



Industria y Comercio
SUPERINTENDENCIA

Delegatura de Propiedad Industrial
División de Nuevas Creaciones

SOLICITUD **PCT**
PATENTE DE INVENCION

21. EXPEDIENTE No.

05-69088

54. TITULO

PROCESO PARA LA REMOCION DE CONTAMINANTES QUE CONTIENEN
NITROGENO PROVENIENTES DE CORRIENTES DE ALIMENTACION
DE GASOLEO

51. CLASIFICACION INTERNACIONAL

71. SOLICITANTE

W.R. GRACE & CO., CONN.

DOMICILIO

Columbia, Maryland, Estados Unidos de América

74. APODERADO

EMILIO FERRERO

22. BOGOTA, D.C.,

C.C. 438,019 de Usaquén.

**Industria y Comercio**

SUPERINTENDENCIA

PETITORIO

SUPERINDUSTRIA Y COMERCIO

Radicación : 05069000 00000000

Folios: 162

Fecha (AMB): 2005-07-13 17:57:44

Trámite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC

Dependencia: 2820 DIVISION DE NUEVAS CREACIONES

FORMULARIO UNICO DE SOLICITUD DE PATENTE**PCT****ENTRADA EN FASE NACIONAL****SOLICITUD DE:****1**☒ Patente de Invención.☐ Patente de Modelo de Utilidad.☐ Capítulo I.☒ Capítulo II.**2****SOLICITANTE
(71)**Nombre: **W.R. GRACE & CO.-CONN.**
sociedad constituida y existente bajo las
leyes del Estado de Connecticut, Estados
Unidos de América.Dirección: 7500 Grace Drive,
Columbia, Maryland 21044,
Estados Unidos de América.
Domicilio: Columbia, Maryland
Estados Unidos de América.**IDENTIFICACIÓN**C.C. ☐ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número _____

3**REPRESENTANTE
APODERADO**Nombre: **EMILIO FERRERO**
Dirección: Carrera 4ª. No. 72-35
Teléfono: 347 36 11
Fax: 217 92 11
E-mail: clientes@camyo.com.
Domicilio: Bogotá, Colombia.**IDENTIFICACIÓN**C.C. ☒ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número 438.019 T.P 31.929**4****INVENTOR (ES)
(72)**1. **Marcus Fredrick Manfred LESEMAN**
Apt. 1034, 105 West 39th Street,
Baltimore, Maryland 21210,
Estados Unidos de América-2. **Constanze SETZER**
Albanusstr 68,
55128 Mainz,
República Federal de Alemania.**5****PCT (86)**Solicitud Internacional No. PCT/US2003/039368Fecha: 12 de diciembre de 2003Publicación Internacional No. WO 2004/060545 A3Fecha: 22 de julio de 2004**6****Título (54)****PROCESO PARA LA REMOCIÓN DE CONTAMINANTES QUE
CONTIENEN NITRÓGENO PROVENIENTES DE CORRIENTES
DE ALIMENTACION DE GASÓLEO****7****Clasificación Internacional (51)** B01J 21/08; C10G 67/06**8****Prioridad****(33) País de Origen****(32) Fecha****(31) Número de Solicitud**SI ☒ NO ☐US.19 de diciembre de 200210/322.614**9****Comprobante de pago No.:** 05. 46.091**Fecha:** 21 de junio de 2005

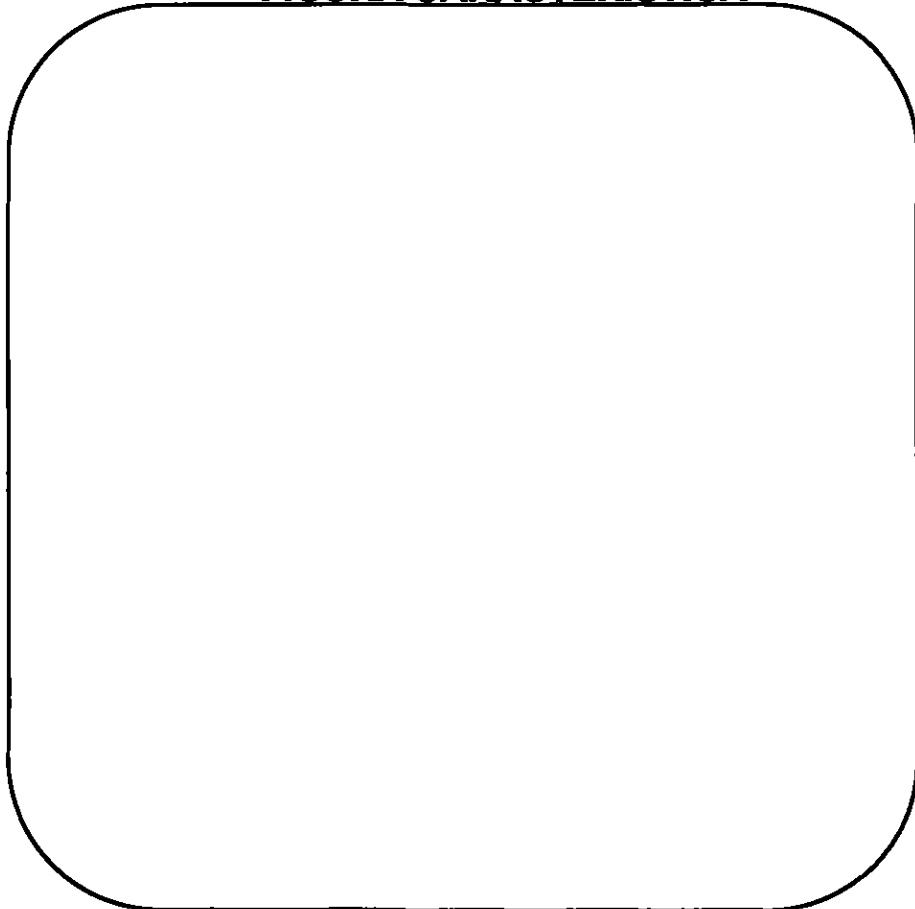
10

An xos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por \$ 422.000.00.
- ☐ 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.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☒ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción 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: (Ver hoja con documentos anexos).

11

FIGURA CARACTERÍSTICA



12

Solicito la concesión de la patente,

N MBRE: EMILIO FERREROFIRMA: *Emilio Ferrero*

C.C. 438.019 de Usaquén T.P. 31.929



3
8:25
06032
5452

The State of Maryland

Office of the Secretary of State

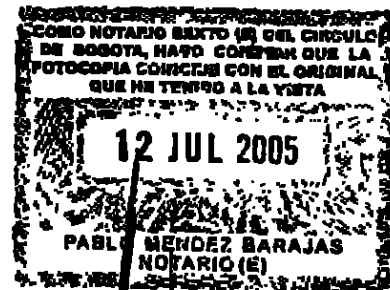
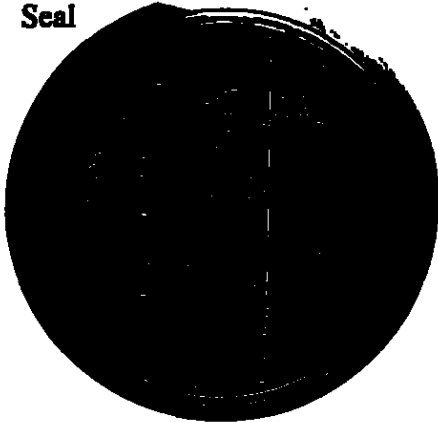
Apostille

(Convention de La Hays 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

Secretary of State

No. 86826

2

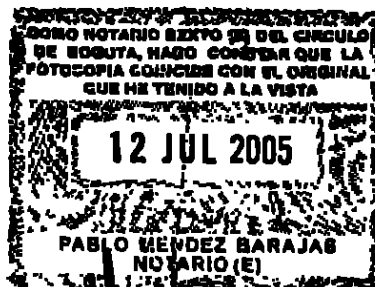
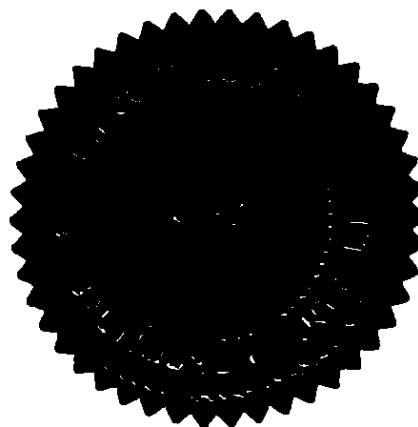


State of Maryland, Baltimore County, to-wit:

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



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

Representation and Power-of-Arrowney with notaria 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 párrafo 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 Público en Colombia, o por Notario u otro Funcionario Público, 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 según 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, especialmente ante las del 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 declare their intention not to exercise the representation through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official of a Colombian Consulate 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 of its exercise will suffice. The exercise of the representation by the first, second or third alternate 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 the unfair competition, for which purpose (we) authorize the said attorneys to represent me (us) before all 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, vegetable varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation; and the registration of license of use of the above rights; b) Actions of unfair competition, protection of 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 oficiales.

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.

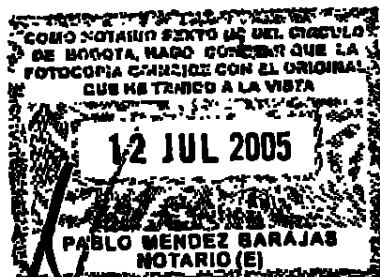
Dado y firmado hoy/Given and signed this October 3, 2002

en/in Columbia, Maryland USA

por/to 

Assistant Secretary

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



CERTIFICADO NOTARIAL (INDIVIDU)

A los 3 días del mes de Octubre
de 2002, ante mí, Notario Público o Funcionario Autorizado
de Baltimore County, Maryland
compareció(ron) 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 Público o Funcionario Autorizado – Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy 3 de Octubre de 2002
Compareció(ron) ante mí Robert A. Maggio
quien(es) conozco personalmente y que firma(n) este
documento en representación de la Sociedad/compañía
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/Compañía 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/Compañía 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/Compañía.

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 Público 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 UNCOMP.
Connecticut, 18 Nov., 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 within the corporation
purposes set forth in the charter of the mentioned
Corporation/Company.

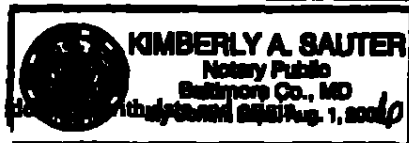
2.4. That Mr.(Messrs.) Robert A. Maggio
is(are) authorized to grant the present Power of Attorney.

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)

1. Country:
This public document
2. has been signed by
3. acting in the capacity of
4. bears the seal/stamp of

Certified

5. at 6. the
7. by
8. No.
9. Seal/stamp 10. Signature

.....

COMPARADO CON EL ORIGINAL DEL CIRCULO
DE NOTARIA, SEGO CONSER QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA

12 JUL 2005

PABLO MENDEZ BARAJAS
NOTARIO (E)



12 JUL 2005

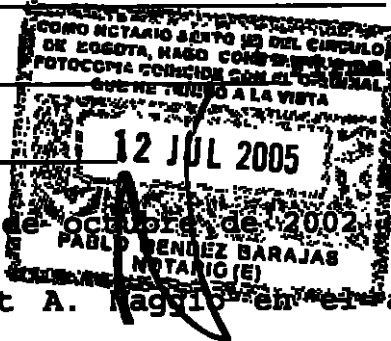
3

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.



CERTIFICADO NOTARIAL (INDIVIDUO) del 3 de octubre de 2002 en donde se autentica la firma del Señor Robert A. Maggio en el 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
DIEGO F. VARGAS

TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999

8

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

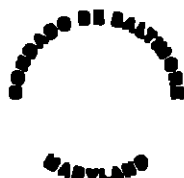
Sello:

KIMBERLY A. SAUTER

Notario Público

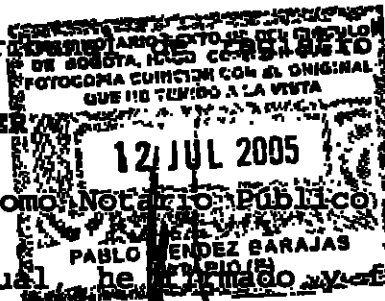
Condado de Baltimore, MD.

