



Industria y Comercio
SUPERINTENDENCIA

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PCT

SOLICITUD

PATENTE DE INVENCION

04-1078

21 EXPEDIENTE N°

54 TÍTULO

REDUCCION DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO CATALITICO FLUIDO

51 CLASIFICACIÓN INTERNACIONAL

71 SOLICITANTE

W.R. GRACE & CO-CONN. Y EXXONMOBIL RESEARCH & ENGINEERING

DOMICILIO

COMPANY

Columbia, Maryland y Fairfax, Virginia Estados Unidos de América
respectivamente.

74 APODERADO

EMILIO FERRERO

Código 1092

22 BOGOTÁ, D C



PETITORIO



04 001078 00

SUPERINDUSTRIA Y COMERCIO
Radicación 84001078 00000000 Folios 184 m
Fecha (AMB) 2004-01 08 17 06 14
Trámite 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia 2020 DIVISION DE NUEVAS CREACIONES

FORMULARIO UNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

1 SOLICITUD DE		
☒ Patente de Invención ☐ Patente de Modelo de Utilidad		
☐ Capítulo I ☒ Capítulo II		
2 SOLICITANTE (71)	Nombre W R GRACE & CO CONN Y EXXONMOBIL RESEARCH & ENGINEERING COMPANY sociedades constituidas y existentes bajo las leyes de los Estados de Conneticut y Virginia Estados Unidos de América respectivamente Direccion 7500 Grace Drive Columbia Maryland 21046 Estados Unidos de América y 3225 Gallows Road Fairfax Virginia 22037 Estados Unidos de América respectivamente Domicilio Columbia Maryland Estados Unidos de America y Fairfax Virginia Estados Unidos de América respectivamente	IDENTIFICACION C C ☐ NIT ☐ C E ☐ Otro ☐ Cual _____ Numero _____
3 REPRESENTANTE O APODERADO	Nombre EMILIO FERRERO Dirección Carrera 4ª No 72 35 Teléfono 347 36 11 Fax 217 92 11 E mail clientes@camvp.com Domicilio Bogotá Colombia	IDENTIFICACION C C ☒ NIT ☐ C E ☐ Otro ☐ Cual _____ Numero <u>438 019</u> T P <u>31 929</u>
4 INVENTOR (ES) (72)	1 Terry G ROBERIE 2613 Liter Drive Ellicott City Maryland 21046 Estados Unidos de América 2 Ranjit KUMAR 6412 Tara Place Clarksville Maryland 21029 Estados Unidos de América 3 Wu-Cheng CHENG 10308 Paddington Court Ellicott City Maryland 20142 Estados Unidos de América 4 Xinjin ZHAO 1731 Cattail Meadows Drive Woodbine Maryland 21797 Estados Unidos de América 5 Michael S ZIEBARTH 12071 Little Patuxent Parkway Columbia Maryland 21046 Estados Unidos de América 6 Nazeer BHORE 10509 Tyler Terrace Potomac Maryland 20854 Estados Unidos de América	

5	PCT (86)		
Solicitud Internacional No <u>PCT/US02/23243</u>		Fecha <u>Julio 9 de 2002</u>	
Publicación Internacional No <u>WO 03/006578 A3</u>		Fecha <u>Enero 23 de 2003</u>	

6	Titulo (54) <u>REDUCCION DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO CATALITICO FLUIDO</u>		
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7	Clasificacion Internacional (51) <u>C10G 11/05</u>		
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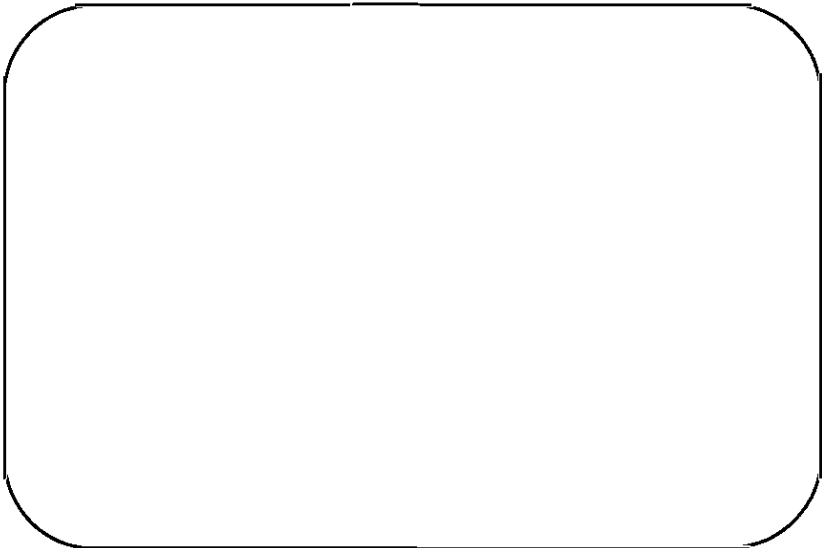
8	Prioridad	(33) Pais de Origen	(32) Fecha	(31) Numero de Solicitud
	SI ☒ NO ☐	<u>US</u>	<u>10 de Julio de 2001</u>	<u>09/901 939</u>

9	Comprobante de pago No <u>03-85 522</u> Fecha <u>Noviembre 24 de 2003</u>		
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10	Anexos		
☒	Comprobante de pago de la tasa de presentación de la solicitud por \$ 400 000 oo		
☐	Comprobante de pago por reivindicación de prioridad		
☒	Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica		
☒	Poderes si fuere el caso (Poder de WR GRACE & CO –CONN)		
☐	Documento de cesión del inventor al solicitante o a su causante		
☒	Declaraciones (Regla 4 17(ii))		
☒	Copia de la solicitud internacional (Resumen descripción reivindicaciones dibujos)		
☒	Traduccion de la solicitud internacional al castellano (Resumen descripción reivindicaciones dibujos)		
☐	Copia del examen preliminar efectuado por la IPEA		
☐	Traduccion del examen preliminar efectuado por la IPEA		
☐	De ser el caso copia del contrato de acceso		
☐	De ser el caso documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas		
☐	De ser el caso certificado de depósito del material biológico		
☐	Arte final 12x12		
☐	De ser el caso información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante relacionadas parcial o totalmente con la invención de esta solicitud		
☐	Otros		

11

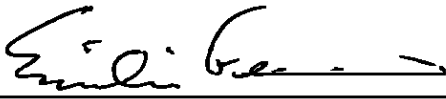
FIGURA CARACTERISTICA



12

Solicito la concesión de la patente

NOMBRE EMILIO FERRERO

FIRMA 

C C 438 019 de Usaquén T P 31 929

00002

MRE/lms



The State of Maryland

Office of the Secretary of State

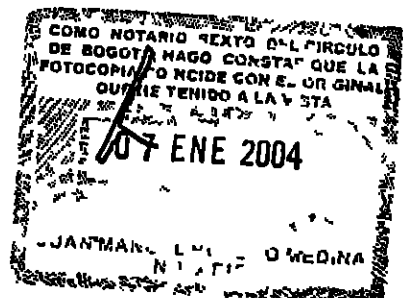
Apostille

(Convention de La Haye du 5 Octobre 1961)

- 1 Country United States of America
This public document
2 has been signed by Suzanne Mensh
3 acting in the capacity of Clerk of the Circuit Court for Baltimore County
4 bears the seal/stamp of the Circuit Court for Baltimore County

Certified

- 5 at Annapolis, Maryland
6 the 9th day of October, 2002
7 by The Secretary of State of Maryland
8 Seal



- 10 Signature

John J. Willis

Secretary of State

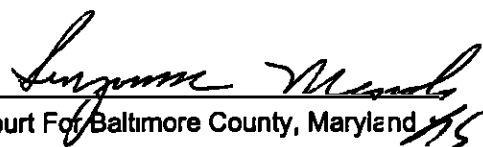
No 86826



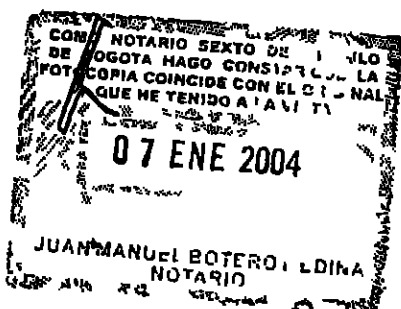
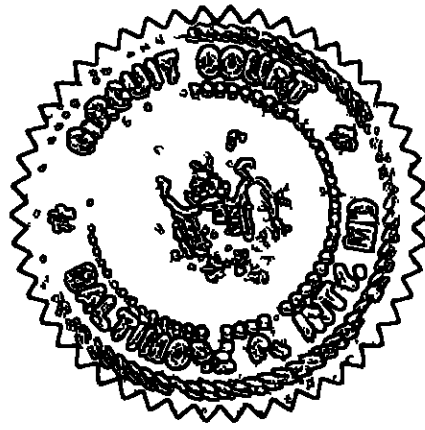
State of Maryland, Baltimore County, to-wit:

I **Suzanne C. Mensh** Clerk of the Circuit Court for Baltimore County, Maryland a court of record
do hereby certify that **KIMBERLY A. SAUTER**
was a commissioned/appointed and qualified a Notary Public commencing on **07/31/2002** In Testimony

Whereof I have hereunto set my hand and affixed the seal of the Court this 9th day of October 2002



Clerk of the Circuit Court For Baltimore County, Maryland



CAVELIER

ABOGADOS
EDIFICIO SISKI
CARRERA 4a N 72-35
BOGOTA 8 COLOMBIA

181

Representación y Poder con autenticación notarial y Apostille para patentes, modelos de utilidad, diseños industriales, marcas de fábrica, nombres comerciales, enseñas, nombres de dominio, lemas comerciales, licencias

Representation and Power-of-Attorney with notarial authentication and Apostille for patents, utility models, industrial designs, trademarks, commercial names, trade emblems, domain names, slogans, licenses

REPRESENTACION Y PODER**REPRESENTATION AND POWER-OF-ATTORNEY**

Yo (nosotros), abajo firmado (s)/I (we), the undersigned

W. R. GRACE & CO -CONN.

domiciliado (s) en/or 7500 Grace Drive,

Columbia, Maryland 21044, U S.A

por el presente nombramos a EMILIO FERRERO tpa 31929 GONZALO PERDOMO tpa 831 LUZ CLEMENCIA DE PAEZ tpa 23555 y GERMAN CAVELIER, tpa 832, domiciliados en la Carrera 4a N° 72 35 Bogotá Colombia en obediencia a lo dispuesto en el parágrafo 1o del Artículo 543 del Código de Comercio el primero como principal y los demás como suplentes en su orden como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero o el tercero al segundo En tales casos el representante principal, o el primero o segundo suplente, en su caso, o ambos declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Publico en Colombia, o por Notario u otro Funcionario Publico o Cónsul de Colombia, en el extranjero y si se tratare de impedimento con el certificado respectivo Si alguno de los nombrados faltare definitivamente el siguiente tomará su lugar Cuando cesare la ausencia o impedimento del representante principal o de su primero o segundo suplentes en su caso podrán ejercer la representación en su orden uno u otros segun el caso asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero segundo o tercer suplente en su caso Además, confiero (conferimos) poder a los abogados arriba nombrados para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas ejerzan o no jurisdicción especial o ante la de orden administrativo contencioso administrativo y judicial así como los tribunales de arbitramento en todo lo concerniente a los siguientes asuntos a) Obtención de patentes de invención modelos de utilidad y diseños industriales el registro de marcas de fábrica colectivas defensivas, de servicio lemas comerciales, nombres comerciales enseñas, nombres de dominio, variedades vegetales y denominaciones de origen su renovación traspaso cambio de nombre o domicilio cancelación voluntaria, y el registro de licencias de uso de esos derechos b) Las acciones de competencia desleal protección del consumidor oposiciones u observaciones cancelación administrativa y judicial nulidad medidas cautelares concesión de licencias la tutela la protección de secretos industriales y en general los juicios civiles penales administrativos o contencioso administrativos relacionados con

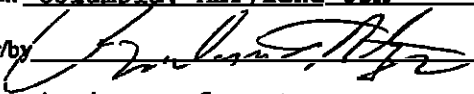
in due compliance with the terms of paragraph 1st of article 543 of the Commercial Code do hereby appoint EMILIO FERRERO tpa 31929 GONZALO PERDOMO, tpa 831, LUZ CLEMENCIA DE PAEZ, tpa 23555 and GERMAN CAVELIER tpa 832 domiciled at Carrera 4a N° 72 35 Bogotá, Colombia the first as principal and the others as alternates in the order of their appointment as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment The same rule will apply when the second alternate representative is to replace the first one or when the third is to replace the first or second alternates in their turn or both of them, second In such cases, the principal representative, or the first or second alternates in their turn or both of them, shall state their intention not to act as representatives through a declaration given before a Notary Public in Colombia or before a Notary or another Public Official or a Colombian Consul abroad and in case of impediment the appropriate certificate shall suffice If any of the appointees were to be definitely absent the following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternate in their turn ceases the representation can be taken again in their sequence by the principal the first or second alternate depending on case and the mere fact or its exercise will suffice The exercise of the representation by the first second or third alternates in their turn shall end at such time In addition, we grant a Power of Attorney in favor of the above named attorneys at law so that they may obtain the protection of my (our) industrial property and against unfair competition for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons with or without jurisdiction specially those administrative, administrative contentious, and judicial as well as before Arbitration Court, in all matters concerning the following a) Obtainment of patents, utility models and industrial designs the registration of trademarks, collective, defensive and service marks slogans commercial names trade emblems domain names vegetal varieties and denominations of origin its renewal assignment change of name or domicile voluntary cancellation and the registration of licenses of use of the above rights b) Actions of unfair competition protection to the consumer oppositions or observations administrative or Court cancellation nullity infringement granting of licenses the action for writ mandamus the protection of trade secrets and in general the civil penal and administrative suits relating to those rights actions and suits

estos derechos acciones y procesos que promovamos o se nos promuevan Y para que en todos los asuntos arriba determinados puedan sustituir este mandato transigir conciliar admitir los hechos del proceso desistir cancelar recibir renunciar y ratificar los actos de agentes oficiosos

instituted by me (us) or against me (us) And that in all the above matters they may substitute this Power of Attorney compromise conciliate admit the facts of the case desist cancel receive resign and ratify acts done by representatives without a power of attorney

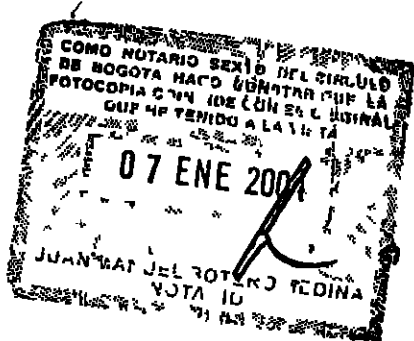
Dado y firmado hoy/Given and signed this October 3, 2002

en/in Columbia, Maryland USA

por/by 

Assistant Secretary

Firma W. R. Grace & Co.-Conn. Signature



CERTIFICADO NOTARIAL (INDIVIDUO)

A los 3 dias del mes de Octubre
de 2002, ante mi Notario Publico o Funcionario Autorizado
de Baltimore County, Maryland
compareció(eron) personalmente Robert A. Maggio
a quien(es) yo fe de conocer y me consta que es(son) la(s)
persona(s) firmante(s) del documento que precede, y quien(es)
tiene(n) capacidad legal para otorgarlo

Notario Publico o Funcionario Autorizado - Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy 3 de Octubre de 2002
Compareció(eron) ante mi
Robert A. Maggio
quien(es) conozco personalmente y que firma(n) este
documento en representacion de la Sociedad/compañia
denominada W. R. GRACE & CO.-CONN.

Certifico

- 1 Que he visto los siguientes documentos *

Certificado de Constitución
Connecticut, 18 Nov, 1899

- 2 Que dichos documentos prueban lo siguiente

- 2.1 Que W. R. GRACE & CO -CONN

es una Sociedad/Compañia legalmente constituida y existente
de acuerdo con las leyes del Estado de Connecticut
Estados Unidos de América

- 2.2 Que el domicilio de dicha Sociedad/Compañia es 7500 Grace Drive,
Columbia, Maryland 21044 E U A

- 2.3 Que el objeto u objetos para los cuales se otorga el presente
poder están comprendidos dentro del objeto social de la
mencionada Sociedad/Compañia

- 2.4 Que el(los) Sr (Sres) Robert A. Maggio
está(n) autorizado(s) para otorgar el presente Poder

Ciudad Columbia

Estado Maryland

Hoy 3 de Octubre de 2002

Notario Publico o Funcionario Autorizado - Notary Public or Attesting Official

* Los documentos deben identificarse con fecha y origen

NOTARIAL CERTIFICATE (INDIVIDUAL)

On this 3rd day of October
2002 before me, a Notary Public or Attesting Official of
Baltimore County, Maryland
personally appeared Robert A. Maggio

to me known, and known to me to be the person(s) who
executed that foregoing document, and who has(have) legal
capacity to execute it

Kimberly A. Sauter
Kimberly A. Sauter, Notary Public

NOTARIAL CERTIFICATE (CORPORATION)

On this 3 day of October 2002
appeared before me
Robert A. Maggio
who(m) I know personally and who(m) signed this document as
representative(s) of the Corporation/Company named
W. R. GRACE & CO.-CONN

I certify

- 1 That I have seen the following documents *

CERT of UNCOND
Connecticut, Nov 18, 1899

- 2 That the above documents duly prove the following

- 2.1 That W. R. GRACE & CO -CONN

is a Corporation/Company legally constituted and in existence
in accordance with the laws of State of Connecticut,
United States of America

- 2.2 That the domicile of said Corporation/Company is 7500 Grace Drive,
Columbia Maryland 21044, U.S.A.

