, which have broad MWDs, have improved ease
6 of processing, better melt behavior, and other desirable properties such as impact resistance
7 and environmental stress crack resistance. Large blow molded products have superior
8 processability when made with broad MWD polymers. Additionally, film is more puncture
9 resistant when made from polymers with a high molecular weight and broad MWD. The
10 polymers made in accordance with this invention using aluminum phosphate supported
11 catalysts possess high molecular weight and either a narrow or broad MWD depending upon
12 the pre-heating conditions for the aluminum phosphate. Additionally, the MWD can be
13 modified by the presence of hydrogen or a co-monomer.

14

15 The catalyst systems of the present invention comprise at least one cyclopentadienyl Group
16 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b
17 metal trialkaryl complex anion in which the Group 6b metal has an oxidation state of +3 and
18 wherein said complex anion is balanced by an alkali metal cation selected from lithium,
19 sodium, potassium and cesium, and which is catalytically active when deposited on an
20 inorganic metal oxide or inorganic metal phosphate support. Optionally, the alkali metal
21 cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom
22 selected from oxygen, nitrogen, phosphorus and sulphur.

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As used herein, the term "cyclopentadienyl" refers to unsubstituted cyclopentadienyl as well as substituted derivatives of cyclopentadienyl in which the cyclopentadienyl ring contains one or more substituents which do not interfere with the Group 6b metal compound's ability to function as an alpha-olefin polymerization catalyst. Examples of substituted cyclopentadienyl include pentamethylcyclopentadienyl, methylcyclopentadienyl, t-butylcyclopentadienyl, and pentaphenylcyclopentadienyl, as well as compounds where the substituent forms a multi-cyclic ring with the cyclopentadienyl ring. Examples of these multi-cyclic rings include indenyl and fluorenyl rings. For the sake of simplicity, the abbreviation "Cp" will be used herein to refer to unsubstituted cyclopentadienyl, and the abbreviation "Cp*" will be used to refer to pentamethylcyclopentadienyl. Cp* is a preferred cyclopentadienyl group as it stabilizes the organometallic compound of this invention.

The Group 6b metal compounds useful in the present invention include compounds wherein the metal is chromium, molybdenum or tungsten. Compounds in which the metal is chromium are preferred. The Group 6b metal atom in the compound has an oxidation state of +3.

These Group 6b metal compounds have, in addition to one cyclopentadienyl group, at least one alkaryl group bonded to the metal atom. Exemplary alkaryl radicals include, but are not limited to, benzyl, 3-methyl benzyl and 3, 5-dimethyl benzyl, and other similar groups. Additionally, silicon can be incorporated into such group as phenyl silyl, and the like. If more than one alkaryl group is bonded to the metal atom, they can be independent or linked.

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1 The alkaryl group is sigma bonded to the Group 6b metal.

2

3 The Group 6b metal, cyclopentadienyl-alkaryl groups form a complex anion which is
4 balanced in charge by an alkali metal cation selected from the group consisting of lithium,
5 sodium, potassium and cesium.

6

7 Examples of the Group 6b metal compounds useful in this invention include, but are not
8 limited to, compounds having the following general formula:

9

10
$$[A]^+ - [Q]_b [(C_5(R')_5)_a MX_a]^-$$

11

12 wherein M is a Group 6b metal such as chromium, molybdenum and tungsten;

13

14 $(C_5(R')_5)_a$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

15

16 R' is at each independent occurrence hydrogen, a hydrocarbyl radical having 1-20 carbon
17 atoms, or adjacent R' groups may together form one or more rings;

18

19 X is an alkaryl radical having 7-20 carbon atoms;

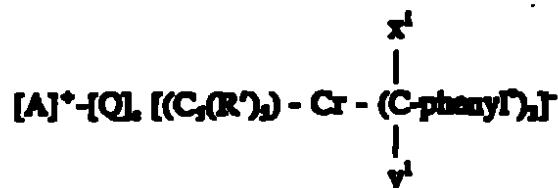
20

21 a=1 or 2, b=1, 2 or 3 where a+b=4; A is a cation selected from the group consisting of
22 lithium, sodium, potassium and cesium; Q is at each independent occurrence a neutral

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hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulfur and coordinately linked to the alkali metal cation and c is 0, 1, 2 or 3. Preferably the Group 6b metal compounds useful in this invention have the general formula:



wherein Cr is chromium; $(C_5(R'))_5$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' at each independent occurrence is hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R' groups may together form one or more rings; x^1 and y^1 are the same or different and are selected from hydrogen or hydrocarbyl radicals having from 1-6 carbon atoms; phenyl is phenyl or a substituted phenyl ring where the substituents at each independent occurrence can be hydrogen or a hydrocarbyl radical having from 1-6 carbon atoms; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0 to 3 inclusive.

As used herein, term "hydrocarbyl" refers to the alkyl, alkenyl, aryl, aralkyl and alkaryl radicals and the like. Exemplary hydrocarbyl radicals include, but are not limited to, methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, neopentyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, benzyl and other similar groups. Additionally, organosilyl-groups, such

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1 as trimethylsilyl methyl, i.e., $(\text{CH}_3)_3\text{SiCH}_2$, and the like can be used. If more than one
2 hydrocarbyl group is bonded to the metal atom, they can be independent or linked, i.e., they
3 can form a 3-, 4-, 5-, 6-, or 7-membered metallocycle. Preferably, the hydrocarbyl group is
4 sigma bonded to the Group 6b metal.

5
6 In part, the choice of Group 6b metal compound is based on the thermal stability of the
7 compound and its ease of preparation. Of the Group 6b compounds useful in this invention,
8 the organochromium compounds are preferred.

9
10 Theopold, J. Am. Chem. Soc. (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as
11 Olefin Polymerization Catalysts," Theopold, Acc. Chem. Res. (1990), 23, 263 entitled-
12 "Organochromium (III) Chemistry: A Neglected Oxidation State," and Thomas et al., J. Am.
13 Chem. Soc., 113 (1991), p. 893 et seq. (all of which are incorporated herein by reference)
14 describe syntheses useful in making some of the Group 6b metal compounds where the
15 Group 6b metal is in the +3 oxidation state. Anyone with ordinary skill in the art, knowing
16 the above references and reading the working examples below, would know how to prepare
17 the Group 6b metal-alkali metal compound(s) which when deposited on a support form the
18 catalysts of this invention. For example, benzyl lithium can be used — as shown in Example
19 2 below — to make a compound catalyst precursor of this invention.

20
21 In the catalyst systems of the present invention, the Group 6b metal compound is deposited
22 on an inorganic support. Suitable inorganic metal oxide supports include silica, alumina

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1 silica-alumina mixtures, thoria, zirconia, magnesium oxide and similar oxides. Suitable
2 inorganic metal phosphates include aluminum phosphate, zirconium phosphate, magnesium-
3 containing alumina phosphate, silica aluminum phosphate, silica alumina-aluminum
4 phosphate, and alumina aluminum phosphate. Silicas, aluminum phosphates and alumina
5 aluminum phosphates are preferred. Suitable silica supports include Davison 952, Davison
6 955, Croscfield EP-10 and Croscfield EP17MS. Further examples of useful supports are the
7 following: alumina aluminum phosphates with aluminum to phosphorus ratios of about 5:1
8 to 1:1 as disclosed in the U.S. Patents Nos. 4,080,311 and 4,219,444; magnesia-alumina-
9 aluminum phosphates as described in U.S. Patent No. 4,210,560; zinc oxide-cadmium oxide-
10 alumina-aluminum phosphates such as those disclosed in the U.S. Patent No. 4,367,067; and
11 the calcium, barium, and/or strontium oxide-alumina-aluminum phosphates described in U.S.
12 Patents Nos. 4,382,877 and 4,382,878. The acidity of these supports can be adjusted by
13 judicious inclusion of basic metals such as alkali and alkaline earth metals (Ca, Be, Mg, K,
14 Li) to counteract excessive acidity. Other useful supports include magnesium halides,
15 particularly magnesium chloride, such as those described in "Transition Metals and
16 Organometallics as Catalysts for Olefin Polymerization" (1988, Springer-Verlag) edited by
17 W. Kaminsky and H. Sinn and "Transition Metal Catalyzed Polymerizations-Ziegler-Natta
18 and Metathesis Polymerizations" (1988, Cambridge University Press) edited by R. Quirk.

19
20 The supports useful in this invention should have a high surface area. In general, these
21 supports should have the characteristics listed in the following table:
22

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1	<u>Property</u>	<u>Broad Range</u>	<u>Preferred Range</u>
2	Surface area	25-600 m ² /g	100-370 m ² /g
3	Pore volume	0.25-4 cm ³ /g	0.7-3 cm ³ /g
4	Mean particle	30-200 microns	60-140 microns
5	diameter		

6

7 Preferably, the pore size distribution is broad, with a significant percentage of the pores in

8 the macropore range (>500 Angstroms). Preferably, at least 50% of the pores are

9 macropores. It is also desirable that the support be substantially anhydrous before the Group

10 6b metal compound is deposited on it. Thus, it is desirable to calcine the support prior to

11 deposition of the Group 6b metal compound.

12

13 The supported catalysts of this invention are readily prepared by techniques well known in

14 the art. For example, a solution of the Group 6b metal alkali metal compound in aliphatic,

15 aromatic or cycloaliphatic hydrocarbons, or ethers such as diethyl ether or tetrahydrofuran

16 can be stirred with the support until the Group 6b metal alkali metal compound is adsorbed

17 on or reacted with the support. The amount of Group 6b metal alkali metal compound

18 relative to the amount of support will vary considerably depending upon such factors as the

19 particle size of the support, its pore size and surface area, the solubility of the Group 6b

20 metal compound in the solvent employed, and the amount of Group 6b metal compound

21 which is to be deposited on the support. However, in general the amount of Group 6b metal

22 alkali metal compound used is adjusted so that the final metal content (calculated as the

23 element), relative to the support, is in the range of from about 0.01 to about 10 weight

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1 percent. In most cases, the most desirable level is in the range of about 0.1 to about 5
2 weight percent.

3
4 Preferably the supported Group 6b metal compounds of this invention are employed in
5 conjunction with a co-catalyst in order to obtain increased activity. The co-catalysts useful in
6 the practice of the present invention are Group 2 and Group 3 metal alkyls. As used herein,
7 the term "Group 2 and Group 3 metal alkyls" refers to compounds containing a metal from
8 Group 2 or Group 3 of the Periodic Table (such as Mg, Zn, B, or Al) to which is bonded at
9 least one alkyl group, preferably a C₁ to C₄ alkyl group. Suitable Group 2 and Group 3
10 metal alkyls include dialkyl magnesium, dialkyl zinc, trialkylboranes, and aluminum alkyls.
11 Suitable aluminum alkyls include trialkylaluminums (such as trimethylaluminum,
12 triethylaluminum, triisobutylaluminum and trioctylaluminum). Trialkylaluminums with alkyl
13 groups of four carbons or greater are preferred. Other aluminum alkyls useful in the
14 practice of the present invention include alkylaluminum alkoxides (such as diethylaluminum
15 ethoxide and ethylaluminum diethoxide), and alkylaluminum halides (such as
16 diethylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide,
17 diethylaluminum fluoride, ethyl aluminum dichloride, ethyl aluminum dibromide, ethyl
18 aluminum diiodide, ethyl aluminum difluoride, and ethyl aluminum sesquichloride).
19
20 Other suitable aluminum alkyls are aluminoxanes, including those represented by the general
21 formula (R-Al-O)_n for the cyclic form and R(R-Al-O)_n-AlR₂ for the linear form. In these
22 formulas, R is, at each independent occurrence, an alkyl group (such as methyl, butyl,

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1 isobutyl and the like) preferably with more than two carbon atoms, more preferably with 3-5
2 carbon atoms, and n is an integer, preferably from 1 to about 20. Most preferably, R is an
3 isobutyl group. Mixtures of linear and cyclic aluminoxanes may also be used. Examples of
4 aluminoxanes useful in this invention include, but are not limited to, ethyl aluminoxane,
5 isobutyl aluminoxane, and methyl aluminoxane. Aluminoxanes (also known as
6 "aluminoxanes") suitable for use in this invention are described in Pasynkiewicz,
7 "Aluminoxanes: Synthesis, Structures, Complexes and Reactions," *Polyhedron* 9, p. 429
8 (1990), which is incorporated by reference herein in its entirety.

9
10 The preferred Group 2 and Group 3 metal alkyls are the aluminoxanes and the
11 trialkylaluminums.

12
13 When used, the Group 2 and Group 3 metal alkyls are used in a Group 2 or 3 metal alkyl to
14 Group 6b metal compound mole ratio of from about 1:1 to about 1,000:1. The preferred
15 mole ratio is from about 10:1 to about 200:1.

16
17 The catalyst systems of the present invention may be used in either solution, slurry or gas
18 phase polymerization processes. After the catalysts have been formed, the polymerization
19 reaction is conducted by contacting the monomer charge with a catalytic amount of the
20 catalyst at a temperature and at a pressure sufficient to initiate the polymerization reaction.
21 If desired, an organic solvent may be used as a diluent and to facilitate materials handling.
22 The polymerization reaction is carried out at temperatures of from about 30°C or less up to

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1 about 200°C or more, depending to a great extent on the operating pressure, the pressure of
2 the entire monomer charge, the particular catalyst being used, and its concentration.
3 Preferably, the temperature is from about 30°C to about 125°C. The pressure can be any
4 pressure sufficient to initiate the polymerization of the monomer charge, and can be from
5 atmospheric up to about 1,000 psig. As a general rule, a pressure of about 20 to about 800
psig is preferred.

7
8 When the catalyst is used in a slurry-type process, an inert diluent medium is used. The
9 diluent should be one which is inert to all other components and products of the reaction
10 system, and be stable at the reaction conditions being used. It is not necessary, however,
11 that the inert organic diluent medium also serve as a solvent for the polymer produced. The
12 inert organic diluents which may be used include saturated aliphatic hydrocarbons (such as
13 hexane, heptane, pentane, isobutane, isopentane, isooctane, purified kerosene and the like),
saturated cycloaliphatic hydrocarbons (such as cyclohexane, cyclopentane,
15 dimethylcyclopentane, methylcyclopentane and the like), aromatic hydrocarbons (such as
16 benzene, toluene, xylene and the like), and chlorinated hydrocarbons (such as chlorobenzene,
17 tetrachloroethylene, o-dichlorobenzene and the like). Particularly preferred diluents are
18 cyclohexane, pentane, isopentane, isobutane, hexane and heptane.

19
20 When the catalyst is used in a gas phase process, it is suspended in a fluidized bed with,
21 e.g., ethylene. Temperature, pressure and ethylene flow rates are adjusted so as to maintain
22 acceptable fluidization of the catalyst particles and resultant polymer particles. Further

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1 descriptions of such a fluidized bed may be found in British Patent No. 1,253,063, to
2 Karapinka, which is incorporated by reference herein.

3
4 The following examples are intended to further illustrate the present invention:

5
6 **EXAMPLE 1**

7 **SUPPORTS**

8
9 The AlPO₄ support was purchased from Grace-Davison. The silica support was an HP-10
10 purchased from Crosfield Catalysts. Some properties of the HP-10 support are:

11

<u>Property</u>	<u>Crosfield HP-10</u>
12 Surface area	320 m ² /g
13 Pore volume	1.80 cm ³ /g
14 Mean particle diameter	105 microns

15
16
17
18
19

20 **CATALYST PREPARATIONS**

21
22 In the preparation of the following catalysts, all manipulations were performed under argon
23 using glove box or Schlenk techniques. All solvents were thoroughly dried over

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Na/benzophenone or calcium hydride and distilled prior to use.