Mi Comisión vence el 1 de Agosto de 2004



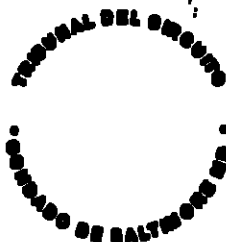
Estado de Maryland, Ciudad de Baltimore, a saber:

Yo, Suzanne C. Mensh, Secretario del Tribunal de Circuito para el
Condado de Baltimore, Maryland, un trámite 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 afijado 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 Estad de Maryland

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

Oficina del Secretario d 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
- 8. Sello:

SECRETARIO
DE ESTADO
MARYLAND



- 10. Firma:

Firma ilegible

COMO NOTARIO SEPTO ME DEL CIRCULO DE JUDICA, HAGO CONSTAR QUE LA FOTOCOPIA COINCIDE CON EL ORIGINAL

Secretario de Estado

12 JUL 2005

PAULO MENDEZ BARAJAS
NOTARIO (E)

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 SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) FIRMA(S) DE

Diego Vargas

CONFIERE CON LA FIRMA REGISTRADA POR ELLOS EN ESTA NOTARIA

SANTAFE DE BOGOTA, 09 ABR 2003



RESEALADO
FOLIO 11 DEL TERCERO
2003
P 1:08

MINISTERIO DE
RELACIONES EXTERIORES

DE 2003
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPENA
LAS FUNCIONES INDICADAS

[Handwritten signature]

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA FOTOCOPIA QUINCE CON EL ORIGINAL QUE ME TRAYO A LA VISTA

12 JUL 2005

PABLO MENDEZ BARAJAS
NOTARIO (E)

DOCUMENTOS ANEXOS

1. ☒ **Publicación Internacional WO 2004/060545 A3**

Descripción:

Páginas 1 - 42 en el idioma original

Páginas 1 - 76 en español

Reivindicaciones: Número (s) 44

Figuras: Número (s) 3

2. ☒ **Forma PCT/RO/101. PCT Reques. (Contiene declaraciones de acuerdo con la regla 4.17 del PCT).**
3. ☐ **Forma PCT/RO/106. Invitation to Correct Defects.**
4. ☒ **Forma PCT/ISA/210. Informe de Búsqueda Internacional.**
5. ☒ **Forma PCT/ISA/220. Notificación De La Transmisión Del Informe De Búsqueda Internacional Y De La Opinión Escrita De La Administración Encargada De La Búsqueda Internacional, O De La Declaración.**
6. ☐ **Forma PCT/ISA/237. Opinión Escrita De La Administración Encargada De La Búsqueda Internacional.**
7. ☒ **Forma PCT/ISA/301. Notification Of Receipt of Record Copy**
8. ☒ **Forma PCT/IB/304. Notification Concerning Submission Or Transmittal Of Priority Document.**
9. ☐ **Forma PCT/IB/306. Notification Of The Recoding Of A Change.**
Descripción De Modificación:
10. ☒ **Forma PCT/IB/308. Notice Informing The Applicant Of The Communication Of The International Application To The Designated Offices.**
11. ☐ **Forma PCT/IB/332. Information Concerning Elected Offices Notified Of Their Election.**
12. ☒ **Forma PCT/IPEA/401. PCT Demand**
13. ☐ **Forma PCT/IPEA/402. Notification Of Receipt Of Demand By Competent International Preliminary Examining Authority.**
14. ☐ **Forma PCT/IPEA/408. Written Opinion.**
15. ☐ **Forma PCT/IPEA/416. Notification Of Transmittal Of The International Preliminary Examination Report.**
16. ☐ **Forma PCT/IPEA/409. Informe Del Examen Preliminar Internacional.**
17. ☐ **Traducción Al Español Del Informe Del Examen Preliminar Internacional.**
18. ☐ **Traducción Al Español De Los Anexos Presentados Junto Con El Informe Del Examen Preliminar Internacional.**

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

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(54) Title: PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS

(57) Abstract: The present invention is directed to the removal of nitrogen and sulfur containing impurities from high molecular weight petroleum feedstock obtained from fluid cracking catalyst or distillation zone of a petroleum treatment plant. The present process comprises first treating C₁₂ and higher hydrocarbon petroleum feedstock having nitrogen and sulfur containing compounds therein with a porous, particulate adsorbent comprising a silica matrix having an effective amount of metal atoms therein to cause the adsorbent to have Lewis acidity of at least 500 $\mu\text{mol/g}$ and then treating the resultant feedstock to catalytic hydrodesulfurization to produce a hydrocarbon fuel having low sulfur and nitrogen content.

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PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS

FIELD OF THE INVENTION:

The present invention is directed to an improved method of producing a petroleum fuel, in particular a diesel fuel, substantially free of nitrogen and sulfur containing compounds. Specifically, the present method comprises treating petroleum hydrocarbon feedstock having a boiling point range of from about 125 to 560°C (preferably a petroleum cut of C₁₂ and higher hydrocarbon) with an inorganic oxide adsorbent having high Lewis acidity imparted thereto prior to subjecting the feedstock to conventional catalytic hydrodesulfurization. The presently required pretreatment has been found to readily remove nitrogenous compounds from the feedstock and permit the hydrodesulfurization to take place more efficiently and more effectively to yield a petroleum product of reduced nitrogen and sulfur content.

BACKGROUND OF THE INVENTION

Environmental pollution problems, especially air quality degradation, have become a high concern throughout the world and especially in industrial developed countries. Such concerns have led to environmental regulatory policies imposing tight quality regulations on transportation fuels. Of such fuels, diesel fuel is considered to be a major contributor of known harmful pollutants, such as SO_x, NO_x and particulate matter and, therefore, stringent regulatory standards have been proposed and enacted to reduce the emission of such pollution by diesel fuels.

The sulfur content in fuels is a critical concern, as it is known to form sulfur dioxide when subjected to a combustion process. The sulfur dioxide, together with atmospheric moisture, forms sulfuric acid in the atmosphere. This is the cause of acid rain, which has been attributed to causing substantial damage on the environment as well as man-made structures.

In addition, the generated sulfur oxides have been found to poison noble metal catalysts conventionally used as part of automobile emission after-treatment devices. For this reason, automobile manufacturers have suggested that sulfur

content in diesel fuels be reduced to less than 30 weight parts per million (ppm) to meet new tail-pipe emission regulations contemplated to become law. Thus, an ultra-low sulfur diesel (ULSD) market is emerging to replace conventional sulfur diesel fuel standards of 500 ppm. In various countries, such as in the United States and in a number of European countries, regulations have been proposed or enacted to require sulfur content to be reduced to levels of less than 50 ppm and, in certain instances, to levels of less than 15 ppm. In view of the ever-increasing regulatory pressures, petroleum refiners and catalyst producers have invested considerable time, money and effort to produce environment-friendly petroleum products.

Hydrodesulfurization (HDS) processes most commonly used reduce sulfur content in petroleum feedstock by converting sulfur compounds present in the feedstock to hydrogen sulfide. Since the 1960's various HDS processes have been developed which, in general, subject the feedstock to hydrogen under elevated temperatures and pressures in the presence of a catalyst. One mode of reducing the sulfur content is to develop innovative improvements in one or more of the operating parameters of catalyst activity, reaction temperature, bed volume and/or hydrogen partial pressure of the HDS process.

Although catalyst activity has been doubled since HDS catalysts were first introduced, it has been calculated that a factor of 3.2 fold activity improvement is required to meet the present 500 ppm sulfur content and a factor of about 17 is needed to reach the 50 ppm level more highly desired. Thus, if one relies on catalyst activity alone, the number of HDS reactors must be substantially increased and/or, the charge rate substantially decreased unless the catalyst activity is dramatically improved.

As stated above, the reaction temperature can be increased to cause reduction in sulfur content. However, such temperature increase can only be done to a small degree due to the design limitations of present equipment. In addition, very high temperatures are known to cause degradation to the product stream. Similarly, increased pressure would aid in achieving reduced sulfur content but presently designed reactors establish a limit on this parameter, and new equipment capable of handling very high pressures would be costly.

Thus, conventional processes for treating diesel feedstock (also known as light gas oil, LGO) have technical limitations while breakthroughs in catalyst activity have not been realized. Therefore, methods, which use different feedstock instead of LGO, or using innovative reaction pathways, are being studied.

For example, a process developed by Shell Oil Company polymerizes natural gas to produce a distillate composed of C_{12} - C_{25} products, similar to diesel feedstock. In this process natural gas is converted to syn-gas through a Fischer-Tropsch reaction and the product is polymerized to yield diesel distillate free of sulfur compounds. This process has the drawbacks of using fairly expensive feed and requiring three distinct reaction steps to result in a high cost process.

U.S. Patent 5,454,933 discloses an adsorption process to produce sulfur-free diesel fuel by removing remaining sulfur compounds from LGO material that has already undergone hydrodesulfurization. The disclosed post-HDS process utilizes adsorbents designed to directly remove residual sulfur compounds from post-HDS treated material.

It has been proposed that reduction or removal of nitrogen containing compounds from streams being fed to a catalytic HDS unit causes HDS to take place in a more efficient manner and, thus, make the system capable of producing a product with very low sulfur content using conventional operating parameters.

It is well known that heteroatom containing compounds, particular nitrogen and sulfur containing compounds can be readily removed from light cuts, such as C_4 - C_8 streams, as is obtained from a conventional FCC unit or etherized streams. Different processes, such as adsorption and extraction have been proposed for this purpose. Heteroatom contaminant compounds that are found in such light cut streams are few in number, readily identified, have low molecular weights and have low boiling points consistent with the light hydrocarbons forming this type of cut. As a consequence, these contaminants are easily removed from the feedstream in which they are contained. These features are not applicable with respect to the more complex mixture of heteroatom containing compounds found in heavier hydrocarbon streams.

The heavier LGO streams, composed primarily of C_{12} - C_{30} and higher compounds obtained from distillation or FCC units or the like, contain a vast mixture of heteroatom species. These compounds have been difficult to identify, are generally composed of high molecular weight compounds and have high boiling points. Some of the sulfur species have been identified and studied by Whitehurst et al. in Adv. Catal. 42, 345-471 (1998). Attempts to identify the nitrogen species of such gas oil cuts have been illusive and challenging due to the concentration in the hydrocarbon matrix and the complexity of the mixture of species. A group of scientists from Kyushu University at Fukuoka, Japan and Chevron Research and Technical Company at Richmond, California, have attempted to identify nitrogen containing compounds of gas oils and were only capable of reporting broad classes including alkyl substituted aniline, quinoline and its alkyl derivatives, and, carbazole derivatives (S. Shin et al., Energy & Fuels (2000), 14(3), 539-544. Wiwel et al. in "Assessing Compositional Changes of Nitrogen Compounds of Typical Diesel Range Gas Oils..." (Industrial & Engineering Chemistry Research (2000), 39(2), 533-540) reported that crude oil generally contains from about 0.1 to 2 percent nitrogen compounds but the nitrogen content rapidly increases with increasing boiling point of the oil fraction. Recognizing that diesel fuels are commercially prepared from straight run distillates and cracked products of heavier feedstock, the nitrogen levels normally range from 20-1000 $\mu\text{gN/ml}$. They report that such compounds are generally made up of four different chemical classes: aliphatic amines, anilines, and five- and six-membered pyridinic ring system compounds. They have identified some 64 compounds (using the method of ASTM D-4629-91) and stated that many more unidentified compounds are contained in this heavier fraction of material.

Removal of nitrogen containing compounds from light cut (C_4 - C_8) petroleum streams has been accomplished because the nitrogen compounds are fewer in number, are readily identifiable and have lower molecular weight. However, because nitrogen containing compounds in heavier fraction material are difficult to identify and, at best, are a complex mixture of compounds, removal has been illusive.

U.S. Patent 2,384,315 discloses filtering crude oil through a bed of bauxite prior to subjecting the oil to catalytic cracking treatment. Such procedure would produce a product still having high amounts of nitrogen compounds relative to today's required standards.

U.S. Patent 2,744,053 discloses the removal of nitrogen compounds from low boiling gasoline hydrocarbon stock by passing the feedstock through an adsorption bed formed from silicon oxide alone or a mixture of silicon oxide and alumina. It is well known that silicon oxide and other conventional adsorbents do not exhibit the Lewis acidity required by the adsorbent used in the present invention.

U.S. Patent 4,708,786 discloses a fluid catalytic cracking process in which the feedstock is treated with a mixture of cracking catalyst and micro-porous refractory oxide capable of sorbing pyridine at room temperature and retaining a portion of the sorbed material. This sorbent is to be used in conjunction with the catalyst in the FCC zone.

U.S. Patent 5,051,163 discloses a process wherein the initial feed to a catalytic cracking reactor is first treated with a small amount of the cracking catalyst. The reference suggests that the nitrogenous material will bind with sacrificial catalyst present in the pre-cracking zone to thus prevent poisoning of the cracking catalyst used in the cracking zone. No suggestion is made as to removal of nitrogenous compounds just prior to hydrodesulfurization that would further decrease the sulfur content after HDS, to enhance the effectiveness of the HDS and to inhibit poisoning of HDS catalyst.

U.S. 5,210,326 and U.S. 5,378,250 are directed to processes which include treating light ($C_3 - C_8$) hydrocarbon stream obtained from a FCC process zone with a super activated alumina to remove nitrogen compounds, mercaptans and water prior to further processing.

U.S. 6,107,535 and U.S. 6,118,037 also teach processes, which include treatment low molecular weight ($C_3 - C_8$) hydrocarbon streams with silica gels to remove contaminant compounds that contain sulfur, nitrogen and/or oxygen.

U.S. Patent 6,248,230 discloses a process for manufacturing cleaner fuels by removing natural polar compounds (NPC) from a wide range boiling point

petroleum feedstream prior to subjecting the stream to catalytic hydrodesulfurization. The reference teaches that petroleum hydrocarbon product streams obtained from FCC or the like process can be contacted with an adsorbent, such as silica gel, hydrated alumina, activated carbon, active alumina, or clay. The reference states that silica or hydrated alumina are each preferred adsorbent. Such adsorbents are known to be substantially free or have only limited degrees of Lewis acidity. Although this reference indicates that large amounts of the NPC contained in the treated petroleum feedstock can be removed, such removal, especially from an LGO stream, requires uneconomically high ratios of adsorbent to feed.

The above references illustrate the desire by the petroleum refining industry to remove hetero-atom containing compounds from light cut petroleum products. Unfortunately, heavier fraction material, such as diesel fuel fractions have not been successfully treated to remove nitrogen and sulfur containing contaminants commonly found therein in a cost-effective, efficient manner to provide an environmentally friendly product. The removal of organic nitrogen is important to many different refinery processes and is essential to provide a diesel fuel products, which meet the environmental needs and associated regulations being proposed and enacted into law. It is highly desired to provide a cost-effective process to remove a majority or substantially all of nitrogenous compounds from diesel fuel fractions so that the treated diesel fuel feedstream can be effectively and efficiently treated by conventional HDS processes to produce a resultant material having less than 50 ppm and more preferably less than 15 ppm of sulfur containing compounds in the resultant product stream.

An object of the present process is to provide a cost-effective and efficient means of removing nitrogenous compounds from a diesel fuel fraction (C_{12} and greater, e.g. C_{12} - C_{30} petroleum feedstream) prior to subjection to HDS treatment.

Another object of the present invention is to provide an economical and efficient means of removing at least about 75 weight percent, preferably at least about 80 weight percent and more preferably at least about 90 weight percent of nitrogenous compounds from a diesel fuel fraction prior to subjection to HDS treatment.

Another object of the present invention is to effectively produce a diesel fuel, which meets present and contemplated environmental regulations with respect to emission of NO_x and SO_x pollutants.