- 2.3 That the purpose or purposes for which the present Power
of Attorney is granted are comprised within the corporation
purposes set forth in the Charter of the mentioned
Corporation/Company

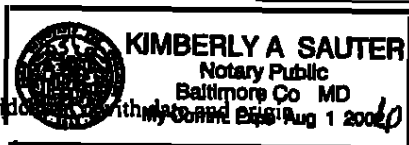
- 2.4 That Mr (Messrs) Robert A. Maggio
is(are) authorized to grant the present Power of Attorney

City Columbia

State Maryland

This 3rd day of October 2002

Kimberly A. Sauter



* Documents must be identified with date and origin

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1Country

This public document

2has been signed by

3acting in the capacity of

4bears the seal/stamp of

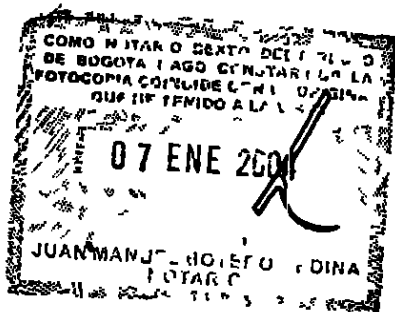
Certified

5at6 the

7by

8No

9Seal/stamp10 Signature

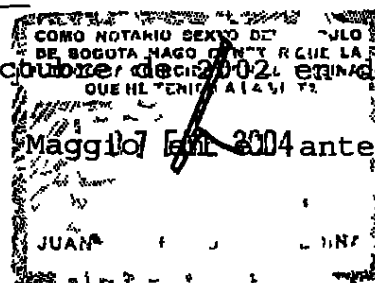


TRADUCCIÓN OFICIAL No 09 04/03 realizada por Diego Vargas, Traductor Oficial, Resolución No 0001 de 1999 del Ministerio de Justicia y registrado ante el Ministerio de Relaciones Exteriores de Colombia

A continuación se traducen los sellos y legalizaciones de un documento de Representación y Poder escrito en inglés y español por medio del cual el W R GRACE & CO -CONN domiciliado en el 7500 Grace Drive, Columbia, Maryland 21044, Estados Unidos de América otorga derechos de Representación y Poder a los Doctores EMILIO FERRERO, tpa 31929, GONZALO PERDOMO, tpa 831, LUZ CLEMENCIA DE PÁEZ, tpa 23555 y GERMÁN CAVELIER, tpa 832, domiciliados en la Carrera 4 No 72-35, Bogotá, Colombia

Dado y firmado hoy 3 de octubre de 2002
en Columbia, Maryland, Estados Unidos de América
por Firma Ilegible
Subsecretario
Firma W R Grace & Co -Conn Firma

CERTIFICADO NOTARIAL (INDIVIDUO) del 3 de octubre de 2002 en donde se autentica la firma del Señor Robert A Maggio en 2004 anterior documento



Firma Ilegible

Kimberly A Sauter, Notario Público

CERTIFICADO NOTARIAL (SOCIEDAD) en donde se certifica la firma anterior del Señor Robert A Maggio en representación de la compañía

DIEGO F. VARGAS

TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL INGLÉS - INGLÉS ESPAÑOL

RES 0001 DE ENERO 4 DE 1999

MINISTERIO DE JUSTICIA

W R GRACE & CO -CONN y se certifica que la anterior es una
compañía legalmente constituida y existente de conformidad con las
leyes del Estado de Connecticut, Estados Unidos de América, y que
está domiciliada en el 7500 Grace Drive, Columbia, Maryland 21044,
Estados Unidos de América Adicionalmente se certifica que el Señor
Robert A Maggio está autorizado para otorgar el presente Poder
Dado y firmado en Columbia, Estado de Maryland el 3 de octubre de
2002

Notario Público o Funcionario Autorizado Firma Ilegible

Sello

KIMBERLY A SAUTER

Notario Público

Condado de Baltimore, MD

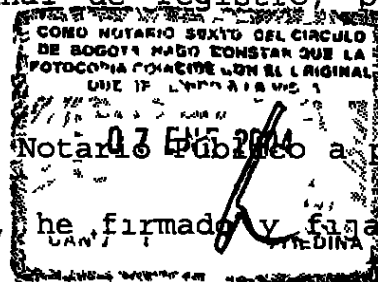
Mi Comisión vence el 1 de Agosto de 2004



Estado de Maryland, Ciudad de Baltimore, a saber

MARYLAND

Yo, Suzanne C Mensh, Secretario del Tribunal de Circuito para el
Condado de Baltimore, Maryland, un tribunal de registro, por el
presente certifico que KIMBERLY A SAUTER
fue comisionado/nombrado y calificado como Notario Público a partir
del 07/31/2002 En Testimonio de lo cual, he firmado y fijado el
sello del Tribunal al presente hoy 9 de octubre de 2002



Firma Ilegible

Secretario del Tribunal de Circuito para el Condado de Baltimore Maryland



SELLO FACSIMILAR

El Estado de Maryland

Diego F. Vargas
DIEGO F. VARGAS
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL INGLES - INGLES ESPAÑOL
RES 0001 DE ENERO 4 DE 1990
MINISTERIO DE JUSTICIA

Oficina del Secretario de Estado

Apostilla

(Convention de La Haye du 5 Octobre 1961)

- 1 País Estados Unidos de América
- Este documento público
- 2 ha sido firmado por Suzanne Mensh
- 3 actuando en calidad de Secretario del Tribunal de Circuito para
- el Condado de Baltimore
- 4 lleva el sello/estampilla del Tribunal de Circuito para el
- Condado de Baltimore

Certificado

- 5 en Annapolis, Maryland
- 6 el 9 de Octubre de 2002
- 7 por el Secretario de Estado de Maryland

COPIA

8 Sello

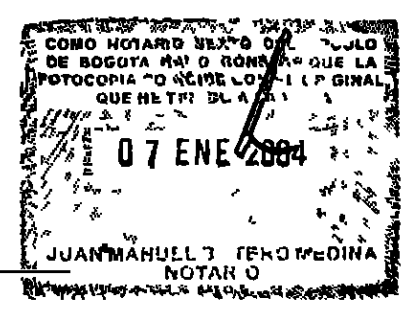


10 Firma

Firma ilegible

Secretario de Estado

N 86826



Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación

DVZ/ID-4317/WPCL002G/COLO 06032-708-002-8

Diego F. Vargas
DIEGO F. VARGAS Z
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL INGLES - INGLES ESPAÑOL
RES 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

COMO NOTARIO JEFATO DEL CIRCULO DEL SA (T) SE UL
BO (T) A HAGO CONSTAR QUE LA(S) FIRMA(S) DE
Diego Vargas
CON LA FIRMA REGISTRADA POR
LOS EN ESTA NOTARIA
CAN 09 ABR 2003



NO SE AÑHE
T... DEL TEXTO
P 1 08
FIRMA

MINISTERIO DE
RELACIONES EXTERIORES

DE 214543
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPEÑA
LAS FUNCIONES INDICADAS

COMO NOTARIO JEFATO DEL CIRCULO
DE BOGOTA HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
O SE HE VERIFICADO LA VERDAD
07 EN 2004
JUAN AIL... EDINA

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF RECEIPT
OF DEMAND BY COMPETENT INTERNATIONAL
PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59 3(e) and 61 1(b) first sentence
and Administrative Instructions Section 601(a))

To BEVERLY J ARTALE W R GRACE & CO CONN 7500 GRACE DRIVE COLUMBIA MARYLAND 21044 MAR - 3 2003		Date of mailing (day/month/year) 27 FEB 2003	
Applicant's or agent's file reference W9517 01		IMPORTANT NOTIFICATION	
International application No PCT/US02/23243	International filing date (day/month/year) 09 Jul 2002	Priority date (day/month/year) 10 Jul 2001	
Applicant W R GRACE & CO CONN			
1 The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application 06 FEB 03 2 That date of receipt is ☒ the actual date of receipt of the demand by this Authority (Rule 61 1(b)) ☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59 3(e)) ☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404) received the required corrections. 3 ☐ ATTENTION That date of receipt is AFTER the expiration of 19 months from the priority date. Consequently the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the <i>PCT Applicant's Guide</i> Volume II ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on _____ 4 Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau			
Name and mailing address of the IPEA/ Assistant Commissioner for Patent, Box PCT Washington D C 20231 Attn RO/US Facsimile No 703 305 3230		Authorized officer Larry Hammond Telephone No 703 308-6517	

Form PCT/IPEA/402 (July 1998)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

February 6, 2003

W R Grace & Co -Conn

RO/US

PCT/US02/23243

International Division

Filed July 9, 2002

Docket No W9517-01

For Gasoline Sulfur Reduction in Fluid Catalytic Cracking

Box PCT
Commissioner of Patents and
Trademarks
Washington, D C 20231

LETTER

Dear Sir

Submitted herewith for filing is Form PCT/IPEA/401 and Annex for
requesting International Preliminary Examination of the subject application

Respectfully submitted,



Beverly J. Antale
Reg No 32,366
Attorney for Applicant

Tel (410) 531-4769

W R Grace & Co -Conn
7500 Grace Drive
Columbia, Maryland 21044

The demand must be filed directly with the competent International Preliminary Examining Authority or if two or more Authorities are with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line

IPEA/ _____

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated)

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND	
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's file reference	
International application No PCT/US02/23243	International filing date (day/month/year) 09 July 2002 (09/07/2002)	(Earliest) Priority date (day/month/year) 10 July 2001 (10/07/2001)	
Title of invention Gasoline Sulfur Reduction in Fluid Catalytic Cracking			
Box No. II APPLICANT(S)			
Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country) W R GRACE & CO -CONN 7500 Grace Drive Columbia Maryland 21044 4098 United States of America		Telephone No (410) 531 4769	
		Facsimile No (410) 53 4195	
		Teleprinter No	
		Applicant's registration No. with the Office	
State (that is country) of nationality United States of America		State (that is country) of residence United States of America	
Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country) ExxonMobil Research & Engineering Company 3225 Gallows Road Fairfax Virginia 22037 United States of America			
State (that is country) of nationality United States of America		State (that is country) of residence United States of America	
Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country)			
State (that is country) of nationality		State (that is country) of residence	
☐ Further applicants are indicated on a continuation sheet			

Sheet No 2

International application No
PCT/US02/23243**Box No. III AGENT OR COMMON REPRESENTATIVE, OR ADDRESS FOR CORRESPONDENCE**

The following person is ☐ agent ☒ common representative
 and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination
☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.
☐ is hereby appointed specifically for the procedure before the International Preliminary Examining Authority in addition to the agent(s)/common representative appointed earlier

Name and address *(Family name followed by given name for a legal entity full official
The address must include postal code and name of country)*

ARTALE Beverly J
 W R GRACE & CO -CONN
 7500 Grace Drive
 Columbia Maryland 21044 4098
 United States of America

Telephone No
(410) 531 4769

Facsimile No
(410) 531 4195

Teleprinter No

Agent registration No with the Office

☐ Address for correspondence Mark this check box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**Statement concerning amendments ***

1 The applicant wishes the international preliminary examination to start on the basis of

☒ the international application as originally filed

the description ☒ as originally filed
☐ as amended under Article 34

the claims ☒ as originally filed
☐ as amended under Article 19 (together with any accompanying statement)
☐ as amended under Article 34

the drawings ☐ as originally filed
☐ as amended under Article 34

2 ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed

3 ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69 1(d)) (This check box may be marked only where the time limit under Article 19 has not yet expired)

* Where no check box is marked international preliminary examination will start on the basis of the international application as originally filed or where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report as so amended.

Language for the purposes of international preliminary examination **English**

- ☒ which is the language in which the international application was filed.
☐ which is the language of a translation furnished for the purposes of international search.
☐ which is the language of publication of the international application
☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination

Box No. V ELECTION OF STATES

The applicant hereby elects all eligible States (that is all States which have been designated and which are bound by Chapter II of the PCT)

excluding the following States which the applicant wishes not to elect

Sheet No 3

International application No
PCT/US02/23243**Box No. VI CHECK LIST**

The demand is accompanied by the following elements in the language referred to in Box No IV for the purposes of international preliminary examination

1 translation of international application

sheets

For International Preliminary
Examining Authority use only
received not received☐☐

2 amendments under Article 34

sheets

☐☐3 copy (or where required translation)
of amendments under Article 19

sheets

☐☐4 copy (or where required translation)
of statement under Article 19

sheets

☐☐

5 letter

sheets

☐☐

6 other (specify)

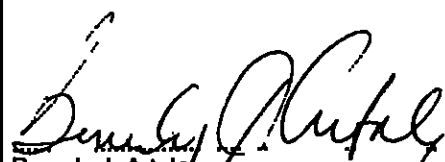
sheets

☐☐

The demand is also accompanied by the item(s) marked below

1 ☒ fee calculation sheet5 ☐ statement explaining lack of signature2 ☐ original separate power of attorney6 ☐ sequence listings in computer readable form3 ☐ original general power of attorney7 ☐ tables in computer readable form related to
sequence listings4 ☐ copy of general power of attorney
reference number if any8 ☒ other (specify) Letter return receipt postcard**Box No VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

Next to each signature indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

Beverly J. Artale
Common Representative for the Applicant
Reg No 32 396

For International Preliminary Examining Authority use only

1 Date of actual receipt of DEMAND

2 Adjusted date of receipt of demand due
to CORRECTIONS under Rule 60 1(b)3 ☐ The date of receipt of the demand is AFTER the expiration of 19 months
from the priority date and item 4 or 5 below does not apply☐ The applicant has been
informed accordingly4 ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of
Rule 80 55 ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date the delay in arrival is
EXCUSED pursuant to Rule 82

For International Bureau use only

Demand received from IPEA on

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No PCT/US02/23243	For International Preliminary Examining Authority use only
Applicant or agent's file reference W9517-01	Date stamp of the IPEA
Applicant W R GRACE & CO -CONN and EXXONMOBIL RESEARCH & ENGINEERING COMPANY	
CALCULATION OF PRESCRIBED FEES	
1 Preliminary examination fee	750 00 P
2 Handling fee <i>(Applicants from certain States are entitled to a reduction of 75% of the handling fee Where the applicant is (or all applicants are) so entitled the amount to be entered at H is 25% of the handling fee)</i>	146 00 H
3 Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	896 00
TOTAL	
MODE OF PAYMENT	
☒ authorization to charge deposit account with the IPEA (see below)	☐ cash
☐ cheque	☐ revenue stamps
☐ postal money order	☐ coupons
☐ bank draft	☐ other (specify)
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT <i>(This mode of payment may not be available at all IPEAs)</i>	
☒ Authorization to charge the total fees indicated above	IPEA/ <u>EPA</u>
☐ <i>(This check box may be marked only if the conditions for deposit accounts of the IPEA so permit)</i> Authorization to charge any deficiency or credit any overpayment in the total fees indicated above	Deposit Account No <u>07-1770</u>
	Date <u>February 6 2003</u>
	Name <u>Beverly J Artale</u>
	Signature <u><i>Beverly J Artale</i></u>

PATENT COOPERATION TREATY

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To

ARTALE, Beverly, J
W R Grace & Co -Conn
7500 Grace Drive
Columbia, MD 21044
United States of America
RECEIVED
PATENT DEPT
OCT - 9 2002

Date of mailing (day/month/year) 27 September 2002 (27 09 02)	
Applicant's or agent's file reference W9517-01	IMPORTANT NOTIFICATION
International application No PCT/US02/23243	International filing date (day/month/year) 09 July 2002 (09 07 02)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 10 July 2001 (10 07 01)
Applicant W R GRACE & CO -CONN et al	

- 1 The applicant is hereby notified of the date of receipt (except where the letters NR appear in the right hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt or by the letters NR in the right hand column the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17 1(a) or (b)
- 2 This updates and replaces any previously issued notification concerning submission or transmittal of priority documents
- 3 An asterisk(*) appearing next to a date of receipt, in the right hand column denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17 1(a) or (b). In such a case the attention of the applicant is directed to Rule 17 1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity upon entry into the national phase to furnish the priority document within a time limit which is reasonable under the circumstances
4. The letters "NR" appearing in the right hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau as provided by Rule 17 1(a) or (b) respectively. In such a case the attention of the applicant is directed to Rule 17 1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity upon entry into the national phase to furnish the priority document within a time limit which is reasonable under the circumstances

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
10 July 2001 (10 07 01)	09/901,939	US	30 Augu 2002 (30 08 02)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20 Switzerland Facsimile No (41 22) 740 14 35	Authorized officer PETRESKA Gorca Telephone No (41 22) 338 83 38
--	--

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To
 W R Grace & Co -Conn
 Attn Artale, Beverly J
 7500 Grace Drive
 Columbia, Maryland 21044
 UNITED STATES OF AMERICA

RECEIVED
 PATENT DEPT

SEP - 9 2002

NOTIFICATION OF RECEIPT
 OF SEARCH COPY

(PCT Rule 25.1)

Date of mailing
 (day/month/year)

02/09/2002

Applicant's or agent's file reference

W9517-01

IMPORTANT NOTIFICATION

International application No

PCT/US 02/ 23243

International filing date (day/month/year)

09/07/2002

Priority date (day/month/year)

10/07/2001

Applicant

W R GRACE & CO -CONN

1 Where the International Searching Authority and the Receiving Office are not the same office

The applicant is hereby notified that the search copy of the international application was received by this International Searching Authority on the date indicated below

Where the International Searching Authority and the Receiving Office are the same office

The applicant is hereby notified that the search copy of the international application was received on the date indicated below

09/08/2002 (date of receipt)

- 2 ☐ The search copy was accompanied by a nucleotide and/or amino acid sequence listing in computer readable form

3 Time limit for establishment of International Search Report

The applicant is informed that the time limit for establishing the International Search Report is 3 months from the date of receipt indicated above or 9 months from the priority date, whichever time limit expires later

4. A copy of this notification has been sent to the International Bureau and, where the first sentence of paragraph 1 applies, to the Receiving Office

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

ISA/EP

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To:
 BEVERLY J ARTALE
 W R GRACE & CO - CONN
 7500 GRACE DRIVE
 COLUMBIA MARYLAND 21044

PCT

NOTIFICATION OF THE INTERNATIONAL
 APPLICATION NUMBER AND OF THE
 INTERNATIONAL FILING DATE

(PCT Rule 20 5(c))

Date of mailing
 (day/month/year) 08 Aug 2002

Applicant's or agent's file reference
 W9517-01

IMPORTANT NOTIFICATION

International application No
 PCT/US02/23243

International filing date (day/month/year)
 09 Jul 2002

Priority date (day/month/year)
 10 Jul 2001

Applicant

W R GRACE & CO - CONN

Title of the invention

GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

1 The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2 The applicant is further notified that the record copy of the international application.



was transmitted to the International Bureau on

08 Aug 2002



has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*



because the necessary national security clearance has not yet been obtained.



because (reason to be specified)

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22 1(c))

3 FOREIGN TRANSMITTAL LICENSE INFORMATION

Completed by: LH



Additional license for foreign transmittal not required. This subject matter is covered by a license already granted or the equivalent U.S. national application. Refer to that license for information concerning its scope.



License for foreign transmittal not required. 37 CFR 5.11(e)(1) or 37 CFR 5.11(e)(2). However, a license may be required for additional subject matter. See 37 CFR 5.15(b).