EXAMPLE 2



Lithium (η^5 -pentamethylcyclopentadienyl)tris(benzyl)chromate(III) was formed by reacting $CrCl_3(THF)_3$ (1.845 g, 4.92 mmol) with Cp^*Li (0.700 g, 4.92 mmol) in the THF overnight. The THF was then removed in vacuo and the solid residue redissolved in 30 ml of toluene. To this solution 28.4 ml (3.00 eq.) of $BzylLi$ (0.52 M in Et_2O) was added dropwise. Within minutes the color of the solution changed to bright purple. After stirring for 45 minutes the solvent was evaporated under vacuum. The residual solid was extracted with toluene. Crystallization from a mixture of pentane and toluene at $-40^\circ C$ gave purple crystals of $Li^+[Cp^*Cr(Bzyl)_3]^-$ in 63 % yield.

X-ray diffraction indicates that the most unusual feature of the structure is the position of the lithium atom, which is sequestered by the benzyl groups and thereby forced into close proximity to the transition metal ($Cr-Li: 2.54 \text{ \AA}$). The lithium atom is bonded equally to all three benzyl groups in an allylic fashion.

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EXAMPLE 3**SUPPORTED [Li]⁺ [Cp⁺Cr(Bzyl)₂]⁻**

The organochromium compound [Li]⁺ [Cp⁺Cr(Bzyl)₂]⁻ (0.042 g, 7.81 x 10⁻⁵ mole), prepared as described in Example 2, was dissolved in 20 ml of benzene, giving a purple solution to which was added 0.5 g of the AlPO₄. The resulting mixture was stirred for 5 minutes, giving a purple colored solid and a clear supernatant. The resulting solid catalyst was washed with benzene and pentane, and dried to a free-flowing powder.

EXAMPLE 4**[Li(TMEDA)₂] [Cp⁺Cr(Bzyl)₂]⁻**

The catalyst for this example was prepared as follows:

Stir CrCl₃(THF)₃ (1.501 g, 3.98 mmol) and Cp⁺Li (0.568 g, 4.00 mmol) together in 50 ml of THF for one hour. 6.0 ml (3.00 eq.) of BzylMgCl (2.05 M in THF, 12.30 mmol) was added dropwise to this blue solution. 1,4-dioxane (3 ml) was added after an hour and the solution was allowed to stir for an additional hour. The purple solution was filtered and 3 ml of TMEDA added to it. This solution was allowed to stir for an additional hour. After removing all volatiles the residue was extracted with ether and dried. Crude yield: 2.39 g (85 %).

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EXAMPLE 5**SUPPORTED [Li(TMEDA)]⁺ [Cp⁺Cr(Bzyl)₃]⁻**

Bis(tetramethylethylenediamine) lithium (μ^3 -pentamethylcyclopentadienyl) tris(benzyl) chromate (III) (0.086 g, 11.2×10^{-5} mole) was dissolved in 20 ml of benzene and treated all at once with 0.5 g of Crosfield HP-10 silica. The resulting mixture was stirred for 15 minutes resulting in a very dark purple colored solid and a clear supernatant. The solid was washed with benzene and pentane, and dried to a free-flowing powder.

COMPARATIVE EXAMPLE A**ETHYLENE POLYMERIZATION USING AN UNSUPPORTED CATALYST**

0.112 mmol of the catalyst from Example 2 above were dissolved in 50 ml of heptane in a 250 ml Fisher-Porter bottle, and pressured to 50 psig with ethylene. The reactor was stirred at 25°C for 2.6 hours. Initially, the ethylene uptake was rapid, but this rate decreased rapidly over the first half hour. The reaction was stopped by venting the pressure. The polymer produced was washed with isopropanol and then with acetone. The polymer was then dried under vacuum. The results of this polymerization are indicated in Run 1 in Table I below.

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COMPARATIVE EXAMPLE B**ETHYLENE-BUTENE-1 COPOLYMERIZATION USING AN UNSUPPORTED CATALYST**

Comparative Example A was repeated except 20 ml of butene-1 in 20 ml of benzene were added to the reactor which was stirred for 4 hours. The results are shown as Run 2 in Table I below.

EXAMPLE 6**ETHYLENE POLYMERIZATION USING A SUPPORTED CATALYST**

Polymerization runs were conducted in two-liter autoclave reactors under particle form (slurry) conditions using 300 ml heptane as diluent, and a weighed amount of catalyst (typically 0.050 to 0.250 g). Run times of 0.5 to 1.0 hour were normally employed. For example, in a typical run, 0.050 g of the catalyst prepared in Example 3, i.e., $(\text{Li})^+(\text{Cp}^*\text{Cr}(\text{Bzyl})_2)^-$ adsorbed on AlPO_4 , was charged to a two-liter stirred autoclave along with 300 ml of heptane and 0.3 ml of a 1.0 M heptane solution of isobutylaluminumoxane purchased from AKZO. The reactor temperature and pressure were adjusted to 80°C and 200 psig (with ethylene), respectively except in Run 6 where a partial pressure of 20 psig of hydrogen was used. The ethylene was supplied on demand from a pressurized reservoir. After 1.0 hour, the reaction was stopped by deactivating the stirrer and venting the pressure. The polymer produced was washed with isopropanol and acetone, and dried under vacuum to

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1 yield 140 g of white, granular solid. The results of these polymerizations are indicated in
2 Runs 3, 4, 5, and 6 in Table I below.

3
4 It is to be noted that the AlPO_4 support used in Runs 3, 4, 5, and 6 was heat treated at a
5 temperature of 600°C (Run 3) for 16 hours or at 400°C for 16 hours for Runs 4, 5 and 6.

6
7 In addition in Run 5, 30 ml of butene-1 were added to the reactor to determine if a co-
8 polymerization product could be obtained.

9
10 Referring to Table I, it can be seen that the polymerization using the homogeneous chromium
11 compound has extremely low activity (Runs 1 and 2).

12
13 In contrast, Runs 3 and 4 show an approximately 5,000-fold improvement in activity using a
14 supported catalyst system of this invention.

15
16 A comparison of Runs 2 and 5 shows that while some butene-1 was co-polymerized with
17 ethylene using the unsupported catalyst, no butene was incorporated, surprisingly, into the
18 product using the supported catalyst systems of this invention. It also appears the butene is a
19 molecular weight control agent and has an effect on MWD.

20
21 Additionally, higher molecular weight products are obtained with the catalyst system of the
22 present invention compared to products obtained using an unsupported catalyst in a

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1 homogeneous type polymerization reaction. Compare the results in Run 1 in Table I below
2 (a homogeneous operation) where the molecular weight of the product was 171,100 to the
3 results in Run 3 in Table I below using the supported catalyst system of this invention where
4 the molecular weight of the product is 1,408,000.

5

6 A comparison of Runs 3 and 6 shows the sensitivity of the catalysts of this invention to
7 hydrogen. The molecular weight goes from 1,408,000 (Run 3) without hydrogen to 166,500
8 (Run 6) with a partial pressure of hydrogen of 20 psig.

9

10 The procedure of Example 6 was repeated except using the supported catalyst of Example 5
11 above. The results are shown in Table II below.

12

13 Referring to Table II below, it can be seen that 3 runs were made, i.e., Runs 7, 8, and 9. In
14 each run the silica support was dehydrated at a temperature of 600°C for 16 hours. In each
15 case, a co-catalyst (IBAO) was used and in Run 8, 20 psig of hydrogen was employed. In
16 Run 9, 40 ml of butene-1 were added to determine if co-polymerization would occur.

17

18 Referring to Table II, it is again seen that the catalyst systems of this invention appear to be
19 unsuitable for the co-polymerization of ethylene with other alpha-olefins (compare Runs 7
20 and 9). In Run 9, 0 % SCB (Side Chain Branching) was observed when butene was added to
21 the reactor.

22

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1 A comparison of Runs 7 and 8 shows that the catalyst systems of this invention are
2 particularly sensitive to the presence of hydrogen to affect the molecular weight of the
3 product. Thus, in Run 7, (without the presence of hydrogen), the molecular weight of the
4 product was 436,200, whereas with a partial pressure of hydrogen (Run 8) the molecular
5 weight of the product was 116,200.

7 The applicant's invention is not to be limited by the examples shown above, but only by the
8 claims set forth below.

TABLE I
POLYMERIZATION DATA FOR Li⁺ [Cp⁺Cr(BzyI)₃]⁻

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RUN	Support ^a	μ MOL Cr	Co-Catalyst	Al Cr ^b	C ₂ H ₄ psig	Co-Monomer psig	Temp. °C	Activity ^c	Activity ^d	MW ^e	MWD ^f	SCB ^g
1	None	128	None	0	50	0	25	4.9	0.54	171,100	9.54	0
2	None	128	None	0	50	24 ml C ₂ H ₄	25	5	0.56	20,440	2.41	12.37
3	AlPO ₄	9	IBAO ^h	33	200	0	80	301,000	2800	1,408,000	2.61	0
4	AlPO ₄	9	IBAO	29	200	0	80	397,436	3720	-----	-----	0
5	AlPO ₄	9	IBAO	29	200	30 ml C ₂ H ₄	80	188,034	1760	742,900	19.29	0
6	AlPO ₄	9	IBAO	29	180 ⁱ	0	80	288,462	2700	166,300	10.36	0

- ^a Precalcined at 400°C for Runs 4, 5 and 6 and 600°C for Run 3
- ^b Mole Ratio
- ^c g Polymer per g Cr per hour
- ^d g Polymer per g catalyst per hour
- ^e MW = Weight Average Molecular Weight
- ^f MWD = $M_w + M_n$ = Weight Average Molecular Weight + Number Average Molecular Weight
- ^g SCB = Ethyl Side Chain Branching/1000C
- ^h Milliliters of Butene-1
- ⁱ IBAO = Isobutylaluminumoxane
- ^j 20 psig of hydrogen also employed

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TABLE II

POLYMERIZATION DATA FOR [Li(TMEDA)]⁺ [Cr⁺Cr(Bayl)₃]⁻

RUN	Support ^a	μ MOL Cr	Co- Catalyst	Al:Cr ^b	C ₄ H ₈ psig	H ₂ psig	Co- Monomer Psig	Temp. °C	Activity ^c	Activity ^d	MW ^e	MWD ^f	SCB ^g
7	EP-10	11.2	IBAO ^h	29	200	0	0	80	137,362	1600	436,200	14.84	0
8	EP-10	11.2	IBAO	29	180	20	0	80	46,360	540	116,200	9.72	0
9	EP-10	11.2	IBAO	29	200	0	40 ml C ₄ H ₈	80	42,582	496	320,400	14.88	0

- ^a Precalcined at 600°C for Runs 7, 8 and 9
- ^b Mole Ratio
- ^c g Polymer per g Cr per hour
- ^d g Polymer per g catalyst per hour
- ^e MW = Weight Average Molecular Weight
- ^f MWD = $M_w + M_n$ = Weight Average Molecular Weight + Number Average Molecular Weight
- ^g SCB = Ethyl Side Chain Branching/1000C
- ^h Milliliters of Butene-1
- IBAO = Isobutylaluminumoxane

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PROPOSED CLAIMS FOR CASE T-5105:

1. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support.
2. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium said Group 6b-alkali metal compound being supported on an inorganic support.
3. The catalyst system of claim 2 wherein the Group 6b metal is chromium.
4. The catalyst system of claim 1 wherein the Group 6b alkali metal compound has the

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formula:



wherein M is a Group 6b metal such as chromium, molybdenum and tungsten;

$(C_5(R'))_a$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' is at each

independent occurrence hydrogen, a hydrocarbyl radical having from 1-20 carbon

atoms, or adjacent R' groups may together form one or more rings; X is an alkaryl

radical having from 7-20 carbon atoms; a is 1 or 2; b is an integer from 1-3

inclusive; and a+b is 4; A is an alkali metal cation selected from lithium, sodium,

potassium or cesium; Q is at each occurrence a neutral hydrocarbyl based ligand

containing a heteroatom selected from the group consisting of oxygen, nitrogen,

phosphorus and sulphur and coordinately linked to the alkali metal cation and c is 0-3

inclusive.

5. The catalyst system of claim 4 wherein M is chromium; $C_5(R')$ is pentamethylcyclopentadienyl and c is zero.
6. The catalyst system of claim 5 wherein A is lithium and X is benzyl.
7. The catalyst system of claim 2 wherein the support is an inorganic metal oxide or inorganic metal phosphate.
8. The catalyst system of claim 7 wherein the support is selected from the group

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consisting of silica and aluminum phosphate.

9. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support.
10. The catalyst system of claim 9 wherein Group 6b metal is chromium.
11. The catalyst system of claim 4 wherein c is 1, 2, or 3.
12. The catalyst system of claim 11 wherein $C_5(R')$ is pentamethylcyclopentadienyl and M is chromium.
13. The catalyst system of claim 12 wherein A is lithium and X is benzyl.
14. The catalyst system of claim 10 wherein the support is an inorganic metal oxide

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or inorganic metal phosphate.

15. The catalyst system of claim 14 wherein the support is selected from silica and aluminum phosphate.
16. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium and cesium and wherein said alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbonyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.
17. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium and cesium said Group 6b-alkali metal compound being

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supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

18. The catalyst system of claim 17 wherein the Group 6b metal is chromium.
19. The catalyst system of claim 16 wherein the Group 6b alkali metal compound has the formula:



wherein M is a Group 6b metal such as chromium, molybdenum and tungsten;
(C₅(R')₅) is a cyclopentadienyl or substituted cyclopentadienyl ring; R' is at each independent occurrence hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R' groups may together form one or more rings; X is an alkaryl radical having from 7-20 carbon atoms; a is 1 or 2; b is 1, 2, or 3; and a+b is 4; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0-3 inclusive.

20. The catalyst system of claim 19 wherein M is chromium; C₅(R')₅ is pentamethylcyclopentadienyl and c is zero.
21. The catalyst system of claim 20 wherein A is lithium and X is benzyl.

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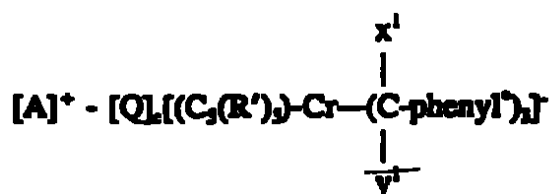
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22. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.
23. The catalyst system of claim 22 wherein the Group 6b metal is chromium.
24. The catalyst system of claim 23 wherein c is 1, 2 or 3.
25. The catalyst system of claim 24 wherein M is chromium; $C_5(R')_3$ is pentamethylcyclopentadienyl and c is 2.
26. The catalyst system of claim 25 wherein A is lithium; X is benzyl and the support is selected from silica and aluminum phosphate.
27. The catalyst system of claim 16 wherein the Group 2 metal alkyl compound is an

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alkyl aluminum compound.

28. The catalyst system of claim 27 wherein the alkyl aluminum compound is selected from the group consisting of trialkylaluminum compounds, alkyl aluminum alkoxides, alkyl aluminum halides and aluminoxanes.
29. The catalyst system of claim 17 wherein the Group 2 metal alkyl compound is an alkyl aluminum compound.
30. The catalyst system of claim 29 wherein the alkyl aluminum compound is an aluminoxane or trialkylaluminum compound.
31. The catalyst system of claim 4 wherein the Group 6 b-alkali metal compound has the formula:



wherein Cr is chromium; $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' at each independent occurrence is hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R' groups may together form one or more rings; x^1 and y^1 are the same or different and are selected from hydrogen or hydrocarbyl radicals having from 1-6 carbon atoms; phenyl¹ is phenyl or a

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substituted phenyl ring where the substituents at each independent occurrence can be hydrogen or a hydrocarbyl radical having from 1-6 carbon atoms; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0-3 inclusive.