SUMMARY OF THE INVENTION

The present invention is directed to an improved method of producing diesel fuel and other high molecular weight petroleum products substantially free of nitrogen and sulfur containing organic contaminants. Specifically, the present method comprises first contacting a petroleum feedstream composed of LGO and higher molecular weight petroleum materials obtained from a distillation or FCC catalytic cracking zone or the like with certain inorganic adsorbents having high levels of Lewis acid sites, as fully described herein below, to remove nitrogen compounds from said LGO, and subsequently subjecting the treated LGO to deep catalytic hydrodesulfurization. The present method has been found to provide a means of removing organic nitrogen containing compounds from C_{12} and higher gas oil feedstreams in an effective and efficient manner.

The present invention is directed to an improved and economical process of producing diesel fuels capable of exhibiting very low levels of pollutants, especially nitrogen oxides and sulfur oxide products and other pollutants derived therefrom, when utilized in combustion engines.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graphic representation of the adsorption capacity for nitrogen containing compounds with respect to an adsorbent labeled "Sample I", illustrative of the present invention (silica xerogel having zirconia therein to impart a Lewis acidity of $1940 \mu\text{mole/g}$, formed according to Example 1. This material is compared to high surface area silica gel adsorbent materials labeled "Sample III Si/1" and "Sample III Si/2" formed according to Example 5. These comparative adsorbents do not exhibit Lewis acidity. Figure 1 graphically shows that the adsorbent of the present invention provides substantially greater adsorption capacity for nitrogen containing molecules in LGO than conventional silica gel adsorbent materials.

Figure 2 is a graphic representation of the adsorption capacity for nitrogen containing compounds with respect to adsorbents illustrative of the present invention (silica xerogel having alumina in amounts to impart high Lewis acidity) as fully described in Example 2. These materials are compared to known high surface area silica gel adsorbent materials labeled Sample III Si/1 and Sample III Si/2 formed according to Example 5. Figure 2 graphically shows that the adsorbents of the present invention provide substantially greater adsorption capacity for nitrogen containing molecules than conventional silica gel adsorbent materials. The sample materials vary substantially in surface area, but when the data of the examined silica/alumina gel of high Lewis acidity is normalized with respect to surface area, the data follows a single line. All of the illustrative samples exhibited significantly higher adsorption capacity than known high surface area silica gel adsorbent materials.

Figure 3 is a graphic presentation of the adsorption capacity for nitrogen containing compounds with respect to adsorbents illustrative of the present invention (silica xerogel having alumina therein in amounts to impart high Lewis acidity) as fully described in Example 2. These materials are compared to known, high surface area alumina adsorbent formed of Example 5. Figure 3 graphically shows that adsorbents of the present invention provide substantially greater adsorption capacity for nitrogen containing molecules than such conventional alumina adsorbent material.

DETAILED DESCRIPTION

Petroleum refining conventionally treats petroleum crude to a process, such as a fluid cracking catalyst (FCC) process, wherein the crude is contacted with a FCC catalyst under elevated temperature and pressure and/or a distillation process, to produce a plurality of petroleum product streams of different molecular weight compounds and related ranges of boiling points. For example, the product streams may be defined as light cut material composed of C_4 - C_8 hydrocarbons normally having a boiling range of from about 0°C to about 115°C; light gas oils (LGO) or diesel fuel product stream composed of C_{12} - C_{30} (e.g. C_{12} - C_{25}) hydrocarbons which

normally has a boiling range of from about 200 to about 550°C, such as from about 225 to about 460°C. The heavy bottom product stream of the FCC unit (resids) is composed of high molecular weight material. The residuals are not conventionally used as fuel for combustion engines although they may be used for such purpose in certain applications.

The product stream composed of LGO or diesel fuel is the target material to which the present invention relates although even heavier petroleum feed streams can be similarly treated to remove nitrogen contaminants therein. It is immaterial as to the exact mode of forming this material although they are commonly formed by distillation or FCC processing of petroleum crude. As stated above, one of the concerns with LGO streams is that they normally contain a large amounts and many different complex nitrogen-containing compounds that, in general, are not readily identified but are believed to reduce the effectiveness of the HDS processing of the feedstream. The exact amount and composition of these compounds depends on the source of petroleum crude being processed.

Removal of nitrogen containing compounds from petroleum feed stream prior to a hydrodesulfurization (HDS) unit is believed to cause the HDS process to take place in a more efficient manner to produce a desired, more environmentally friendly diesel fuel. It is believed, though not meant to be a limitation of the present invention, that nitrogen containing compounds combine with the active sites of HDS catalysts and, therefore, the removal of such compounds aids in causing the catalysts to provide for enhanced HDS processing. By using low nitrogen content material as the feed for a conventional HDS unit, one enhances the effectiveness of the HDS process to enable the process to be conducted at lower processing temperatures or higher flow rates while extending the life of conventional desulfurization catalyst utilized. The product of the HDS unit has been found to have very low sulfur content, such as less than 50 ppm or even less than 30 ppm and even less than 15 ppm sulfur content.

The present inventors have discovered that LGO (diesel fuel) streams of C₁₂ and higher composition can be readily treated in a cost-effective and efficient manner to remove nitrogen contaminants from the LGO stream prior to its

introduction to a HDS zone. The present process utilizes certain Lewis acid enhanced inorganic oxide adsorbents fully described herein below. These adsorbents have been found to effectively achieve removal of nitrogen contaminants commonly contained in the LGO feedstream without the need to require multiple passes, the use of economically undesirable low flow rates (liquid hourly space velocity), or economically undesirable ratios of feed to adsorbent (before regeneration of the adsorbent becomes necessary), when treating the stream.

In general, the present process can be achieved by contacting an LGO feedstream with the presently required adsorbent prior to introducing the feedstream to a HDS zone of a refinery. Contact may be done by any known method of contacting a solid and a liquid material, such as by utilization an adsorption zone composed of one (suitable for a batch process) or two or more (suitable for a continuous process) fixed bed (packed bed) columns, fluidized bed columns, or an abullating bed zone. The preferred adsorption zone is a fixed or packed bed system.

The present invention shall be described using the preferred fixed or packed bed system, although other adsorption zone systems can be readily substituted for such systems by those skilled in this art. Normally, columns are packed with the present adsorbent, which is allowed to contact the petroleum feed stream and cause adsorption of the nitrogen contaminant compounds therein. The adsorbent, at a point of exhaustion of its adsorbent capacity or prior thereto, is subjected to desorption to remove the nitrogen contaminants therefrom and finally to regeneration in order to reestablish the adsorbent capacity of the adsorbent. A continuous process can be readily achieved by using a plurality of columns in which at least one column is in an adsorption mode while the adsorbent of at least one other column is being desorbed of nitrogen contaminant and being regenerated.

The nitrogen contaminant is immobilized on the adsorbent. The term "immobilized" and "adsorbed" as used herein and in the appended claims refer to physical and/or chemical adsorption (adhesion of the nitrogen compound to the surface of the adsorbent) and/or physical absorption (penetration into the inner structure of the adsorbent). Without wishing to be bound by any particular theory, it is believed that the nitrogen contaminants form some type of weak bond with the

present adsorbent. The structure of such bond may be merely physical or ionic or dative or a mixture thereof.

The adsorbent required by the present invention is a porous inorganic oxide matrix material having high Lewis acidity imparted thereto. More specifically, the adsorbent used in the present invention is in the form of particulate adsorbent formed from (a) at least one inorganic oxide component selected from three-dimensional matrix or lattice like forms of silica, titania, alumina, zirconia or stannia. The term "inorganic oxide matrix material," as used herein and in the appended claims, refers to a material formed of a three dimensional structure of atoms comprising M atoms (selected from atoms of silicon, titanium, aluminum, zirconium or tin) and oxygen atoms. The oxygen atoms form a bridge between the M atoms. The lattice may further have small amounts of other chemical groups, such as hydroxyl or alkoxy groups and the like. Component (a) is preferably selected from silica, alumina or zirconia or titania. The formed matrix may be composed of lattice-like or amorphous material or a mixture of both (the degree of crystalline lattice-like structure can be determined by conventional X-ray diffraction spectroscopy or similar techniques).

The three dimensional inorganic oxide matrix material (in the form of a gel or the like) (a) forming the present adsorbent, prior to treatment with component (b) described below, usually exhibits very low degrees of Lewis acidity of less than about 300, generally less than about 200 and, in most instances, less than about 100 $\mu\text{mol/gm}$.

The subject adsorbent further contains metal atoms other than M (of a particular adsorbent material) as part of the matrix structure. Such metal atoms may be imparted to the matrix by contacting a matrix material (a) with at least a sufficient amount of a metal containing precursor compound (b) capable of imparting Lewis acidity to the inorganic oxide matrix component (a) of the resultant adsorbent, as described herein below.

Lewis acidity of a high degree, as presently required, may be imparted to matrix material (a) by insertion or substitution of metal atoms into the inorganic oxide matrix to establish electron poor sites within the matrix. The atoms imparting

Lewis acidity may be selected from metal atoms of Group IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA, or VIIA of the Periodic Table (IUPAC format). For example, the metals can be selected from Mg, Ca, Sr, Ba, B, Al, Ga, Zn, Cd, Sc, Y, La, Ti, Zr, Hf, V, Nb, Mo, W, Fe, Co, Ni, or mixtures thereof with Mg, Ca, Zn, La, Ti, Zr, Fe, Co, Ga and Al and mixtures thereof being preferred and Mg, Zn, La, Ti, Zr, Fe and Al and mixtures thereof being more preferred, and Zr, Al, Fe and Ti being most preferred, provided said metal is different from the atoms forming the original matrix component (a). For example, a portion of the Zr atoms of a zirconia gel may be substituted by one of the above described metal atoms or mixtures thereof, such as with cadmium atoms to impart the Lewis acid electron poor sites. Similarly, a portion of the Al atoms of an alumina gel may be substituted by one of the above described metal atoms or mixtures thereof, as more fully described herein below.

The metal atoms of the precursor (b) may be introduced into the component (a) by any method and in amounts whereby the resultant adsorbent has imparted Lewis acidity to at least the degree recited herein below. For example, the metal may be introduced in the form of a precursor material, such as a metal salt or other metal precursor that is soluble in the media selected for forming the matrix or for contacting the matrix with the precursor (b) or mixtures thereof. It is believed, though not meant to be a limitation on the present invention, that when components (a) and (b) are contacted to form the adsorbent or when the initially formed adsorbent is further processed and/or activated, as described herein below, a metal oxide moiety of the metal of precursor (b) is formed as part of the matrix.

The Lewis acidity of the present adsorbent should be at least 500 $\mu\text{mol/gm}$ (e.g. 600 $\mu\text{mol/gm}$, 700 $\mu\text{mol/gm}$, 800 $\mu\text{mol/gm}$), preferably from 600 to 3000 and more preferably from 700 to 2500 (e.g. 750-2000) $\mu\text{mol/gm}$ of adsorbent.

The term "Lewis acidity" as used herein and in the appended claims refers to the ability of a substance to accept electrons from an electron rich substance or atom of such substance. The presence and quantitative values of Lewis acidity can be determined according to the method described by E. Rakiewicz et al., J. Phys. Chem. B, 102, 2890-2896 (1998) entitled "Characterization of Acid Sites in Zeolite and Other Inorganic Systems Using Solid State ^{31}P NMR of the Probe Molecule

Trimethylphosphine Oxide". The teaching of this reference is incorporated herein in its entirety by reference. The described method provides an analytical procedure to quantitatively determine the Lewis acidity of an inorganic substance and to discriminate between the population of Lewis and Bronsted acid sites therein.

The matrix material (a) of the adsorbent is preferably an alumina, zirconia, titania or silica gel (e.g. hydrogel, aerogel, or xerogel). Gels of these inorganic oxides are known solid materials having three-dimensional structures formed by a plurality of metal and O atoms. In the case of silica, it may be in the form of a hydrogel, also known as an aquagel, which is a gel formed in water that has its pores filled with water. A xerogel is a hydrogel with the water removed. An aerogel is a type of xerogel from which the liquid has been removed in such a way as to minimize any collapse or change in the structure as the water is removed. The other inorganic oxides may also be in these forms.

The matrix forming inorganic oxide [Component (a)] of the Lewis acid adsorbent used in the present invention may be formed by known methods. For example, a silica gel may be prepared by conventional means, such as by mixing an aqueous solution of an alkali metal silicate (e.g., sodium silicate) with a strong acid such as nitric or sulfuric acid (preferred), the mixing being done under suitable conditions of agitation to form a clear silica sol which sets into a hydrogel in less than about one-half hour. The concentration of the SiO_2 in the hydrogel which is formed is usually in the range of typically between about 15 and about 40, preferably between about 20 and about 35, and most preferably between about 30 and about 35 weight percent, with the pH of the gel being from about 1 to about 9, preferably 1 to about 4. A wide range of mixing temperatures can be employed, this range being typically from about 20 to about 50°C.

Similarly, alumina sols and alumina gels can be formed by conventional means, such as by the hydrolysis of aluminum salts. For example, an alumina sol is formed by introducing aluminum metal to an acidic solution (e.g. hydrochloric acid, nitric acid and the like) at elevated temperature. The resultant sol is then aged at elevated temperatures of from about 100 to 360°C. for a period of time of from 0.5 to 24 hours followed by spray drying to form a solid powder product. Alumina gels

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(gelatinous boehmites) are formed by controlled hydrolysis of aluminum alkoxides in an aqueous or alcoholic solution.

Similarly, known methods of forming titania particles includes hydrolysis of titanium alkoxide, such as titanium ethoxide (TEOT) with water at elevated temperature.

The choice of metal suitable to impart Lewis acidity to a particular matrix will depend on the electron configuration of the atoms M of the matrix and that of the Lewis acid imparting metal of precursor (b). These can be determined by minor trial and with the aid of the teachings of Tanabe et al., *infra*. Further methods of forming inorganic oxide matrix materials found useful in the present invention are described by J-E. Otterstedt and D. Brandreth in "Small Particle Technology, Chapter 3, 85-155 (1998); by K. Tanabe et al. in "Studies in Surface Science and Catalysis" 51, 108-113 (1989); and by C.J. Brinker, G.W. Scherer, in "Sol-Gel Science The physics and Chemistry of Sol-Gel Processing", Academic Press, (1990). The teachings of these references are incorporated herein in their entirety by reference.