Foreign transmittal license granted. 35 U.S.C. 184, 37 CFR 5.11 on

05 Aug 2002

(date)

☐ 37 CFR 5.15(a)

37 CFR 5.15(b)

Name and mailing address of the receiving Office

Assistant Commissioner for Patent, Box PCT
 Washington, D.C. 20231 Attn: RO/US

Facsimile No 703-305-3230

Authorized officer

LARRY HAMMOND

Telephone No 703-308-6517

TRANSMITTAL LETTER TO THE UNITED STATES RECEIVING OFFICE

PTO-1382 (Rev. 4-1995) (Modified)

PCTUS2.FRP/REV03

Date	July 9 2002
International Application No	
Attorney Docket No	W9517-01

I. Certification under 37 CFR 1.10 (if applicable)

ET 170356131 US

July 9 2002
Date of Deposit

I hereby certify that the application/correspondence attached hereto is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, D C 20231


Signature of person mailing correspondence

RACHEL H SCRIVEN
Typed or printed name of person mailing correspondence

II. ☒ New International Application

TITLE	GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING
-------	---

Earliest priority date (Day/Month/Year)
10/07/2001

SCREENING DISCLOSURE INFORMATION In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied (Note check as many boxes as apply)

- A. ☐ The invention disclosed was not made in the United States
- B. ☐ There is no prior U S application relating to this invention
- C. ☐ The following prior U S application(s) contain subject matter which is related to the invention disclosed in the attached international application (NOTE priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority)

application no	09/901 939	filed on	July 10 2001
application no		filed on	

- D. ☒ The present international application ☒ is identical ☐ contains less subject matter than that found in the prior U S application(s) identified in paragraph C
- E. ☐ The present international application ☐ contains additional subject matter not found in the prior U S application(s) identified in paragraph C above The additional subject matter is found on pages and ☐ DOES NOT ALTER ☐ MIGHT BE CONSIDERED TO ALTER the general nature of the invention in a manner which would require the U S application to have been made available for inspection by the appropriate defense agencies under 35 U S C 181 and 37 CFR 5.1 See 37 CFR 5.15

III. ☐ A Response to an Invitation from the RO/US The following document(s) is (are) enclosed

- A. ☐ A Request for An Extension of Time to File a Response
- B. ☐ A Power of Attorney (General or Regular)
- C. ☐ Replacement pages

pages		of the request (PCT/RO/101)	pages		of the figures
pages		of the description	pages		of the abstract
pages		of the claims			

- D. ☐ Submission of Priority Documents

Priority document		Priority document	
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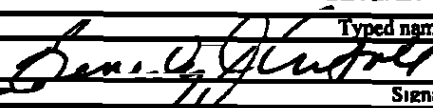
- E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☐ A Request for Rectification under PCT 91 ☐ A Petition ☐ A Sequence Listing Diskette

V. ☒ Other (please specify) FEE CALCULATION SHEET CORRESPONDENCE RECEIPT CARD GENERAL POWER OF ATTORNEY POWER OF ATTORNEY

The person signing this form is the

☐ Applicant
☒ Attorney/Agent (Reg No) 32 366
☐ Common Representative

BEVERLY J ARTALE
Typed name of signer

Signature

U S Department of Commerce Patent and Trademark Office

○
PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty

○ For receiving Office use only

International Application No

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) W9517-01

Box No I TITLE OF INVENTION
GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

Box No. II APPLICANT ☐ This person is also inventor

Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

W R GRACE & CO -CONN
7500 Grace Drive
Columbia
Maryland 21046
United States of America

Telephone No
(410) 531 4789

Facsimile No
(410) 531 4195

Teleprinter No

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☒ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address (Family name followed by given name, for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ExxonMobil Research & Engineering Company
3225 Gallows Road
Fairfax
Virginia 22037
United States of America

This person is.

☒ applicant only

☐ applicant and inventor

☐ inventor only (if this check-box is marked, do not fill in below)

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV 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 ☐ common representative

Name and address (Family name followed by given name for a legal entity, full official designation. The address must include postal code and name of country.)

ARTALE Beverly J
W R GRACE & CO -CONN
7500 Grace Drive
Columbia
Maryland 21044
United States of America

Telephone No
(410) 531 4789

Facsimile No
(410) 531 4195

Teleprinter No

Agent's registration No with the Office
32 386

☐ Address for correspondence Mark this check box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)*If none of the following sub-boxes is used this sheet should not to be included in the request*

Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

ROBERIE Terry G
2613 Lter Drive
Ellicott City
Maryland 21046
United States of America

This person is

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below)

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

KUMAR Ranjit
6412 Tara Place
Clarksville Maryland 21029
United States of America

This person is

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below)

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

CHENG Wu-Cheng
10308 Paddington Court
Ellicott City Maryland 20142
United States of America

This person is

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below)

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name for a legal entity full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

ZHAO Xinjin
1731 Cattail Meadows Drive
Woodbine Maryland 21797
United States of America

This person is

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below)

Applicant's registration No with the Office

State (that is country) of nationality
US

State (that is country) of residence
US

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Continuation of Box No III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not to be included in the request

Name and address (Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) ZIEBARTH Michael S 12071 Little Patuxent Parkway Columbia Maryland United States of America	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below)
	Applicant's registration No with the Office

State (that is country) of nationality US	State (that is country) of residence US
--	--

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) BHOE Nazeer 10509 Tyler Terrace Potomac Maryland 20854 United States of America	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below)
	Applicant's registration No with the Office

State (that is country) of nationality US	State (that is country) of residence US
--	--

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below)
	Applicant's registration No with the Office

State (that is country) of nationality	State (that is country) of residence
--	--------------------------------------

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address (Family name followed by given name, for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below)
	Applicant's registration No with the Office

State (that is country) of nationality	State (that is country) of residence
--	--------------------------------------

This person is applicant for the purposes of ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No V DESIGNATION OF STATES*Mark the applicable check boxes below at least one must be marked.*

The following designations are hereby made under Rule 4 9(a)

Regional Patent

- ☒ **AP** ARIPO Patent GH Ghana, GM Gambia, KE Kenya, LS Lesotho MW Malawi MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland TZ United Republic of Tanzania, UG Uganda, ZM Zambia, ZW Zimbabwe and any other State which is a Contracting State of the Harare Protocol and of the PCT (if other kind of protection or treatment desired, specify on dotted line)
- ☒ **EA** Eurasian Patent AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation TJ Tajikistan TM Turkmenistan and any other State which is a Contracting State of the Eurasian
- ☒ **EP** European Patent AT Austria, BE Belgium, CH & LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA** OAPI Patent BF Burkina Faso BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GQ Equatorial Guinea, GW Guinea Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line)

- | | | |
|---|--|--|
| ☒ AE United Arab Emirates | ☒ GM Gambia | ☒ NZ New Zealand |
| ☒ AG Antigua and Barbuda | ☒ HR Croatia | ☒ OM Oman |
| ☒ AL Albania | ☒ HU Hungary | ☒ PH Philippines |
| ☒ AM Armenia | ☒ ID Indonesia | ☒ PL Poland |
| ☒ AT Austria | ☒ IL Israel | ☒ PT Portugal |
| ☒ AU Australia | ☒ IN India | ☒ RO Romania |
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| ☒ BA Bosnia and Herzegovina | ☒ JP Japan | |
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| ☒ BR Brazil | ☒ KP Democratic People's Republic of Korea | ☒ SG Singapore |
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| ☒ CA Canada | ☒ LC Saint Lucia | ☒ SL Sierra Leone |
| ☒ CH & LI Switzerland and Liechtenstein | ☒ LK Sri Lanka | ☒ TJ Tajikistan |
| ☒ CN China | ☒ LR Liberia | ☒ TM Turkmenistan |
| ☒ CO Colombia | ☒ LS Lesotho | ☒ TN Tunisia |
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| ☒ EC Ecuador | ☒ MK The former Yugoslav Republic of Macedonia | ☒ UZ Uzbekistan |
| ☒ EE Estonia | ☒ MN Mongolia | ☒ VN Viet Nam |
| ☒ ES Spain | ☒ MW Malawi | ☒ YU Yugoslavia |
| ☒ FI Finland | ☒ MX Mexico | ☒ ZA South Africa |
| ☒ GB United Kingdom | ☒ MZ Mozambique | ☒ ZM Zambia |
| ☒ GD Grenada | ☒ NO Norway | ☒ ZW Zimbabwe |
| ☒ GE Georgia | | |
| ☒ GH Ghana | | |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet



Precautionary Designation Statement In addition to the designations made above, the applicant also makes under Rule 4 9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI

PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is		
		national application country	regional application * regional Office	international application receiving Office
item (1) 10 July 2001 (10 07 01)	09/901 939	US		
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as

☐ all items ☒ item (1) ☐ item (2) ☐ item (3) ☐ item (4) ☐ item (5) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii))

Box No. VII

INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen, the two-letter code may be used)

ISA/ EP

Request to use results of earlier search, reference to that search (If an earlier search has been carried out by or requested from the International Searching Authority)

Date (day/month/year)NumberCountry (or regional Office)

Box No. VIII

DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check boxes below and indicate in the right column the number of each type of declaration)

	Number of declarations
☐ Box No. VIII (i) Declaration as to the identity of the inventor	
☒ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	1
☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	
☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America)	
☐ Box No. VIII (v) Declaration as to non prejudicial disclosures or exceptions to lack of novelty	

Box No VIII (u) DECLARATION ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212 see Notes to Boxes Nos VIII VIII (i) to (v) (in general) and the specific Notes to Box No VIII (ii) If this Box is not used, this sheet should not be included in the request

Declaration as to the applicant's entitlement, as at the international filing date to apply for and be granted a patent (Rules 4 17(ii) and 51bis 1(a)(ii)), in a case where the declaration under Rule 4 17(iv) is not appropriate

in relation to this international application

W R GRACE & CO CONN is entitled to apply for and be granted a patent by the virtue of the following
an assignment from

ROBERIE Terry G of 2613 Litter Drive Ellicott City Maryland 21046 United States of America

KUMAR Ranjit of 6412 Tara Place Clarksville Maryland 21029 United States of America

ZIEBARTH Michael S of 12071 Little Patuxent Parkway Columbia Maryland United States of America

CHENG Wu-Cheng of 10308 Paddington Court, Ellicott City Maryland 21042 United States of America

ZHAO Xinjin of 1731 Cattail Meadows Drive Woodbine Maryland 21797 United States of America

BHORE Nazeer of 10509 Tyler Terrace Potomac Maryland 20854 United States of America

to W R GRACE & CO -CONN dated July 13 2001

This declaration is made for the purposes of all designations

in relation to the international application

ExxonMobil Research & Engineering Company is entitled to apply for and be granted a patent by the virtue of the
following assignment from

BHORE Nazeer of 10509 Tyler Terrace Potomac Maryland 20854 United States of America

to ExxonMobil Research & Engineering Company dated July 2 2002

This declaration is made for the purposes of all designations

☐ This declaration is continued on the following sheet, "Continuation of Box No VIII (u)"

Box No. IX CHECK LIST, LANGUAGE OF FILING

This international application contains		This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item)	Number of items
(a) the following number of sheets in paper form		1 ☒ fee calculation sheet	1
request (including declaration sheets)	7	2 ☒ original separate power of attorney	1
description (excluding sequence listing part)	20	3 ☒ original general power of attorney	1
claims	3	4 ☐ copy of general power of attorney, reference number if any	
abstract	1	5 ☐ statement explaining lack of signature	
drawings	0	6 ☐ priority document(s) identified in Box No. VI as item(s)	
Sub total number of sheets	31	7 ☐ translation of international application into (language)	
sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form see (b) below)		8 ☐ separate indications concerning deposited microorganism or other biological material	
Total number of sheets	31	9 ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	
(b) sequence listing part of description filed in computer readable form		(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	
(i) ☐ only (under Section 801 (a)(i))		(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	
(ii) ☐ in addition to being filed in paper form (under Section 801.(a)(ii))		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	
Type and number of carriers (diskette, CD ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii) in right column)		10 ☒ other (specify) CORRESPONDENCE RECEIPT CARD	1
Figure of the drawings which should accompany the abstract		Language of filing of the international application	ENGLISH

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request)


 ARTALE Beverly
 Attorney for the Applicant
 Reg No 32,888

For receiving Office use only		2 Drawings
1 Date of actual receipt of the purported international application		☐ received
3 Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application		☐ not received
4 Date of timely receipt of the required corrections under PCT Article 11(2)		
5 International Searching Authority (if two or more are competent) ISA/	6 ☐ Transmittal of search copy delayed until search fee is paid	

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Date of receipt of the record copy by the International Bureau

This sheet is not part of and does not count as a sheet of the international application.

PCT
FEE CALCULATION SHEET
Annex to the Request

For receiving Office use only

International Application No

Applicant's or agent's
file reference

W9517-01

Date stamp of the receiving Office

Applicant
W R. GRACE & CO -CONN

CALCULATION OF PRESCRIBED FEES

1 TRANSMITTAL FEE

240 00 T

2 SEARCH FEE

866 00 S

International search to be carried out by EPO

(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3 INTERNATIONAL FEE

Basic Fee

Where item (b) of Box No IX applies enter Sub-total number of sheets } 31
Where item (b) of Box No IX does not apply enter Total number of sheets }

b1 first 30 sheets 407 00 b1

b2 1 x 9 00 = 9 00 b2
number of sheets fee per sheet

b3 additional component (only if sequence listing part of description
is filed in computer readable form under Section 801(a)(i), or both
in that form and on paper under Section 801(a)(ii))

400 x = b3
fee per sheet

Add amounts entered at b1, b2 and b3 and enter total at B 416 00 B

Designation Fees

The international application contains 5 designations

5 x 88 00 = 440 00 D
number of designation fees amount of designation fee
payable (maximum 5)

Add amounts entered at B and D and enter total at I 856 00 I

(Applicants from certain States are entitled to a reduction of 75% of the
international fee Where the applicant is (or all applicants are) so entitled, the

4 FEE FOR PRIORITY DOCUMENT (if applicable)

15 00 P

5 TOTAL FEES PAYABLE

1,977 00

Add amounts entered at T S I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time

MODE OF PAYMENT

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☐ postal money order

☐ cash

☐ coupons

☐ cheque

☐ bank draft

☐ revenue stamps

☐ other (specify)

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all receiving Offices)

Receiving Office RO/ US

☒ Authorization to charge the total fees indicated above

Deposit Account No 07-1770

☒ (This check box may be marked only if the conditions for deposit accounts of
the receiving Office so permit) Authorization to charge any deficiency or
credit any overpayment in the total fees indicated above.

Date July 9, 2002

Name ARTALE, Beverly J.

☒ Authorization to charge the fee for priority document.

Signature

Beverly J. Artale

See Notes to the fee calculation sheet

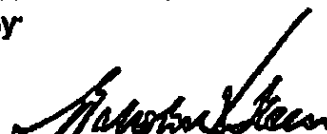
Power of Attorney

ExxonMobil Research and Engineering Company appoints the following attorneys whose names and registration numbers in the United States Patent and Trademark Office are set out below:

Beverly J. Artale, Reg. No. 32,366
Charles A. Cross, Reg. No. 32,406
Robert A. Maggio, Reg. No. 28,032

to act on its behalf before the International Patent Examining Authority in the matter of a PCT Application corresponding to USSN 09/901,938, entitled Gasoline Sulfur Reduction in Fluid Catalytic Cracking

ExxonMobil Research and Engineering Company
By



Malcolm D. Keen
Authorized Attorney in Fact
U.S. PTO Registration No. 27,728

PATENT COOPERATION TREATY

(4)

20

From the INTERNATIONAL BUREAU

PCT

To

ARTALE Beverly J
W R Grace & Co -Conn

7500 Grace Drive

Columbia MD 21044
ETATS-UNIS D AMERIQUE

W9517 01

NOV 18 2003

CAL/65A

W

BT
12/11/02

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(10) International Publication Number
WO 03/006578/A3(51) International Patent Classification⁷ C10G 11/05
11/18

(21) International Application Number PCT/US02/23243

(22) International Filing Date 9 July 2002 (09 07 2002)

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(26) Publication Language English

(30) Priority Data
09/901 939 10 July 2001 (10 07 2001) US(71) Applicants WR GRACE & CO-CONN [US/US]
7500 Grace Drive Columbia MD 21046 (US) EXXON-
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[US/US] 3225 Gallows Road Fairfax VA 22037 (US)(72) Inventors ROBERIE, Terry, G 2613 Liler Drive El
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10308 Paddington Court Ellicott City MD 21042 (US)
ZHAO, Xinjin 1731 Cattail Meadows Drive Woodbine,
MD 21797 (US) ZIEBARTH, Michael, S. 12071 Little
Patuxent Parkway Columbia, MD 21046 (US) BHOZE,
Nazeer 10509 Tyler Terrace, Potomac MD 20854 (US)(74) Agent ARTALE Beverly, J WR Grace & Co Conn
7500 Grace Drive Columbia MD 21044 (US)(81) Designated States (*national*) AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CQ, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW(84) Designated States (*regional*) ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW)
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European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR) OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG)

Declarations under Rule 4.17

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations

Published

- with international search report

(88) Date of publication of the international search report
6 November 2003

For two-letter codes and other abbreviations refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

(57) Abstract The sulfur content of liquid cracking products especially the cracked gasoline is reduced in a catalytic cracking process employing a cracking catalyst containing a high content of vanadium. The cracking process involves introducing at least one vanadium compound into a hydrocarbon sulfur containing feedstock to be charged to a fluid catalytic cracking reactor operating under steady state conditions and containing an equilibrium fluid cracking catalyst inventory within the reactor. The amount of sulfur in the liquid products in particular gasoline and LCO fractions, is reduced as a result of the increased vanadium content on the equilibrium catalyst. Advantageously sulfur reduction is achieved even in the presence of other metal contaminants such as nickel and iron on the equilibrium catalyst.



WO 03/006578 A3

INTERNATIONAL SEARCH REPORT

 Intern Application No
 PCT/US 02/23243

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Columbia, MD 21046
ETATS-UNIS D'AMERIQUE

NOV 18 2003



Datum/Date

12/11/03

Zeichen/Pat./Ref	Anmeld.-Nr./Application No./Demande n°/Patent Nr./Patent No./Brevet n°
	02752505 4-1213-PCT/US0223243
Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire	
W R Grace & Co -Comm, et al	

The international search report, or the declaration under Article 17(2)(a) PCT, has been published under Article 21(3) and Rule 48 PCT on 06 11 03. That publication takes the place of the mention of publication of the European search report (Article 157(1) EPC).

The request for examination must be filed within SIX months from the above date (Article 94(2) in conjunction with Article 157(1) EPC). It is not deemed to have been filed until the examination fee has been paid. However, under Article 22 or 39 PCT in conjunction with Article 150(2) and Rule 107(1) EPC, the time limit for filing it does not expire before the end of the 31st month from the filing date (or earliest priority date). Payment of the designation fees must also be made within the above-mentioned period (Rule 107(1) EPC). The same applies also for the extension fees.

If the request for examination is not filed in due time, and at least one designation fee is not paid, the European patent application is deemed to be withdrawn (Article 94(3), 79(3) and Rule 108(1) EPC).

For more details see the Guide for applicants Part 2 PCT proceedings before the EPO-"Euro-PCT".