32. The catalyst system of claim 31 wherein $C_5(R')$ is pentamethylcyclopentadienyl and c is zero.
33. The catalyst system of claim 32 wherein x^1 and y^1 are hydrogen and phenyl¹ is phenyl.
34. The catalyst system of claim 33 wherein A is lithium.
35. The catalyst system of claim 34 wherein the support is an inorganic metal oxide or an inorganic metal phosphate.
36. The catalyst system of claim 35 wherein the support is selected from silica and aluminum phosphate.
37. The catalyst system of claim 36 wherein $C_5(R')$ is pentamethylcyclopentadienyl

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and c is 1, 2, or 3.

38. The catalyst system of claim 37 wherein x^1 and y^1 are hydrogen; phenyl¹ is phenyl; A is lithium and wherein the support is an inorganic metal oxide or an inorganic metal phosphate.

39. The catalyst system of claim 38 wherein the support is selected from silica and aluminum phosphate.

40. The catalyst system of claim 31 which contains in addition a group 2 or 3 metal alkyl compound.

41. The catalyst system of claim 40 wherein $C_5(R')_5$ is pentamethylcyclopentadienyl and c is zero.

42. The catalyst system of claim 41 wherein x^1 and y^1 are hydrogen; phenyl¹ is phenyl; A is lithium and wherein the support is an inorganic metal oxide or an inorganic metal phosphate.

43. The catalyst system of claim 42 wherein the support is selected from silica and aluminum phosphate.

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44. The catalyst system of claim 41 wherein the Group 2 or 3 metal alkyl compound is an alkyl aluminum compound.
45. The catalyst system of claim 44 wherein the alkyl aluminum compound is an aluminosilane or trialkylaluminum compound.
46. A process for the polymerization of alpha-olefins having from 2-8 carbon atoms which comprises contacting said alpha-olefins under polymerization reaction conditions in the contact presence of a catalyst system according to any of claims 1 to 45.
47. A process according to claim 46 wherein the alpha-olefin is ethylene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/01224

A. CLASSIFICATION OF SUBJECT MATTER

IPC(S) : COF 4/022,10/00

US CL : 502/117; 526/155,134

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/103,113,117; 526/114,160,155,134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Acc. Chem. Res., Volume 23, Published 1990, Theopold, "Organochromium (III) Chemistry, A Neglected Oxidation State", pages 263-270, particularly, page 264.	1-6
Y	US, A, 5,183,868 (Nordquest) 2 February 1993, col. 2, lines 23-24	7-47
Y	EP, A, 0,509,294 (Carney et al), 21 October 1992, See page 3, lines 14-16, See also page 5, lines 5-20.	7-47
T	U., A 5,418,200 (CARNEY ET AL) 23 MAY 1995	1-47



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents	*T	later document published after the international filing date or priority date and not in conflict with the application but aimed to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*T*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
T earlier document published on or after the international filing date	*T*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (to specify)	*A*	document member of the same patent family
O document relating to an oral disclosure, use, exhibition or other means		
T document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

24 APRIL 1996

Date of mailing of the international search report

21 MAY 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3600

Authorized officer

for GLENN CALDAROLA

Telephone No. (703) 305-6118

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US 20020013432A1

(19) United States

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(54) POLYMERIZATION CATALYST AND
PROCESS

(76) Inventors: MAX P. MCDANIEL,
BARTLESVILLE, OK (US);
ELIZABETH A. BENHAM,
BARTLESVILLE, OK (US)

Correspondence Address:
CHEVRON PHILLIPS CHEMICAL
COMPANY, LP
1301 MCKINNEY
SUITE 3447
HOUSTON, TX 77010 (US)

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(57) ABSTRACT

An olefin polymerization process is provided comprising contacting an olefin monomer with chromium oxide on a titanium containing silica support having less than about 3 weight percent titanium in combination with an organoboron promoter. Polymers thus produced are useful for blow molding applications.

POLYMERIZATION CATALYST AND PROCESS

BACKGROUND OF THE INVENTION

[0001] This invention relates to modified supported chromium oxide olefin polymerization catalyst systems.

[0002] It further relates to a method of making ethylene polymers and copolymers.

[0003] Supported chromium oxide catalyst systems have been used for many years in the polymerization of olefins. Ethylene can be polymerized by contacting the monomer with a silica-supported chromium oxide catalyst systems, the reaction being carried out in an inert liquid at temperatures below 110° C. for producing solid polymer suspended in the liquid or at temperatures above 110° C. for solution polymerization. The properties of the resulting polymer depend upon a number of factors, including the type of catalyst system employed and its activation temperature, the reaction pressure, and the reaction temperature. It is generally known that titanium can be added to the supported chromium oxide catalyst systems to produce a polymer having an increased melt index and a broader molecular weight distribution. It is also generally known that certain substances called promoters or adjuvants can be used in combination with chromium oxide catalyst systems to modify the properties of the polymer.

[0004] The use of chromium catalyst systems with certain organoboron promoters generally is known to broaden the polymer molecular weight distribution. Use of titanium in the catalyst system support or boron adjuvants in the reactor can result in improvements in the environmental stress crack resistance (ESCR) of the resultant polymers, as well as increased catalyst system productivity. Unfortunately, these modifications can increase the amount of low molecular weight polymer and oligomers that are formed. Low molecular weight polymers and oligomers can contribute smoke and odor during the processing of the polymer, or resin, as it is molded into bottles and other articles of manufacture.

[0005] Another important characteristic of a blow molding resin is the swell properties of the resin. Two kinds of swell are critical during blow molding. These are "weight swell" and "diameter swell"; the later also is referred to herein as "die swell". As polymer, or resin, is extruded under pressure through a die opening and into a mold, a polymer has a tendency to swell as it exits the die. This is known as weight swell and can be determinative of the thickness of bottle wall, as well as the overall weight of the resultant blow molded product. For example, a resin which is extruded through a 0.02 inch die gap might yield a bottle wall thickness of 0.06 inches, in which case the weight swell is said to be 300%. A resin that swells too much can produce a bottle with too thick of a wall. To compensate, the die opening, or gap, can be narrowed by manual adjustment. However, any decrease in die gap can increase the resistance to the flow of the resin through the die. Narrower die gaps can result in higher shear rates during extrusion which also can increase melt fracture leading to a rough bottle surface. Thus, a resin which can be described as easily processable must exhibit low weight swell, which allows a wide die gap.

[0006] Diameter, or die, swell refers to how much a parison flares out as it is extruded from the die. For example, a resin extruded through a circular die of one (1) inch diameter can yield a parison tube of 1.5 inches in diameter; the die swell is said to be 50%. Die swell is significant because molds usually are designed for a certain amount of flare; too much die swell can interfere with molding of a bottle handle. A high degree of weight swell often causes high die swell because of the narrow die gap. Unfortunately, a narrow gap also increases the resistance to polymer flow. Thus, as used herein, a polymer which is considered easily processable also should exhibit low die swell.

[0007] Attempts have been made to obtain ethylene polymers having a broader molecular weight distribution (MWD) and consequent improved environmental stress crack resistance imparted by organoboron promoters and titania-containing catalyst systems. One of the most prevalent problems associated with such attempts is an increase of the amount of swell exhibited by the resin as it exits the die. Swell can be decreased by raising the activation temperature of the catalyst system, however, this also can reduce the polymer ESCR. Swell also can be decreased by lowering the melt index (MI), but this generally makes the resin more difficult to process, as measured by output rate and melt fracture. Swell also can be decreased by adding more chromium to the catalyst system, but this tends to impart a dirty color to the final polymer product. Thus, it has been difficult to produce a resin that maintains good swell and processing characteristics, high ESCR, and a low volatiles content.

SUMMARY OF THE INVENTION

[0008] It is an object of this invention to provide a process by which high density ethylene polymers and copolymers can be manufactured having a high stress crack resistance are prepared in high yield.

[0009] It is a further object of the invention to minimize the production of oligomers and low molecular weight polymer during the polymerization process.

[0010] It is a further object of this invention to minimize the amount of die swell and weight swell exhibited by the resin during molding.

[0011] It is a further object of this invention to provide a blow molding polymer which processes well in the blow molding machine.

[0012] In accordance with one embodiment of the invention, a polymerization catalyst system is provided which comprises chromium oxide on a silica-titania, wherein said support comprises less than about 3 weight percent titanium, in combination with an organoboron promoter. Further according to the invention, an ethylene polymer or copolymer is produced by contacting an ethylene monomer, and an optional comonomer, with an activated catalyst system comprising chromium oxide on a silica-titania, wherein said support comprises less than about 3 weight percent titanium, in the presence of an organoboron promoter. The resulting polymer is produced in high yield and has a combination of improved properties, including high shear response, good environmental stress crack resistance, and high density.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The silica containing substrates, or supports, used in the invention catalyst systems are silica or silica-alumina gels. Such gels conventionally are prepared by mixing an acid such as sulfuric acid with an aqueous solution of an alkali metal silicate such as sodium silicate to produce an aqueous gel, or hydrogel. The silicate preferably is added to the acid, and the reaction mixture is strongly agitated. The mixing temperature can range from about 1° C. to about 43° C. The resulting hydrogel is approximately 3 to about 12 weight percent SiO_2 and has a pH in a range of about 3 to about 9. The hydrogel is aged at a temperature of about 18° C. to 98° C. for a suitable time, generally more than one hour. Silica gels often have a minor portion, generally not exceeding 20 weight percent, of alumina or other metal oxides, and the support of the invention includes composite silica gels comprising silica and alumina, thorium, zirconium and like substances.

[0014] As used in this disclosure, the term "support" refers to a carrier for another catalytic component. However, by no means, is a support necessarily an inert material; it is possible that a support can contribute to catalytic activity and selectivity.

[0015] The hydrogel then is washed with water and either an ammonium salt solution or a dilute acid to reduce the alkali metal content of the hydrogel to less than about 0.1 weight percent. The ammonium salt solution is preferably one such as ammonium nitrate or an ammonium salt of an organic acid which volatilizes upon subsequent calcination.

[0016] Water in the hydrogel can be removed by any conventional method, such as, for example, by spray drying, vacuum oven drying, or air oven drying at temperatures above 100° C. If the hydrogel is dried by heating, it is not necessary to add an agent to the gel to prevent shrinkage of the pores.

[0017] The support must comprise titanium. Titration of the silica can be effected using a variety of methods. The titrated catalyst systems must comprise no more than about 3 weight percent titanium, based on the weight of the catalyst system (not including the organoboron component), after calcining. All or part of the titanium can be supplied by coprecipitation of silica and titania. In the coprecipitation method, a titanium compound, such as, for example, a titanium halide, nitrate, sulfate, oxalate, or alkyl titanate, can be incorporated with the acid or the silicate in an amount such that the amount of titanium present as titanium dioxide in the final calcined catalyst system is less than about 3 weight percent. The amount of titanium in the calcined catalyst system generally will be about 0.5 weight percent to about 3.0 weight percent, preferably within a range of about 0.5 to about 2.6 weight percent. Most preferably, the amount of titanium in the catalyst system support is within a range of 0.8 to 1.5 weight percent. The coprecipitation of titania with silica is disclosed in U.S. Pat. No. 3,887,494, the disclosure of which is hereby incorporated by reference.

[0018] Titration of the catalyst system support alternatively can be effected by impregnation of the hydrogel or

zirconium before or after incorporation of the chromium component of the catalyst system. For example, an aqueous solution of a hydrolysis-resistant titanium compound can be incorporated into a silica hydrogel and dried by conventional techniques.

[0019] Titration of the silica support also can be accomplished by adding a titanium compound to the silica zirconium, usually with heat to vaporize the solvent and cause titanium to be deposited on the support.

[0020] Particularly advantageous catalyst systems useful in this invention are silica-titanium created by twice aging, as disclosed in U.S. Pat. No. 4,981,831, the disclosure of which is hereby incorporated by reference.

[0021] The chromium component of the catalyst system comprises about 0.5% to about 4% weight percent chromium, preferably about 0.8 to about 2.0 weight percent, based on the weight of the calcined catalyst system and most preferably between 0.8 and 1.5% weight percent. The chromium component can be coprecipitated with the silica or the silica-titanium or added by means of an aqueous solution of a chromium compound such as tertiary butyl chromate to the zirconium, but preferably it is introduced by incorporating an aqueous solution of a water soluble chromium compound into the hydrogel after washing the hydrogel to remove alkali metal ions. Suitable chromium compounds include chromium acetate, chromium nitrate, chromium sulfate, chromium trioxide, ammonium chromate or any other chromium compound which can be converted to chromium oxide by calcination with at least part of the chromium being converted to the hexavalent state. As used herein, the term "chromium oxide", as used to describe the chromium compound present in the catalyst system after calcining, includes fixed surface chromates formed by the reaction of chromium oxide and silica, as discussed in Hogan, J. Poly. Sci. A-1, 8, 2637-2652 (1970). The chromium compound can be employed in any amount so as to provide the desired weight percent chromium in the final catalyst system.

[0022] The catalyst system can be activated by calcining at a temperature within the range of about 530° C. to about 650° C. in a dry atmosphere containing oxygen, usually dry air, for a time of about 10 minutes to 20 hours or longer. Activation can follow titration of the catalyst system in the activator, as described above, by heating the fluidized catalyst system sample to about 316° C., substituting dry air for the nitrogen atmosphere present during titration, raising the temperature to at least about 400° C., and calcining the fluidized catalyst system at this elevated temperature for any appropriate activation time. Following activation, the catalyst system must be stored in a dry, inert atmosphere until used.

[0023] Catalyst systems of this invention do not require a reduction step using carbon monoxide or other reducing treatments. In fact, such reduction treatments can be detrimental to this invention because they can narrow the molecular weight distribution and lower the density of the resin beyond that which is desirable for blow molding.

[0024] The resultant chromium on silica-titanium catalyst system must be of a certain porosity. The pore volume of the

resultant catalyst system preferably is within a range of about 0.6 to about 1.4 milliliters per gram and preferably within a range of about 0.7 to about 1.3 milliliters per gram. Most preferably, for best catalyst system activity and most improved polymer product properties, the pore volume of the catalyst system is within a range of 0.8 to 1.1 milliliters per gram. Higher pore volumes tend to give higher swell in the resin, and lower pore volumes destroy the activity of the catalyst system.

[0025] The surface area of the catalyst system must be within a range of about 100 m²/gram to about 500 m²/gram, preferably within a range of about 200 m²/gram to about 400 m²/gram. Most preferably, the surface area of the catalyst system, for best catalyst system productivity and best resultant polymer processing properties is within a range of 300 m²/gram to 400 m²/gram.

[0026] The resultant pore diameter is important because it can affect the amount of swell in the resin. As used here, the pore diameter is calculated by the equation: Pore diameter=4(Pore Volume)/(Surface Area). The pore diameter must be from about 50 angstroms (Å) to about 150 Å, preferably between 60 Å and 140 Å, and most preferably between 70 Å and 120 Å.