The formed material is then washed. Washing is accomplished simply by immersing the newly formed hydrogel in a continuously moving stream of water, which leaches out the undesirable salts, leaving substantially pure inorganic oxide polymer behind. The pH, temperature, and duration of the wash water will influence the physical properties of the formed matrix, such as surface area (SA) and pore volume (PV). For example, silica gel washed at 65-90°C at pH's of 8-9 for 28-36 hours will usually have SA's of 290-350 m²/g and form xerogels with PV's of 1.4 to 1.7 cc/gm. Silica gel washed at pHs of 3-5 at 50-65°C for 15-25 hours will have SAs of 700-850 m²/g and form xerogels with PV's of 0.3-0.6 cc/g.

The present adsorbent can be formed by contacting the inorganic oxide matrix forming material with a precursor material of a metal capable of imparting Lewis acidity to the resultant product to the degree required herein. The metal atom containing precursor material may be contacted with the inorganic oxide matrix forming material either during gel formation or subsequent to said formation. For example, the Lewis acid forming metal precursor component (b) may be cogelled

with the inorganic oxide matrix forming component (a) or, alternately, the already formed inorganic oxide matrix material can be treated with a Lewis acid metal precursor in a manner to impart Lewis acidity to the matrix.

The Lewis acid forming metals of the Lewis acid imparting precursor components (e.g. metal salts, metal oxide and the like having solubility in the media used to form the present adsorbent and mixtures thereof) may be incorporated as part of the inorganic oxide matrix by various techniques, namely (1) by being intimately incorporated into the gel structure upon formation, e.g., by formation of the inorganic matrix material in the presence of one or more Lewis acid metal precursor materials; (2) by admixing the Lewis acid metal precursor material with the initially formed gel particles of the inorganic oxide matrix material prior to milling or after milling in slurry form just prior to spray drying to cause agglomeration of the components, as described herein below; (3) by addition of the Lewis acid metal precursor material to an already formed inorganic oxide matrix or gel material by means of impregnation or the like; or (4) by contacting the Lewis acid metal precursor material with formed inorganic oxide matrix particles during after-treatment procedure, such as during aging at elevated temperature.

Thus, materials representing the first category are mixed gels such as, for example, alumina-zirconia, alumina-titania, titania-zirconia, titania-silica, zirconia-silica, alumina-silica, silica-alumina, silica-zirconia, silica-titania, silica-titania-alumina, silica-alumina-zirconia, silica-iron, titania-copper oxide, titania-alumina, titania-iron oxide, zirconia-cadmium oxide, alumina-magnesia and the like cogels. Such cogels show a substantially homogeneous distribution of the Lewis acid imparting metal throughout the bulk and on the surface of the resultant adsorbent. The weight ratio of the primary inorganic oxide to the Lewis acid imparting metal may range from about 100:1 to about 1:3. The preferred weight ratio will depend on the identity of the Lewis acid imparting metal and the degree of Lewis acidity desired.

In the second category, component (b) may be admixed, usually in slight proportions, with a inorganic oxide matrix material, prior to milling and/or just prior to agglomeration. This method is most suitable when it is contemplated to form the

resultant adsorbent from a gel material which is to undergo physical mixing, milling and/or agglomeration to prepare the resultant particulate adsorbent for use in the present improved process.

In the third category, the metal precursor material or other material used to impart Lewis acidity can be contacted with the already formed inorganic oxide matrix material by known techniques, such as that of incipient wetness impregnation wherein the inorganic oxide matrix material is contacted with a solution (aqueous or low molecular weight organic solvent) of a soluble (with respect to solvent of the solution) metal precursor followed by removal of the solvent. The treated material is normally subjected to elevated temperature to aid in causing the Lewis acid imparting metal atom to be oxidized to become part of the matrix configuration. When employing this method, the Lewis acid sites imparting metal ions are located almost entirely on the surface area of the adsorbent.

In the fourth category, the inorganic oxide matrix material may be a gel, such as an alumina gel or titania gel, which, following an impregnation step, is subjected to an aging procedure. Aging of gels can be conducted at elevated temperatures such as, for example at a temperature of from about 50 to 200°C (e.g. 65-90°C) and elevated pH of from about 7.5 to 10 (e.g. pH of 8-9) for 4-12 hours. In this case, the resulting product shows a surface enrichment in Lewis acid sites with a decreasing concentration of such sites into the bulk of the matrix.

In each of the above resultant adsorbents, the Lewis acid imparting metal can be present (as metal oxide) in from 1 to 80 weight percent of the resultant adsorbent with, preferably, from 1 to 30 and from 1 to 20 weight percent being most preferred.

The preferred adsorbent is a highly porous inorganic oxide matrix material having pores of large diameter. The average pore diameter should preferably be from about 40 to about 400, more preferably from about 45 to about 100 and most preferably from 45 to 75 Angstroms.

The preferred adsorbents are formed by producing a silica gel with an aluminate to provide a silica gel having Lewis acidity imparted by the aluminum atoms to the degree described herein above; or by cogelling an alkali metal silicate in the presence of a zirconium salt; or by treating a silica sol with carbon dioxide,

aging at elevated temperature and then adding aluminate to the sol to cause gel formation to provide the desired Lewis acidity. Combinations of the above are also preferred materials, such as, for example, silica gel having zirconium atoms and aluminum atoms present.

Other constituents which may be present, include those constituents not adversely affected by water, spray drying or calcination, as appropriate with respect to the method of forming the adsorbent particulate, such as finely divided oxides or chemical compounds. Similarly, it is possible to add powders or particles of other constituents to the gel particles to impart additional properties to the resultant adsorbent. Accordingly, there may be added materials that possess additional adsorbent properties, such as synthetic zeolites. In addition, one may add materials that act as a binder to aid in the attrition resistance of the resultant particulate. Such binders may be selected from clays, such as, for example, attapulgite, bentonite, sepiolite and the like and mixtures thereof usually in colloidal or powder form. The skilled artisan will appreciate that the amounts of such additional components must be restricted in order to avoid compromising the desired adsorption properties described herein.

Also, it is feasible to add constituents to the inorganic oxide matrix material which may be eliminated after agglomeration in order to control porosity within a desired range; such agents as cellulose, graphite, wood charcoal, and the like being particularly useful for this purpose. When such materials are to be employed, they may be added in conventional manners prior to gel formation or prior to agglomeration. However, when milling and agglomeration is used in the formation of the resultant particulate adsorbent, it is preferable that they be present in the gel during or prior to milling as described since they will be less likely to disturb the desired agglomerate morphology after spray drying when they are also subjected to milling.

In view of the above, the term "gel" (e.g. "alumina gel", "titania gel" and the like), as used herein and in the appended claims, is intended to include the optional inclusion of the aforementioned non-gel constituents permitted to be present in the inorganic oxide adsorbent.

The present adsorbent has a surface area (BET technique described by S. Brunauer, P. Emmett and E. Teller in J.A.C.S. 60, 209-319 (1939)) of greater than about 200 m²/g, preferably from 300 to 1000, more preferably from 400 to 600 and most preferably from 400 to 550 m²/g. Further the present adsorbent has nitrogen pore volume (BET) of at least 0.5, preferably from 0.5 to 1.8, more preferably from 0.6 to 1.5 and most preferably from 0.6 to 1.2 cc/g. Still further, the average pore diameter of the adsorbent should be preferably from about 40 to 400, such as from 45 to 200, more preferably from 45 to 100 and most preferably from 45 to 75 Angstroms.

The metal precursor material or other material used to impart Lewis acidity may be added to the matrix forming inorganic raw materials as part of the hydrogel or xerogel or aerogel formation or can be added to the formed hydrogel or xerogel or aerogel prior to milling, spray drying or extrusion to provide the resultant particulate adsorbent of the present invention. It is preferred to incorporate the metal precursor material or other material for imparting Lewis acidity into an inorganic oxide sol as part of hydrogel or xerogel or aerogel formation.

The subject adsorbent may be formed into particulate material in accordance with methods well known to the art, such as by spray drying, grinding and screening of larger particles of gelled material, pelletizing, extrusion, shaping into beads in a rotating coating drum, and the like as well as by a nodulizing technique whereby composite particles having a diameter of not greater than about 0.05 mm are agglomerated to particles with a diameter of at least about 1mm by means of granulation. A liquid may also be employed.

The particle size of the adsorbent will depend on the contemplated mode of contact of the adsorbent and the petroleum feedstream for a particular process system. For example, when the adsorbent is contemplated for use in a packed bed column or the like, the particle size of the adsorbent should be from about 0.2 to about 20, such as from about 0.5 to about 5 mm, with from about 0.6 to 1.5 mm being preferred. Particles of smaller or larger particle size may be used and will depend on the design of the particular column used. The exact particle size can be determined by known methods by those skilled in the art. Similarly, when contact

of the adsorbent and petroleum feedstream is to be done in a fluidized bed, the particle size of the adsorbent should be from about 10 to about 100 micrometer.

A preferred adsorbent is formed by cogelling an alkali metal silicate with an inorganic acid (e.g. sulfuric acid) (the sol is formed after the two raw materials have been contacted) that contains dissolved zirconium, titanium or aluminum salt or mixtures thereof, such as a zirconium, titanium or aluminum sulfate salt in sulfuric acid. The resultant cogelled material will contain the elected Lewis acid imparting metal atoms (e.g. zirconium atoms) as a substitute for some of the silicon atoms in the formed gel matrix to thus impart Lewis acidity to the formed material. Another preferred adsorbent is formed by gellation of an alkali metal silicate using carbon dioxide in the presence of aluminum sulfate. The resultant gel is then ground or milled to reduce the average particle size of the material to about 0.2 to about 20 (e.g. 0.2 to about 10), preferably from about 0.5 to about 5 mm, with from 0.6 to about 1.5 mm being still more preferred and from 0.7 to about 1.2 mm being most preferred.

Alternatively, the present adsorbent may be made by drying, preferably spray drying, a slurry of the Lewis acid metal precursor material and a matrix producing inorganic oxide (e.g. alumina gel) or of an already formed Lewis acid metal containing alumina gel followed by agglomeration. More specifically, in this embodiment, the adsorbent is formed into a slurry, preferably an aqueous slurry, comprising typically at least 50, preferably at least 75 (e.g., at least 80), and most preferably at least 85 (e.g., at least 90) weight percent water based on the slurry weight. However, organic solvents, such as C₃ to C₁₂ alkanes, alcohols (e.g. isopropyl alcohol), may also be employed although they represent a fire hazard relative to water and often make agglomerates too fragile for use as subject adsorbent.

To render a gel suitable for agglomerate (particulate) formation, e.g. by spray drying, various milling procedures are typically employed (although not required). The goal of a milling procedure is to ultimately provide gel material with an average particle size of typically from about 0.2 to about 10 (e.g. 2 to about 10) preferably from about 4 to about 9, and most preferably from 4 to 8 microns. In addition, to aid

in the formation of agglomerate particulate material, the gel may contain a binder material, such as a silica sol having known binding properties or additional material that has a particle diameter in the colloidal range of typically less than about 1, preferably less than about 0.5, and typically from about 0.4 to about 1 micron. All particle size and particle size distribution measurements described herein are determined by laser light diffraction and is known to all familiar in the art of small particle analysis.

Once the target average particle size is imparted to the inorganic oxide matrix material, a slurry, preferably an aqueous slurry, is prepared for agglomeration, preferably by spray drying. Agglomerate particles formed in the above manner are of a size normally suitable for slurry or fluidized bed application for contacting the subject adsorbent with the LGO petroleum feedstock.

Another suitable method for making the present adsorbent is by the agglomeration or extrusion of the inorganic oxide gel or of an already formed Lewis acid metal containing inorganic oxide matrix material. More specifically, in this process the gel material with an average particle size of 3 to about 100 preferably from about 4 to about 30, and most preferably from 4 to 10 microns is agglomerated or extruded in the presence of a binder. Such binders may be selected from clays or colloidal clays such as, for example, attapulgite, bentonite, sepiolite and the like and mixtures thereof, colloidal or submicron silica, silica hydrogels, aluminas and the like and mixtures thereof. Extrusion and agglomeration may be carried out by known methods which include, but are not limited to, single- and twin-screw extruders, pelletizer, different types of shear impact mixers, such as screw mixer, or pelletizing mixer. For example, the gel-binder mixture is processed to a paste using a solvent (e.g. water) and then extruded. In the case of agglomeration, the gel-binder mixture is beaded in the presence of a liquid, such as water, diluted citric acid or silica sol.

The resultant particulate material is normally dried to remove the processing liquid (water or organic solvent). The drying is normally conducted at elevated temperatures of from about 50 to 250°C, although lower or higher temperatures may be used. Drying is normally conducted at atmospheric pressure although reduced

pressure may be employed. The dried particulate material is then activated by calcination of the material. Thus, the material is subjected to elevated temperature such as, for example, from about 200 to 600, preferably from 400 to 600°C, under an oxygen laden atmosphere, such as air.

Accordingly, whatever overall process is utilized, the particulate formation is controlled to preferably impart the following properties to the adsorbent:

- (1) A surface area (BET) of typically at least about 200, preferably at least about 300, and most preferably from at least about 450 m²/g, which surface area can range typically from about 300 to about 1000, preferably from about 400 to about 600, and most preferably from about 400 to about 550 m²/g.
- (2) An average pore diameter (BET) of from about 40 to about 400, preferably from about 45 to 200, more preferably from about 45 to 100, and most preferably from about 45 to about 75 Angstroms (In instances where the particles are in the form of beads or extrudate, the particles may also contain pores of greater than 1000 Angstroms which can be detected and measured by utilizing mercury diffusion method of measurement);
- (3) A total pore volume of at least 0.5 with from 0.5 to about 1.8, preferably from about 0.6 to about 1.5, and most preferably from about 0.6 to about 1.2 cc/g; and
- (4) A bulk density of the adsorbent particles of typically at least about 0.2, preferably at least about 0.3, and most preferably at least about 0.4 g/ml, which bulk density can range typically from about 0.2 to about 1, preferably from about 0.3 to about 0.8, and most preferably from about 0.4 to about 0.7 g/ml.
- (5) An attrition resistance that provides sufficient strength to allow the adsorbent to undergo multiple adsorption/desorption cycles (e.g. 50 to 1000).