RECEIVING SECTION



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

(43) International Publication Date
23 January 2003 (23 01 2003)

PCT

(10) International Publication Number
WO 03/006578 A2

- (51) International Patent Classification⁷ C10G (81) Designated States (*national*) AE, AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE, DK DM DZ, EC EE ES FI GB GD GE, GH GM HR HU ID IL IN IS JP KE, KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL, TJ TM TN TR TT TZ, UA UG UZ VN YU ZA ZM ZW
- (21) International Application Number PCT/US02/23243
- (22) International Filing Date 9 July 2002 (09 07 2002)
- (25) Filing Language English
- (26) Publication Language English
- (30) Priority Data 09/901 939 10 July 2001 (10 07 2001) US
- (71) Applicants WR. GRACE & CO-CONN [US/US] 7500 Grace Drive Columbia, MD 21046 (US) EXXON-MOBIL RESEARCH & ENGINEERING COMPANY [US/US] 3225 Gallows Road Fairfax VA 22037 (US)
- (72) Inventors ROBERIE, Terry, G 2613 Liler Drive Ellicott City MD 21046 (US) KUMAR, Ranjit 6412 Tara Place Clarksville, MD 21029 (US) CHENG, Wu-Cheng 10308 Paddington Court, Ellicott City MD 20142 (US) ZHAO, Xinjin 1731 Cattail Meadows Drive Woodbine MD 21797 (US) ZIEBARTH, Michael, S. 12071 Little Patuxent Parkway Columbia, MD 21046 (US) BHOORE, Nazeer 10509 Tyler Terrace, Potomac MD 20854 (US)
- (74) Agent ARTALE, Beverly, J WR Grace & Co-Conn 7500 Grace Drive, Columbia MD 21044 (US)
- (84) Designated States (*regional*) ARIPO patent (GH GM KE, LS MW MZ, SD SL, SZ TZ UG ZM ZW) Eurasian patent (AM AZ BY KG KZ, MD RU TJ TM) European patent (AT BE, BG CH CY CZ, DE DK, EE, ES FI FR, GB GR IE IT LU MC NL, PT SE, SK, TR) OAPI patent (BF BJ CF CG CI, CM GA GN GQ GW ML, MR, NE SN TD TG)
- Declarations under Rule 4.17**
- as to applicant's entitlement to apply for and be granted a patent (Rule 4 17(ii)) for all designations
 - as to applicant's entitlement to apply for and be granted a patent (Rule 4 17(i)) for all designations
- Published**
- without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette*

(54) Title GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

(57) Abstract The sulfur content of liquid cracking products especially the cracked gasoline is reduced in a catalytic cracking process employing a cracking catalyst containing a high content of vanadium. The cracking process involves introducing at least one vanadium compound into a hydrocarbon sulfur containing feedstock to be charged to a fluid catalytic cracking reactor operating under steady state conditions and containing an equilibrium fluid cracking catalyst inventory within the reactor. The amount of sulfur in the liquid products in particular gasoline and LCO fractions, is reduced as a result of the increased vanadium content on the equilibrium catalyst. Advantageously sulfur reduction is achieved even in the presence of other metal contaminants such as nickel and iron, on the equilibrium catalyst.

WO 03/006578 A2

GASOLINE SULFUR REDUCTION IN FLUID CATALYTIC CRACKING

FIELD OF THE INVENTION

[0001] This invention relates to the reduction of sulfur in gasoline and other petroleum products produced by a catalytic cracking process. In particular, this invention relates to an improved catalytic cracking process, which provides catalytic cracked product streams of light and heavy gasoline fractions having a reduced sulfur content.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application is related to Application Serial No. 09/144,607, filed August 31, 1998.

[0003] This application is also related to Application Serial Nos. 09/221,539 and 09/221,540, both filed December 28, 1998.

[0004] This application is also related to Application Serial No. 09/399,637, filed September 9, 1999.

[0005] This application also relates to Application Serial No. 09/649,627, filed August 28, 2000.

BACKGROUND OF THE INVENTION

[0006] Catalytic cracking is a petroleum refining process which is applied commercially on a very large scale, especially in the United States where the majority of the refinery gasoline blending pool is produced by catalytic cracking, with almost all of this coming from the fluid catalytic cracking (FCC) process. In the catalytic cracking process, hydrocarbon feedstocks containing heavy hydrocarbon fractions are cracked in a FCC reactor or unit to form lighter products. Cracking is accomplished by reactions taking place at elevated temperature in the presence of a catalyst, with the majority of the conversion or cracking occurring in the vapor phase. The feedstock is thereby converted into gasoline, distillate and other liquid cracking products as well as lighter gaseous cracking products of four or less carbon atoms per molecule. The gas partly consists of olefins and partly of saturated hydrocarbons.

[0007] During the cracking reactions some heavy material, known as coke, is deposited onto the catalyst. This reduces its catalytic activity and regeneration is desired.

After removal of occluded hydrocarbons from the spent cracking catalyst, regeneration is accomplished by burning off the coke to restore catalyst activity. The three characteristic steps of the catalytic cracking can therefore be distinguished: a cracking step in which the hydrocarbons are converted into lighter products, a stripping step to remove hydrocarbons adsorbed on the catalyst and a regeneration step to burn off coke from the catalyst. The regenerated catalyst is then reused in the cracking step.

[0008] Catalytic cracking feedstocks normally contain sulfur in the form of organic sulfur compounds such as mercaptans, sulfides and thiophenes. The products of the cracking process correspondingly tend to contain sulfur impurities even though about half of the sulfur is converted to hydrogen sulfide during the cracking process, mainly by catalytic decomposition of non-thiophenic sulfur compounds. The distribution of sulfur in the cracking products is dependent on a number of factors including feed, catalyst type, additives present, conversion and other operating conditions but, in any event a certain proportion of the sulfur tends to enter the light or heavy gasoline fractions and passes over into the product pool. With increasing environmental regulation being applied to petroleum products, for example in the Reformulated Gasoline (RFG) regulations, the sulfur content of the products has generally been decreased in response to concerns about the emissions of sulfur oxides and other sulfur compounds into the air following combustion processes.

[0009] One approach has been to remove the sulfur from the FCC feed by hydrotreating before cracking is initiated. While highly effective, this approach tends to be expensive in terms of the capital cost of the equipment as well as operationally since hydrogen consumption is high. Another approach has been to remove the sulfur from the cracked products by hydrotreating. Again, while effective, this solution has the drawback that valuable product octane may be lost when the high octane olefins are saturated.

[0010] From the economic point of view, it would be desirable to achieve sulfur removal in the cracking process itself since this would effectively desulfurize the major component of the gasoline blending pool without additional treatment. Various catalytic materials have been developed for the removal of sulfur during the FCC process cycle. For example, a FCC catalyst impregnated with vanadium and nickel metal has been shown to reduce the level of product (See Mystrad et al, *Effect of Nickel and Vanadium on Sulfur Reduction of FCC Naphtha*, Applied Catalyst A General 192(2000) pages 299-305). This reference also showed that a sulfur reduction additive based on a zinc impregnated alumina is effective to reduce product sulfur in FCC products. However, when mixed with a metal impregnated catalyst, the effect of the additive to reduce sulfur was inhibited.

[0011] Other developments for reducing product sulfur have centered on the removal of sulfur from the regenerator stack gases. An early approach developed by Chevron used alumina compounds as additives to the inventory of cracking catalyst to adsorb sulfur oxides in the FCC regenerator, the adsorbed sulfur compounds which entered the process in the feed were released as hydrogen sulfide during the cracking portion of the cycle and passed to the product recovery section of the unit where they were removed. See Krishna et al, *Additives Improve FCC Process*, Hydrocarbon Processing, November 1991, pages 59-66. The sulfur is removed from stack gases emitted from the regenerator but product sulfur levels are not greatly affected, if at all.

[0012] An alternative technology for the removal of sulfur oxides from regenerator stack gases is based on the use of magnesium-aluminum spinels as additives to the circulating catalyst inventory in the FCCU. Under the designation DESOX™ used for the additives in this process, the technology has achieved a notable commercial success. Exemplary patents disclosing this type of sulfur removal additives include U.S. Patent Nos. 4,963,520, 4,957,892, 4,957,718, 4,790,982 and others. Again, however, product sulfur levels are not greatly reduced.

[0013] Catalyst additives for the reduction of sulfur levels in the liquid cracking products was proposed by Ziebarth et al. in U.S. Patent 6,036,847, using compositions containing a titania component, and Wormsbecher and Kim in U.S. Patents 5,376,608 and 5,525,210, using a cracking catalyst additive of an alumina-supported Lewis acid for the production of reduced-sulfur gasoline but this system has not achieved significant commercial success.

[0014] In Application Serial No. 09/144,607, filed August 31, 1998, catalytic materials are described for use in the catalytic cracking process, which are capable of reducing the content of the liquid products of the cracking process. These sulfur reduction catalysts comprise, in addition to a porous molecular sieve component, a metal in an oxidation state above zero within the interior of the pore structure of the sieve. The molecular sieve is in most cases a zeolite and it may be a zeolite having characteristics consistent with the large pore zeolites such as zeolite beta or zeolite USY or with the intermediate pore size zeolites such as ZSM-5. Non-zeolitic molecular sieves such as MeAPO-5, MeAPSO-5, as well as the mesoporous crystalline materials such as MCM-41 may be used as the sieve component of the catalyst. Metals such as vanadium, zinc, iron, cobalt, and gallium were found to be effective for the reduction of sulfur in the gasoline, with vanadium being the preferred metal. The amount of the metal component in the sulfur reduction additive catalyst is normally from

0.2 to 5 weight percent, but amounts up to 10 weight percent were stated to give some sulfur removal effect. The sulfur reduction component may be a separate particle additive or part of an integrated cracking/sulfur reduction catalyst. When used as a separate particle additive catalyst, these materials are used in combination with an active catalytic cracking catalyst (normally a faujasite such as zeolite Y and REY, especially as zeolite USY and REUSY) to process hydrocarbon feedstocks in the FCC unit to produce low-sulfur products

[0015] In Application Serial Nos 09/221,539 and 09/221,540, both filed December 28, 1998, sulfur reduction catalyst similar to the one described in Application No 09/144,607 were described, however, the catalyst compositions in those applications also comprise at least one rare earth metal component (e.g. lanthanum) and a cerium component, respectively. The amount of the metal component in the sulfur reduction catalysts is normally from 0.2 to 5 weight percent, but amounts up to 10 weight percent were suggested to give some sulfur removal effect.

[0016] In Application Serial No 09/399,637, filed September 20, 1999, an improved catalytic cracking process for reducing the sulfur content of the liquid cracking products, especially cracked gasoline, produced from hydrocarbon feed containing organosulfur compounds is described. The process employs a catalyst system having a sulfur reduction component containing porous catalyst and a metal component in an oxidation state greater than zero. The sulfur reduction activity of the catalyst system is increased by increasing the average oxidation state of the metal component by an oxidation step following conventional catalyst regeneration.

[0017] Application Serial No 09/649,627, filed August 28, 2000, is a continuation in part of Application Serial No 09/399,637 and discloses improved sulfur reduction additives for use in a catalytic cracking process for reduction of sulfur content. The sulfur reduction additive comprises a non-molecular sieve support material (preferably an inorganic oxide support such as Al_2O_3 , SiO_2 , and mixtures thereof) containing a high concentration of vanadium. The amount of vanadium contained in the sulfur reduction additive catalyst is normally from about 2.0 to about 20 weight percent, typically from about 3 to about 10 weight percent (metal based on the total weight of the additive).

[0018] Despite recent sulfur reduction technologies, there continues to exist a need for effective ways to reduce the sulfur content of gasoline and other liquid cracking products. The present invention was developed in response to this need.

SUMMARY OF THE INVENTION

[0019] An improved catalytic cracking process has now been developed which is capable of improving the reduction in the sulfur content of the products of the cracking process, including the gasoline and middle distillate cracking fractions. In accordance with the process of the invention at least one vanadium containing compound is added to a liquid hydrocarbon feedstock containing sulfur, and optionally, vanadium and/or nickel, as impurities to selectively increase the concentration of vanadium in the feedstock. The vanadium-enriched feedstock is thereafter charged into a FCC unit operating under steady state conditions to contact an inventory of FCC equilibrium catalyst *in situ* with a high concentration of vanadium, expressed as elemental vanadium.

[0020] The mechanism by which the present invention acts to enhance the removal of sulfur components normally present in cracked hydrocarbon products is not precisely understood. However, the presence of high concentration of a vanadium compound in the feedstock enables the rapid transportation of vanadium over the entire circulating catalyst inventory, thereby increasing the activity of the cracking catalyst to remove sulfur.

[0021] Accordingly, it is an advantage of the present invention to provide an improved catalytic cracking process, which provides liquid products having improved sulfur reduction when compared to the sulfur reduction activity typical in conventional catalyst cracking processes.

[0022] It is also an advantage of the present invention to provide a catalytic cracking process which allows for the rapid dispersion of vanadium over the entire cracking catalyst inventory, thereby enhancing the removal of sulfur components from cracked hydrocarbon products.

[0023] An additional advantage of the present invention is to provide a catalytic cracking process having improved product sulfur reduction without the need for the addition of sulfur reduction additives, including zeolite/vanadium additives as disclosed in related Application Serial Nos. 09/144,607, 09/221,539, 09/221,540, 09/399,637 and 09/649,627.

[0024] Another advantage of the present invention is to provide catalytic cracking compositions *in situ* during a catalytic cracking process which compositions are capable of improving the reduction in the sulfur content of liquid cracking products in the presence of metal contaminants, e.g. nickel and iron.

[0025] Other objects and advantages will become apparent from the detailed description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] The Figure outlines a typical catalytic cracking process for the reduction of product sulfur content in accordance with the present invention

DETAIL DESCRIPTION OF THE INVENTION

[0027] For purposes of this invention the term "fresh catalyst" is used to indicate a catalyst composition as manufactured and sold

[0028] The term "equilibrium catalyst" or "ecat" is used herein to indicate the inventory of circulating fluid cracking catalyst composition in an FCC unit operating under catalytic cracking conditions. For purpose of this invention the terms "equilibrium catalyst", "spent catalyst" (catalyst taken from an FCC unit) and "regenerated catalyst" (catalyst leaving a regeneration unit) shall be deemed equivalent.

[0029] The term "steady state" is used herein to indicate operating conditions within a FCC reactor unit wherein there exists within the unit a constant amount of catalyst inventory having a constant catalyst activity at a constant rate of feed of a feedstock having a defined composition to obtain a constant conversion rate of products

[0030] The term "conversion rate" is used herein to indicate the rate at which a hydrocarbon feedstock is converted to lower molecular weight, lower boiling hydrocarbon products

[0031] The term "catalyst activity" is used herein to indicate the quantity of cracked product formed per unit time per unit volume of reactor

[0032] In accordance with the present invention, a conventional FCC process is modified to provide a high concentration of vanadium (expressed as elemental vanadium) directly onto the equilibrium catalyst inventory to reduce the sulfur content of cracked liquid products. The process involves charging a hydrocarbon feedstock, containing at least one organo-sulfur compound as an impurity, into a FCC unit operating under catalytic cracking conditions to contact the equilibrium catalyst inventory contained in the unit. During the FCC process, fresh FCC catalyst is added and equilibrium catalyst is withdrawn to create a steady state condition within the FCC reactor unit. Once a steady state environment is reached within the FCC unit, the hydrocarbon feedstock is treated to add at least one vanadium compound to feedstock. The vanadium treated feedstock is charged into the FCC unit operating under steady state condition to contact the equilibrium catalyst inventory and selectively provide a high content of vanadium, expressed as elemental vanadium, on the equilibrium catalyst. The vanadium-treated catalyst is thereafter re-circulated throughout the

FCC unit in a continuous reaction/regeneration process to reduce the sulfur content of cracked liquid products fractions, in particular light and heavy gasoline fractions

[0033] The catalytic cracking process of the invention may be conducted using any suitable catalytic cracking unit or reactor. For convenience, the invention will be described with reference to the FCC process although the present process could be used in the older moving bed type (TCC) cracking process with appropriate adjustments to suit the requirements of the process. Apart from the addition of the vanadium compound/s to the hydrocarbon feedstock and some possible changes in the product recovery section, discussed below, the manner of operating the process will remain unchanged. Thus, conventional FCC catalysts may be used, for example, zeolite based catalysts with a faujasite cracking component as described in the seminal review by Venuto and Habib, *Fluid Catalytic Cracking with Zeolite Catalysts*, Marcel Dekker, New York 1979, ISBN 0-8247-6870-1 as well as in numerous other sources such as Sadeghbeigi, *Fluid Catalytic Cracking Handbook*, Gulf Publ. Co. Houston, 1995, ISBN 0-88415-290-1

[0034] Generally, the fluid catalytic cracking process in which the heavy hydrocarbon feedstock containing the organosulfur compounds will be cracked to lighter products takes place in a catalytic cracking reactor unit by contact of the feedstock in a cyclic catalyst recirculation cracking process with a circulating fluidizable catalytic cracking catalyst inventory consisting of particles having a size ranging from about 20 to about 100 microns. The significant steps in the cyclic process are

[0035] (i) the hydrocarbon-containing feedstock or feed is charged into a catalytic cracking unit, normally containing one or more risers, operating at catalytic cracking conditions by contacting the feedstock with a source of hot, regenerated cracking catalyst to produce an effluent comprising cracked products and spent catalyst containing coke and strippable hydrocarbons,

[0036] (ii) the effluent is discharged and separated, normally in one or more cyclones, into a vapor phase rich in cracked product and a solids rich phase comprising the spent catalyst,

[0037] (iii) the vapor phase is removed as product and fractionated in the FCC main column and its associated side columns to form liquid cracking products including gasoline,

[0038] (iv) the spent catalyst is stripped, usually with steam, to remove occluded hydrocarbons from the catalyst, after which the stripped catalyst is oxidatively regenerated to

produce hot, regenerated catalyst which is then recycled to the cracking zone for cracking further quantities of feed

[0039] As fresh catalyst equilibrates within an FCC unit or reactor, the equilibrium catalyst is exposed to various conditions, such as the deposition of feedstock contaminants and the severe regeneration of operation conditions. Thus, equilibrium catalyst may contain high levels of metal contaminants, including but not limited to, vanadium, nickel and iron. In normal operation of a FCC unit, fresh catalyst is added daily at the same rate that equilibrium catalyst is withdrawn. This provides a constant amount of catalyst inventory having a constant catalyst activity, which maintains a constant conversion of feed and selectivity of desired products.

[0040] Thus, at steady state operation conditions, the amount of equilibrium catalyst in the FCC unit is constant, i.e. the amount of fresh catalyst added to the FCC unit is equal to the amount of equilibrium catalyst withdrawn from the unit plus the amount of equilibrium catalyst lost due to attrition. Also, during steady state operation of a FCC unit, the rate at which a feedstock having a defined composition is added to the unit is held constant. This feed can be characterized by a number of properties such as API gravity, specific gravity, total sulfur (wt %), total nitrogen (wt %), metals content (wt %), Conradson carbon, K factor, and boiling point and molecular weight distributions.