[0027] Organoboron compounds used as promoters with the silica-titania chromium oxide catalyst systems of the invention can be expressed as BR₃, wherein each R is selected independently from hydrogen, alkyl, cycloalkyl and aryl, at least one R in each compound being a hydrocarbon radical having from 1 to 12 carbon atoms, with the total number of carbon atoms not exceeding 30 in each compound. Examples of suitable boron promoters include trimethylborane, triethylborane, tri-n-dodecylborane, tricyclohexylborane, tri(2-methylcyclopentyl)borane, triphenylborane, tribenzylborane, tri(2-ethylphenyl)borane, methyldiethylborane, and like compounds. Boron compounds such as diborane which can form an organoboron compound in-situ, on contact with the olefin monomer(s), also are suitable. Trialkylboranes presently are preferred because of their availability.

[0028] The amount of boron compound used is generally within a range of about 0.1 to about 10 weight percent, based on the weight of the calcined catalyst system fed to the polymerization reactor. In a continuous particle form process using a loop reactor, for example, it is convenient to introduce the organoboron compound as a separate stream into the reactor, either continuously or in pulses, as a dilute solution in an inert hydrocarbon, e.g., 0.1 weight percent in isobutane. The concentration of the organoboron compound also can be expressed in parts per million (ppm) based on the diluent used in the polymerization reactor. Weight percent ranges of organoboron compounds should be from about 0.1 ppm to about 2 ppm organoboron compound, based on the amount of diluent charged in a continuous particle form process using a loop reactor. Preferably it should be from 0.3 ppm to 1.5 ppm, and most preferably it should be from 0.8 ppm to 1.3 ppm. Higher levels of the boron compound can generate more volatile components, and lower amounts do not give sufficiently high ESCR.

Reactants

[0029] Polymers produced in accordance with the process of this invention are homopolymers of ethylene and copolymers of ethylene and higher alpha-olefin comonomers. Preferably, the ethylene concentration in the polymerization reactor is within a range of from about 2 weight percent to about 20 weight percent, based on the total liquid content of the reactor. Most preferably, the ethylene concentration in the polymerization reactor is within a range of from about 4 to about 15 weight percent. Measured in another manner, ethylene concentration in the polymerization reactor flash gas is within a range of from about 2 weight percent to about 12 weight percent. Most preferably, the ethylene concentration in the polymerization reactor flash gas is within a range of from about 3 to about 8 weight percent. Ethylene concentration in the reactor can significantly affect the molecular weight of the resultant polymer and also catalyst system activity.

[0030] Alpha-olefin comonomers used in the present invention must be selected from the group consisting of 1-butene, 1-hexene, and mixtures thereof in order to produce a copolymer with desirable properties as well as ease of use in a loop/slurry polymerization reaction process. The most preferred comonomer is 1-hexene to produce a copolymer with the best product properties. If a comonomer is present during polymerization, the comonomer concentration in the polymerization reactor is within a range of from about 0.1 to about 10 weight percent. Most preferably, comonomer is present within a range of about 0.2 to about 2 weight percent.

Polymerization Process

[0031] Polymerization of the olefin monomer(s) must be carried out under loop/slurry polymerization conditions wherein the temperature is kept below the temperature at which polymer swells. Such polymerization techniques are well known in the art and are disclosed, for instance, in Norwood, U.S. Pat. No. 3,248,179, the disclosure of which is herein incorporated by reference. A light diluent, loop polymerization process is much more preferred than a stirred tank reactor because a stirred tank cannot contain isobutane, which is necessary to produce other commercially popular high density polyethylene polymer grades. A loop reactor also has an advantage in that isobutane diluent can be flashed off during polymer recovery, eliminating the necessity of separating polymer product from solvent. Additionally, the greater heat transfer surface of a loop reactor offers much more versatility for plant operation, and often less polymer swelling during polymerization.

[0032] Polymerization reaction temperature in the reactor, or reaction zone, according to this invention, is critical and is dependent on the type of catalyst system employed. Polymerization reaction temperatures usually must be within a range of about 200° F. to about 230° F. (93° C. to 110° C.), preferably within a range of about 210° F. to about 225° F. (99° C. to 107° C.). Most preferably, the reaction zone temperature is within a range of 210° F. to 220° F. (99° C. to 104° C.). Too high of a reactor temperature can produce a polymer with too low of a molecular weight; or

even to a fouled reactor. Too low of a reactor temperature can make the polymerization process inoperable because a lower reactor temperature can be difficult to maintain due to the exothermic polymerization reaction, flashing off reactor diluent can be difficult, and can produce a polymer with a commercially unacceptable high molecular weight.

Products

[0033] Polymers produced in accordance with this invention are homopolymers of ethylene and copolymers of ethylene and higher alpha-olefin comonomers. Polymers produced according to this invention are much more easily processed than polymers produced in accordance with different polymerization processes. The high load melt index (HLMI) usually is within a range of about 5 g/10 mins to about 25 g/10 mins, preferably within a range of about 8 g/10 mins to about 20 g/10 mins. Most preferably, the HLMI of the polymer product is within a range of 10 g/10 mins to 16 g/10 mins. The HLMI/MI ratio of polymers produced in accordance with this invention is relatively high and usually is within a range of about 100 to about 250, preferably within a range of about 140 to about 230; most preferably the HLMI/MI ratio is within a range of 160 to 200.

[0034] These polymers also have a broad molecular weight distribution as evidenced by M_w/M_n . Usually the M_w/M_n ratio is within a range of about 15 to about 30, preferably within a range of about 15 to about 26. Most preferably the M_w/M_n ratio is within a range of 18 to 23. These polymers also have a very narrow density range, usually within a range of about 0.950 g/cc to about 0.960 g/cc. Preferably the density is within a range of about 0.952 g/cc to about 0.958 g/cc and most preferably the density is within a range of 0.953 g/cc to 0.957 g/cc.

[0035] Polymers produced in accordance with this invention also have a very high environmental stress crack resistance (ESCR). Generally, under Condition A, the ESCR is greater than about 400 hours, preferably greater than about 500 hours and most preferably the ESCR, condition A is greater than 600 hours. The modified Condition B ESCR usually is greater than about 50 hours, preferably greater than about 65 hours, and most preferably greater than 80 hours.

[0036] Polymers of this invention also have excellent processing characteristics, as indicated by a high shear rate at the onset of melt fracture. The shear rate at onset of melt fracture is at least about 2000 sec^{-1} , preferably greater than about 2100 sec^{-1} , and most preferably greater than 2200 sec^{-1} . Polymers of this invention also have high output rates from a blow molding machine, at least 1200 grams per minute (g/min), preferably greater than 1300 g/min, and most preferably greater than 1350 g/min.

[0037] Polymers of this invention are characterized as having low swell characteristics, too. They usually exhibit less than about 42% diameter swell, preferably less than about 39%, and most preferably less than 35%. The weight swell of polymers of this invention usually is less than about 380%, preferably less than about 350%, and most preferably less than 330%.

[0038] Polymers of this invention also are characterized as having a low volatile content, or smoke content. This means that they should contain less than 2% of their weight as oligomeric components having less than 1000 molecular weight. Preferably, these polymers comprise less than about 1.6 weight % below 1000 MW, and most preferably these polymers comprise less than 1.4% material below 1000 in molecular weight. These polymers should also contain less than about 0.7% xylene solubles, preferably less than about 0.65%, and most preferably less than 0.6 % xylene solubles.

[0039] The following examples are provided to further assist a person skilled in the art with understanding the invention. The particular reactants, conditions, and other variables are intended to be generally illustrative of these inventions and are not meant to be construed to the unduly limiting the reasonable scope of the invention.

EXAMPLE

[0040] Catalyst systems used for the production of the inventive resins, Runs 17-22, was a low porosity Cr/silica-titania commercially available from W.R. Grace Company as 965 Sylopor®. It contained 2.5 weight percent titanium as titania and originally 1.0 weight percent chromium. Sylopor® has a pore volume of about 1.0 cc/g and a surface area of usually about 380 m^2/g . Specific measurements may be shown in the Tables that follow. In some Runs, both inventive Runs and control Runs, extra chromium was added through impregnation of a 0.5% methanol solution of chromium nitrate, as indicated in the Tables.

[0041] Control resins were made from several other types of commercial catalyst systems commercially available from W.R. Grace. The catalyst 969 MS (sometimes also referred to as 1%Cr on Grade 952 silica), used for Runs 1-10, had a pore volume of about 1.6 cc/g and a surface area around 300 m^2/g .

[0042] Run 11 was made using a HA30 support, from W.R. Grace, having the properties listed in the Tables.

[0043] Runs 12-14, were made by a catalyst system described as chromium on HPV8A silica. This silica also was made by W.R. Grace and had a surface area of about 580 m^2/g and a pore volume of about 2.2 cc/g.

[0044] Another silica support used in Runs 15 and 16, labeled HPV, had a pore volume of 2.5 cc/g and a surface area of 300 m^2/g .

[0045] Some polymers, or resins, were made from 964 Magnapore®, Runs 23-34, and 963 Magnapore®, Runs 35-48, and which contained 1.0, 2.0 or 3.0 weight percent chromium on a high porosity silica-titania and either 2.5 or 5.0 weight percent titanium, as indicated. 964 Magnapore® has a pore volume of 2.3 cc/g and a surface area of 540 m^2/g . 963 Magnapore® has a pore volume of 2.6 cc/g and a surface area of 520 m^2/g .

[0046] The catalyst system used in Runs 49-61 was similar to 963 Magnapore®, but had only one (1) weight percent titania in the support.

[0047] Another catalyst system was used in Runs 62-64 and was prepared by W.R. Grace by depositing aluminophosphate (P/Al molar ratio of 0.6) into the pores of silica. This material had a pore volume of 1.3 cc/g and a surface area of 250 m^2/g .

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[0048] Ethylene polymers were prepared using these catalyst systems in a continuous particle form process (also known as a slurry loop process) by contacting a catalyst system with ethylene and 1-hexene. The medium (diluent) and temperature thus were selected such that the copolymer was produced as solid particles and is recovered in that form. Ethylene that had been dried over activated alumina was used as the monomer.

[0049] The reactor was a liquid full 15.2 cm diameter pipe loop having a volume of 23 gallons (87 liters). Liquid isobutane, degassed by fractionation and dried over alumina, was used as the diluent, and occasionally some hydrogen was added to regulate the molecular weight of the polymer product. The reactor pressure was about 3.8 MPa (about 580 psi). The reactor temperature was varied over the range of 180° F. to 230° F. (82° C. to 110° C.), as indicated in the Tables below. The reactor was operated to have a residence time of 1.25 hours. Catalyst system was added through a 0.35 cc circulating ball-check feeder. At steady state conditions, the isobutane feed rate was about 46 liters per hour, the ethylene feed rate was about 30 lbs/hr, and the 1-hexene feed rate was varied to control the density of the polymer product. Catalyst system concentrations in the reactor can be such that the catalyst system content ranges from 0.001 to about 1 weight percent, based on the weight of the reactor contents. Polymer was removed from the reactor at a rate of about 25 lbs per hour and recovered in a flash chamber. A Vulcan dryer was used to dry the polymer under nitrogen at about 60° C. to about 80° C.

[0050] Cocatalysts triethylaluminum (TEA) and triethylboron (TEB) sometimes were added, as indicated in the Table below. To prevent static buildup in the reactor, a small amount (<5 ppm of diluent) of a commercial antistatic agent sold as Statix 450 was usually added.

[0051] Density (g/ml): ASTM D 1505-68 and ASTM D 1928, Condition C. Determined on a compression molded sample, cooled at about 15 C. per minute, and conditioned at room temperature for about 40 hours.

[0052] High Load Melt Index (HLMI)(g/10 min): ASTM D1238, condition E. Determined at 190 C. with a 21,600 gram weight.

[0053] Molecular Weight Distribution M_w/M_n : Molecular weights and molecular weight distributions were obtained using a Waters 150 CV gel permeation chromatograph with trichlorobenzene (TCB) as the solvent, with a flow rate of 1 mL/minute at a temperature of 140 C. BHT (2,6-di-tert-butyl-4-methylphenol) at a concentration of 1.0 g/L was used as a stabilizer in the TCB. An injection volume of 220 L was used with a nominal polymer concentration of 0.3 g/l (at room temperature). Dissolution of the sample in stabilized TCB was carried out by heating at 160-170 C. for 20 hours with occasional, gentle agitation. The column was two Waters HT-GE columns (7.8x300 mm). The columns were calibrated with a broad linear polyethylene standard (Phillips Marlex® BHB 5003) for which the molecular weight had been determined. As a measure of volatile oligomeric components, or smoke, the amount of material found in the range of molecular weights from 100 to 1000 are listed in the table below.

[0054] Xylene solubles (%): ASTM D5494-94. A measurement of the amount of low molecular weight oligomers and thus, of the potential of the resin to smoke during processing.

[0055] A "Quantachrome Autosorb-6 Nitrogen Pore Size Distribution Instrument" was used to determine the surface area and pore volume of the supports. This instrument was acquired from the Quantachrome Corporation, Syosset, N.Y.

[0056] Polymer resins obtained by this invention are useful for blow molding applications. In these examples blow molding evaluations were conducted by blowing a one gallon (105.0±0.5 gm) bottle on a Uniloy 2016 single head blow molding machine using a 2.5 inch diameter die, 20 degree diverging die, 32% accumulator position, 8.5 second blow time, 0.10 second blow delay, 0.75 second pre-blow delay and a 45° F. mold temperature. A reciprocating screw speed of 45 rpm was used, providing parison extrusion at shear rates greater than 10,000/sec⁻¹ through the die.

[0057] Three measurements of polymer processability during blow molding were determined in the following three tests:

[0058] 1-Minute Output. Describes the speed at which one part of the blow molding operation was accomplished. For this test, the extruder on the blow molding machine was set at 45 rpm and it was allowed to extrude resin for one full minute at the same die gap used to make the desired bottles. After 1 minute, the test was stopped and extruded polymer was weighed to determine the 1-minute output value. This value provides an indication of the rate of extrusion of the polymer during the blow molding operation.

[0059] Processing Rating: A subjective rating given by the machine operator based on their unbiased observations during the test. Each resin was given a rating of from 1 to 5, with 5 being the worst and 1 being the best. The operator considered such factors as head pressure, temperature, cycle time, pinch-off, and difficulties trimming.

[0060] Shear Rate at Melt Fracture. The onset of melt fracture of each resin was evaluated on the same Uniloy machine used in the previous two tests, by opening the die gap and extruding the resin. Shear rate was increased steadily by increasing the screw rpm. Onset of melt fracture was the rpm at which the parison showed visible signs of melt fracture, such as a shark skin appearance or a distorted rippled surface.

[0061] Percent Weight Swell: Measures the amount the molten resin expands immediately as the resin exits the die. Percent weight swell is a measure of the "memory" of polymer chains as the chains seek to relax and reform the original polymer shape. Weight swell is important because it measures how tightly the die gap must be adjusted to provide a constant bottle weight. If a resin has high weight swell, the die gap required will be tighter to make the proper part weight. In so doing, higher stress will be required to push the resin through the die than a lower weight swell resin. Weight swell is defined as the ratio of the die gap to the final bottle wall thickness.

[0062] Diameter Swell (Die Swell): The ratio of the parison diameter to the die diameter.

Example 1

[0063] A total of 64 polymers were produced for this test in accordance with the above procedures. Information about the catalyst system, the polymerization reaction, and evaluation of the polymers are listed in Table 1 below.