The particle size and particle size distribution sought to be imparted to the adsorbent particles is dictated and controlled by the contemplated mode of contact

by which the adsorbent and the petroleum feedstock will be employed as well as by the specific design parameters of the contacting operation (e.g. pressure drop within a column). For example, when a packed column is to be employed, the particulate should have a particle size distribution wherein the majority of particles (>95%) are less than 2, preferably less than 1.6 and more preferably less than 1.4 mm while only a minority of particulate (<10%, preferably <7%, most preferably <5%) are less than 0.6mm in average diameter.

The petroleum feedstock may be contacted with the adsorbent under temperature and pressure conditions that maintain the petroleum feedstream material in a liquid state during the adsorption operation. For example, the temperature conditions may range from about 0 to 100°C, preferably from about 20 to 60°C and with pressures of from about 1 to 15 bar, preferably from about 1 to 5 bar. The pressure conditions depend on the specific design of the column, the adsorbent particle size and the feed viscosity, so that even higher pressures than those mentioned here may to be applied under conditions well known to the artisan. Preferably, the feedstream may be contacted with the subject adsorbent under atmospheric pressure conditions and at a temperature dictated by the petroleum feedstream obtained from prior processing. The particular temperature and pressure for optimization of the adsorption can be readily determined by simple experimentation.

The present adsorbent has been found to effectively remove nitrogen compounds from C₁₂ and higher petroleum feedstock. Such feed streams are known to contain a varied and complex mixture of nitrogen compounds normally believed difficult to remove in an efficient manner.

The present adsorbent can be contacted with the feedstream by using any conventional means of contacting a solid and liquid material, such as using a packed column, a fluidized bed column or an ebullated bed column. It is preferred to utilize the present adsorbent by using it as the packing of a packed column. The size and residence time of the column design can be determined by the nature of the feedstream contemplated for treatment. Normally, when a continuous system is desired, a plurality of columns are used in parallel so that at least one column is in

the adsorption mode while the remaining columns are in a desorption or regeneration mode for continuous treatment of a petroleum feedstream.

When the subject adsorbent is spent (that is, has a reduction in adsorption rate below a certain predetermined design level), the adsorbent is removed from service for adsorption of the nitrogen compounds, and regenerated for return to service as an adsorbent. In a continuous system, when one column containing spent adsorbent is removed from service, a second column having regenerated adsorbent is placed into service. It has been found that the present adsorbent can be treated to adsorption, desorption and regeneration in a cyclic manner for extended periods (multiple cycles) prior to needing to be removed from service.

The continuous process can be described as first feeding a petroleum feed obtained from a distillation or FCC unit or its equivalent into one of at least two adsorption columns packed with the presently described adsorbent. The adsorption columns are located prior (normally just prior) to the HDS units of a flow diagram of the total petroleum process being utilized. The stream is fed into the column for a predetermined time to utilize substantially all of the adsorption capacity of the subject adsorbent. Such time can be determined for a particular column unit by conventional experimentation. Once substantially all of the adsorption capacity is utilized, the feedstock is directed to another adsorption column while taking the first unit out of the adsorption mode.

The first adsorption column is then subjected to desorption to remove collected nitrogen containment compounds from the adsorbent therein. It is believed, though not meant to be a limitation on the claimed invention, that, because the nitrogen contaminant compounds are merely adsorbed and/or absorbed either physically or through ionic or dative bonding or the like and not, in general, bound to the adsorbent by covalent bonds, the nitrogen contaminants can be readily removed by use of a polar organic solvent or other compound that is a solvent for a majority or, preferably, substantially all of the nitrogenous compounds. The solvent needs to be inert, that is inert with respect to the adsorbent, residual petroleum feedstock and other compounds in the adsorbent and will not cause formation of a solid precipitate with the nitrogenous compounds. In general, the adsorbent is

treated with an inert, low boiling liquid that is preferably selected from a polar organic liquid, although non-polar liquids may also be used. The desorption liquid is usually selected from C₁-C₆ alcohols such as straight and branched chain alkanols as, for example, methanol, ethanol, propanol (all isomers), butanol (all isomers), pentanol (all isomers), hexanol (all isomers), mixtures thereof and the like; C₁-C₆ ethers such as dialkyl ethers and alkyl cycloalkyl ethers as, for example, dimethyl ether, diethyl ether, dipropyl ether, methyl t-butyl ether, methyl cyclopropyl ether, methyl cyclobutyl ether, ethyl cyclobutyl ether, mixtures thereof and the like; C₁-C₆ aldehydes such as alkyl and cycloalkyl containing aldehydes, as acetaldehyde, propionaldehyde, butylaldehyde, malonaldehyde, mixtures thereof and the like; C₁-C₆ ketones such as dialkyl ketones as for example, acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, ethyl propyl ketone, methyl cyclopropyl ketone, methyl cyclobutyl ketone, mixtures thereof and the like. Higher molecular weight desorption liquids may be used although their increased boiling point requires more energy for stripping the liquid from the nitrogen material and, therefore, are less preferred.

The desorption solvent is contacted with the nitrogen compound laden adsorbent usually by merely passing the solvent through the packed column for a predetermined time to remove substantially all of the nitrogenous compounds therefrom. Such time can be readily determined by simple experimentation and may be done in coordination with the determination of suitable adsorption time for the adsorbent, as described above. Resultant solvent that contains the nitrogenous contaminants is then removed. Optionally, the solvent is separated from the nitrogen contaminants and recycled for additional desorption.

Determination of both the adsorption and desorption times to effectively adsorb and desorb the nitrogenous compounds will depend on the column design, petroleum feedstock being treated, temperature of the feedstock as well as other known factors.

The desorbed column may be directly returned to adsorption function or may, optionally, be further treated to remove any remaining solvent, petroleum

residue capable of fouling the column, or the like before being returned to service as an adsorption column.

The high boiling petroleum product stream obtained from the adsorption process described above is subsequently treated to a hydrodesulfurization process (HDS). In general, such processes entail contacting the obtained petroleum material with a conventional HDS catalyst at elevated temperatures (e.g. 250 to 450°C) and pressure (e.g. 10 to 150 bars) with a hydrogen to oil ratio of 36 to 620 m³/m³. HDS catalysts in general have acidic sites, which are poisoned by the presence of nitrogen containing compounds. Thus, the present process, where these nitrogen compounds are removed prior to the HDS processing, provides an efficient manner to remove the nitrogen and sulfur contaminants from the high boiling cuts obtained from petroleum feedstock.

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements in Hawley's Condensed Chemical Dictionary, 12th Edition. Also, any references to the Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of Elements using the IUPAC notation system for numbering groups.

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified.

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.

EXAMPLE 1

Formation of Silica-Zirconia Adsorbent

A cogel of silica-zirconia was formed using a mixing nozzle having the capability for concurrent introduction of two liquid streams followed by passage of the introduced liquids through a tortuous path capable of providing rapid mixing of the streams. An aqueous solution of sodium silicate (analysis: 24.2% SiO_2 , 7.5% Na_2O) was introduced into the mixing nozzle at the rate of 29.5 l/hr while simultaneously introducing, at a rate of 10.5 l/hr, a sulfuric acid solution having zirconium orthosulfate dissolved therein (analysis: 30.7% H_2SO_4 ; 3.2% ZrO_2). Upon exiting from the mixing apparatus, a silica hydrogel having zirconium metal as the Lewis acid promoter was formed within 11 minutes. 2500 parts of the resultant hydrogel was washed by passing 2100 parts of water maintained at 60°C through the hydrogel product over a one hour period. This washing step was repeated three additional times. After the final wash, the resultant hydrogel was sequentially treated

- (a) with a first solution of 2100 parts water containing 103 parts of an aqueous 12.5% ammonia solution for 4 hours at 90°C;
- (b) repeating treatment (a) above;
- (c) repeating treatment (a) above except only 5 parts of the aqueous ammonia solution was introduced with the water and the duration was 2 hours;
- (d) contacting the hydrogel with 2100 parts water containing 24 parts of an aqueous 45% sulfuric acid solution for 2 hours at 60°C; and
- (e) washing 4 times, each with 2100 parts water for 1 hour at 60°C.

The washed hydrogel was dried for 15 hours at 200°C followed by heating at 400°C for 2 hours. The resultant activated silica-zirconia aerogel was cooled to ambient conditions under a dry atmosphere.

The resultant gel contained 3.2 weight percent zirconium (as ZrO_2) (SAMPLE I). The Lewis and Bronsted acidities were measured by the procedure of

E. Bakiewicz et al, described in J. Phys. Chem. B 102 2890-2896 (1998). The physical properties of BET surface area, pore volume and pore diameter were measured using conventional methodology for these properties. Table I below shows the Lewis and Bronsted acidity as well as physical properties of the resultant adsorbent.

Table I
Physical Properties of
SiO₂ gel- ZrO₂ Adsorbent

	Lewis Acidity μmol/g	Bronsted Acidity μmol/g	Surface Area m ² /g	Pore Vol. cc/g	Avg. Pore Diameter Å
SiO ₂ with 3.2% Zr (as ZrO ₂)	1940	0	467	0.78	67

EXAMPLE 2:

Formation of Alumina modified Silica Adsorbents

Four samples of spray dried silica gel having aluminum atoms in the matrix to impart Lewis acidity were formed as follows.

IIA. An aqueous silica sol was formed by initially dissolving sodium silicate (analysis: 24.2% SiO₂, 7.5% Na₂O) in water heated to 85°C at a silicate/H₂O ratio of 0.15 to produce an aqueous silica sol. The silica sol was mixed with carbon dioxide at a rate such that the gel time of the silica sol was between 10 and 30 seconds. The mixing was performed using a pipe reactor to enable intimate mixing of the materials. The gel was further mixed in the reactant water for approximately 140 minutes to allow gel structure development to be completed. The gel was then pumped through a static mixer while adding an aluminum sulfate solution at the

silica to alumina ratio 28/5. Due to the change in pH, carbon dioxide gas expelled from the gel mixture. The resultant alumina-silica hydrogel was dewatered at 200°C for 15 hours and spray dried to form spherical particles (1100 psi). The resultant powdered product was then slurried in water and washed with ammonium sulfate solution to exchange soda in the same manner as described in Example 1 above. The resultant material was flash dried at 182°C. The dried spherical particles (about 60 μm in diameter) were then milled to about 8 μm particle size using a jet mill. The powder was then formed into beads of about 1mm in diameter according to the procedure described below.

II B. The process of IIA described above was repeated except that the sol was initially formed at about 35°C instead of 85°C; using a silicate/H₂O ratio of 0.24 instead of 0.15; and aging the gel for 60 minutes instead of 140 minutes.

II C. A sample was prepared in the same manner as described for Sample II B, except that additional sodium aluminate (19% Al₂O₃) was added after the aging step to produce a product having an alumina content of 25 weight percent.

II D. This sample was formed in the same manner as described for Sample II B except that the resultant material was used in powder form with a particle size of between 20 and 70 micrometers. The material was not formed into beads as described below.

Example 3

Formation of Alumina-Titania Adsorbent

Aluminum isopropoxide is hydrolyzed by introducing it into water being maintained at 85°C over a 10 minute period to produce a solution having 15% by weight aluminum in water. The resultant suspension is maintained at 85°C for 20 minutes. The material is then peptized by the addition of a solution of titanium tetrachloride in isopropanol. The resulting material is dried by heating at 200°C for 20 hours to produce an alumina-titania cogel.

Example 4

Formation of beads from alumina modified silica powders:

800 parts of each of the above Samples of Example II (except II E) was separately mixed with 200 parts of binder (Sample II A with boehmite; Samples II B and II C with attapulgite clay) in an Eirich mixer for half an hour. The resulting powder mixtures were each agglomerated by adding an appropriate amount of water to observe bead formation. The water content differed depending on the silica-alumina powder and on the binder system used. The particle size of the beads was between 0.6 and 1.4 mm.

The resultant samples were dried for 15 hours at 120°C and then activated at 550°C for about 2 hours. The Lewis and Bronsted acidities were measured by the procedure of E. Bakiewicz et al, described in J. Phys. Chem. B 102 2890-2896 (1998). The physical properties of BET surface area, pore volume and pore diameter were measured using conventional methodology for these properties. The resultant particulate adsorbents were analyzed to have the properties shown in Table II below.

Table II

<u>Sample</u>	Lewis Acidity ($\mu\text{mol/g}$)	Bronsted Acidity ($\mu\text{mol/g}$)	Al content (as Al_2O_3) (wt. %)	Surface Area (m^2/g)	Pore Vol. (cc/g)	Av. Pore Dia. (Å)
II A	1050	270	13.1	338	0.69	81
II B	1000	30	13.3	267	0.93	140
II C	1240	100	25.0	364	0.64	70
II D	1100	260	13.1	329	1.1	134

The alumina-titania cogel of Example III is treated (using attapulgite as the binder) in the same manner as above to form beads of this material. The resultant

material has a high Lewis acidity of about 1000 $\mu\text{mol/g}$ and a high pore diameter of about 75.

Example 5

Formation of Silica Gel (Comparative)

Two silica xerogels (Samples III-Si/1 and III-Si/2) were formed in the same manner as described in Example I above except that the initial sulfuric acid solution did not contain zirconium or other Lewis acid metal precursor agent. The washing and aging conditions were altered for each sample in order to adjust the desired pore structure.

Sample III-Si/1:

2500 parts of the resultant hydrogel was washed by passing 2100 parts of water maintained at 60°C through the hydrogel product over a one hour period. This washing step was repeated three additional times. After the final wash, the resultant hydrogel was sequentially treated

- (a) with a first solution of 2100 parts water containing 103 parts of an aqueous 12.5% ammonia solution for 4 hours at 60°C;
- (b) contacting the hydrogel with 2100 parts water containing 24 parts of an aqueous 45% sulfuric acid solution for 2 hours at 60°C; and
- (c) washing 3 times, each with 2100 parts water for 1 hour at 60°C.