[0041] Typically, during the cracking reaction in the FCC unit, the sulfur in the feed becomes distributed in the liquid and gaseous fractions of the cracked products. These products include H_2S gasoline, light cycle oil (LCO), heavy cycle oil (HCO), coke and unconverted feed. Under steady state conditions, the amount of sulfur (on a wt % basis) generated in these products is constant. Unexpectedly, however, it has been found that the addition of vanadium from a secondary source to the feed being charged into a FCC unit operating under a steady state environment selectively increases the concentration of vanadium on the equilibrium catalyst circulating inventory to effectively reduce the sulfur content of the cracked products. The amount of sulfur in the liquid products, especially the gasoline fractions, is lowered as a result of the increased vanadium on the equilibrium catalyst, even in the presence of metal contaminants such as nickel and iron.

[0042] Accordingly, the process in accordance with the present invention generally comprises

[0043] (i) providing a substantially liquid heavy hydrocarbon feed stream comprising at least one organosulfur compound as an impurity,

[0044] (ii) charging the hydrocarbon feed stream into a FCC reactor unit operating under catalytic cracking conditions and having a circulating inventory of an equilibrium catalyst composition,

[0045] (iii) removing a portion of the equilibrium catalyst inventory from the FCC reactor unit while replacing all removed equilibrium catalyst inventory with fresh catalyst to create a steady state environment within the unit,

[0046] (iv) contacting the hydrocarbon feed stream with at least one vanadium compound in an amount sufficient to increase the concentration of vanadium in or on the equilibrium catalyst inventory by about 100 to about 20,000 ppm, relative to the amount of vanadium initially present in or on the catalyst inventory, and

[0047] (v) contacting the vanadium containing hydrocarbon feed stream with the equilibrium catalyst inventory in the FCC reactor unit under steady state conditions to produce a cracking zone effluent comprising cracked products having a reduced sulfur content

[0048] Vanadium compounds useful in the present invention may be any vanadium containing compound which permits the transport and deposition of the vanadium species to the cracking catalyst under catalytic cracking conditions. Non-limiting examples of suitable vanadium compounds are ammonium ortho-, pyro- or meta vanadates, vanadium oxides (e.g. V_2O_5), vanadic acids, organometallic vanadium complexes (e.g. vanadyl naphenate), vanadium sulfate, vanadium nitrate, vanadyl nitrate, vanadium halides and oxyhalides (e.g. vanadium chlorides and oxychlorides) and mixtures thereof. Preferably, the vanadium compound is selected from the group consisting of vanadium oxalate, vanadium sulfate, vanadium naphthenate, vanadium halides, and mixtures thereof.

[0049] In a preferred embodiment, the vanadium compound/s are blended into the feed as a solution prior to injection of the feed into the reactor. Suitable vanadium solutions include those solutions wherein the desired vanadium compound/s are dissolved in water or a non-aqueous solvent, e.g. a suitable organic solvent such as pentane, toluene and the like. In a preferred embodiment, a non aqueous vanadium naphthenate solution is used.

[0050] The amount of the vanadium solution added to the feed stream will typically be relatively small. Consequently, the vanadium solution can be added to the feedstock using any commercially available pump. For practical application, the delivery of the vanadium solution may be continuous or intermittent.

[0051] As shown in the Figure, in a typical FCC process in accordance with the invention, a vanadium solution 2 is added directly into the feedstock 1 to be charged into the

riser reactor unit 4 to provide a vanadium containing hydrocarbon feed 3. The vanadium containing hydrocarbon feed 3 is thereafter introduced in the riser reactor 4 containing a equilibrium catalyst inventory and operating under a steady state environment. The effluent from the riser reactor 4 is separated into a cracked product stream 5 and a spent catalyst stream 6 containing coke and strippable hydrocarbons. The spent catalyst stream is thereafter recirculated in the cracking unit through a regenerator 7 to regenerate the catalyst.

[0052] The cracking catalyst used in the cracking process of the invention will normally be based on a faujasite zeolite active cracking component, which is conventionally zeolite Y in one of its forms such as calcined rare-earth exchanged type Y zeolite (CREY), the preparation of which is disclosed in U S Patent No. 3,402,996, ultrastable type Y zeolite (USY) as disclosed in U S Patent No. 3,293,192, as well as various partially exchanged type Y zeolites as disclosed in U S Patents Nos. 3,607,043 and 3,676,368. The active cracking component is routinely combined with a matrix material such as alumina in order to provide the desired mechanical characteristics (attrition resistance etc.) as well as activity control for the very active zeolite component or components. The particle size of the cracking catalyst is typically in the range of 10 to 120 microns for effective fluidization.

[0053] The feedstocks useful in the catalytic cracking process of this invention include a liquid or substantially liquid hydrocarbon feed containing sulfur as a contaminant. The feedstocks include those which are conventionally utilized in catalytic cracking processes to produce gasoline and light distillate fractions from heavier hydrocarbon feedstocks. The feedstocks generally have an initial boiling point above about 400°F (204°C) and include fluids such as gas oils, fuel oils, cycle oils, slurry oils, topped crudes, shale oils, oils from tar sands, oils from coal, mixtures of two or more of these, and the like. By "topped crude" is meant those oils which are obtained as the bottoms of a crude oil fractionator. If desired, all or a portion of the feedstock can constitute an oil from which a portion of the metal content previously has been removed, e.g., by hydrotreating or solvent extraction.

[0054] Optionally, the feedstock utilized in this process may contain as impurities one or more of the metals nickel, vanadium and iron at the following typical ranges: nickel at a level of about 0.02 to about 100 ppm, vanadium at a level of about 0.02 to 500 ppm, and iron at a level of 0.02 to 500 ppm. In a preferred embodiment, the feedstock contains vanadium as an impurity.

[0055] In accordance with the process of the invention, the vanadium compound is added to the feed during operation of the FCC unit under steady state conditions. The amount of vanadium compound added to the feed will vary depending upon such factors as the nature

of the feedstock used, the cracking catalyst used and the results desired. Generally, the vanadium compound is added to the feed at a rate sufficient to increase the concentration of vanadium in or on the equilibrium catalyst inventory by about 100 to about 20,000 ppm, preferably about 300 to about 5000 ppm, most preferably about 500 to about 2000 ppm, relative to the amount of vanadium initially present in or on the catalyst inventory.

[0056] The concentration of vanadium on the equilibrium catalyst inventory under state steady conditions can be determined by the following equation

$$\text{ppm V on ecats} = \frac{\text{ppm V in feed} \times \text{feed rate (Tons/Day)}}{\text{Catalyst Addition Rate (T/D)}}$$

[0057] The catalytic cracking process of the invention is conducted in conventional FCC reactor units wherein the reaction temperature ranges from about 400 °C to 700 °C and regeneration temperatures from about 500 °C to 850 °C are utilized. Conditions within the cracking and regeneration zone, as will be understood by the skilled artisan, are not critical and depend upon several parameters, such as the feed stock used, the catalyst, and the results desired.

[0058] The effect of the improved process of the invention is to reduce the sulfur content of the liquid cracking products, especially the light gasoline fractions although reductions are also noted in the light cycle oil, making the products more suitable for use as a diesel or home heating oil blend component. Gasoline sulfur reduction of 25% or more is readily achievable using the process according to the present invention, as shown by the Examples below. The sulfur removed by the use of the process is converted to the inorganic form and released as hydrogen sulfide which can be recovered in the normal way in the product recovery section of the FCC unit. The increased load of hydrogen sulfide may impose additional sour gas/water treatment requirements but with the significant reductions in gasoline sulfur achieved, these are not likely to be considered limitative.

[0059] To further illustrate the present invention and the advantages thereof, the following specific examples are given. The examples are given as specific illustrations of the claim invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

[0060] All parts and percentages in the examples as well as the remainder of the specification are by weight unless otherwise specified.

[0061] Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers within any range so recited

EXAMPLES

Example 1

(Catalytic Evaluation of Vanadium Added to Feed)

[0062] The process of the invention was tested in the Davison circulation riser (DCR) for catalytic performance for gasoline sulfur reduction. A gas oil feed with about 1.04 wt% of sulfur in feed was used as the base feed. The feed properties are shown in Table 1

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Table 1
Feed Properties
Heavy Vacuum Gas Oil

API Gravity @60 °F	25.3
Specific Gravity @60 °F	0.9023
Aniline Point, °F	178
Sulfur, wt. %	1.041
Total Nitrogen, wt. %	0.07
Basic Nitrogen, wt. %	0.0308
Conradson Carbon, wt. %	0.21
Ni, ppm	0.2
V, ppm	0.4
Fe, ppm	3.7
Na, ppm	0
Cu, ppm	0
K Factor	11.67
Refractive Index	1.501736
Average Molecular Weight	348
% Paraffinic Ring Carbons, C _p	59.8
% Naphthenic Ring Carbons, C _n	21.1
% Aromatic Ring Carbons, C _a	19
Simulated Distillation, vol %, °F	
IBP	309
5	462
10	525
20	601
30	653
40	703
50	748
60	792
70	835
80	885
90	941
95	981
FBP	1063
Percent Recovery	100

[0063] 2.50 grams of a vanadium naphthenate solution containing about 3 wt % of vanadium was blended with 3000 grams of the feed. The resulting feed contained about 25ppm of vanadium as analyzed by ICP and a vanadium to nickel ratio of 125.

[0064] A commercial FCC catalyst was used for the study. The catalyst was steamed deactivated for 4 hours at 1500°F in 100% steam. The catalyst properties are shown in Table 2.

Table 2
Catalyst Properties

<u>Chemical Analyses (Fresh)</u>		
Al ₂ O ₃	57.4	wt %
SiO ₂	37.9	wt %
RE ₂ O ₃	2.05	wt %
Na ₂ O	0.30	wt %
SO ₄	1.18	wt %
TiO ₂	0.99	wt %
Fe ₂ O ₃	0.64	wt %
P ₂ O ₅	0.14	wt %
CaO	0.09	wt %
MgO	0.05	wt %
<u>Physical Properties (3 hrs./1000°F)</u>		
BET Surface Area	259	m ² /g
Zeolite Area	147	m ² /g
Matrix Area	112	m ² /g
Unit Cell Size	24.56	(Å)
<u>Steam Deactivation (4 hr/1500°F / 100% steam)</u>		
BET Surface Area	141	m ² /g
Zeolite Area	65	m ² /g
Matrix Area	76	m ² /g
Unit Cell Size	24.36	(Å)

[0065] The catalyst and feed combinations were tested for cracking activity and selectivity as well as gasoline sulfur effect in the DCR. The liquid product from each run was analyzed for sulfur using a gas chromatograph with an Atomic Emission Detector (GC-AED). Analysis of the liquid products with the GC-AED allowed each of the sulfur species in the gasoline region to be quantified. For purposes of this example, the cut gasoline will be defined as C₃ to C₁₂ hydrocarbons that have a boiling point up to 430° F. The sulfur species included in the cut of gasoline range include thiophene, tetrahydrothiophene, C₁-C₅ alkylated thiophenes and a variety of aliphatic sulfur species. Benzothiophene is not included in the cut gasoline range.

[0066] The DCR data for the catalysts is shown in Table 3 below.

Table 3
Effect of Feed Added V on Gasoline Sulfur

Vanadium, ppm	0	360	773	1250
Conversion, wt%	77.06	76.49	74.68	76.32
Kinetic Conv	3.36	3.25	2.95	3.22
C/O Ratio	8.10	8.31	8.73	8.54
H ₂ Yield, wt%	0.02	0.03	0.06	0.06
C ₁ + C ₂ 's, wt%	1.65	1.69	1.70	1.70
Total C ₃ , wt%	5.67	5.66	5.27	5.42
Total C ₄ , wt%	10.52	10.71	10.06	10.50
Gasoline, wt%	54.22	53.24	52.19	53.41
LCO, wt%	18.21	18.51	19.52	18.81
Bottoms, wt%	4.74	5.00	5.80	4.87
Coke, wt%	4.51	4.66	4.92	4.74
Cut Gasoline Sulfur, ppm	610	500	393	412
<i>Percent Gasoline S Reduction</i>		<i>18.0%</i>	<i>35.5%</i>	<i>32.4%</i>
Relative to 0 ppmV				

[0067] The first column shows the FCC catalyst without the addition of vanadium to the feed. The next three columns show the product yields and gasoline sulfur as the vanadium accumulated on the catalyst at about 360 ppm, 773 ppm, and 1250 ppm. The data shows that the added vanadium decreased cut gasoline range sulfur content from 18 to 35% as compared to the base FCC catalyst. The H₂ increased modestly as the vanadium increased but the effect on coke was small.

Example 2

(Catalytic Evaluation of Vanadium Added to Feed)

[0068] This example shows the effect of feed vanadium gasoline in the DCR. A commercial equilibrium FCC catalyst and a commercial FCC gas oil feed with about 0.05 wt% of S was used. The equilibrium catalyst contained 24 ppm Ni and 110 ppm V. The catalyst properties are shown in Table 4 below.

Table 4
Ecat Properties

<u>Chemical Analyses</u>		
SiO ₂	64.87	wt %
Al ₂ O ₃	31.6	wt %
RE ₂ O ₃	2.69	wt %
Na ₂ O	0.29	wt %
SO ₄	0.13	wt %
Fe	0.5	wt %
TiO ₂	1.1	wt %
MgO	0.052	wt %
P ₂ O ₅	0.271	wt %
CaO	0.086	wt %
Ni	54	ppm
V	110	ppm
<u>Physical Analyses (3hrs. / 1000 °F.)</u>		
BET Surface Area	181	m ² /g
Zeolite Area	137	m ² /g
Matrix Area	44	m ² /g

The feed properties are shown in Table 5 below

Table 5
Feed Properties

API Gravity @60 °F	22.3
Specific Gravity @60 °F	0.92
Aniline Point, °F	157
Sulfur, wt. %	0.055
Total Nitrogen, wt. %	0.2
Basic Nitrogen, wt. %	0.056
Conradson Carbon, wt. %	0.05
Ni, ppm	0
V, ppm	0.1
Fe, ppm	0
Na, ppm	0.6
Cu, ppm	0
K Factor	11.36
Refractive Index	1.50846
Average Molecular Weight	324
% Paraffinic Ring Carbons, C _p	46.4
% Naphthenic Ring Carbons, C _n	34.2
% Aromatic Ring Carbons, C _a	19.4
Simulated Distillation, vol. %, °F	
IBP	264
	433
	490
	577
	635
	685
	728
	771
	814
	860
	926
	988
FBP	1415
Percent Recovery	100

[0069] The DCR was operated with a riser temperature of 970°F and a regenerator temperature of 1300°F. All the liquid products were analyzed by GC-AED for gasoline sulfur levels. The DCR data for the catalysts is shown in Table 6 below.

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Table 6
DCR Study with Vanadium Added to Feed
970 °F Riser Temperature

	<u>Column A</u>	<u>Column B</u>
	E-Cat	E-Cat V Feed
Added		
Total V in System, ppm	110	640
V on ECAT Only, ppm	110	110
Conversion	68	
Activity	6 18	6 88
H ₂ Yield wt%	0 03	0 06
C ₁ + C ₂ 's wt%	1 86	1 87
Total C ₃ wt%	5 06	4 97
C ₃ wt%	0 69	0 77
C ₃ = wt%	4 37	4 19
Total C ₄ wt%	9 42	9 01
IC ₄ wt%	3 05	3 08
nC ₄ wt%	0 55	0 58
Total C ₄ = wt%	5 82	5 34
Gasoline wt%	49 13	49 03
LCO wt%	24 90	24 90
Bottoms wt%	6 91	6 84
Coke wt%	2 33	2 85
<u>ppm S Gasoline</u>		
Mercaptans	9	7
Thiophene	6	5
MethylThiophenes	21	18
TetrahydroThiophene	2	1
C ₂ -Thiophenes	17	13
Thiophenol	2	0

Table 6 continued

C ₃ -Thiophenes	7	2
MethylThiophenol	7	0
C ₄ -Thiophenes	7	0
BenzoThiophene	11	10
<u>ppm S Gasoline</u>		
Light Cut Sulfur	45	38
Heavy Cut Sulfur	14	2
Cut Gasoline Sulfur	60	41
Total Sulfur	71	50
Thiophenols	9	0
Total Sulfur + Thiophenols	80	51
<u>% Gasoline S Reduction</u>		
Light Cut Sulfur		16%
Heavy Cut Sulfur		85%
Cut Gasoline Sulfur		32%
Total Sulfur		29%
Thiophenols		100%
Total Sulfur + Thiophenols		36%

[0070] The product selectivity was interpolated to a constant conversion of 68 wt%. The first set of yield data was obtained on the base feed and base catalyst without the feed vanadium. At the end of the first set of yield data, the DCR was operated with the same feed, but added 39 grams of vanadium naphthenate solution into 3000 grams of feed. The newly made feed contained about 390 ppm vanadium. Since nickel was below the detection limit, the ratio of vanadium and nickel was not calculated. The DCR continuously operated for 3 hours and the vanadium level on the catalyst was about 750 ppm.

[0071] The Ecat data with vanadium added to the feed (Column B) showed about 32% reduction in cut gasoline sulfur as compared to the base Ecat (Column A).

[0072] Reasonable variations and modifications, which will be apparent to those skilled in the art, can be made in this invention without departing from the spirit and scope thereof.

What is claimed is

1 A process of reducing the sulfur content of cracking products from a fluid catalytic cracking (FCC) process in which a heavy hydrocarbon feed comprising organosulfur compounds is catalytically cracked to lighter products by contact in a cyclic catalyst recirculation cracking process with a circulating fluidizable catalytic cracking equilibrium catalyst inventory, the process comprising

(i) providing a substantially liquid heavy hydrocarbon feed stream comprising at least one organosulfur compound as an impurity,

(ii) introducing the hydrocarbon feed stream into a FCC reactor unit operating under catalytic cracking conditions and comprising a circulating inventory of an equilibrium catalyst composition,

(iii) removing a portion of the equilibrium catalyst inventory from the FCC reactor unit while replacing all the equilibrium catalyst inventory removed from the unit with fresh catalyst to create a steady state environment within the FCC reactor unit;

(iv) contacting the hydrocarbon feed stream with at least one vanadium compound in an amount sufficient to increase the concentration of vanadium in or on the equilibrium catalyst inventory by about 100 to about 20,000 ppm, relative to the amount of vanadium initially present in or on the catalyst inventory;

(v) contacting the equilibrium catalyst inventory in the FCC reactor unit with the vanadium containing hydrocarbon feed stream under a steady state environment to produce a cracking zone effluent comprising cracked products, including gasoline, having a reduced sulfur content

2 The process of claim 1 further comprising simultaneously producing a spent catalyst containing coke and strippable hydrocarbons in step (iii)

3 The process of claim 2 further comprising

(i) discharging and separating the effluent mixture into a cracked product rich vapor phase and a solid rich phase comprising spent catalyst, and

(ii) removing the vapor phase as a product and fractionating the vapor to form liquid cracking products, including gasoline, having a reduced sulfur content.