[0064] Only the unique combination of catalyst system properties (pore diameter, activation temperature, Ti and Cr level) and reactor properties (TEB level) yields a polymer that is especially well suited to the desired blow molding operations. This is evidenced by the high level of ESCR, good processing characteristics (as indicated by the 1-minute output test, operator evaluations, and the shear at onset of melt fracture), and low volatile or smoke content (as indicated by the xylene solubles test, the amount of material found in the GPC molecular weight decade of 10^2 - 10^3 , i.e., less than 1000 molecular weight, and by the subjective odor rating given by the machine operator (5=worst, 1=best).

TABLE 1

Catalyst Characteristics					
Run Number	Support	Weight Percent Chromium	Weight Percent Titanium	Pore Volume cc/g	Pore Surface Area m ² /g
1	Silica	0.6	0.0	1.6	300
2	Silica	0.6	0.0	1.6	300
3	Silica	1.0	0.0	1.6	300
4	Silica	1.0	0.0	1.6	300
5	Silica	1.0	0.0	1.6	300
6	Silica	1.0	0.0	1.6	300
7	Silica	1.0	0.0	1.6	300
8	Silica	1.0	0.0	1.6	300
9	Silica	1.0	0.0	1.6	300
10	Silica	1.0	0.0	1.6	300
11	Silica	1.0	0.0	1.6	300
12	Silica	1.0	0.0	2.2	577
13	Silica	1.0	0.0	2.2	577
14	Silica	1.0	0.0	2.2	577
15	Silica	1.0	0.0	2.5	300
16	Silica	1.0	0.0	2.5	300
17	Silica-Thin	1.0	2.5	1.0	380
18	Silica-Thin	1.0	2.5	1.0	380
19	Silica-Thin	1.0	2.5	1.0	380
20	Silica-Thin	1.0	2.5	1.0	380
21	Silica-Thin	1.0	2.5	1.0	380
22	Silica-Thin	2.0	2.5	1.0	380
23	Silica-Thin	1.0	5.0	2.3	540
24	Silica-Thin	1.0	5.0	2.3	540
25	Silica-Thin	2.0	5.0	2.3	540
26	Silica-Thin	2.0	5.0	2.3	540
27	Silica-Thin	2.0	5.0	2.3	540
28	Silica-Thin	2.0	5.0	2.3	540
29	Silica-Thin	2.0	5.0	2.3	540
30	Silica-Thin	2.0	5.0	2.3	540
31	Silica-Thin	2.0	5.0	2.3	540

TABLE 1-continued

Catalyst Characteristics					
Run Number	Support	Weight Percent Chromium	Weight Percent Titanium	Pore Volume cc/g	Pore Surface Area m ² /g
32	Silica-Thin	3.0	5.0	2.3	540
33	Silica-Thin	3.0	5.0	2.3	540
34	Silica-Thin	3.0	5.0	2.3	540
35	Silica-Thin	2.0	2.5	2.6	320
36	Silica-Thin	2.0	2.5	2.6	320
37	Silica-Thin	2.0	2.5	2.6	320
38	Silica-Thin	2.0	2.5	2.6	320
39	Silica-Thin	2.0	2.5	2.6	320
40	Silica-Thin	2.0	2.5	2.6	320
41	Silica-Thin	2.0	2.5	2.6	320
42	Silica-Thin	2.0	2.5	2.6	320
43	Silica-Thin	2.0	2.5	2.6	320
44	Silica-Thin	2.0	2.5	2.6	320
45	Silica-Thin	2.0	2.5	2.6	320
46	Silica-Thin	2.0	2.5	2.6	320
47	Silica-Thin	2.0	2.5	2.6	320
48	Silica-Thin	2.0	2.5	2.6	320
49	Silica-Thin	2.0	1.0	2.6	335
50	Silica-Thin	2.0	1.0	2.6	335
51	Silica-Thin	2.0	1.0	2.6	335
52	Silica-Thin	2.0	1.0	2.6	335
53	Silica-Thin	2.0	1.0	2.6	335
54	Silica-Thin	2.0	1.0	2.6	335
55	Silica-Thin	2.0	1.0	2.6	335
56	Silica-Thin	2.0	1.0	2.6	335
57	Silica-Thin	2.0	1.0	2.6	335
58	Silica-Thin	2.0	1.0	2.6	335
59	Silica-Thin	2.0	1.0	2.6	335
60	Silica-Thin	2.0	1.0	2.6	335
61	Silica-Thin	2.0	1.0	2.6	335
62	Silica-A1PO4	1.0	0.0	1.3	250
63	Silica-A1PO4	1.0	0.0	1.3	250
64	Silica-A1PO4	1.0	0.0	1.3	250

[0065]

TABLE 2

Run Number	Reaction Conditions		Coat. Type	Coat. ppm	Polymer Properties				M _w /M _n
	Calcining Temp. ° F.	Reactor Temp. ° F.			MI g/10 min	HLMI g/10 min	HLMI/MI	density g/mL	
1	1300	220	TEB	2.23	0.01	7.9	794	0.9526	16.8
2	1300	221	TEB	1.77	0.02	9.0	452	0.9547	13.1
3	1450	214	None	ND	0.30	30.0	100	0.9535	8.4
4	1450	217	None	ND	0.41	37.6	91.6	0.9540	10.4
5	1450	218	None	ND	0.31	31.5	102	0.9531	7.9
6	1200	217	TEB	2.0	0.06	8.9	148	0.9545	16.4
7	1200	220	TEB	2.0	0.05	11.8	236	0.9544	14.9
8	1200	220	TEB	2.0	0.06	13.6	230	0.9546	14.4
9	1300	222	TEB	1.0	0.07	11.4	1637	0.9536	8.4
10	1300	222	TEB	1.0	0.09	14.3	159	0.9537	8.4
11	1300	218	TEB	2.08	0.01	10.2	1040	0.9524	11.4
12	1000	218	TEB	2.0	0.15	20.7	138	0.9539	17.5
13	1000	217	TEB	2.0	0.14	19.3	138	0.9541	14.4
14	1000	220	TEB	2.13	0.02	10.7	536	0.9539	20.0
15	1200	217	TEB	2.0	0.06	12.4	207	0.9546	15.2
16	1200	218	TEB	2.0	0.10	15.7	157	0.9544	14.2
17	1100	211	TEB	1.0	0.14	19.8	141	0.9512	23.5
18	1100	213	TEB	1.0	0.06	11.1	184	0.9532	19.4
19	1100	214	TEB	1.0	0.07	12.8	182	0.9545	21.5
20	1100	216	TEB	1.0	0.07	12.5	178	0.9530	17.2
21	1100	218	TEB	1.0	0.05	11.5	230	0.9540	23.0
22	1100	216	TEB	2.0	0.09	19.4	216	0.9532	24.1
23	1000	210	TEB	2.0	0.17	28.7	169	0.9502	22.2
24	1000	204	TEB	2.0	0.09	17.3	191	0.9547	38.8
25	1100	216	TEA	2.0	0.12	16.7	139	0.9545	30.2
26	1100	198	TEB	2.0	0.06	14.9	248	0.9545	41.9
27	1100	203	TEB	2.0	0.18	32.5	180	0.9560	ND
28	1100	203	TEB	2.0	0.15	27.4	183	0.9565	29.0
29	1100	199	TEB	2.0	0.05	13.1	263	0.9544	35.1
30	1000	203	TEB	2.0	0.11	21.0	191	0.9534	38.1
31	1000	203	TEB	2.0	0.04	12.8	320	0.9581	37.2
32	1000	199	TEB	2.0	0.08	17.8	222	0.9532	37.2
33	1000	205	TEB	4.0	0.13	27.1	208	0.9561	35.6
34	1000	197	TEB	4.0	0.06	17.4	291	0.9564	43.9
35	1000	211	TEB	2.0	0.13	21.7	167	0.9544	25.6
36	1000	210	TEB	2.0	0.11	19.2	174	0.9545	24.7
37	1100	219	None	ND	0.23	20.1	87.2	0.9506	12.6
38	1100	219	None	ND	0.31	23.6	73.8	0.9507	13.2
39	1100	219	None	ND	0.34	26.7	78.5	0.957	14.0
40	1100	218	TEA	2.0	0.11	12.5	113	0.9530	22.8
41	1100	219	TEA	2.0	0.15	17.0	113	0.9533	24.0
42	1100	208	TEB	2.0	0.09	17.2	191	0.9539	21.4
43	1100	219	TEB/A	2.0/0.5	0.19	25.4	134	0.9587	21.2
44	1100	219	TEB/A	1.4/0.3	0.21	26.4	126	0.9585	21.0
45	1100	219	TEB/A	1.9/0.5	0.22	24.8	113	0.9549	21.6
46	1100	219	TEB/A	2.3/2.3	0.15	21.8	146	0.9547	22.7
47	1100	219	TEB/A	2.0/2.0	0.35	33.5	95.7	0.9482	21.2
48	1200	206	TEB	2.05	0.05	12.5	250	0.9537	23.4
49	1100	220	TEB	1.83	0.04	11.9	289	0.9577	23.7
50	1100	219	TEB	1.94	0.07	15.2	217	0.9537	19.8
51	1200	219	TEB	1.89	0.06	13.7	228	0.9545	18.8
52	1200	220	TEB	2	0.12	19.7	164	0.956	22.8
53	1200	220	TEB	2.1	0.15	22.6	151	0.9569	20.8
54	1200	220	TEB	1.9	0.2	24.2	121	0.9582	17.5
55	1200	220	TEB	1.9	0.21	26.9	128	0.9569	18.5
56	1200	220	TEB	1.9	0.2	25.7	129	0.9568	18.1
57	1200	220	TEB	2.1	0.19	24.9	131	0.9586	18.5
58	1200	220	TEB	2.1	0.16	22.8	142	0.9586	18.7
59	1200	218	TEB	2.02	0.07	14.3	204	0.9526	20.3
60	1200	220	TEB	1.96	0.02	10.8	540	0.9523	20.4
61	1200	213	TEB	2.01	0.02	10.3	514	0.9545	22.9
62	1300	212	TEB	1.94	0.08	18.2	228	0.9574	17.9
63	1300	214	TEB	2.15	0.04	13.7	342	0.9567	21.7

Note:

TEB is Triethylborane; TEA is triethyl aluminum; and TEB/A is a combination of triethylborane and triethyl aluminum.

[0066]

TABLE 3

Run Number	Processing Character					Volatiles				
	ESCR		Swell		Process Rating 1 to 5	Melt		Ode Rating 1 to 5	Xylene Solubles %	MW Denda 10 ⁴ -10 ⁵ (<1000 MW)
	Cond. A hours	Cond. mod B hours	Dls Swell %	Weight Swell %		Fract. Shear Rate	1 min output @ 75 g			
1	104	48	31.4	246	3	1240	743	3	0.08	0.73
2	90	48	31.7	247	3	1250	752	3	0.12	0.61
3	115	115	42.9	389	1	1930	ND	3	0.23	0.00
4	42	24	44.6	445	2	2440	1465	3	0.80	0.35
5	64	24	46.7	405	2	2420	1454	2	0.12	0.33
6	261	82	32.4	312	2	2290	1378	2	ND	0.69
7	196	56	34.2	314	2	2350	1412	2	ND	0.81
8	234	44	38.0	314	2	2270	1364	2	ND	0.45
9	71	39	29.9	239	2	1440	865	2	0.20	0.01
10	60	57	30.4	263	2	1920	1154	2	0.08	0.01
11	408	139	36.7	283	2	1260	756	3	0.20	0.44
12	395	90	42.3	401	2	2460	1476	2	ND	0.94
13	395	73	45.4	375	2	2240	1348	2	ND	0.62
14	>1000	185	41.8	316	3	735	442	2	0.58	0.55
15	316	54	35.0	334	2	2370	1424	2	ND	0.65
16	248	61	41.3	349	2	2440	1465	2	ND	0.51
17	>1000	411	42.3	368	3	2330	1412	2	0.56	1.54
18	>1000	127	36.7	321	2	2300	1382	2	0.56	1.29
19	594	104	37.3	328	2	2310	1391	2	0.44	1.04
20	726	87	36.5	327	2	2330	1413	2	0.52	1.19
21	428	87	39.0	313	2	2230	1339	2	0.48	1.61
22	283	115	34.5	290	3	2360	ND	5	1.29	1.27
23	>1000	233	43.9	399	4	2290	ND	4	0.99	2.03
24	>1000	429	42.6	395	4	2200	ND	4	1.07	2.44
25	304	102	44.1	330	3	1620	976	3	0.75	2.83
26	>1000	170	43.9	434	4	2200	1321	3	1.12	3.73
27	>1000	86	39.3	430	3	2260	1359	3	1.59	ND
28	414	75	39.0	402	4	2320	1393	3	0.99	2.14
29	>1000	226	37.3	485	5	2170	1304	3	1.28	2.67
30	>1000	317	40.1	392	5	2160	ND	5	0.80	2.34
31	>1000	257	40.1	397	5	2210	ND	5	1.21	2.60
32	>1000	300	38.0	410	5	2190	ND	5	1.20	2.42
33	>1000	139	40.6	475	5	2180	ND	5	1.57	2.40
34	>1000	261	40.1	457	5	2170	ND	5	1.10	2.92
35	>1000	329	42.3	455	2	2260	1362	2	0.92	1.46
36	>1000	241	44.4	436	3	2230	1339	3	0.96	1.97
37	209	45	51.0	353	3	1010	428	3	0.28	0.00
38	202	45	52.0	379	3	N/A	493	3	0.32	0.14
39	271	45	53.0	403	3	N/A	570	3	0.34	0.29
40	534	125	43.4	321	2	1130	689	2	0.56	1.53
41	400	85	45.1	325	2	1030	620	2	0.60	1.22
42	>1000	144	44.9	414	3	2230	1343	3	0.80	1.43
43	485	69	47.0	489	3	1870	1378	2	1.04	0.37
44	417	61	48.0	489	3	1890	1442	2	0.64	0.44
45	637	90	47.0	407	3	1660	973	2	0.40	0.73
46	500	110	46.0	409	3	1500	915	3	0.20	0.85
47	>1000	500	46.0	474	4	1640	1402	3	0.60	0.81
48	>1000	180	40.3	386	2	2090	1257	3	0.92	1.58
49	258	120	43.1	332	2	848	510	3	0.68	1.38
50	441	120	42.9	338	2	1180	711	3	0.56	0.91
51	564	139	41.3	330	2	496	399	3	0.92	0.74
52	321	76	45.0	404	3	1560	1125	3	0.32	0.66
53	329	78	44.0	392	3	1680	1009	3	0.48	0.44
54	251	71	45.0	400	3	1910	991	3	0.60	0.33
55	373	56	45.0	429	3	1430	1182	3	0.76	0.49
56	378	69	46.0	412	3	1650	996	3	0.68	0.30
57	368	58	45.0	384	3	1640	948	3	0.64	0.31
58	346	56	46.0	389	3	1580	871	3	0.92	0.31
59	912	139	40.8	398	2	1820	1096	2	0.72	1.03
60	672	139	42.3	369	3	1490	898	2	0.40	1.08
61	>1000	146	40.8	317	3	777	467	2	0.64	1.22
62	131	48	35.7	332	2	2370	1425	2	0.92	1.09
63	131	48	35.2	322	2	2340	1410	2	0.66	1.38
64	112	48	36.7	325	2	2410	1431	3	0.68	0.89

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[0067] By studying the data in Tables 1-3, it can be seen that ESCR is improved by high levels of TEB and Ti, which unfortunately also yields high volatiles or smoke. Swell is decreased by lowering the HLMI, which also makes processing more difficult, as indicated by lower values from the melt fracture and output tests. Swell is also decreased by increasing the activation temperature, but this also hurts ESCR. Notice also that the output test drops significantly if TEB is omitted, and the ESCR drops significantly if Ti is omitted. However, if TEB rises too much volatiles becomes a problem. Finally, notice also that swell becomes too high if the pore diameter increases much.