Sample III-Si/2:

2500 parts of the resultant hydrogel was washed by passing 2100 parts of water maintained at 60°C through the hydrogel product over a one hour period. This washing step was repeated three additional times. After the final wash, the resultant hydrogel was sequentially treated

- (a) with a first solution of 2100 parts water containing 103 parts of an aqueous 12.5% ammonia solution for 4 hours at 70°C;
- (b) contacting the hydrogel with 2100 parts water containing 24 parts of an aqueous 45% sulfuric acid solution for 2 hours at 60°C;
- (c) washing 2 times, each with 2100 parts water for 1 hour at 60°C; and

- (d) washing with a solution of 2100 parts water containing 103 parts of an aqueous 12.5% ammonia solution for 3 hours at 90°C

Alumina Adsorbent (Comparative)

A commercially available alumina adsorbent product, Hi Q 30 sold by Alcoa World Chemicals, was labeled Sample III-AI/1 and compared to the subject adsorbent of the present invention. The sample was in powder form with particle sizes between 20 and 70 micrometer.

Each of the comparative samples described above was dried at 200°C for 15 hours and then heated at 400°C for 2 hours. The samples were then allowed to cool to ambient temperature under a dry atmosphere. The Lewis and Bronsted acidities for each sample were measured by the procedure of E. Bakiewicz et al, described in J. Phys. Chem. B 102 2890-2896 (1998). The physical properties of BET surface area, pore volume and pore diameter were measured using conventional methodology for these properties.

Table III below shows the Lewis and Bronsted acidity as well as physical properties of the comparative adsorbents.

Table III
Physical Properties of SiO₂ and Alumina Gels

<u>Sample</u>	Lewis Acidity μmol/g	Bronsted Acidity μmol/g	Surface Area m²/g	Pore Vol. cc/g	Avg. Pore Diameter Å
III-Si/1	0	0	498	0.88	71
III-Si/2	0	0	275	1.16	168
III-AI/1	80	60	116	0.50	172

Example 6

Each of the silica-zirconia adsorbent formed according to Example I, the silica-alumina adsorbents formed according to Example II; and the comparative adsorbents of Example III was heated in a muffle oven at for 15 hours at 200°C followed by heating at 750°F (400°C) for 2 hours. The samples were then allowed to cool to ambient temperature under a dry atmosphere.

Each of the samples was tested according to the following procedure:

Various amounts of each adsorbent were charged into separate test columns followed by certain amounts of an LGO petroleum feedstream material (B.P. range of 164 to 458°C; total nitrogen of about 220 ppm, total sulfur 1.56 wt-%). For details of the feed to adsorbent ratios see Tables below. The total nitrogen content of the LGO petroleum feedstream material was analyzed by photometric spectrometry using a commercial nitrogen analyzer (ANTEK Analyzer).

Each of the test columns was maintained under agitation for 4 hours at 40°C to allow adsorption equilibrium to occur. The remaining petroleum material was removed from each column by centrifuging and analyzed for total nitrogen content in the same manner as done with the LGO petroleum feedstream material. The nitrogen adsorption capacity attained by the adsorbent of each test column was calculated according to the formula:

$$C = (c_o - c) m (\text{feed}) / m (\text{adsorbent})$$

where: C is the equilibrium nitrogen adsorption capacity in mg/g; c_o is nitrogen concentration of feed, c is nitrogen concentration of feed product after equilibration in contact with adsorbent; m (feed) is mass of LGO petroleum tested; and m (adsorbent) is mass of adsorbent in column.

For each test the calculated adsorption capacity was normalized with respect to the surface area (BET) of the adsorbent. The results are reported in Tables IV through XI below as adsorption capacity (mg/m²).

Table IV

Sample I				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.67	20	103	0.46	0.0078
1.33	20	67	0.30	0.0051
2.66	20	38	0.17	0.0030
4.00	10	10	0.04	0.0012

Table V

Sample IIA				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.17	10	151	0.66	0.0138
0.33	10	108	0.47	0.0110
0.37	10	70	0.30	0.0071
1.34	10	42	0.18	0.0042
4.00	10	10	0.04	0.0016

Table VI

Sample IIB				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.67	20	125	0.55	0.0113
1.33	20	86	0.38	0.0079
2.66	20	52	0.23	0.0049
4.00	10	16	0.07	0.0020

Table VII

Sample IIC				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.35	20	137	0.59	0.0149
0.37	20	108	0.46	0.0102
1.33	20	71	0.31	0.0066
2.66	20	45	0.19	0.0039
8.00	20	14	0.061	0.0015

Table VIII

Sample IID				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.18	10	140	0.58	0.0189
0.35	10	101	0.42	0.0121
0.67	10	70	0.29	0.0077
1.33	10	43	0.18	0.0045
4.00	10	13	0.05	0.0017

Table IX

Sample III-Si/1				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.66	20	129	0.62	0.0048
1.33	20	86	0.42	0.0037
2.66	20	55	0.26	0.0023
4.00	10	18	0.08	0.0010

Table X

Sample III-Si/2				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.66	20	128	0.62	0.0087
1.33	20	100	0.48	0.0059
2.66	20	70	0.34	0.0038
4.00	10	27	0.13	0.0016

Table XI

Sample III-Al 2				
m(ads) (g)	m(feed) (g)	c (ppm)	c/co	Capacity (mg / m ²)
0.18	10	205	0.85	0.0172
0.35	10	189	0.78	0.0128
0.67	10	161	0.67	0.0102
1.33	10	119	0.50	0.0079
4.00	10	43	0.18	0.0043

The principals, preferred embodiments and modes of operation of the invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than

restrictive. Variations and changes may be made by those skilled in the art, without departing from the spirit of the invention.

WE CLAIM:

1. A method of manufacturing C₁₂ and higher hydrocarbon fuel having reduced nitrogen and sulfur content comprising (a) contacting, prior to hydrodesulfurization, a C₁₂ or greater petroleum feedstream having nitrogen and sulfur containing compounds therein with a porous, particulate adsorbent comprising an inorganic metal (M) oxide matrix material wherein M is selected from Ti, Al, Zr, Si, Sn or mixtures thereof, having Lewis acidity of at least about 500 $\mu\text{mol/g}$; and (b) subsequently treating the feedstream product derived from (a) to catalytic hydrodesulfurization to produce a hydrocarbon fuel.
2. The method of Claim 1 wherein the adsorbent has a surface area of at least 200 m²/gm; a N₂ pore volume of at least about 0.5 cc/gm; and an average pore diameter of from 40 to 400 Å and an effective amount of metal atoms of Group IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA or VIIA of the Periodic Table other than M to cause Lewis acidity of at least 500 $\mu\text{mol/g}$ to the adsorbent.
3. The method of Claim 1 wherein the petroleum feedstream comprises C₁₂-C₃₀ hydrocarbons prior formed by fluid catalytic cracking or by distillation of petroleum feed.
4. The method of Claim 1 wherein the petroleum feedstream is contacted with adsorbent in a packed bed zone comprising at least one packed bed adsorption column.
5. The method of Claim 2 wherein the petroleum feedstream is contacted with adsorbent in a packed bed zone comprising at least one packed bed adsorption column.
6. The method of Claim 3 wherein the petroleum feedstream is contacted with adsorbent in a packed bed zone comprising at least one packed bed adsorption column.

7. The method of Claim 1 wherein said petroleum feedstream is contacted with adsorbent in an adsorption zone selected from a fluidized bed adsorption zone or an embullating bed adsorption zone.
8. The method of Claim 2 wherein said petroleum feedstream is contacted with adsorbent in an adsorption zone selected from a fluidized bed adsorption zone or an embullating bed adsorption zone.
9. The method of Claim 3 wherein said petroleum feedstream is contacted with adsorbent in an adsorption zone selected from a fluidized bed adsorption zone or an embullating bed adsorption zone.
10. The method of Claim 4 wherein the packed bed adsorption zone comprises at least two adsorption columns.
11. The method of Claim 5 wherein the packed bed adsorption zone comprises at least two adsorption columns.
12. The method of Claim 6 wherein the packed bed adsorption zone comprises at least two adsorption columns.
13. The method of Claim 7 wherein the adsorption zone comprises at least two adsorption columns.
14. The method of Claim 8 wherein the adsorption zone comprises at least two adsorption columns.
15. The method of Claim 9 wherein the adsorption zone comprises at least two adsorption columns.

16. The method of Claim 10 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

17. The method of Claim 11 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

18. The method of Claim 12 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

19. The method of Claim 13 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

20. The method of Claim 14 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

21. The method of Claim 15 wherein the petroleum feedstock is contacted with said adsorbent in at least one first adsorption column and the spent adsorbent in at least one second adsorption column is subjected to desorption to remove prior adsorbed nitrogen containing compounds therefrom.

22. The method of Claim 16 wherein the desorption comprises contacting adsorbent containing nitrogen compound with a liquid compound that is a solvent for the nitrogen compounds selected from C₁ – C₆ alkyl and cycloalkyl alcohols, C₁ – C₆ alkyl and cycloalkyl ethers, C₁ – C₆ alkyl and cycloalkyl aldehydes and C₁ – C₆ dialkyl ketones.

23. The method of Claim 19 wherein the desorption comprises contacting adsorbent containing nitrogen compound with a liquid compound that is a solvent for the nitrogen compounds selected from C₁ – C₆ alkyl and cycloalkyl alcohols, C₁ – C₆ alkyl and cycloalkyl ethers, C₁ – C₆ alkyl and cycloalkyl aldehydes and C₁ – C₆ dialkyl ketones.

24. The method of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22 or 23 wherein the adsorbent comprises a composite formed by contacting (a) a silica selected from silica matrix-forming material or silica matrix formed material or mixtures thereof with (b) a Lewis acid precursor compound in an effective amount to impart at least 500 $\mu\text{mol/g}$ Lewis acidity to the resultant adsorbent.

25. The method of Claim 24 wherein component (b) comprises a precursor compound having metal atoms of Group IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA or VIIA of the Periodic Table and the adsorbent has Lewis acidity of at least 600 $\mu\text{mol/g}$.

26. The method of Claim 24 wherein the Lewis acid imparting metal is selected from Mg, Ca, Sr, Ba, B, Al, Ga, Zn, Sc, Y, La, Ti, Zr, Hf, V, Nb, Mo, W, Fe, Co, Ni, and mixtures thereof.

27. The method of Claim 24 wherein the Lewis acid imparting metal is selected from Mg, Zn, La, Ti, Zr, Fe and Al and mixtures thereof.

28. The method of Claim 24 wherein the Lewis acid imparting metal is selected from Ti, Zr, Fe, Al and mixtures thereof.
29. The method of Claim 24 wherein component (a) of the adsorbent is selected from silica hydrogel, silica aerogel or silica xerogel or mixtures thereof.
30. The method of Claim 26 wherein component (a) of the adsorbent is selected from silica hydrogel, silica aerogel or silica xerogel or mixtures thereof.
31. The method of Claim 27 wherein component (a) of the adsorbent is selected from silica hydrogel, silica aerogel or silica xerogel or mixtures thereof.
32. The method of Claim 28 wherein component (a) of the adsorbent is selected from silica hydrogel, silica aerogel or silica xerogel or mixtures thereof.
33. The method of Claim 24 wherein the adsorbent has Lewis acidity of from about 500 to 2500 $\mu\text{mol/g}$.
34. The method of Claim 32 wherein the adsorbent has Lewis acidity of from about 500 to 2500 $\mu\text{mol/g}$.
35. The method of Claim 32 wherein the adsorbent is selected from a silica hydrogel, silica aerogel or silica xerogel having aluminum atoms therein in sufficient amount to impart Lewis acidity of from 500 to 2500 $\mu\text{mol/g}$.
36. The method of Claim 32 wherein the adsorbent is selected from a silica hydrogel, silica aerogel or silica xerogel having zirconium atoms therein in sufficient amount to impart Lewis acidity of from 500 to 2500 $\mu\text{mol/g}$.

37. The method of Claim 24 wherein the adsorbent has a surface area of from 400 to 550 m²/gm; a N₂ pore volume of from 0.6 to 0.9 cc/gm; and an average pore diameter of from 45 to 75 Å.

38. The method of Claim 32 wherein the adsorbent has a surface area of from 400 to 550 m²/gm; a N₂ pore volume of from 0.6 to 0.9 cc/gm; and an average pore diameter of from 45 to 75 Å.

39. The method of Claim 16 wherein the adsorbent is formed from a slurry of silica and Lewis acid metal precursor compound in a weight ratio of silica to metal (as metal oxide) of from 0.25:1 to 99:1.

40. The method of Claim 18 wherein the adsorbent comprises particulate material having a particle size distribution such that less than 5 weight percent have a diameter of less than 0.6 mm and at least about 95 weight percent have diameter of less than 2 mm.

41. The method of Claim 32 wherein the adsorbent comprises particulate material having a particle size distribution such that less than 5 weight percent have a diameter of less than 0.6 mm and at least about 95 weight percent have diameter of less than 2 mm.

42. A method of manufacturing hydrocarbon fuel comprising forming a feedstream comprising C₁₂ and higher hydrocarbon compounds wherein said feedstream further comprises nitrogen and sulfur containing compounds, introducing said feedstream to an adsorption zone comprising at least two packed adsorption columns followed by introducing said feedstream to a catalytic hydrodesulfurization zone, wherein said feedstream is introduced to at least one column of the adsorption zone having adsorbent comprising porous particulate selected from silica hydrogel, silica aerogel or silica xerogel or mixtures thereof having from about 1 to 80 weight percent of atoms (as metal oxide) of at least one Lewis acid imparting metal selected

from metal atoms of Group IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA or VIIA of the Periodic Table and having Lewis acidity of at least about 500 $\mu\text{mol/g}$; surface area of at least 200 m^2/gm ; N_2 pore volume of at least about 0.5 cc/gm ; and average pore diameter of at least 40 Å.

43. The process of Claim 42 wherein the Lewis acid imparting metal is selected from Ti, Zr, Fe, Al or mixtures thereof; and the adsorbent has Lewis acidity of from 600 to 3000 $\mu\text{mol/g}$; and average pore diameter of from 40 to 400 Å.