4 The process of claim 1 wherein said at least one vanadium compound is selected from the group consisting of ammonium ortho-, pyro- or meta vanadates, hydrated vanadium oxides, vanadic acids, organometallic vanadium complexes, vanadium sulfate, vanadyl sulfate, vanadium nitrate, vanadium halides and oxyhalides and mixtures thereof

5 The process of claim 4 wherein said at least one vanadium compound is selected from the group consisting of vanadium oxalate, vanadium sulfate, vanadium naphthenate, vanadium halides, and mixtures thereof

6 The process of claim 1 wherein the hydrocarbon feed stream is contacted with the vanadium compound in an amount sufficient to increase the concentration of vanadium in or on the cracking catalyst by about 300 to about 5000 ppm, relative to the amount of vanadium initially present in or on the cracking catalyst.

7 The process of claim 6 wherein the hydrocarbon feed stream is contacted with the vanadium compound in an amount sufficient to increase the concentration of vanadium in or on the cracking catalyst by about 500 to about 2000 ppm, relative to the amount of vanadium initially present in or on the cracking catalyst.

8 The process of claim 1 wherein the cracking catalyst comprises a large pore size zeolite

9 The process of claim 8 wherein the large pore size zeolite comprises a faujasite

10 The process of claim 1 wherein the hydrocarbon feed further comprises vanadium as an impurity

11 The process of claim 10 wherein the hydrocarbon feed further comprises nickel as an impurity

12 An improved process for catalytic cracking of a hydrocarbon feedstock which contains at least one organic sulfur compounds comprising contacting in a fluid catalytic cracking (FCC) reactor an inventory of fluid catalytic cracking equilibrium catalyst, removing a portion of the catalyst inventory while replacing the same amount of fresh

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catalyst composition to provide a steady state environment within the FCC reactor, the improvement comprising,

(i) contacting the hydrocarbon feed with at least one vanadium compound in an amount sufficient to increase the concentration of vanadium in or on the equilibrium fluid cracking catalyst inventory by about 100 to about 20,000 ppm, relative to the amount of vanadium initially present in or on the catalyst inventory,

(ii) contacting the equilibrium catalyst with the vanadium containing hydrocarbon feed in a FCC reactor unit under a steady state environment to produce a cracking zone effluent comprising cracked products, including gasoline, having a reduced sulfur content

13 The process of claim 3 wherein the process further comprises the addition steps of;

(i) stripping the solids rich spent catalyst phase to remove occluded hydrocarbons from the catalyst,

(ii) transporting stripped catalyst from the stripper to a catalyst regenerator,

(iii) regenerating stripped catalyst by contact with oxygen containing gas to produce regenerated catalyst, and

(iv) recycling the regenerated catalyst to the cracking unit to contact further quantities of heavy hydrocarbon feed

REDUCCION DEL AZUFRE EN LA GASOLINA EN EL CRAQUEO

CATALITICO FLUIDO

CAMPO DE LA INVENCION

Esta invención se relaciona con la reducción del azufre en la gasolina y otros productos de petróleo producidos por un proceso de craqueo catalítico. En particular esta invención se relaciona con un proceso de craqueo catalítico mejorado, el cual suministra corrientes de producto de craqueo catalítico de fracciones de gasolina liviana y pesada que tienen un contenido en azufre reducido.

REFERENCIAS CRUZADAS A SOLICITUDES RELACIONADAS

Esta solicitud esta relacionada con la solicitud serie No 09/144,607, presentada en Agosto 31,1998

Esta solicitud esta tambien relacionada con la solicitud serie No 09/221,539 y 09/221,540, ambas presentadas en Diciembre 28,1998

Esta solicitud está también relacionada con la solicitud serie No 09/399,637, presentada en Septiembre 09,1999

Esta solicitud esta tambien se relaciona con la solicitud serie No 09/649,627, presentada en Agosto 28,2000

ANTECEDENTES DE LA INVENCION

El craqueo catalitico es un proceso de refinacion de petroleo que es aplicado comercialmente a gran escala, especialmente en los Estados Unidos en donde la mayoría del grueso del mezclado de la gasolina en refinarias es producido por craqueo catalitico, con la mayoría de este viniendo del craqueo catalitico fluido el proceso de craqueo catalitico fluido (FCC) En le proceso de craqueo catalítico, los materiales de partida de hidrocarburos contienen fracciones de hidrocarburos pesados que son craqueados en un reactor FCC o unidad para formar productos más livianos El craqueo es llevado a cabo por reacciones que tienen lugar a temperaturas elevadas en la presencia de un catalizador, con la mayoría de la conversion o del craqueo ocurriendo en la fase de vapor

El material de partida es por lo tanto convertido en gasolina, destilados y otros productos de craqueo líquidos lo mismo que productos de craqueo gaseosos livianos de cuatro o menos átomos de carbono por molécula. El gas consiste parcialmente de olefinas y parcialmente de hidrocarburos saturados.

Durante las reacciones de craqueo algunos materiales pesados, conocidos como coque, se depositan en el catalizador. Esto reduce su actividad catalítica y la regeneración es deseada.

Después de remover los hidrocarburos que ocluyen del gasto de catalizador de craqueo, la regeneración es llevada a cabo por el quemado del coque para restaurar la actividad catalizadora. Las tres etapas características del craqueo catalítico pueden por lo tanto distinguirse como sigue: una etapa de craqueo en la cual los hidrocarburos son convertidos en productos más livianos, una etapa de separación para remover los hidrocarburos absorbidos en el catalizador y una etapa de regeneración para quemar el coque del catalizador. El catalizador regenerado es entonces reutilizado en la etapa de craqueo.

Los materiales de partida de craqueo catalítico normalmente contienen azufre en la forma de compuesto de azufre orgánico tales como mercaptanos, sulfuros y tiofenos. Los productos del proceso de craqueo correspondientemente tiende a contener la impurezas de azufre aun cuando cerca de la mitad del azufre es convertido en sulfito de hidrogeno durante el proceso de craqueo, principalmente por descomposición catalítica de los compuestos de azufre no-tiofenicos. La distribucion del azufre en los productos de craqueo es dependiente de un numero de factores que incluyen la alimentacion el tipo de catalizador, los aditivos presentes, la conversión y otras condiciones de operacion pero, en cualquier caso una cierta proporcion del azufre tiende a ingresar en las fracciones de gasolina liviana y pesadas y pasan adelante a el grueso del producto. Con el incremento en las regulaciones ambientales aplicadas a los productos de petróleo, por ejemplo en las regulaciones reformuladas de gasolina (RFG) el contenido de azufre en los productos generalmente ha disminuido en respuesta a las preocupaciones acerca de las emisiones de oxidos de azufre y otros compuestos de azufre al aire luego del proceso de combustion.

Una enseñanza ha sido retirar el azufre de la alimentación FCC por hidrotratamiento antes de que se inicie el craqueo. Aunque es altamente efectivo, esta enseñanza tiende a ser costosa en términos de costo de capital del equipo y lo mismo que operacionalmente ya que el consumo de hidrógeno es alto. Otra enseñanza ha sido la de remover el azufre de los productos craqueados por hidrotratamiento. Nuevamente, aunque es efectivo, esta solución tiene el inconveniente de que el producto de octano valioso puede perderse cuando las olefinas de alto octano están saturadas.

Desde el punto de vista económico, sería deseable lograr remover el azufre en el proceso de craqueo mismo ya que esto desulfurizaría efectivamente el mayor componente del grueso de la mezcla de gasolina sin tratamiento adicional. Varios materiales catalizadores han sido desarrollados para la remoción del azufre durante el ciclo de proceso FCC. Por ejemplo, un catalizador de FCC impregnado con vanadio y metal níquel ha sido mostrado que reduce el nivel del producto (ver Mystrad et al, Effect of Nickel and Vanadium on Sulfur Reduction of FCC Naphtha, Applied Catalyst A General

192(2000) paginas 299-305) Esta referencia tambien mostro que un aditivo para reducir el azufre con base en un zinc impregnado de alumina es efectivo para reducir el producto de azufre en los productos FCC Sin embargo, cuando se ha mezclado con un catalizador impregnado con metal, el efecto del aditivo para reducir el azufre fue inhibido

Otros desarrollos para la reduccion del azufre en los productos se han centrado en la remocion del azufre a partir de los gases apilados en el regenerador. Una enseñanza primera desarrollada por Chevron uso compuestos de alumina como aditivos en el inventario del catalizador de craqueo para absorber oxidos de azufre en el regenerador FCC, los compuestos de azufre absorbidos que ingresaron en el proceso en la alimentación fueron liberados como sulfuro de hidrogeno durante la porcion de craqueo del ciclo y pasaron a la sección de recuperacion de producto de la unidad en donde fueron removidos. Ver Krishna et al, Additives Improve FCC Process, Hydrocarbon Processing, Noviembre 1991, paginas 59-66. El azufre es removido de los gases apilados emitidos por el regenerador pero los niveles de azufre del producto no fueron afectados grandemente, si es que lo fueron.

Una tecnología alternativa para la remoción de óxidos de azufre de los gases de chimenea del regenerador se basa en el uso de espineles de magnesio-aluminio como aditivos en el inventario de catalizador circulante en el FCCU. Bajo la designación de DESOX™ usada para los aditivos en este proceso, la tecnología logró un notable éxito comercial. Patentes ejemplares o ilustrativas que describen este tipo de aditivos para remover azufre incluyen la patente estadounidense No 4,963,520, 4,957,892, 4,957,718, 4,790,982 y otras. Nuevamente, sin embargo, los niveles de azufre en el producto no fueron reducidos grandemente.

Aditivos de catalizador para la reducción de niveles de azufre en los productos de craqueo líquido fue propuesta por Ziebarth et al en la patente Estadounidense 6,036,847, usando composiciones que contenían un componente de titanio, y Wormsbecher y Kim en las patentes Estadounidenses 5,376,608 y 5,525,210, usando un aditivo de catalizador de craqueo de un ácido Lewis soportado por alumina para la producción de gasolina con azufre reducido pero este sistema no logró un éxito comercial significativo.

En la solicitud serie No 09/144,607, presentada en Agosto 31,1998, los materiales catalizadores son descritos para ser usados en el proceso de craqueo catalitico, los cuales son capaces de reducir el contenido de los productos líquidos del proceso de craqueo Estos catalizadores de reduccion de azufre comprenden, en adición a un componente de tamiz molecular poroso, un metal en un estado de oxidacion por encima de cero dentro del interior de la estructura porosa del tamiz El tamiz molecular es en la mayoría de los casos una zeolita y esta puede ser zeolita que tenga características consistentes con las zeolitas de poros grandes tales como zeolita beta o zeolita USY o con zeolitas de tamaño de poro intermedio tales como la ZSM-5 Los tamices moleculares no zeolíticos tales como MeAPO-5, MeAPSO-5, lo mismo que los materiales cristalinos mesoporosos tales como MCM-41 pueden ser usados como componentes de tamiz del catalizador Los metales tales como vanadio, zinc, hierro, cobalto, y galio se encontraron que eran efectivos para la reduccion del azufre en la gasolina, con el vanadio siendo el metal preferido La cantidad del componente de metal en el catalizador aditivo para la reducción de azufre esta

normalmente entre 0,2 a 5% en peso, pero cantidades de hasta 10% en peso fueron establecidas para dar algun efecto en la remocion del azufre El componente de reduccion de azufre puede ser un aditivo de partículas separadas o parte de un catalizador integrado de craqueo/reducción de azufre Cuando es usado como un catalizador de aditivo de partículas separa, estos materiales son usados en combinacion con un catalizador de craqueo catalitico activo (normalmente una faujasita tal como la zeolita Y y REY, especialmente, como zeolita USY y REUSY) para los materiales de partida de hidrocarburos el de proceso en la unidad FCC para producir productos de bajo azufre

En las solicitudes serie Nos 09/221,539 y 09/221/540, ambas presertadas en diciembre 28,1998, el catalizador de reduccion de azufre similar aquel descrito en la solicitud No 09/144,607 fue descrito, sin embargo, las composiciones catalizadoras en aquellas solicitudes también contenían por lo menos un componente de metal de tierra rara (por ejemplo lantanio) y un componente de cerio, respectivamente La cantidad del componente metálico en los catalizadores de reducción de azufre está normalmente entre 0,2 a 5% en peso, pero cantidades de

hasta 10% en peso fueron sugeridas para dar algun efecto de remoción de azufre

En la solicitud serie No 09/399,637 presentada en septiembre 20,1999, un proceso de craqueo catalítico mejorado para reducir el contenido de azufre en los productos de craqueo liquido, especialmente la gasolina de craqueo Producida a partir de alimentacion de hidrocarburos que contenían compuestos de organo azufre fue descrito El proceso emplea un sistema de catalizador que tienen un componente de reduccion de azufre que contiene un catalizador poroso y un componente metalico en un estado de oxidacion mayor a cero La actividad de reduccion de azufre en el sistema catalizador incrementando el promedio de estado de oxidacion del componente metalico por una etapa de oxidacion luego de la regeneracion catalizadora convencional

La solicitud serie No 09/649,627, presentada en Agosto 28,2000, es una continuacion en parte de la solicitud serie No 09/399,637 y describe aditivos para la reduccion de azufre mejorados para el uso en un proceso de craqueo catalitico para la reducción del contenido de azufre El aditivo para la reduccion de

azufre comprende un material de soporte de tamiz no molecular (preferiblemente un oxido inorganico tal como Al_2O_3 , SiO_2 , y mezclas de ellos) que contiene una alta concentracion de vanadio. La cantidad de vanadio contenida en el catalizador de aditivo para reduccion de azufre esta normalmente entre cerca de 2,0 a cerca de 20% en peso, tipicamente entre cerca de 3 a cerca de 10% en peso (metal con base en el peso total del aditivo)

Si importar las tecnologias para la reduccion de azufre recientes, estas continuan la existencia de una necesidad de maneras efectivas para reducir el contenido de azufre de la gasolina y de otros productos de craqueo liquido. La presente invencion fue desarrollada en respuesta a esta necesidad.

RESUMEN DE LA INVENCION

Un proceso de craqueo catalitico mejorado ha sido ahora desarrollado el cual es capaz de mejorar la reduccion en el contenido de azufre de los productos del proceso de craqueo, incluyendo la gasolina y fracciones de craqueo de destilados intermedios. De acuerdo con el proceso de la invencion por lo menos un compuesto que

contiene vanadio es agregado a un material de partida de hidrocarburo liquido que contiene azufre, y opcionalmente vanadio y / o níquel, como impurezas para incrementar selectivamente la concentracion de vanadio en el material de partida. El material de partida enriquecido con vanadio es de ahí en adelante cargado en la unidad de FCC que opera bajo condiciones estables para poner en contacto un inventario de catalizador de equilibrio FCC in situ con una concentración de vanadio, expresada, como vanadio elemental.

El mecanismo por el cual la presente invención actúa para mejorar la remoción de los componentes de azufre normalmente presentes en los productos de hidrocarburo de craqueo no es entendido precisamente. Sin embargo, la presencia de la alta concentracion de un compuesto de vanadio en el material de partida permite el transporte rápido del vanadio sobre el inventario de catalizador circulante completo, y por lo tanto incrementa la actividad de catalizador de craqueo para remover el azufre.

De acuerdo con lo anterior, es una ventaja de la presente invencion el suministrar un proceso de craqueo

catalítico mejorado, que suministra productos líquidos que tienen una reducción de azufre mejorada cuando se compara con la actividad de reducción de azufre típica en los procesos de craqueo catalítico convencionales

También es una ventaja de la presente invención suministrar un proceso de craqueo catalítico que permite una dispersión rápida del vanadio sobre el inventario de catalizador de craqueo completo, mejorando así la remoción de los componentes de azufre de los productos de hidrocarburo de craqueo

Una ventaja adicional de la presente invención es suministrar un proceso de craqueo catalítico que tiene una reducción de azufre del producto mejorada sin la necesidad de la adición de aditivos para la reducción de azufre, incluyendo aditivos de zeolita/vanadio como se describió en las solicitudes serie No 09/144,607, 09/221,539, 09/221,540, 09/399,637 y 09/649,627

Otra ventaja de la presente invención es suministrar composiciones de craqueo catalítico in situ durante un proceso de craqueo catalítico que dichas composiciones son capaces de mejorar la reducción del contenido de

azufre de los productos de craqueo liquido en la presencia de contaminantes metalicos, por ejemplo níquel y hierro

Otros objetivos y ventajas se harán evidentes de la descripción detallada y las reivindicaciones adjuntas

BREVE DESCRIPCION DE LOS DIBUJOS

La figura muestra un proceso de craqueo catalitico tipico para la reduccion del contenido de azufre en el producto de acuerdo con la presente invención

DESCRIPCION DETALLADA DE LA INVENCION

Para los propósitos de esta invencion el termino "catalizador fresco" se usa para indicar una composición catalizadora como se fabrica y se vede

El termino "catalizador de equilibrio" o "ecat" se usa aqui para indicar el inventario de la composicion catalizadora de craqueo fluido circulante en una unidad FCC que opera bajo condiciones de craqueo catalítico
Para propositos de esta invencion los terminos

"catalizador de equilibrio", "catalizador de gasto" (catalizador tomado de una unidad FCC) y "catalizador regenerado" (catalizador que deja una unidad de regeneracion) deben considerarse equivalentes

El término "estable" es usado aquí para indicar condiciones de operación dentro de una unidad de reactor FCC en donde existe dentro de la unidad una cantidad constante de inventario de catalizador que tiene una actividad catalizadora constante a una velocidad de alimentacion constante de un material de partida que tienen una composicion definida para obtener una velocidad de conversion constante de los productos

El término "velocidad de conversion" se usa aquí para indicar la velocidad a la cual un material de partida de hidrocarburos es convertido a productos de hidrocarburos hirvientes menores de bajo peso molecular

El término "actividad catalizadora" se usa aquí para indicar la cantidad de producto craqueado formado por unidad de tiempo por unidad de volumen del reactor