[0068] Thus the many opposing variables are uniquely balanced by the precise combination of conditions taught in this invention.

[0069] While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed is:

1. A polymerization process comprising contacting under slurry polymerization conditions in an isobutane diluent at a temperature of from about 200° F. to 230° F.

- a) ethylene monomer;
 - b) at least 1 mono-1-olefin comonomer having about three to eight carbon atoms per molecule;
 - c) a catalyst system comprising chromium supported on a silica-titania support, wherein said support comprises from about 0.5 to about 3 weight percent titanium, based on the weight on the support, wherein said catalyst system has a average pore diameter from 50 to about 150 angstroms, and said catalyst system has been activated at a temperature within a range of about 1000° F. to about 1200° F. (about 538° C. to about 649° C.);
 - d) about 0.1 to about 2.0 mg/kg, based on the reactor diluent, of a trialkylboron compound; and
 - e) recovering an ethylene/mono-1-olefin copolymer.
2. A process according to claim 1 wherein said comonomer is selected from the group consisting of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and mixtures thereof.
3. A process according to claim 2 wherein said comonomer is 1-hexene.
4. A process according to claim 1 wherein said reactor temperature is within a range of about 210° F. to 220° F.
5. A process according to claim 1 wherein said titania of the silica-titania support is coprecipitated with the silica.
6. A process according to claim 1 wherein said catalyst system is aged twice and wherein the first aging is at a substantially neutral pH and wherein the second aging is at an alkaline pH.
7. A process according to claim 1 wherein said trialkylboron cocatalyst is present in the reactor in an amount within a range of 0.3 to 1.3 mg/kg of diluent.

8. A composition comprising ethylene and a 1-hexene, wherein said copolymer has a high load melt index (HLMI) within a range of about 5 to about 25 g/10 minutes, a density within a range of about 0.95 to 0.96 g/cc, a shear response (HLMI/MI) is within a range of about 140 to about 230, a weight swell of less than about 350%, and a die swell within a range of about 30% to about 40%, an ESCR (Condition A) of greater than about 400 hours, a M_w/M_n of between about 15 and about 26, the onset of melt fracture of greater than about 2200 sec-1, and 1-minute output test value of greater than 1300 grams per minute, xylene solubles of less than 0.65%, and less than 2.0% material of molecular weight less than 1000.

9. A composition according to claim 8 wherein the density is within the range of 0.952 to 0.958 g/cc.

10. A composition according to claim 9 wherein said high-load melt index is within a range of 10 to 16 grams/10 minutes.

11. A composition according to claim 9 wherein said shear response (HLMI/MI) is within a range of 160 to 200.

12. A composition prepared from a polymerization process comprising contacting under slurry polymerization conditions in an isobutane diluent at a temperature of from 210° F. to 220° F.

- a) ethylene monomer;
- b) 1-hexene;
- c) a catalyst system comprising chromium supported on a silica-titania support, wherein said support comprises from about 0.5 to about 3 weight percent titanium, based on the weight on the support, wherein said catalyst system has a average pore diameter from 70 to about 120 angstroms, and said catalyst system has been activated at a temperature within a range of about 1000° F. to about 1200° F. (about 538° C. to about 649° C.);
- d) about 0.3 to about 1.5 mg/kg, based on the reactor diluent, of a trialkylboron compound; and
- e) recovering an ethylene/mono-1-olefin copolymer, and, wherein said composition has a high load melt index (HLMI) within a range of about 5 to about 25 g/10 minutes, a density within a range of about 0.95 to 0.96 g/cc, a shear response (HLMI/MI) is within a range of about 140 to about 230, a weight swell of less than about 350%, and a die swell within a range of about 30% to about 40%, an ESCR (Condition A) of greater than about 400 hours, a M_w/M_n of between about 15 and about 26, the onset of melt fracture of greater than about 2200 sec-1, and 1-minute output test value of greater than 1300 grams per minute, xylene solubles of less than 0.65%, and less than 2.0% material of molecular weight less than 1000.

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(54) **PROCESS THAT PRODUCES POLYMERS**

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(75) Inventors: **Joseph J. Bergmeister, Bartlesville, OK (US); Steven J. Secora, Bartlesville, OK (US); Gerhard Guenther, Kemah, TX (US); Elizabeth A. Benham, Bartlesville, OK (US); Max McDaniel, Bartlesville, OK (US)**

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Correspondence Address:
Chevron Phillips Chemical Company LP
Suite 3490
1301 McKinney
Houston, TX 77010 (US)

(57) **ABSTRACT**

(73) Assignee: **Phillips Petroleum Company, Bartlesville, OK (US)**

A process comprising polymerizing ethylene, or polymerizing ethylene and at least one other olefin, to produce a polymer is provided.

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PROCESS THAT PRODUCES POLYMERS

FIELD OF THE INVENTION

[0001] This invention is related to the field of processes that polymerize ethylene, or that polymerize ethylene and at least one other olefin, to produce a polymer.

BACKGROUND OF THE INVENTION

[0002] There are many processes that polymerize ethylene, or that polymerize ethylene and at least one other olefin, to produce a polymer. There are also many manufacturing processes that use these types of polymers to produce useful items. One of these manufacturing processes is called blow molding.

[0003] In general, blow molding is useful for producing hollow plastic products. A principle advantage of blow molding is its ability to produce hollow shapes without having to join two or more separately molded parts.

[0004] In order to produce a good quality blow molded product, one needs to start with a good quality polymer. However, producing such good quality polymers is difficult. It has been especially difficult to produce a good quality polymer that has a high environmental stress crack resistance (ESCR) and that is useful for blow molding applications.

[0005] Therefore, the inventors provide this invention so that such good quality polymers with high ESCR's are more readily obtainable, and readily useable in blow molding applications.

SUMMARY OF THE INVENTION

[0006] It is an object of this invention to provide a process to polymerize ethylene, or ethylene and at least one other olefin to produce a polymer.

[0007] It is also an object of this invention to provide said polymer.

[0008] In accordance with this invention a process is provided. The process comprises (or optionally "consists essentially of", or "consists of") polymerizing ethylene, or polymerizing ethylene and at least one other olefin, to produce a polymer.

[0009] wherein said polymerizing is conducted in a polymerization zone, and

[0010] wherein said polymerizing is conducted using a catalyst and a cocatalyst, and

[0011] wherein said catalyst comprises chromium on a support, and

[0012] wherein the amount of said chromium on said support is from about 0.5 to 5 weight percent, and

[0013] wherein said support comprises silica, in major part, and

[0014] wherein the amount of titanium in said support is greater than about 3.5 to about 10 weight percent based on the weight of said support, and

[0015] wherein said support has a surface area from about 400 to about 800 square meters per gram, and

[0016] wherein said support has a pore volume from about 1.8 to about 4 cubic centimeters per gram, and

[0017] wherein said catalyst has been activated at a temperature in the range of about 600° F. to about 1100° F. in the presence of an oxidizing ambient, and

[0018] wherein said cocatalyst is an organoboron compound.

[0019] In accordance with this invention a polymer comprising the following properties: a density from about 0.94 to about 0.96, a high load melt index from about 5 to about 45 g/10 min., a shear ratio (high load melt index/melt index) from about 150 to about 400, a heterogeneity index from about 15 to about 55, an ESCR condition A greater than about 1000 hours, and ESCR Condition B greater than about 200 hours, a normalized die swell from about 0.8 to about 1.1, a weight swell from about 300 to about 500 percent, and an onset of melt fracture greater than about 2000 sec⁻¹.

[0020] These and other objects will become more apparent with the following.

[0021] The terms "comprise", "comprises" and "comprising" are open-ended and do not exclude the presence of other steps, elements, or materials that are not specifically mentioned in this specification.

[0022] The phrases "consists of" and "consisting of" are closed ended and do exclude the presence of other steps, elements, or materials that are not specifically mentioned in this specification, however, they do not exclude impurities normally associated with the elements and materials used.

[0023] The phrases "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials that are not specifically mentioned in this specification, as long as such steps, elements, or materials, do not affect the basic and novel characteristics of the invention, additionally, they do not exclude impurities normally associated with the elements and materials used.

[0024] The previous terms and phrases are intended for use in areas outside of U.S. jurisdiction. Within the U.S. jurisdiction the above terms and phrases are to be applied as they are construed by U.S. courts and the U.S. Patent Office.

DETAILED DESCRIPTION OF THE INVENTION

[0025] This polymerization can be carried out in any manner known in the art such as gas phase, solution or slurry polymerization conditions. A stirred reactor can be utilized for a batch process, or the reaction can be carried out continuously in a loop reactor.

[0026] This polymerization is conducted in a polymerization zone. It is preferred to conduct this polymerization in a loop reactor. It is more preferred when said polymerization is conducted in a loop reactor under slurry polymerization conditions. Currently, the preferred diluent for slurry polymerization is isobutane.

[0027] Loop reactors are known in the art, see, for example, U.S. Pat. Nos. 3,248,179; 4,424,341; 4,501,855; and 4,613,484; the entire disclosures of which are hereby incorporated by reference. Especially preferred processes are disclosed in U.S. Pat. Nos. 4,589,957; 4,737,280; 5,597,

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892; and 5,575,979 the entire disclosures of which are also hereby incorporated by reference.

[0028] A preferred polymerization technique is that which is referred to as a particle form, or slurry process, wherein the temperature is kept below the temperature at which polymer swells and fouls the reactor. Such polymerization techniques are well known in the art and are disclosed, for example, in Norwood, U.S. Pat. No. 3,248,179, the disclosure of which is hereby incorporated by reference.

[0029] Two preferred polymerization methods for the slurry process are those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel or combinations thereof wherein the reaction conditions are different in the different reactors.

[0030] The diluent, before it enters the reactor, comprises isobutane. Additionally, before the diluent enters the reactor, the majority of said diluent is isobutane. It is preferred when the diluent contains 60-100, more preferably, 70-100, and most preferably 80-100 weight percent isobutane based on the weight of the diluent before it enters the reactor.

[0031] The polymerization is conducted at a temperature from about 190° F. to about 230° F. However, it is preferred when said polymerizing is conducted at a temperature from about 195° F. to about 225° F. and it even more preferred when said polymerizing is conducted at a temperature from 200° F. to 220° F. At temperatures below about 190° F. the efficiency of the catalyst and the reactor is adversely affected. At temperatures above about 230° F. the reactor could foul due to the swelling of the polymer.

[0032] The pressure that the polymerization is conducted at is in the range of about 400 psia to about 800 psia, preferably about 500 psia to about 700 psia. The catalyst used in this invention comprises chromium on a support, preferably in the form of chromium oxide on a support. The amount of chromium on said support is in the range of about 0.5 to about 5 weight percent, preferably about 1 to about 4 weight percent, and most preferably from 1.5 to 3 weight percent, where such weight percents are based on the weight of the support.

[0033] The support comprises silica and titania. Additionally, such support has silica, as its major component by weight, and titania, as its minor component by weight. It is most preferred when said support consists essentially of silica and titania, with little, if any, impurities. It is even more preferred when the silica and titania are cogelled.

[0034] It is preferred when the amount of titanium in the support is from about 3.5 to about 10 weight percent, preferably about 4 to about 8 percent, and most preferably from 4 to 6 weight percent, where said weight percents are based on the weight of the support. When the amount of titanium is less than about 3.5 weight percent, the ESCR of the resin produced tends to be too low. When the amount of titanium is greater than about 10 weight percent, the catalyst becomes thermally unstable and processability of the resin produced tends to be undesirable.

[0035] The support should have a surface area from about 400 to about 800 square meters per gram. It is more preferred when the support has a surface area from about 425 to 700 square meters per gram, and it is most preferred

when said support has a surface area from 450 to 650 square meters per gram. Surface areas below about 400 m²/g tend to have less activity, less ESCR, and too little die swell, while surface areas above about 800 m²/g produces polymers that have a die swell that is too high, an amount of long chain branching that is too low, and possibly, a melt index that is too low.

[0036] The support should have a pore volume from about 1.8 to about 4 cubic centimeters per gram. It is more preferred when the support has a pore volume from about 1.9 to about 3 cm³/g, and it is most preferred when said support has a pore volume from 2 to 2.7 cm³/gram. Pore volumes below about 1.8 cm³/g produce polymer with low ESCR, while pore volumes above about 4 cm³/g are difficult to handle in commercial operations.

[0037] Methods of producing these types of catalysts are known in the art. See for example, U.S. Pat. Nos. 3,900,457; 4,081,407; 4,392,990; 4,405,501; 4,735,931; 4,981,831; the disclosures of which are hereby incorporated by reference.

[0038] The catalyst should be activated in the presence of an oxidizing ambient (sometimes referred to as "atmosphere") at a temperature greater than about 600° F. to about 1100° F. It is even more preferred when the temperature is from about 700° F. to less than 1100° F., and it is even more preferred when the temperature is from about 900° F. to about 1050° F., and it is most preferred when the temperature is from about 900° F. to about 1050° F. At temperatures below about 600° F. the activity of the catalyst is reduced and the physical properties of the polymer are adversely affected. At temperatures above about 1100° F. there is a loss of ESCR in the polymer. Currently, the preferred oxidizing ambient is air. This activation is carried out for a time period of about 1 minute to about 50 hours. This allows a portion of the chromium in a lower valence state to be converted to a hexavalent state.

[0039] The ethylene used should be polymerization grade ethylene. The other olefins that can be used are alpha-olefins having from 4 to 12 carbon atoms. Currently, 1-butene, 1-hexene, and 1-octene are the most preferred olefins.

[0040] The catalyst must be used in the presence of a cocatalyst that is an organoboron compound. Organoboron compounds, as used in this invention, have the following general formula: B(X)₃.

[0041] In this formula (X) is a hydrocarbyl having from 1-20 carbon atoms. Currently, it is preferred when (X) is an alkyl having from 1 to 10 carbon atoms. However, it is most preferred when (X) is selected from the group consisting of methyl, ethyl, propyl, butyl, and isobutyl.

[0042] Examples of such compounds are as follows:

- [0043] trimethylboron;
- [0044] triethylboron;
- [0045] tripropylboron;
- [0046] tributylboron; and
- [0047] triisobutylboron.

[0048] Currently, triethylboron is preferred.

[0049] The amount of organoboron compound to use in this invention is from about 1 to about 15 parts per million

by weight, based on the weight of the diluent before it enters the reactor. However, it is preferred when the amount is from about 1 to about 10, and it is most preferred when the amount is from 2 to 4 parts per million.

[0050] The polymer produced needs to have the following properties in order to be a polymer that is good for blow molding applications.

[0051] The density needs to be from about 0.94 to 0.96 grams per cubic centimeter. However, it is preferred when the density is from about 0.95 g/cm³ to 0.96 g/cm³ and it is more preferred when the density is from 0.953 g/cm³ to 0.958 g/cm³. This density is determined in accordance with ASTM D1505.

[0052] The high load melt index needs to be from about 5 to about 45 grams per ten minutes. However, it is preferred when the high load melt index is from about 8 g/10 min to about 35 g/10 min. and it is even more preferred when the high load melt index is from 10 g/10 min. to 25 g/10 min. This high load melt index is determined in accordance with ASTM D 1238.