44. The process of Claim 42 wherein the Lewis acid imparting metal is selected from aluminum or zirconium or mixtures thereof; and the adsorbent has Lewis acidity of from 750 to 2500 $\mu\text{mol/g}$; and average pore diameter of from 40 to 400 Å.

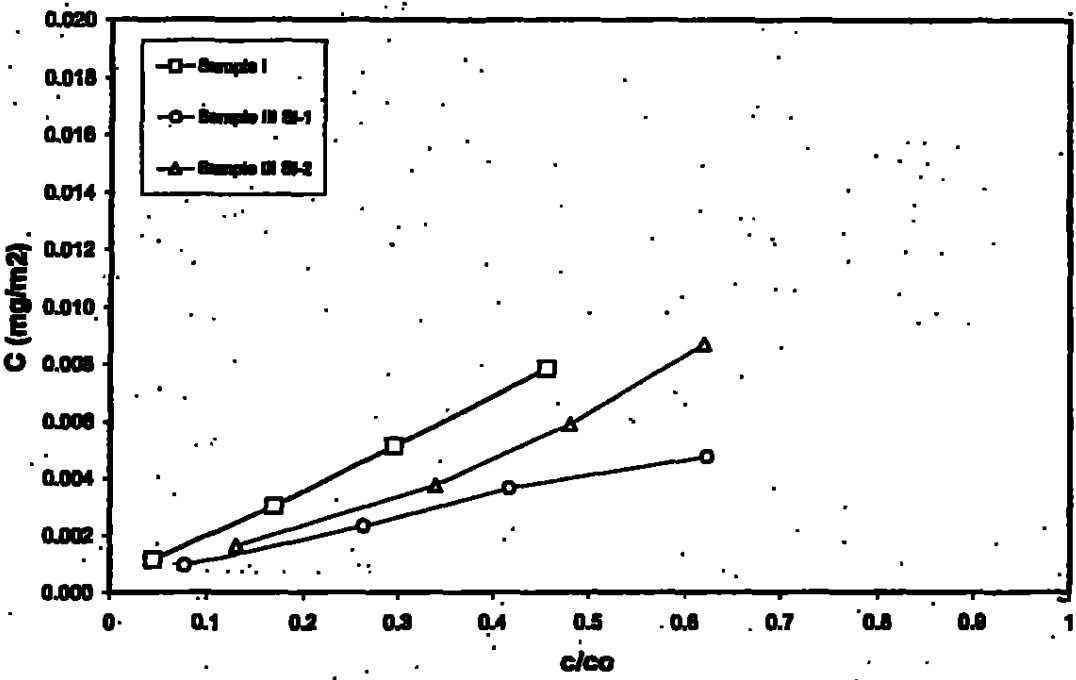


Fig. 1

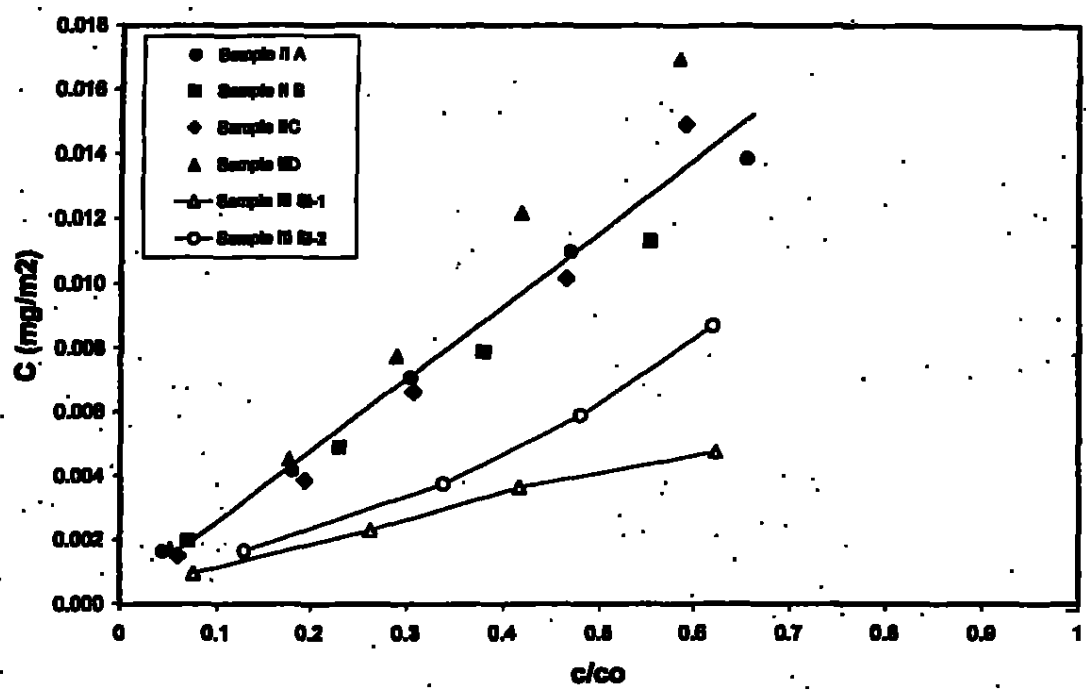


Fig. 2

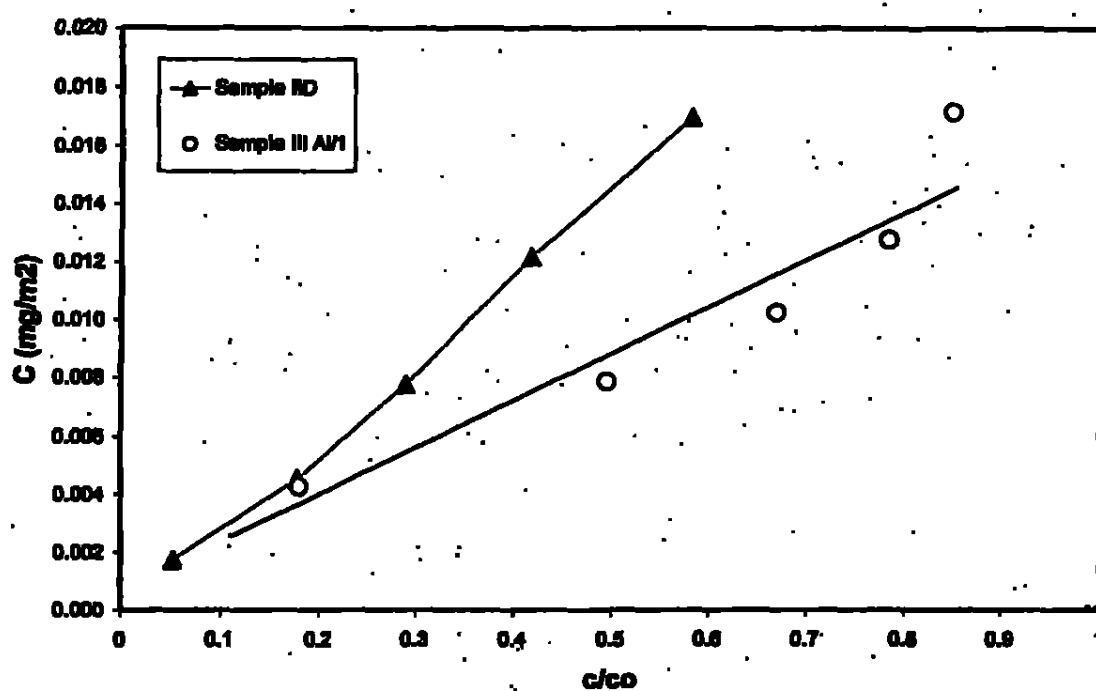


Fig. 3

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The Patent & Trademark Office stamp affixed hereto indicates date of receipt of International Application under the Patent Cooperation Treaty, PCT Request, Fee Calculation Sheet (in triplicate), General Power of Attorney, Specification [description (35 sheets), claims (7 sheets), abstract (1 sheet), drawings (3 sheets)], and Return Receipt Acknowledgement Postal Card for U S Serial No(s) 10/322 814, filed 12/19/2002, Inventor Lesemann et al
TITLE PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS"

Ref HJT:dpd
Atty Docket W9563-01
Mailed 12/12/2003

2

PCT INTERNATIONAL APPLICATION TRANSMITTAL LETTER	Date December 12, 2003
Regarding The International Application Of W.R. Grace & Co.-Conn.	Docket or Reference Number W9563-01

Entitled "PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS"

EV 311098556 US Certification Under 37 CFR 1.10 (If applicable) December 12, 2003
 "Express Mail" mailing number Date of Deposit

I hereby certify that this application 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 the Assistant Commissioner for Patents, Washington, D.C. 20231.

Debra P. Darcey
 (Typed or printed name of person mailing application) (Signature of person mailing application)

To the United States Receiving Office (RO/US): Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450
 Accompanying this transmittal letter is the above-identified International application, including a completed Request form (PCT/RO/101). Please process the application according to the provisions of the Patent Cooperation Treaty:

The following requests are made of the RO/US:

1. ☒ PREPARATION AND TRANSMITTAL OF CERTIFIED COPY OF PRIORITY DOCUMENTS - Please prepare and transmit to the International Bureau a certified copy of the United States origin priority documents identified in Box VI of the Request form (37 CFR 1.451).
 To cover the cost of copy preparation and certification (37 CFR 1.19(a)(3) and (b)(1)),
☐ a (check) (money order) in the amount of \$___ is attached to this transmittal letter.
☒ the RO/US is hereby authorized to charge the following deposit account no.: 07-1770

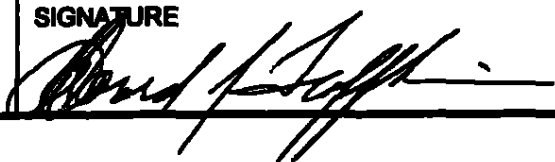
2. ☒ CHOICE OF INTERNATIONAL SEARCHING AUTHORITY - It is requested that the International Search be performed by the following International Searching Authority:
☐ United States Patent and Trademark Office (ISA/US)
☒ European Patent Office (ISA/EP)
 The appropriate Search fee for the above-named Authority is indicated on the Fee Calculation Sheet (PCT/RO/101 Annex).

3. ☐ SUPPLEMENTAL SEARCH FEES (ONLY WHEN ISA/US CONDUCTS THE INTERNATIONAL SEARCH.) - Please charge any Supplemental Search fees that may be required by the United States International Searching Authority (ISA/US) to deposit account no.: 07-1770.
 I understand that this authorization is subject to my oral confirmation thereof in each instance and that it in no way limits my right to submit a protest against payment of the Supplemental Search fees, but is merely an administrative aid to assure that the ISA/US may timely complete the Search Report.

NOTE: SUPPLEMENTAL SEARCH FEES FOR ISA/EP ARE PAYABLE DIRECTLY TO THE EUROPEAN PATENT OFFICE

4. ☐ 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:
 A. ☐ There is no prior filed application relating to this invention.
 B. ☐ There is a prior application, serial number _____ filed on _____ which contains subject matter that is
 1. ☐ substantially identical to that of the accompanying International application.
 2. ☐ less than that of the accompanying International application. The additional subject matter of the International application appears on page(s) and line(s) _____.
 3. ☐ more than that of the accompanying International application.
 C. ☐ Disclosure information cannot be covered by the language of Points 4A or 4B above due to the involvement of several prior applications or for other reasons. A separate sheet on which the disclosure information is explained is attached to this transmittal letter.

5. ☒ REQUEST FOR FOREIGN TRANSMITTAL LICENSE - According to the provisions of 35 U.S.C. 164 and 37 CFR 5.11, a license to transmit the accompanying International application to foreign agencies or International authorities is hereby requested.

SIGNER IS THE ☐ APPLICANT ☐ COMMON REPRESENTATIVE ☒ (ATTORNEY) (AGENT) REG. NO. 25,184	NAME OF SIGNER (typed) Howard J. Troffkin
	SIGNATURE 

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 derived) (12 characters maximum) W9563-01**Box No. I TITLE OF INVENTION**
PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS**Box No. II APPLICANT** ☐ This person is also inventor

Name and address: (Family name followed by given names; 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 21044
United States of America

Telephone No.
410-531-4883Facsimile No.
410-531-4195

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:
United States of AmericaState (that is, country) of residence:
United States of AmericaThis 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 names; 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.)

LESEMANN, Marcus Fredrick Manfred
Apt. 1034, 105 West 38th Street
Baltimore, Maryland 21210
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:
GermanyState (that is, country) of residence:
United States of AmericaThis 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 names; for a legal entity, full official designation. The address must include postal code and name of country.)

TROFFKIN, Howard J.
W. R. GRACE & CO.-CONN.
7500 Grace Drive
Columbia, Maryland 21044
United States of America

Telephone No.
301-299-9328Facsimile No.
301-299-4575

Teleprinter No.

Agent's registration No. with the Office
25,184☐ 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 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.) SETZER, Constanze Albanusstr 68 Mainz, Germany 55128		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: Germany
State (that is, country) of residence: Germany		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
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. 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 or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) 19 December 2002 (19.12.02)	10/322,614	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)

Number

Country (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 | : | |
| ☒ 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 (II) 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:

W. R. GRACE & CO.-CONN. is entitled to apply for and be granted a patent by the virtue of the following:

An Assignment from:

LESEMANN, Marcus Frederick Manfred of Apt. 1034, 105 West 39th Street, Baltimore, Maryland 21210, United States of America

and

SETZER, Constanze, of Albanusstr 68, Mainz, Germany 55128

to W. R. GRACE & CO.-CONN. dated 5 June 2003.



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

Box No. VIII (iii) DECLARATION: ENTITLEMENT TO CLAIM PRIORITY

The declaration must conform to the standardized wording provided for in Section 213; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iii). 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 claim the priority of the earlier application specified below, where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4.17(iii) and 51bis.1(a)(iii)):

W. R. GRACE & CO.-CONN. is entitled to claim priority of earlier Application No. 10/322,614 filed in the United States of America by virtue of the following:

An Assignment from:

LESMANN, Marcus Frederick Manfred of Apt. 1034, 105 West 39th Street, Baltimore, Maryland 21210, United States of America

and

SETZER, Constanze of Albenusstr 68, Mainz, Germany 55128

to W. R. GRACE & CO.-CONN. dated 5 June 2002.