De acuerdo con la presente invencion, un proceso FCC convencional es modificado para suministrar una alta concentración de vanadio (expresado como vanadio elemental) directamente el inventario de catalizador de equilibrio para reducir el contenido de azufre de los productos líquidos craqueados. El proceso involucra cargar un material de partida de hidrocarburo, que contiene por lo menos un compuesto organoazufre como una impureza, en una unidad FCC que opera bajo condiciones de craqueo catalítico para poner en contacto el inventario de catalizador de equilibrio contenido en la unidad. Durante el proceso FCC, el catalizador FCC fresco es agregado y el catalizador de equilibrio es retirado para crear una condición estable dentro de la unidad del reactor FCC. Una vez el ambiente estable se ha alcanzado dentro de la unidad FCC, el material de partida de hidrocarburo es tratado para agregarle por lo menos un compuesto de vanadio a dicho material. El material de partida tratado con vanadio es cargado en la unidad FCC que opera bajo condición estable para poner en contacto el inventario de catalizador de equilibrio y selectivamente suministrar un alto contenido de vanadio expresado como vanadio elemental, al catalizador de equilibrio. El catalizador tratado con vanadio es luego

recirculado por la unidad FCC en un proceso continuo de reacción/regeneración para reducir el contenido de azufre de las fracciones de productos líquidos craqueados en particular fracciones de gasolina liviana y pesada

El proceso de craqueo catalítico de la invención puede ser conducido usando una unidad craqueo catalítico adecuada o reactor. Para conveniencia la invención será descrita con referencia al proceso FCC aunque el presente proceso podría utilizarse en el proceso de craqueo tipo cama movable antiguo (TCC) con ajustes apropiados para adecuar los requerimientos del proceso. A parte de la adición de compuestos de vanadio al material de partida de hidrocarburo y algunos posibles cambios en la sección de recuperación de producto, discutidos más adelante, la manera de operar el proceso permanece sin cambio. Así, los catalizadores FCC convencionales pueden ser usados, por ejemplo, catalizadores con base en zeolita con un componente de craqueo de faujasita como se describió en la revisión seminal por Venuto y Habib, Fluid Catalytic Cracking with Zeolite Catalysts, Marcel Dekker, New York 1979, ISBN 0-8247-6870-1 lo mismo que en numerosas otras fuentes tales como Sadeghbeigi, Fluid Catalytic Cracking

Handbook, GulfPubl Co Houston, 1995, ISBN 0-88415-290-1

Generalmente, el proceso de craqueo catalítico fluido en el cual el material de partida de hidrocarburos pesados que contienen en los compuestos de organoazufre seran craqueados a productos mas livianos lo que tiene lugar en una unidad de reactor de craqueo catalítico poniendo en contacto el material de partida en un proceso de craqueo de recirculacion catalizadora ciclica con un inventario de catalizador de craqueo catalítico fluidizable que consiste de partículas que tienen un tamaño que varia entre cerca de 20 a cerca 100 micrones Las etapas significativas en el proceso ciclico son

- (1) El material de partida que contiene el hidrocarburo o alimentación es cargado en la unidad de craqueo catalitico normalmente contiene uno o más elevadores, condiciones de craqueo catalitico en operación por el contacto del material de partida con una fuente de catalizador de craqueo regenerado caliente para producir un efluente que comprende productos de craqueo y

catalizador de gasto que contiene coque y hidrocarburos separables,

(11) El efluente es descargado y separado, normalmente en uno o mas ciclones, en una fase vapor rica en producto craqueado y una fase de sólidos ricos que comprende catalizador de gasto,

(111) La fase de vapor es retirada como producto y fraccionada en la columna principal del FCC y sus columnas laterales asociadas para formar productos de craqueo liquido incluyendo gasolina,

(1V) El catalizador de gasto es separado, usualmente con vapor, para remover los hidrocarburos que ocluyen del catalizador, después de lo cual el catalizador separado es regenerado oxidativamente para producir catalizador regenerado caliente el cual es entonces reciclado a la zona de craqueo para craquear cantidades adicionales de la alimentacion

Un catalizador fresco equilibra dentro de la unidad FCC o reactor, el catalizador de equilibrio es expuesto a diversas condiciones, tales como la deposición de contaminantes del material de partida y regeneración severa de las condiciones de operación. Así, el catalizador de equilibrio puede contener altos niveles de contaminantes metálicos, incluyendo pero no limitado a, vanadio, níquel y hierro. En operación normal de una unidad FCC, el catalizador fresco es agregado diariamente a la misma velocidad que el catalizador de equilibrio es retirado. Esto suministra una cantidad constante de inventario de catalizador que tiene una actividad catalizadora constante, la cual mantiene una conversión constante de la alimentación y selectividad de productos deseados.

Así, en condiciones de operación estables, la cantidad de catalizador de equilibrio en la unidad FCC es constante, por ejemplo la cantidad de catalizador fresco agregado a la unidad FCC es igual a la cantidad de catalizador de equilibrio retirada de la unidad más la cantidad de catalizador de equilibrio perdido durante la atrición. También, durante la operación estable de una unidad FCC, la velocidad a la cual el material de partida

tienen una composición definida que es agregada a la unidad se mantiene constante Esta alimentación puede ser caracterizada por un número de propiedades tales como gravedad API, gravedad específica, azufre total (% en peso) nitrógeno total (% en peso), contenido de metales (% en peso), carbono Conradson, factor K, y punto de ebullición y distribuciones de peso molecular

Tipicamente, durante la reacción de craqueo en la unidad FCC, el azufre en el material de partida o de alimentación se distribuye en las fracciones líquidas y gaseosas de los productos craqueados Estos productos incluyen gasolina H_2S , aceite de ciclo liviano (LCO), aceite de ciclo pesado (HCO), coque y alimentación no convertida Bajo condiciones estables, la cantidad de azufre (en una base de % en peso) generado en estos productos es constante Inesperadamente, sin embargo, se ha encontrado que la adición de vanadio de una fuente secundaria a la alimentación que está siendo cargada en la unidad FCC que opera bajo ambiente estable selectivamente incrementa la concentración de vanadio en el catalizador de equilibrio circulante para reducir de manera efectiva el contenido de azufre de los productos careados La cantidad de azufre en los productos líquidos

especialmente las fracciones de gasolina, se ha reducido como un resultado del vanadio incrementado en el catalizador de equilibrio, aun en la presencia de contaminantes metalicos tales como niquel y hierro

De acuerdo a lo anterior, el proceso de acuerdo con la presente invencion generalmente comprende

(1) Suministrar una corriente de alimentacion de hidrocarburos pesados sustancialmente líquidos que comprende por lo menos un compuesto de organoazufre como una impureza,

(11) Cargar la corriente de material de alimentación de hidrocarburos en una unidad de reactor FCC que opera bajo condiciones de craqueo catalitico y que tiene un inventario circulante de una composicion catalizadora de equilibrio,

(111) Remover una porcion del inventario de catalizador de equilibrio de la unidad de reactor FCC mientras se reemplaza todo el inventario de catalizador de equilibrio removido con

catalizador fresco para crear un ambiente estable dentro de la unidad,

(iv) Poner en contacto la corriente de alimentacion de hidrocarburos con por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar la concentracion de vanadio en o sobre el inventar o de catalizador de equilibrio en cerca de 100 a cerca de 20 000 ppm, en relacion con la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador, y

(v) Poner en contacto la corriente de alimentacion de hidrocarburo que contiene vanadio con el inventario de catalizador de equilibrio en la unidad de reactor FCC bajo condiciones estables para producir un efluente de zona de craqueo que comprende productos craqueados que tienen un contenido de azufre reducido

Los compuestos de vanadio utiles en la presente invencion pueden ser cualquier compuesto que contenga vanadio que permita el transporte y deposición de las

especies de vanadio en el catalizador de craqueo bajo condiciones de craqueo catalítico. Ejemplo no limitativos de compuestos de vanadio adecuados son los orto-piro-meta vanadatos de amonio, óxidos de vanadio (por ejemplo V_2O_5), ácidos vanádicos, complejos de vanadio organometálicos (por ejemplo naftenato de vanadilo), sulfato de vanadio, nitrato de vanadio, nitrato de vanadilo, haluros de vanadio y oxihaluros de vanadio (por ejemplo cloruros y oxiclорuros de vanadio) y mezcla de ellos. Preferiblemente, el compuesto de vanadio se selecciona del grupo que consiste de oxalato de vanadio, sulfato de vanadio, naftenato de vanadio, haluros de vanadio y mezcla de ellos.

En una modalidad preferida, los compuestos de vanadio son mezclados en el producto de alimentación como una solución antes de la inyección de la alimentación en el reactor. Soluciones de vanadio adecuadas incluyen aquellas soluciones en donde los compuestos de vanadio deseados son disueltos en agua o en un disolvente no acuoso, por ejemplo un disolvente orgánico adecuado tal como pentano, tolueno y similares. En una modalidad preferida, una solución de naftenato de vanadio no acuosa es usada.

La cantidad de la solución de vanadio agregada a la corriente de alimentación típicamente será relativamente pequeña. Consecuentemente, la solución de vanadio puede agregarse al material de partida usando cualquier bomba comercialmente disponible. Para aplicación práctica, el suministro de la solución de vanadio puede ser continuo o intermitente.

Como se muestra en la figura, en un proceso FCC típico de acuerdo con la invención, una solución de vanadio 2 es agregada directamente a 1 material de partida 1 que va a ser cargado dentro de la unidad reactiva de elevación 4 para suministrar una alimentación de hidrocarburo que contiene vanadio 3. La alimentación de hidrocarburo que contiene vanadio 3 es luego introducida en el reactor de elevación 4 que contiene un inventario de catalizador de equilibrio y opera bajo un ambiente estable. El efluente del reactor de elevación 4 es separado en una corriente de producto craqueado 5 y una corriente de catalizador de gastos 6 que contiene coque e hidrocarburos separables. La corriente de catalizador de gasto se hace recircular luego en la

unidad de craqueo por un regenerador 7 para regenerar el catalizador

El catalizador de craqueo utilizado en el proceso de craqueo de la invención normalmente estara en base a componente de craqueo activo de zeolita faujasita, que es convencionalmente zeolita Y en una de sus formas tales como zeolita tipo Y intercambiada con tierra rara calcinada (CREY), la preparación de la cual se describe en la patente Estadounidense No 3,402,996, zeolita tipo Y ultra estable (USY) como se describe en la patente Estadounidense No 3,293,192, lo mismo que varios zeolitas tipo Y intercambiadas parcialmente como se describe en las patentes Estadounidenses Nos 3,607,043 y 3,676,368 El componente de craqueo activo es combinado rutinariamente con un material de matriz tal como alumina para poder suministrar las característica mecanicas deseadas (resistencia a la atricion etc) lo mismo que el control de actividad para el componente de zeolita muy activo o componentes de zeolita muy activos El tamaño de partícula del catalizador de craqueo esta típicamente en el rango entre 10 a 120 micrones para fluidizacion efectiva

Los materiales de partida utiles en el proceso de craqueo catalítico de esta invención incluyen una alimentacion de hidrocarburos liquida o sustancialmente liquida que contiene azufre como contaminante. Los materiales de partida incluyen aquellos que son utilizados convencionalmente en procesos de craqueo catalítico para producir gasolina o fracciones destiladas livianas a partir de materiales de partida de hidrocarburos mas pesados. Los materiales de partida generalmente tienen un punto de ebullicion inicial por encima de 400° F (204° C) e incluye fluidos tales como aceites de gas, aceites de combustibles, aceites de ciclo, aceites de lodos, crudos de destilacion primaria, aceites de esquisto, aceites de arenas de brea, aceites de carbón, mezclas de dos o más de estos, y similares. Por "crudo de destilacion primaria" se quiere decir aquellos aceites que han sido obtenidos en la parte inferior de un fraccionador de aceite crudo. Si se desea, toda o una porcion del material de partida puede constituir un aceite del cual una porcion del contenido metálico previo ha sido removida, por ejemplo, por hidrotratamiento o extracción por disolvente.

Opcionalmente, el material de partida utilizado en este proceso puede contener como impurezas uno o más metales de níquel, vanadio y hierro en los rangos siguientes típicos níquel a un nivel entre 0,02 a cerca de 100 ppm, vanadio a un nivel entre cerca de 0,02 a 500 ppm, y hierro a en un nivel de 0,02 a 500 ppm. En una modalidad preferida el material de partida contiene vanadio como una impureza.

De acuerdo con el proceso de la invención, el compuesto de vanadio es agregado a la alimentación durante la operación de la unidad FCC bajo condiciones estables. La cantidad de compuesto de vanadio agregado a la alimentación variará dependiendo de tales factores como la naturaleza del material de partida usado, el catalizador de craqueo utilizado y los resultados deseados. Generalmente el compuesto de vanadio es agregado a la alimentación a una velocidad suficiente para incrementar la concentración de vanadio sobre el inventario de catalizador de equilibrio desde cerca de 100 a cerca de 20 000 ppm, preferiblemente cerca de 300 a cerca de 5 000 ppm, más preferiblemente cerca de 500 a cerca de 2 000 ppm, relativo a la cantidad de vanadio inicialmente presente sobre el inventario catalizador.

La concentracion de vanadio sobre el inventario de catalizador de equilibrio bajo condiciones estables puede determinarse por la siguiente ecuacion

$$\text{Ppm V sobre ecat} = \frac{\text{Ppm V en la alimentacion x velocidad de alimentación (Toneladas/Dia)}}{\text{Velocidad de Adicion de Catalizador (T/D)}}$$

El proceso de craqueo catalítico de la invención es conducido en unidades de reactor FCC convencionales en donde la temperatura de reacción varia entre cerca de 400° C a 700° C y las temperaturas de regeneración entre 500° C a 850° C son utilizadas Las condiciones dentro de la zona de craqueo y regeneracion, como sera entendido por aquellos versados en la técnica, no son criticas y dependen de varios parametros tales como el material de partida de alimentación usado, el catalizador, y los resultados deseados

El efecto del proceso mejorado de la invencion es reducir el contenido de azufre de los productos de

craqueo liquido, especialmente las fracciones de gasolina liviana aunque reducciones tambien se notaron en el aceite de ciclo liviano, haciendo los productos mas adecuados para uso como diesel o componente de mezcla de aceite para calentamiento domestico La reduccion de azufre en la gasolina del 25% o mas es evidentemente lograble usando el proceso de acuerdo con la presente invención, como se muestra en los ejemplos que siguen El azufre removido por el uso del proceso es convertido en una forma inorganica y liberado como sulfuro de hidrogeno el cual puede ser recuperado de una manera normal en la sección de recuperacion del producto en la unidad FCC La carga incrementada de sulfuro de hidrogeno puede imponer requerimientos de tratamientos adicionales de gas amargo/agua pero con las reducciones significativas en el azufre en la gasolina logrado, no se debe considerar esto como una limitación

Para ilustrar adicionalmente la presente invencion y las ventajas de la misma, los siguientes ejemplos especificos se han dado Los ejemplos se han dado como ilustraciones especificas de la reivindicacion de la invencion reivindicada

Debe entenderse, sin embargo, que la invención no esta limitada a detalles específicos establecidos en los ejemplos

Todas las partes y porcentajes en los ejemplos lo mismo que el resto de la especificacion se da en peso a menos que se especifique lo contrario

Adicionalmente, cualquier rango de numeros recitados o dados en la especificación o reivindicaciones, tales los que representan un conjunto particular de propiedades, unidades de medida, condiciones, estados fisicos o porcentajes, tiene el proposito de incorporal literalmente expresamente aquí como referencia o de otra manera cualquier numero que caiga dentro de tal rango, que incluya cualquier subconjunto de numeros den estrógeno de cualquier rango así recitado

EJEMPLOS

Ejemplo 1

(Evaluación Catalítica del vanadio agregado a la alimentación)

El proceso de la invención fue ensayado en el elevador de circulación de visión (DCR) para el comportamiento catalítico en la reducción de azufre en la gasolina. Una alimentación de aceite de gas con cerca de 1,04 % en peso de azufre en la alimentación fue usado como alimentación base. Las propiedades de la alimentación se muestran en la tabla 1.

Tabla 1

Propiedades de la alimentación

Aceite de Gas Pesado en Vacío

Gravedad API @60 °F	25,3
Gravedad Específica @60 °F	0,9023
Punto de Anilina, °F	178

Azufre, % en peso	1,041
Nitrogeno Total, % en peso	0,07
Nitrógeno Básico, % en peso	0,0308
Carbon Conradson, % en peso	0,21
N ₁ , ppm	0,2
V, ppm	0,4
Fe, ppm	3,7
Na, ppm	0
Cu, ppm	0
Factor K	11,67
Indice Refractivo	1,501736
Peso Molecular Promedio	348
% de Carbonos de Anillo	59,8
Parafinico, C _p	
% de Carbonos de Anillo Naftenico,	21,1
C _n	
% de Carbono de Anillo Aromatico,	19
C _a	

Destilacion	Simulada,	%	en
Volumen, °F			
IBP			309
5			462
10			525
20			601
30			653
40			703
50			748
60			792
70			835
80			885
90			941
95			981
FBP			1063
% de Recuperación			100

2,50 gramos de una solución de naftenato de vanadio que contiene cerca de 3% en peso de vanadio fue mezclada con 3 000 gramos de la alimentación. La alimentación resultante que contenía cerca de 25 ppm de vanadio según se analizó por ICP y una proporción de vanadio a níquel de 125

Un catalizador FCC comercial fue utilizado para el estudio. El catalizador fue vaporizado desactivado durante 4 horas a 1500° F en 100% de vapor. Las propiedades catalizadoras se muestran en la Tabla 2.

Tabla 2

Propiedades Catalizadoras

Analisis Químico (Fresco)

Al ₂ O ₃	57,4	% en peso
SiO ₂	37,9	% en peso
RE ₂ O ₃	2,05	% en peso
Na ₂ O	0,30	% en peso
SO ₄	1,18	% en peso
TiO ₂	0,99	% en peso
Fe ₂ O ₃	0,64	% en peso
P ₂ O ₅	0,14	% en peso
CaO	0,09	% en peso
MgO	0,05	% en peso

Propiedades Físicas (3 horas/1000° F)

Area de Superficie BET	259	m ² /g
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Area de Zeolita	147	m ² /g
Area de Matriz	112	m ² /g
Tamaño de celula de la	24,	(Å)
unidad	56	

Desactivacion del vapor (4 horas/1500° F/100% vapor)

Area de Superficie BET	141	m ² /g
Area de Zeolita	65	m ² /g
Area de Matriz	76	m ² /g
Tamaño de celula de la	24,	(Å)
unidad	36	

Las combinaciones de catalizador y alimentacion fueron ensayadas en cuanto actividad de craqueo y selectividad lo mismo que el efecto de azufre en gasolina en el DCR El producto liquido de cada corrida para el azufre usando un cromatografo de gas con un detector de emision atomica (GC-AED) El análisis de los productos líquidos con el GC-AED permitio que cada una de las especies de azufre en la region de gasolina fuera cuantificada Para propositos de este ejemplo, la gasolina cortada sera definida como hidrocarburos con C₁ a C₁₂ que tienen un punto de ebullición hasta de 430° F

las especies de azufre incluidas en el corte de gasolina variaban en el rango de gasolina incluían tiofeno, tetrahidrotiofeno, tiofeno alquilados con 1 a 5 carbonos y una variedad de especies de azufre alifáticos. Los benzotiofenos no estuvieron incluidos en el rango de corte de gasolina.