[0053] The shear ratio (HLMI/MI) needs to be from about 150 to about 400. However, it is preferred when the shear ratio is from about 170 to about 350 and it is even more preferred when the shear ratio is from 180-320.

[0054] The heterogeneity index (Mw/Mn) needs to be from about 15 to about 55. However, it is preferred when the heterogeneity index is from 20 to 50 and it is even more preferred when the heterogeneity index is from 25 to 45, and it is most preferred when the Heterogeneity index is from 30 to 40. The heterogeneity index was determined by gel permeation chromatography.

[0055] The ESCR Condition A of the polymer is greater than 1000 hours. The ESCR Condition B of the polymer is greater than 200 hours, preferably greater than 300 hours. These ESCR's are measured according to ASTM D1693, Conditions A and B. Additionally, the polymer should have a bottle ESCR greater than 700 hours as measure in accordance with the examples below.

[0056] The die swell is an indication of how much the molten polymer tends to flare out as it is extruded from the die. The normalized die swell should be between about 0.8 and about 1.1, preferably, about 0.9 and about 1.05, and most preferably, from 0.95 to 1.05. Normalized die swell outside this range leads to poor bottle molding. High die swell results in the parison extending beyond the mold, leading to, for example, "pinch-off" or other problems. Low die swell can cause a failure to fill the mold.

[0057] Weight swell is a measure of how much memory the polymer retains as it is extruded. A 300 weight percent swell indicates that the final bottle wall thickness is three times the die gap distance. If the polymer has a characteristically high weight swell, it requires a smaller die gap to produce the required wall thickness, and a smaller gap can restrict polymer flow, and thus machine output. The weight swell should be between about 300 and about 500 weight percent, preferably, about 325 and about 475 weight percent, and most preferably, from 350 to 450 weight percent.

[0058] The onset of melt fracture should be greater than 2000 sec⁻¹.

EXAMPLES

[0059] These examples are provided to further illustrate the invention. The scope of the invention should not be limited to these examples.

TESTS

[0060] A "Quantachrome Autosorb-6 Nitrogen Pore Size Distribution Instrument" was used to determine the surface area and pore volume of the supports. This instrument was acquired from the Quantachrome Corporation, Syoset, N.Y.

[0061] Polymer density was determined in grams per cubic centimeter (g/cc) on a compression molded sample, cooled at 15° C. per hour, and conditioned for 40 hours at room temperature in accordance with ASTM D1505 and ASTM D1928, procedure C.

[0062] High load melt index (HLMI, g/10 min) was determined in accordance with ASTM D1238 at 190° C. with a 21,600-grain weight.

[0063] Melt index (MI, g/10 min) was determined in accordance with ASTM D1238 at 190° C. with a 2,160 gram weight.

[0064] Environmental Stress Crack Resistance (ESCR, hr) was determined according to ASTM D1693, Conditions A and B.

[0065] The Heterogeneity index was determined using size exclusion chromatography (SEC) analyses that were performed at 140° C. on a Waters, model 150 GPC with a refractive index detector. A solution concentration of 0.25 weight percent in 1,2,4-trichlorobenzene was found to give reasonable elution times.

[0066] Polymer resins obtained by this invention are useful for blow molding applications. In these examples blow molding evaluations were conducted by blowing a one gallon (105.0±0.5 gm) bottle on a Uniloy 2016 single head blow molding machine using a 2.5 inch diameter die, 20 degree diverging die, 32% accumulator position, 8.5 second blow time, 0.10 second blow delay, 0.75 second pre-blow delay and a 45 degree ° F. mold temperature. A reciprocating screw speed of 45 rpm was used, providing parison extrusion at shear rates greater than 10,000/sec through the die.

[0067] Percent weight swell measures the amount the molten resin expands immediately as it exits the die. It is a measure of the "memory" of the polymer chains as they seek to relax and thus reform the polymer shape. Weight swell is an important parameter as it determines how tight the die gap must be adjusted to provide a constant bottle weight. If a resin has high weight swell, the die gap required will be tighter to make the proper part weight. In so doing, it will require higher stress to push the resin through the die than a lower weight swell resin. Weight swell is defined as the ratio of the final bottle wall thickness to the die gap.

[0068] Another measurement of swell is die swell or diameter swell. This is the ratio of the parison diameter to the die diameter. These numbers are referenced to a standard commercial blow molding polyethylene resin, Marlex 5502, obtained from Phillips Petroleum Company, and are thus called normalized die swell. The normalized die swell for other resins is reported as a ratio of the measured die swell

divided by the die swell of the Marlex 5502 standard which was blown on the same machine as a control run during at about the same time.

[0069] Bottle stress crack resistance was tested using ten 105 gram one gallon bottles made as described above on a Uniloy 2016 machine. The bottles were filled with a 10% Orvus-K detergent solution, capped, and placed in a 140 degrees ° F. hot room. Bottle failures were noted each day, and a 50% mean failure time was calculated for each set.

[0070] Extruder-capillary die melt fracture results were obtained using a 1 inch Killion single screw extruder (KL-100) fitted with a barrier screw. Capillary dies were attached to the end of the extruder with an adaptor. The adaptor was fitted with a Dynisco pressure transducer (model TPT432A) with a measurement range of 0-5000 psi, which was located just upstream of the entry to the capillary die. A two-piece capillary die was used. The first section consisted of a detachable orifice (entry angle 90 degrees and zero land length) with an entry diameter of 1 inch and a exit diameter of 0.15 inches. The second section consisted of a capillary with a 0.150 inch diameter and 2.25 inch land length (L/D=15).

[0071] A typical experiment would consist of extruding a polymer over a range of flow rates (screw RPM) using extruder, adaptor, and die temperature settings of 170° C. Using the capillary die (described earlier) fitted to the orifice die, the pressure in the adaptor, flow rate at various RPM were noted along with the RPM at which the onset of melt fracture occurred. Pressure drop versus flow rate data were also collected using the orifice die alone. Using standard calculations for flow through capillary dies, this data was then converted to true shear stress versus shear rate for each resin examined.

[0072] In some examples and some comparative examples the catalyst contained more than 1 weight percent chromium. In these cases extra chromium was added to the catalyst. This was accomplished by impregnating the catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

Examples 1-4

[0073] These polymers were prepared in a continuous, particle form process by contacting a catalyst system with monomers, which employed a liquid full 15.2 cm diameter pipe loop reactor having a volume of 23 gallons (87 liters), isobutane as the diluent, and occasionally some hydrogen to regulate the molecular weight of the product. The reactor was operated to have a residence time of 1.25 hours. The reactor temperature was varied over a range of 95° C. to 107° C., depending on the particular experiment, and the pressure was four Mpa (580 psi). At steady state conditions the isobutane feed rate was about 46 liters per hour, the ethylene feed rate was about 30 lbs/hr, and the 1-hexene feed rate was varied to control the density of the polymer product. Polymer was removed from the reactor at the rate of about 25 lbs per hour and recovered in a flash chamber. A Vulcan dryer was used to dry the polymer under nitrogen at about 60-80 degrees ° C.

[0074] Ethylene that had been dried over alumina was used as the monomer. Isobutane that had been degassed by

fractionation and dried over alumina was used as the diluent. Triethylboron or triethylaluminum was also sometimes used as a cocatalyst as indicated in the tables below.

[0075] A commercially available chromium catalyst system was purchased from the W. R. Grace Corporation. This chromium catalyst system was the 964 Magnapore Catalyst. It had a chromium content of about 1 weight percent based on the weight of the chromium catalyst system and about 5 weight percent titanium based on the weight of the total catalyst system. In Examples 1-3 extra chromium was added to the 964 Magnapore catalyst. This was accomplished by impregnating the catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

Comparative Examples 1-15

[0076] These polymers were prepared in the same reactor and under the same process parameters as described above.

[0077] Various catalysts and cocatalysts were used in these runs as indicated in the table and descriptions below.

[0078] In comparative example 1 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation. This chromium catalyst system was the 969 catalyst. Titanium was added by first drying the catalyst in dry nitrogen in a fluidized bed at 400-500° F., then lowering the temperature to 250° F.-400° F. during which time titanium isopropoxide liquid was added over a period of about one hour. The titanium isopropoxide evaporated while transported by the nitrogen in a ¾" stainless steel coil which introduced the vapor into the bottom of the bed. After all the titanium had been added, the nitrogen gas stream was replaced by dry air and the temperature was ramped up to the desired activation temperature in the usual fashion. The final catalyst composition was analyzed after activation.

[0079] In comparative examples 2 and 15 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation.

[0080] This chromium catalyst system was sold under the name of 965 Sylopor. This chromium catalyst was treated with titanium during activation as described earlier.

[0081] In comparative example 3 a chromium catalyst system was obtained from the W. R. Grace Corporation by spray drying a silica-titania-chromia hydrogel. This chromium catalyst system was called the SD Tergal catalyst.

[0082] In comparative example 4 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation known as HA-30. This chromium catalyst was treated with titanium during activation as described earlier.

[0083] In comparative examples 5 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation. This chromium catalyst system was sold under the name of 965 Sylopor.

[0084] In comparative example 6 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation. This chromium catalyst system was the 963 Magnapore catalyst. Extra chromium was added to the catalyst. This was accomplished by impregnating the

catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

[0085] In comparative example 7 and 8 a chromium catalyst system was obtained from the W. R. Grace Corporation, designated HPVSA indicating its relatively high pore volume and surface area compared to standard 969MS grades. Extra chromium was added to the catalyst. This was accomplished by impregnating the catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

[0086] In comparative examples 10 to 14 a commercially available chromium catalyst system was purchased from the W. R. Grace Corporation. This chromium catalyst system was sold under the name 964 Magnapore. In examples 10, 11, and 13, extra chromium was added to the catalyst. This was accomplished by impregnating the catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

[0087] In comparative example 9, a 964 Magnapore catalyst was produced except that no chromium was used in the process. Extra chromium was added to the catalyst. This was accomplished by impregnating the catalyst to incipient wetness or somewhat less, with a methanol solution of chromium (III) nitrate containing 0.5 g Cr/100 ml.

TABLE ONE

EXAMPLE NUMBERS	1	2	3	4
PROCESS CONDITIONS				
Surface area of Catalyst (m ² /g)	555	555	555	525
Pore Volume of Catalyst (cm ³ /g)	2.11	2.11	2.11	2.26
Weight Percent	5	5	5	5

TABLE ONE-continued

EXAMPLE NUMBERS	1	2	3	4
of Thionine Weight Percent of Chromium Activation Turpentine (° F)	3	3	2	1
Cocatalyst used Concentration of Cocatalyst (ppm)	TEB 2	TEB 4	TEB 2	TEB 2
POLYMER PROPERTIES				
Shaw Ratio (MLM/ML)	222	291	191	191
High Load Melt Index (g/10 min.)	17.8	17.4	21.0	17.2
Density (g/cm ³)	0.9352	0.9364	0.9354	0.9367
Heterogeneity Index (Mw/Mn)	33.5	43.9	38.1	38.6
ESCR Condition A (hours)	>1000	>1000	>1000	>1000
ESCR Condition B (hours)	300	261	317	429
Bottle ESCR (hours)	>700	>700	>700	>700
Die Swell (normalized)	0.97	1.02	1.02	1.08
Weight Swell (percent)	410	457	392	395
Melt Fracture (m-1)	2194	2169	2155	2200

[0088]

TABLE TWO

PROCESS CONDITIONS															
COMPARATIVE EXAMPLE NUMBERS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Surface area of Catalyst (m ² /g)	300	400	510	500	400	300	577	300	539	530	533	300	530	500	400
Pore Volume of Catalyst (cm ³ /g)	1.7	1	0.85	1.5	1	2.42	2.21	2.5	2.12	2.26	2	2.2	2.26	2.2	1
Weight Percent of Titanium	3	5	5	3.6	3.6	2.5	0	0	5	5	5	5	5	5	5
Weight Percent of Chromium	1	1	1	1	1	2	2	2	0.2	2	2	1	2	1	1
Activation Temperature (° F)	1250	1200	1100	1100	1100	1000	1000	1200	1100	1100	1500	1100	1100	1000	1100
Catalyst used	TB8	TB8	TB8	None	TB8	TB8	TB8	TB8	TB8	TB8	None	None	TEA	None	None
Concentration of Catalyst (ppm)	6.2	0.5	8	0	2.1	2	2	2	5	2	0	0	2	0	0
Shear Rate (RLM/MI)	128.6	108	—	90.5	81	174.5	137.5	156.9	100	248	87	48	139	63.1	86
High Load Melt Index (g/10 min.)	37.3	25	—	18.3	22.9	19.2	19.3	15.7	4	14.9	20.1	21.4	16.7	27	28.3
Density (g/cm ³)	0.958	0.956	—	0.958	0.955	0.955	0.954	0.954	0.958	0.955	0.959	0.956	0.955	0.958	0.961
Heterogeneity Index	21	—	—	—	16.8	24.7	14.4	14.1	20.9	41.9	12.4	—	30.2	16.3	13.9
ESCR Condition A (mm)	200	250	—	100	170	>1000	395	248	—	>1000	209	283	304	116	69
ESCR Condition B (mm)	50	100	—	51	93	341	73	61	—	170	45	121	102	46	44
Beale ESCR (mm)	180	—	—	150	245	>700	>700	508	—	>700	—	575	>700	143	—
D/S Swell (normalized)	1.30	1.03	—	1.07	1.22	1.18	1.16	1.05	—	1.12	1.48	1.24	1.24	1.00	1.26
Weight Swell (percent)	—	—	—	—	—	436	375	349	—	434	353	—	330	—	—
Melt Fracture (no-1)	—	—	—	—	601	2227	2241	2437	—	2196	1014	—	1024	544	601

It should be noted that Comparative Example Three produced no polymer. Additionally, it should be noted that "—" means that no measurement was conducted. It should be noted that even though Comparative Example 16 is considered a comparative run due to the values obtained for ESCR (10) and normalized die swell, these values are considered to be within the experimental error of these measurements.

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That which is claimed is:

1. A process comprising polymerizing ethylene, or polymerizing ethylene and at least one other olefin, to produce a polymer,

wherein said polymerizing is conducted in a polymerization zone, and

wherein said polymerizing is conducted using a catalyst and a cocatalyst, and

wherein said catalyst comprises chromium on a support, and

wherein the amount of said chromium on said support is from about 0.5 to 5 weight percent, and

wherein said support comprises silica, in major part, and

wherein the amount of titanium in said support is greater than about 3.5 to about 10 weight percent based on the weight of said support, and

wherein said support has a surface area from about 400 to about 800 square meters per gram, and

wherein said support has a pore volume from about 1.8 to about 4 cubic centimeters per gram, and

wherein said catalyst has been activated at a temperature in the range of about 600° F. to about 1100° F. in the presence of an oxidizing ambient, and

wherein said cocatalyst is an organoboron compound.

2. A process according to claim 1 wherein said polymerizing is conducted under slurry polymerization conditions.

3. A process according to claim 2 wherein said polymerizing is conducted at a temperature from about 195° F. to about 225° F.

4. A process according to claim 3 wherein said polymerizing is conducted at a pressure from about 500 psia to about 700 psia.

5. A process according to claim 4 wherein said amount of said chromium on said support is in the range of about 1 to about 4 weight percent.

6. A process according to claim 5 wherein said amount of said titanium on said support is in the range of about 4 to about 8 percent.

7. A process according to claim 6 wherein said support has a surface area from about 425 to about 700 square meters per gram.