Los datos DCR para los catalizadores se muestran en la Tabla 3 que sigue.

Tabla 3

Efecto de la Alimentación Agregada sobre el Azufre en la Gasolina

Vanadio, ppm	0	360	773	1250
Conversion, % en peso	77,06	76,49	74,68	76,32
Conversión Cinética	3,36	3,25	2,95	3,22
Proporción C/O	8,10	8,31	8,73	8,54
Producción de H ₂ , % en peso	0,02	0,03	0,06	0,06
C ₁ +C ₂ , % en peso	1,65	1,69	1,70	1,70
Total de C ₃ , % en peso	5,67	5,66	5,27	5,42
Total de C ₄ , % en peso	10,52	10,71	10,06	10,50

Gasolina, % en peso	54,22	53,24	52,19	53,41
LCO, % en peso	18,21	18,51	19,52	18,81
Productos inferiores, % en peso	4,74	5,00	5,80	4,87
Coque, % en peso	4,51	4,66	4,92	4,74
Azufre de corte de gasolina, ppm	610	500	393	412
Porcentaje de reduccion de S en gasolina Relativo a 0 ppm de V		18,0%	35,5%	32,4%

La primera columna muestra el catalizador FCC sin la adición del vanadio a la alimentación. Las siguientes tres columnas muestran en las producciones de producto y de azufre en gasolina como vanadio acumulado en el catalizador alrededor de 360 ppm, 773 ppm y 1250 ppm. Los datos muestran que el vanadio agregado disminuyó el contenido de azufre en el rango de corte de gasolina entre 18 a 35% según se comparó con el catalizador FCC base. El H₂ incrementado modestamente como a medida que el vanadio se incrementó pero el efecto en el coque fue pequeño.

Ejemplo 2

(Evaluación Catalítica del Vanadio agregado a la
alimentación)

Este ejemplo muestra el efecto de la gasolina con vanadio de alimentación en el DCR. Un catalizador FCC de equilibrio comercial y una alimentación de aceite gas FCC comercial con cerca de 0,05% en peso de ese fueron usados. El catalizador de equilibrio contenía 24 ppm de Ni y 110 ppm de V. Las propiedades del catalizador se muestran en la Tabla 4 que sigue.

Tabla 4
Propiedades del Ecat

Analisis Químico

SiO ₂	64,87	% en peso
Al ₂ O ₃	31,6	% en peso
RE ₂ O ₃	2,69	% en peso
Na ₂ O	0,29	% en peso
SO ₄	0,13	% en peso
Fe	0,5	% en peso
TiO ₂	1,1	% en peso
MgO	0,052	% en peso
P ₂ O ₅	0,271	% en peso
CaO	0,086	% en peso
Ni	54	ppm
V	110	ppm

Analisis Físico (3 horas/1000° F)

Area de Superficie BET	181	m ² /g
Area de Zeolita	137	m ² /g
Area de Matriz	44	m ² /g

Las propiedades de la alimentacion se dan en la Tabla 5 que sigue

Tabla 5
Propiedades de la Alimentacion

Gravedad API @60 °F	22,3
Gravedad Especifica @60 °F	0,92
Punto de Anilina, °F	157
Azufre, % en peso	0,055
Nitrogeno Total, % en peso	0,2
Nitrogeno Basico, % en peso	0,056
Carbon Conradson, % en peso	0,05
N1, ppm	0
V, ppm	0,1
Fe, ppm	0
Na, ppm	0,6
Cu, ppm	0

Factor K	11,36
Indice Refractivo	1,50846
Peso Molecular Promedio	324
% de Carbonos de Anillo	46,4
Parafinico, C _p	
% de Carbonos de Anillo Naftenico,	34,2
C _n	
% de Carbono de Anillo Aromatico,	19,4
C _a	
Destilacion Simulada, % en	
Volumen, °F	
IBP	264
	433
	490
	577
	635
	685
	728
	771
	814

	860
	926
	988
FBP	1415
% de Recuperacion	100

El DCR fue operado con un elevador a temperatura de 970° F y una temperatura del regenerador de 1300° F todos los productos líquidos fueron analizados por GC-AED para los niveles de azufre en la gasolina Los datos DCR para los catalizadores se dan en la Tabla 6 que sigue

Tabla 6

Estudio DCR con Vanadio Agregado a la alimentacion

Temperatura del Elevador 970° F

alimentación	<u>Columna A</u>	<u>ColumnaB</u>
	E-Cat	E-Cat
	V	
Agregado		
V Total en el Sistema, ppm	110	640
V en el ECAT solamente, ppm	110	110
Conversion	68	

FBP	1415
% de Recuperación	100

El DCR fue operado con un elevador a temperatura de 970° F y una temperatura del regenerador de 1300° F todos los productos líquidos fueron analizados por GC-AED para los niveles de azufre en la gasolina Los datos DCR para los catalizadores se dan en la Tabla 6 que sigue

Tabla 6

Estudio DCR con Vanadio Agregado a la alimentación
Temperatura del Elevador 970° F

	<u>Columna A</u> E-Cat	<u>ColumnaB</u> alimentación E-Cat V
Agregado		
V Total en el Sistema, ppm	110	640
V en el ECAT solamente, ppm	110	110
Conversion	68	
Actividad	6,18	6,88
Produccion de H ₂ % en peso	0,03	0,06
C ₁ +C ₂ % en peso	1,86	1,87
Total de C ₃ % en peso	5,06	4,97
C ₃ % en peso	0,69	0,77

Actividad	6,18	6,88
Producción de H ₂ % en peso	0,03	0,06
C ₁ +C ₂ % en peso	1,86	1,87
Total de C ₃ % en peso	5,06	4,97
C ₃ % en peso	0,69	0,77
C ₃ =% en peso	4,37	4,19
Total de C ₄ % en peso	9,42	9,01
IC ₄ % en peso	3,05	3,08
nC ₄ % en peso	0,55	0,58
C ₄ Total=% en peso	5,82	5,34
Gasolina % en peso	49,13	49,03
LCO, % en peso	24,90	24,90
Productos Inferiores % en	6,91	6,84
peso		
Coque, % en peso	2,33	2,85

Gasolina S ppm

Mercaptanos	9	7
Tiofeno	6	5
Metiltiofenos	21	18
Tetrahidrotiofeno	2	1
C ₂ -Tiofenos	17	13

Gasolina S ppm

Azufre de Corte Liviano	45	38
Azufre de Corte Pesado	14	2
Azufre en Gasolina de Corte	60	41
Azufre Total	71	50
Tiofenoles	9	0
Azufre + Tiofenoles Total	80	51

% de Reducción de S en Gasolina

Azufre de Corte Liviano	16%
Azufre de Corte Pesado	85%
Azufre en Gasolina de Corte	32%
Azufre Total	29%
Tiofenoles	100%
Azufre + Tiofenoles Total	36%

La selectividad del producto fue interpolada a una conversión constante de 68% en peso. El primer conjunto de datos producidos fue obtenido sobre la alimentación base y el catalizador base sin la alimentación de vanadio. Al final del primer conjunto de datos producidos, el DCR fue operado con la misma alimentación,

pero se le agregaron 39 gramos de una solución de naftenato de vanadio en 3000 gramos de la alimentación. La nueva alimentación hecha contenía cerca de 390 ppm de vanadio. Ya que el níquel estaba por debajo del límite de detección, la proporción de vanadio y níquel no fue calculada. El DCR fue operado continuamente durante 3 horas y el nivel de vanadio en el catalizador era de cerca de 750 ppm.

Los datos Ecat con el vanadio agregado a alimentación (Columna B) mostraron cerca de 32% en la reducción en el azufre de gasolina de corte cuando se comparó con el Ecat base (Columna A).

Variaciones razonables y modificaciones, que serán evidentes para aquellos versados en la técnica, pueden ser hechas a esta invención sin salirse del espíritu y alcance de la misma.

REIVINDICACIONES

1 Un proceso para reducir el contenido de azufre de los productos de craqueo de un proceso de craqueo catalítico fluido (FCC) en el cual una alimentación de hidrocarburos pesados que comprende compuestos de órganoazufre es craqueada catalíticamente en productos mas livianos por medio de ponerla en contacto con un proceso de craqueo de recirculizacion de catalizador cíclico con un inventario de catalizador de equilibrio de craqueo catalítico fluidizable circulante, el proceso comprende

(1) Suministrar una corriente de alimentacion de hidrocarburos pesados sustancialmente líquidos que comprende por lo menos un compuesto de órganoazufre como una impureza,

(11) Introducir la corriente de alimentación de hidrocarburos en una unidad de reactor FCC que opera bajo condiciones de craqueo catalítico y que tiene un inventario

,circulante de una composicion catalizadora de equilibrio,

(iii) Remove una porcion del inventario de catalizador de equilibrio de la unidad de reactor FCC mientras se reemplaza todo el inventario de catalizador de equilibrio removido de la unidad con catalizador fresco para crear un ambiente estable dentro de la unidad,

(iv) Poner en contacto la corriente de alimentación de hidrocarburos con por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar la concentracion de vanadio en o sobre el inventario de catalizador de equilibrio en cerca de 100 a cerca de 20 000 ppm, en relacion con la cantidad de vanadio inicialmente presente en o sobre el inventario de catalizador, y

(v) Poner en contacto el inventario de catalizador de equilibrio en la unidad de reactor FCC con la corriente de alimentacion de hidrocarburo que contiene vanadio

bajo un ambiente estable para producir un efluente de zona de craqueo que comprende productos craqueados, incluyendo gasolina, que tienen un contenido de azufre reducido

2 El proceso de la reivindicación 1 que comprende adicionalmente producir de manera simultanea un catalizador de gasto que contiene coque e hidrocarburos separables en la etapa (111)

3 El proceso de la reivindicación 2 que comprende adicionalmente

(1) Descargar y separar la mezcla efluente en una fase de vapor rica en productos craqueados y una fase rica en sólidos que comprende el catalizador de gasto, y

(11) Retirar la fase de vapor como un producto y fraccionar el vapor para formar productos de craqueo liquido, incluyendo gasolina, que tienen un contenido de azufre reducido

4 El proceso de la reivindicacion 1 en donde dicho por lo menos un compuesto de vanadio es seleccionado a partir del grupo que consiste de orto-piro-o meta vanadatos de amonio, óxidos de vanadio hidratados, ácidos vanádicos, complejos de vanadio órgano-metálico, sulfato de vanadio, sulfato de vanadilo, nitrato de vanadio, haluros de vanadio y oxihaluros de vanadic y mezcla de ellos

5 El proceso de la reivindicacion 4 en donde dicho por lo menos un compuesto de vanadio se selecciona del grupo que consiste de oxalato de vanadio, sulfato de vanadio, naftenato de vanadio, haluros de vanadio y mezcla de ellos

6 El proceso de la reivindicacion 1 en donde la corriente de alimentacion de hidrocarburo es puesta en contacto con el compuesto vanadio en una cantidad suficiente para incrementar la concentracion de vanadio en o sobre el catalizador de craqueo en cerca de 300 a cerca de 5000 ppm, con relación a la cantidad de vanadio inicialmente presente en o sobre el catalizador de craqueo

7 El proceso de la reivindicacion 6 en donde la corriente de alimentación de hidrocarburo es puesta en contacto con el compuesto de vanadio en una cantidad suficiente para incrementar la concentracion de vanadio en o sobre el catalizador de craqueo en cerca de 500 a cerca de 2000 ppm, en relacion con la cantidad de vanadio inicialmente presente en o sobre el catalizador de craqueo

8 El proceso de la reivindicacion 1 en donde el catalizador de craqueo comprende una zeolita con tamaño de poro grande

9 El proceso de la reivindicacion 8 en donde la zeolita con tamaño de poro grande comprende una faujasita

10 El proceso de la reivindicación 1 en donde la alimentación de hidrocarburo comprende adicionalmente vanadio como una impureza

11 El proceso de la reivindicación 10 en donde la alimentación de hidrocarburo comprende adicionalmente níquel como una impureza

12 Un proceso mejorado para craqueo catalítico de un material de partida de hidrocarburos que contiene por lo menos compuestos de azufre orgánicos comprende en contacto en un reactor de craqueo catalítico fluido (FCC) un inventario de catalizador de equilibrio de craqueo catalítico fluido, remover una porción del inventario de catalizador mientras se reemplaza la misma cantidad de composición catalizadora fresca para suministrar un ambiente estable dentro del reactor FCC, la mejora comprende

(1) Poner en contacto la alimentación de hidrocarburo con por lo menos un compuesto de vanadio en una cantidad suficiente para incrementar la concentración de vanadio en o sobre el inventario de catalizador de craqueo de fluido de equilibrio en cerca de 100 a cerca de 20 000 ppm, con relación a la cantidad de vanadio

inicialmente presente en o sobre el inventario de catalizador,

(11) Poner en contacto el catalizador de equilibrio con la alimentacion de hidrocarburo que contiene vanadio en una unida de reactor FCC bajo ambiente estable para producir un efluente de zona de craqueo que comprende productos craqueados, incluyendo gasolina, que tienen un contenido de azufre reducido

13 El proceso de la reivindicacion 3 en donde el proceso comprende adicionalmente la adiccion de las etapas de

(1) Separar la fase de catalizador de gaso rica en sólidos para remover los hidrocarburos que ocluyen del catalizador,

(11) Transportar el catalizador separado del separador al regenerador de catalizador,

(111) Regenerar el catalizador separado poniendolo en contacto con

un gas que contiene oxigeno para producir un catalizador regenerado y

(iv) Reciclar el catalizador regenerado a la unidad de craqueo para poner en contacto con cantidades adicionales de alimentacion de hidrocarburo pesado

SUPERINDUSTRIA Y COMERCIO
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Fecha (AMD) 2004-01-08 17 06 14
Trámite 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia 2020 DIVISION DE NUEVAS CREACIONES

NIT 800176089-2

RECIBO OFICIAL DE CAJA 03 - 85 522
FECHA NOVIEMBRE 24 DE 2003

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº PAGO	FECHA PAGO	Vr PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110 6	17923914	24/11/2003	28 427 560 00

***** CONCEPTO *****

CANT	REPARTICION	CONCEPTO	TOTAL CONCEPTO
1	50005 01 01	SOLICITUDES	
		7 TRAMITES DE SOL DE DISEÑOS INDUS	400 000 00
		TOTAL	\$ 400 000 00

SON CUATROCIENTOS MIL PESOS

RESPONSABLE



RECIBO DE CAJA APLICADO AL EXPEDIENTE N° _____

66 14101-841-001-1

NIT 800176089-2

SUPERINDUSTRIA Y COMERCIO
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Fecha (AND) 2004-01-06 17 06 14
Tramite 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios 104

RECIBO OFICIAL DE CAJA 04 - 892
FECHA ENERO 6 DE 2004

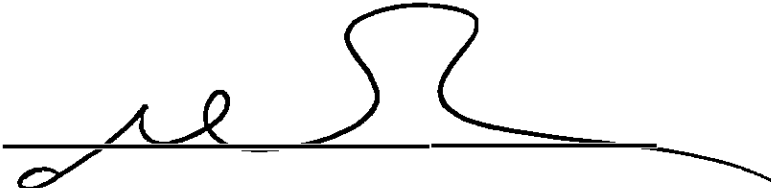
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No PAGO	FECHA PAGO	Vr PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	10497411	06/01/2004	67 154,000 00

***** C O N C E P T O *****

CANT	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		998 VALOR COMPLEMENTO TARIFA AND ANTR	22,000 00
		TOTAL	\$ 22 000 00

SON VEINTIDOS MIL PESOS

RESPONSABLE 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No _____

Colo 14101-84-001-1

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
<u>PATENTE DE INVENCION</u>		
MODELO DE UTILIDAD	()	()
Indicacion de que se solicita la concesion de una patente	()	()
Datos de identificacion del solicitante o de la persona que se presenta la solicitud	()	()
Descripcion de la invencion	()	()
Dibujos de los aspectos pertinentes	()	()
Comprobante de Pago de las tasas establecidas	()	()

COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicacion de que se solicita el registro de Diseño Industrial () ()
- Datos de identificacion del solicitante o de la persona que presenta la solicitud () ()
- Representacion grafica y fotografica del Diseno Industrial o muestra del Material que incorpora el diseno () ()
- Comprobante de pago de las tasas establecidas () ()

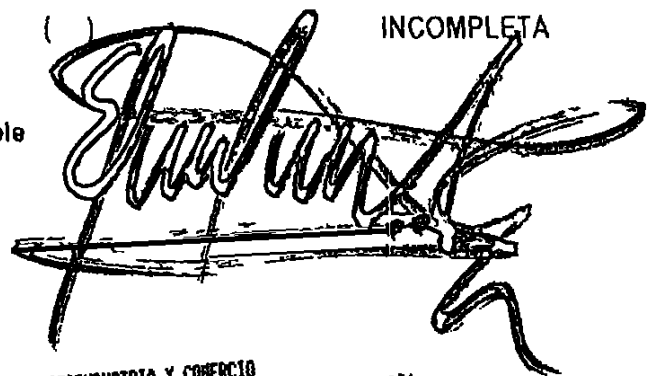
COMPLETA () INCOMPLETA ()

ESQUEMA DE TRAZADO ()

- Indicacion de que solicita el registro de un Esquema de trazado () ()
- Datos de identificación del solicitante o de la persona que presenta la solicitud () ()
- Representacion grafica del esquema de trazado () ()
- Comprobante de pago de las tasas establecidas () ()

COMPLETA () INCOMPLETA ()

Firma Responsable



Fecha

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Dependencia 2020 DIVISION DE NUEVAS CREACIONES



2020
Bogotá, D C ,

Doctor(a)
EMILIO FERRERO

04909

Oficio N°

ASUNTO	Solicitante	W R GRACE & CO-CONN Y EXXONMOBIL RESEARCH & ENGINEERING COMPANY
	Radicación N°	04 - 001078
	Solicitud internacional	PCT/US02/23243
	Fecha inicio fase nacional	10/02/2004
	Trámite	011
	Evento	379
	Actuación	430
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Unica de la Superintendencia de Industria y Comercio, se le comunica que

- La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante (Art 26-k) Decisión 486)
- La solicitud no contiene el poder debidamente otorgado, por el solicitante EXXONMOBIL RESEARCH & ENGINEERING COMPANY con el lleno de los requisitos exigidos por los artículos 63 y subsiguientes del Código de Procedimiento Civil. Adicionalmente, deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante, cuando ésta fuere persona jurídica

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Unica N° 10 de 2001.

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 14 MAYO 2004

202059

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