8. A process according to claim 7 wherein said support has a pore volume from about 1.9 to about 3 cm³/g.

9. A process according to claim 7 wherein said catalyst is activated in the presence of an oxidizing ambient at a temperature from about 700° F. to less than 1100° F.

10. A polymer produced in accordance with claim 1.

11. A polymer produced in accordance with claim 9.

* * * * *

PATENT COOPERATION TREATY

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210481US01

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCTUS2005/009889

International filing date (day/month/year)
24.03.2005

Priority date (day/month/year)
22.04.2004

International Patent Classification (IPC) or both national classification and IPC
C08F10/00, C08F4/22

Applicant
CHEVRON PHILLIPS CHEMICAL COMPANY LP

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of three months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office
D-80299 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4485

Authorized Officer

Balmer, J-P

Telephone No. +49 89 2399-8520



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

319/196
International application No.
PCT/US2005/009669

Box No. I Basis of the opinion

1. With regard to the language, this opinion has been established on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).
2. With regard to any nucleotide and/or amino acid sequence disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
☐ a sequence listing
☐ table(s) related to the sequence listing
 - b. format of material:
☐ in written format
☐ in computer readable form
 - c. time of filing/furnishing:
☐ contained in the international application as filed.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

319 197
International application No.
PCT/US2005/009669

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 38-54, 60-74, 76

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for the whole application or for said claims Nos. 38-54, 60-74, 76

☐ the nucleotide and/or amino acid sequence listing does not comply with the standard provided for in Annex C of the Administrative Instructions in that:

the written form

☐ has not been furnished

☐ does not comply with the standard

the computer readable form

☐ has not been furnished

☐ does not comply with the standard

☐ the tables related to the nucleotide and/or amino acid sequence listing, if in computer readable form only, do not comply with the technical requirements provided for in Annex C-bis of the Administrative Instructions.

☐ See separate sheet for further details

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2005/009669

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA206) to pay additional fees, the applicant has:
- ☒ paid additional fees.
 - ☐ paid additional fees under protest.
 - ☐ not paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is
- ☐ complied with
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
 - ☒ the parts relating to claims Nos. 1-34

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	1-37,55-59,75
Inventive step (IS)	Yes: Claims	
	No: Claims	1-37,55-59,75
Industrial applicability (IA)	Yes: Claims	1-37,55-59,75
	No: Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/US2005/009669

Re Item III.

According to point IV below, only claims 1-34, 55-59, 75 have been searched.
Therefore with regard to Rules 66.1(e) and 66.1 bis (a) PCT this written opinion will be drafted according to the searched claims, namely 1-34 of the present application.

Re Item IV.

The separate inventions or groups of inventions are:

Claims 1-34

A catalyst according to claim 1 and its use according to claim 10.

A method to prepare a supported catalyst according to claim 11.

A method of polymerizing an olefin with a chromium catalyst according to claim 25 and the polymer obtained therewith.

Claims 35-37, 55-59, 75

A polymer composition according to claim 35, its use and article made therewith.

Claims 38-39, 55-59, 75

A polymer composition according to claim 38 its use and article made therewith.

Claims 40-41, 55-59, 75

A polymer composition according to claim 40, its use and article made therewith.

Claims 42-54

A polymer composition according to claim 42

Claims 60-64, 75, 76

A copolymer of ethylene and hexene according to claim 60, its use and article made therewith.

Claims 65-69, 75, 76

A polymer according to claim 65, its use and article made therewith.

Claims 70

A polymer according to claim 70.

Claims 71-72, 75, 76

A polymer according to claim 71, its use and article made therewith.

Claims 73-76

A polymer according to claim 73, its use and article made therewith.

They are not so linked as to form a single general inventive concept (Rule 13.1 PCT) for the following reasons:

The present application is directed to a chromium based catalyst system using a specific type of cocatalyst, namely a non-transition metal Cp compound (CpLi and Cp2Mg are exemplified).

This in order to prepare polyolefins and in particular copolymers of ethylene and hexene, having a broad molecular weight distribution.

This aspect of the invention is clearly shown in the claims 1-34.

But in addition to the latter claims, the applicant filed a set of independent claims of polymers or polymer compositions (not even restricted to polyolefin as it should be according to the description), which are not related by a single inventive concept.

As example, claim 36 discloses a HLMI range from 1 to 10 g/10min, whereas claim 60 discloses a HLMI range from 15 to 50 g/10min.

These polymers disclosed in these different claims aim to different applications and are linked together simply by the fact that they are "polymers" (or "polymer compositions") which is not an inventive concept as such.

Therefore as the claims 35-76 are not clearly linked to the specific polymerization process using the specific chromium catalyst system as disclosed in the description, the present invention lacks non unity a priori according to the set of inventions disclosed above.

Remark

Novelty and inventiveness of a product by process can be acknowledged when the product as such cannot be characterized otherwise than by the process to prepare it.

On the other side the claimed products according to claims 34-76 have to be novel and inventive as such, independently from the process to prepare them.

Re item V.

1. Reference is made to the following documents:

D1: US-A-3 071 493
D2: WO-A-96/23006
D3: US-A-5 418 200
D4: HEINEMANN, OLIVER ET AL: "Bis(indenyl) chromium is a Dimer"
ORGANOMETALLICS , 15(26), 5462-5463 CODEN: ORGND7; ISSN: 0276-
7333, 1996, XP002335284
D5: LIANG, YUANFENG ET AL: "Constrained Geometry Chromium Catalysts for
Olefin Polymerization" ORGANOMETALLICS , 15(25), 5284-5286 CODEN:
ORGND7; ISSN: 0276-7333, 1996, XP002335285
D6: US-A-2001/004663
D2: US-A-2002/013432
D3: US-A-2003/199648

2. The document D1 discloses a metal plating process using a bimetallic organometallic composition which, as in the examples XXIII and XXIV comprises an aluminum(Cp) part and a Cr(CO)₃ part.

These compounds corresponds to the ones as defined in the present claims 1,2, 7-9, 11.12.

— Accordingly D1 is novelty destroying for the present claims 1,2, 7-9, 11.12 with regard to Article 33(2) PCT.

3. The present invention discloses a catalyst system comprising a chromium catalyst which is contacted to a cocatalyst as disclosed in present claim 1.

According to the description presumably the cocatalyst, which is considered as very reactive, will be combined to the chromium atom similarly to the preparation of a Cr(Cp) compound.

Therefore it is strongly assumed, unless the applicant can bring the evidence of the contrary, that the aim of present claim 1 and of the description is in fact the preparation, may be in situ, of a Cr(Cp) catalyst which is already known from the prior art, see D2-D4. In particular D2 discloses in the examples 2-5 such complexes of a chromium atom linked to Cp's and to a non-transition metal (i.e. Lithium).

Therefore, independently from the wording used by the applicant in its invention "cocatalyst" the documents D2-D5 disclose catalyst systems identical to the ones presently disclosed.

Therefore present claims 1-34 are not novel or do not involve an inventive step over D2-D5 with regard to Article 33(2 + 3) PCT.

4. The document D6 discloses in example 9 a copolymer of ethylene and hexene prepared with a chromium-based catalyst wherein both melt index MI and HLMI are within the scope of the ranges disclosed in present claims 35-37.

The molecular weight Mw is not explicitly mentioned, only the heterogeneity index, i.e. the polydispersity which is rather high.

The document D7 discloses in the examples 1,2,6 a copolymer of ethylene and hexene similarly to D6.

The document D8 discloses similar copolymers as in D6 and D7, in particular the examples H-M wherein the Mw is above 600 000 and the HLMI is between 1 and 10 g/10min. The melt index is not mentioned, only the HLMI.

Since the ratio HLMI/MI (i.e. MFR = melt flow ratio) in D6 and D7 and the ratio Mw/Mn (i.e. polydispersity) in D8 are very high it is strongly assumed that the Mw in D6, D7 and the MI in D8 will be within the scope of present claims 35-37. This is supported by the sole inventive example of the present application being within the scope of claims 35-37, namely run 16 of table 3, which shows a high polydispersity together with a high MFR.

Accordingly unless the applicant can unambiguously demonstrate that D6-D8 are not within the scope of the present claims 35-37, the examining division will consider D6-D8 as novelty destroying of present claims 35-37, 55-59,75 with regard to Article 33(2) PCT.

Re Item VIII

1. In example 1, p.16, l.13 there is written "runs 2 and 3 were run using different amounts of the", this is not correct.
Further on l.17-18 the effect of the absence of hydrogen is not demonstrated, according to table 1.
2. In table 2, runs 5 and 6 show a reduction of the PDI when hydrogen is introduced during the polymerization, this is strange. Explanation is requested.
Further, run 12 does not show any analysis of the polymer, despite the fact that this is the sole run without the use of hydrogen....Why ????
3. On page 13 the Charpy measurement of energy is mentioned at 0°C, but in table 7 this is done at 23°C why ???? What is the standard?
4. On table 7 the measurement of the shear rate is somehow very high compared to the

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**WRITTEN PRIORITY
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/US2005/009669

prior art, nearly 5 times higher. There must be an error somewhere. Also the definition of this measurement is not clear for the skilled man to be reproduced correctly.

5. Example 6 relates to figure 2, but in example 6 $\text{Mg}(\text{Cp})_2$ is used, contrary to what is disclosed in figure 2 (CpLi) ????
6. In table 6, runs 10 and 11 show a rather bad Charpy performance, why ???
Further the Charpy energy should be expressed with J/m^2 and not J/m isn't it ???
7. According to the examples the chromium catalyst is always supported and with a reduced oxidation state, so should it be mentioned in the claims as well, as the applicant could not prove anything for his invention for other chromium type catalysts.....
8. Certain claims (see claims 35,36,57 in particular) recite only a polymer or a polymer composition as such, together with different parameter like MI or HLMI. Depending of the type of polymer meant the MI or HLMI method used will differ, for example in temperature or load:
Accordingly as matter of clarity the applicant should draft his claims in order to define clearly the method used to determine the characteristics in relation to the type of polymer covered by the said claim.
In all cases the polymer composition of claim 35 should be reduced at least to a polyolefin composition which is what was achieved in the description.
9. The units used in particular on page 23 and 25 should be in accordance with the international unit system.

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PCT REQUEST

Original (for SUBMISSION)

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form PCT/RO/101 PCT Request	
0-4-1	Prepared Using	PCT-SAFE [EASY mode] Version 3.50 (Build 0002.169)
0-5	Petition The undersigned requests that the present International application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	Applicant's or agent's file reference	210481PCT
I	Title of invention	CATALYST SYSTEMS FOR PRODUCING POLYMERS HAVING BROAD MOLECULAR WEIGHT DISTRIBUTIONS AND METHODS OF MAKING THE SAME
II	Applicant	
II-1	This person is	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	CHEVRON PHILLIPS CHEMICAL COMPANY LP
II-5	Address	10001 Six Pines Drive The Woodlands, TX 77380 United States of America
II-6	State of nationality	US
II-7	State of residence	US
III-1	Applicant and/or Inventor	
III-1-1	This person is	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	MCDANIEL, Max P.
III-1-5	Address	1601 Melmart Drive Bartlesville, Oklahoma 74006 United States of America
III-1-6	State of nationality	US
III-1-7	State of residence	US

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PCT REQUEST

Original (for SUBMISSION)

III-2	Applicant and/or Inventor	
III-2-1	This person is	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	BENHAM, Elizabeth A.
III-2-5	Address	9310 Katie Grace Circle Spring, Texas 77379 United States of America
III-2-6	State of nationality	US
III-2-7	State of residence	US
III-3	Applicant and/or Inventor	
III-3-1	This person is	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	SECORA, Steven J.
III-3-5	Address	5932 Martin Lane Bartlesville, Oklahoma 74006 United States of America
III-3-6	State of nationality	US
III-3-7	State of residence	US
III-4	Applicant and/or Inventor	
III-4-1	This person is	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	JENSEN, Michael D.
III-4-5	Address	2008 Skyline Place Bartlesville, Oklahoma 74006 United States of America
III-4-6	State of nationality	US
III-4-7	State of residence	US
III-5	Applicant and/or Inventor	
III-5-1	This person is	applicant and inventor
III-5-2	Applicant for	US only
III-5-4	Name (LAST, First)	COLLINS, Kathy S
III-5-5	Address	3915 Silver Lake Drive Bartlesville, Oklahoma 74006 United States of America
III-5-6	State of nationality	US
III-5-7	State of residence	US

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PCT REQUEST

Original (for SUBMISSION)

IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	BROWN, Kimberly L.
IV-1-2	Address	Chevron Phillips Chemical Company LP 10001 Six Pines Drive The Woodlands, TX 77380 United States of America
IV-1-3	Telephone No.	832-813-4331
IV-1-4	Facsimile No.	832-813-6060
IV-1-5	Agent's registration No.	48,698
V	DESIGNATIONS	
V-1	The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.	
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	22 April 2004 (22.04.2004)
VI-1-2	Number	10/829,550
VI-1-3	Country	US
VI-2	Priority claim of earlier national application	
VI-2-1	Filing date	22 April 2004 (22.04.2004)
VI-2-2	Number	10/829,842
VI-2-3	Country	US
VI-3	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1, VI-2
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)

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PCT REQUEST

Original (for SUBMISSION)

VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	5	✓
IX-2	Description	31	-
IX-3	Claims	7	-
IX-4	Abstract	1	✓
IX-5	Drawings	3	-
IX-7	TOTAL	47	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-SAFE physical media	-	✓
IX-18	Figure of the drawings which should accompany the abstract		
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative		
X-1-1	Name (LAST, First)	BROWN, Kimberly L.	
X-1-2	Name of signatory		
X-1-3	Capacity		

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PCT REQUEST

Original (for SUBMISSION)

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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PCT (ANNEX - FEE CALCULATION SHEET)

Original (for SUBMISSION)

(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only		
0-1	International Application No.		
0-2	Date stamp of the receiving Office		
0-4	Form PCT/RO/101 (Annex) PCT Fee Calculation Sheet Prepared Using	PCT-SAFE [EASY mode] Version 3.50 (Build 0002.169)	
0-6	Applicant's or agent's file reference	210481PCT	
2	Applicant	CHEVRON PHILLIPS CHEMICAL COMPANY LP	
12	Calculation of prescribed fees	fee amount/multiplier	Total amounts (USD)
12-1	Transmittal fee T	⇒	300
12-2-1	Search fee S	⇒	1920
12-2-2	International search to be carried out by	EP	
12-3	International filing fee (first 30 sheets) I1	1134	
12-4	Remaining sheets	17	
12-5	Additional amount (A)	12	
12-6	Total additional amount I2	204	
12-7	I1 + I2 = I	1338	
12-12	EASY Filing reduction R	-81	
12-13	Total international filing fee (I-R)	⇒	1257
12-14	Fee for priority document		
	Number of priority documents requested	2	
12-15	Fee per document (D)	20	
12-16	Total priority document fee: P	⇒	40
12-17	TOTAL FEES PAYABLE (T+S+I+P)	⇒	3517
12-18	Mode of payment	authorization to charge deposit account	
12-20	Deposit account instructions		
	The receiving Office	United States Patent and Trademark Office (USPTO) (RO/US)	
12-20-1	Authorization to charge the total fees indicated above	✓	
12-20-2	Authorization to charge any deficiency or credit any overpayment in the total fees indicated above	✓	
12-20-3	Authorization to charge the fee for priority document	✓	
12-21	Deposit account No.	50-1629	
12-22	Date	24 March 2005 (24.03.2005)	
12-23	Name and signature	Kimberly L. Brown <i>Kimberly L. Brown</i>	