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

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) In paper form, the following number of sheets:		1. ☒ fee calculation sheet	:
request (including declaration sheets)	: 7	2. ☐ original separate power of attorney	:
description (excluding sequence listings and/or tables related thereto)	: 35	3. ☐ original general power of attorney	:
claims	: 7	4. ☒ copy of general power of attorney; reference number, if any:	:
abstract	: 1	5. ☐ statement explaining lack of signature	:
drawings	: 3	6. ☐ priority document(s) identified in Box No. VI as item(s):	:
Sub-total number of sheets	: 53	7. ☐ translation of international application into (language):	:
sequence listings	:	8. ☐ separate indications concerning deposited microorganism or other biological material	:
tables related thereto	:	9. ☐ sequence listings in computer readable form (Indicate type and number of carriers)	:
(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)	:	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:
Total number of sheets	: 53	(ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:
(b) ☐ only in computer readable form (Section 801(a)(i))		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listings mentioned in left column	:
(i) ☐ sequence listings		10. ☐ tables in computer readable form related to sequence listings (Indicate type and number of carriers)	:
(ii) ☐ tables related thereto		(i) ☐ copy submitted for the purposes of international search under Section 802(b-quarter) only (and not as part of the international application)	:
(c) ☐ also in computer readable form (Section 801(a)(ii))		(ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quarter)	:
(i) ☐ sequence listings		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	:
(ii) ☐ tables related thereto		11. ☒ other (specify): RECEIPT CARD	:
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the			
☐ sequence listings:			
☐ tables related thereto:			
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)			

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).



Howard J. Franklin
Registration No. 25784

For receiving Office use only		2. Drawings: ☐ received: ☐ not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
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	

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

65

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International Application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

W9563-01

Applicant

W. R. GRACE & CO.-CONN.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 240.00 T

2. SEARCH FEE 1,119.00 S

International search to be carried out by

(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) and/or (c) of Box No. IX apply, enter Sub-total number of sheets

Where item (b) and (c) of Box No. IX do not apply, enter Total number of sheets

53

b1 first 30 sheets 476.00 b1

b2 23 x 12.00 = 276.00 b2
number of sheets in excess of 30 fee per sheet

b3 additional component (only if sequence listings and/or tables related thereto are 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 fee per sheet = b3

Add amounts entered at b1, b2 and b3 and enter total at B 752.00 B

Designation Fees

The international application contains >5 designations.

6 x 104.00 = 520.00 D
number of designation fees payable (maximum 5) amount of designation fee

Add amounts entered at B and D and enter total at I 1,272.00 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) 20.00 P

5. TOTAL FEES PAYABLE 2,661.00

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

☒ authorization to charge deposit account (see below)

☐ 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)

☒ Authorization to charge the total fees indicated above.

☐ (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.

☐ Authorization to charge the fee for priority document.

Receiving Office: RO/ US

Deposit Account No.: 07-1770

Date: 12 December 2003

Name: Howard J. Troffklip

Signature

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/060545 A3

(51) International Patent Classification²: C10G 67/06, 45/02, B01J 21/08, 20/16

(21) International Application Number:
PCT/US2003/039368

(22) International Filing Date:
12 December 2003 (12.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/322,614 19 December 2002 (19.12.2002) US

(71) Applicant: W. R. GRACE & CO.-CONN. [US/US];
7500 Grace Drive, Columbia, Maryland 21044 (US).

(72) Inventors: LESEMANN, Marcus, Fredrick, Manfred;
/ Apt. 1034, 105 West 39th Street, Baltimore, MD 21210
(US); SETZER, Constanze; Albanusstrasse 68, 55128
Mainz (DE).

(74) Agent: TROFFKIN, Howard, J.; W.R. 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, 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, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, 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, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the International search report:
13 January 2005

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: PROCESS FOR REMOVAL OF NITROGEN CONTAINING CONTAMINANTS FROM GAS OIL FEEDSTREAMS

(57) Abstract: The present invention is directed to the removal of nitrogen and sulfur containing impurities from high molecular weight petroleum feedstock obtained from fluid cracking catalyst or distillation zone of a petroleum treatment plant. The present process comprises first treating C₁₂ and higher hydrocarbon petroleum feedstock having nitrogen and sulfur containing compounds therein with a porous, particulate adsorbent comprising a silica matrix having an effective amount of metal atoms therein to cause the adsorbent to have Lewis acidity of at least 500 µmol/g and then treating the resultant feedstock to catalytic hydrodesulfurization to produce a hydrocarbon fuel having low sulfur and nitrogen content.

WO 2004/060545 A3



INTERNATIONAL SEARCH REPORT

International Application No

/US 03/39368

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10667/06 C10645/02 B01J21/08 B01J20/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C106 B01J

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 057 879 A (TOPSOE HALDOR AS) 6 December 2000 (2000-12-06) the whole document	1-44
Y	EP 0 609 971 A (GRACE W R & CO) 10 August 1994 (1994-08-10) the whole document	1-44
A	US 5 917 069 A (EBERT HERMANN ET AL) 29 June 1999 (1999-06-29) the whole document	1-44



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"Z" document member of the same patent family

Date of the actual completion of the international search

9 November 2004

Date of mailing of the international search report

18/11/2004

Name and mailing address of the ISA

European Patent Office, P.O. Box 5011 Patentkan 2
NL - 2200 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cagnoli, M

INTERNATIONAL SEARCH REPORT

International Application No

/US 03/39368

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1057879	A	06-12-2000	AU 3784000 A	07-12-2000
			CA 2310555 A1	02-12-2000
			CN 1277988 A	27-12-2000
			EP 1057879 A2	06-12-2000
			JP 2001040370 A	13-02-2001
			NO 20002796 A	04-12-2000
			US 6551501 B1	22-04-2003
EP 0609971	A	10-08-1994	US 5376608 A	27-12-1994
			CA 2113219 A1	28-07-1994
			CN 1093735 A ,B	19-10-1994
			DE 69414278 D1	10-12-1998
			DE 69414278 T2	10-06-1999
			EP 0609971 A1	10-08-1994
			ES 2122154 T3	16-12-1998
			JP 6277519 A	04-10-1994
			US 5525210 A	11-06-1996
US 5917069	A	29-06-1999	DE 19505579 A1	22-08-1996
			DE 59600709 D1	26-11-1998
			WO 9626005 A1	29-08-1996
			EP 0809532 A1	03-12-1997
			JP 11500352 T	12-01-1999

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference W9563-01	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 03/39368	International filing date (day/month/year) 12/12/2003	(Earliest) Priority Date (day/month/year) 19/12/2002
Applicant W. R. GRACE & CO. - CONN.		

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

This International Search Report consists of a total of 3 sheets.



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

1. Basis of the report

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



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

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

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

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



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

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G67/06 C10G45/02 B01J21/08 B01J20/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G B01J

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Classification of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 057 879 A (TOPSOE HALDOR AS) 6 December 2000 (2000-12-06) the whole document	1-44
Y	EP 0 609 971 A (GRACE W R & CO) 10 August 1994 (1994-08-10) the whole document	1-44
A	US 5 917 069 A (EBERT HERMANN ET AL) 29 June 1999 (1999-06-29) the whole document	1-44

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

* Special categories of cited documents:

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

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

Date of the actual completion of the international search

9 November 2004

Date of mailing of the international search report

18/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentplan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 851 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cagnoli, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/39368

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1057879	A	06-12-2000	AU 3784000 A	07-12-2000
			CA 2310555 A1	02-12-2000
			CN 1277988 A	27-12-2000
			EP 1057879 A2	06-12-2000
			JP 2001040370 A	13-02-2001
			NO 20002796 A	04-12-2000
			US 6551501 B1	22-04-2003
EP 0609971	A	10-08-1994	US 5376608 A	27-12-1994
			CA 2113219 A1	28-07-1994
			CN 1093735 A , B	19-10-1994
			DE 69414278 D1	10-12-1998
			DE 69414278 T2	10-06-1999
			EP 0609971 A1	10-08-1994
			ES 2122154 T3	16-12-1998
			JP 6277519 A	04-10-1994
			US 5525210 A	11-06-1996
US 5917069	A	29-06-1999	DE 19505579 A1	22-08-1996
			DE 59600709 D1	26-11-1998
			WO 9626005 A1	29-08-1996
			EP 0809532 A1	03-12-1997
			JP 11500352 T	12-01-1999

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

72

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RECEIVED
PATENT DEPT

JAN 25 2005

[Signature]

To:

TROFFKIN, Howard, J. *[Signature]*
W.R. Grace & Co.-Conn.
7500 Grace Drive
Columbia, MD 21044
ETATS-UNIS D'AMERIQUE

W9563 01 LB

Rockes Jan. 18. 2005
PATENT COOPERATION TREATY

73

NOV 24 2004

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

W.R. GRACE & CO.-CONN
Attn. Troffkin, Howard J. *HTC*
7500 Grace Drive
Columbia
Maryland, 20144
UNITED STATES OF AMERICA *UB*

DAVLE

Date of mailing
(day/month/year)

18/11/2004

Applicant's or agent's file reference

W9563-01

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/US 03/39368

International filing date
(day/month/year)

12/12/2003

Applicant

W. R. GRACE & CO.-CONN.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

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

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

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

Within 18 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 30 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 18 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



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

Authorized officer

Lorena Díaz-Carralero Murcian

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 18. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

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

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 18

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 18 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 18, only the claims may be amended.

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

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

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

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

How?

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

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

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

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

What documents must/may accompany the amendments?

Letter (Section 206(b)):

The amendments must be submitted with a letter.

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

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

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NOTES TO FORM PCT/ISA/220 (continued)

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

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

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

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 18, 19 and 20; new claims 21 and 22 added."

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

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

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

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

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

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

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

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

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

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

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

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

From the INTERNATIONAL BUREAU

PCT**NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES**

(PCT Rule 47.1(c), first sentence)

To:

TROFFKIN, Howard, J.
W.R. Grace & Co.-Conn.
7500 Grace Drive
Columbia, MD 21044
ETATS-UNIS D'AMERIQUE

AUG - 2 2004

Date of mailing (day/month/year)
22 July 2004 (22.07.2004)Applicant's or agent's file reference
W9563-01**IMPORTANT NOTICE**International application No.
PCT/US2003/039368International filing date (day/month/year)
12 December 2003 (12.12.2003)Priority date (day/month/year)
19 December 2002 (19.12.2002)

Applicant

W. R. GRACE & CO.-CONN.

Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this notice:

AU, AZ, BY, CH, CN, CO, DZ, EP, HU, JP, KG, KP, KR, MD, MK, MZ, RU, TM

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BZ, CA, CR, CU, CZ, DE, DK, DM, EA, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, ID, IL, IN, IS, KE, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PG, PH, PL, PT, RO, SC, SD, SE, SG, SK, SL, SY, TJ, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on 22 July 2004 (22.07.2004) under No. WO 2004/060545

4. **TIME LIMITS** for filing a demand for international preliminary examination and for entry into the national phase

The applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be 30 MONTHS from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of 19 months from the priority date, but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

For filing a demand for international preliminary examination, see the *PCT Applicant's Guide*, Volume IA, Chapter IX. Only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

It is the applicant's sole responsibility to monitor all these time limits.

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

Authorized officer

Ellen Moyse

Facsimile No.+41 22 740 14 35

Facsimile No.+41 22 338 89 75

INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated on the cover sheet of this Notification by paying national fees and furnishing translations, as prescribed by Articles 22 and 39 and the applicable national laws. In addition, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure the necessary steps to enter the national phase are taken in a timely fashion. Most Offices do not issue reminders to applicants in connection with the entry into the national phase.

The applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be **30 MONTHS** from the priority date, not only in respect of any elected Office where a demand for international preliminary examination is filed before the expiration of 18 months from the priority date (see Article 39(1)), but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see PCT Gazette No. 44/2001 of 1 November 2001, pages 18826, 18832 and 18834, as well as the PCT Newsletter, October and November 2001 and February 2002 issues.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the PCT Gazette ("Section IV" part published on a weekly basis), to the PCT Newsletter (on a monthly basis) and to the relevant National Chapters in Volume II of the PCT Applicant's Guide (the paper version of which is updated usually twice a year and the Internet version of which is updated usually on a weekly basis). Finally, a cumulative table of all applicable time limits for entering the national phase is available from WIPO's Internet site, via links from various pages the site including those of the Gazette, Newsletter and Guide, at <http://www.wipo.int/pct/en/index.html>.

Information about the requirements for filing a demand for international preliminary examination is set out in the PCT Applicant's Guide, Volume I/A, Chapter IX. Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date (this time limit may not be extended). If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. The Notice of confirmation and payment must reach the receiving Office within the 15-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 18 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the International application, in which case that document will be considered to have been received by the International Bureau on the last day of the 18-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 18-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided 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 the time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 18-month time limit is the filing date of the earliest application whose priority is claimed.

PATENT COOPERATION TREATY

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From the INTERNATIONAL BUREAU

PCT

APR - 7 2004

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

To:

TROFFKIN, Howard, J. *1 CAE*
W.R. Grace & Co.-Conn.
7500 Grace Drive
Columbia, MD 21044
United States of America

Date of mailing (day/month/year) 25 March 2004 (25.03.2004)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference W9563-01	International application No. PCT/US2003/039368

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

W. R. GRACE & CO.-CONN.(all designated States)

International filing date : 12 December 2003 (12.12.2003)
Priority date(s) claimed : 19 December 2002 (19.12.2002)
Date of receipt of the record copy
by the International Bureau : 20 February 2004 (20.02.2004)
List of designated Offices :

AP : BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
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, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase - see updated Important Information (as of April 2002)
☒ confirmation of precautionary designations (if applicable)
☒ requirements regarding priority documents (if applicable)

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: Alison OSBORNE (Fax : 338 89 75)
Facsimile No. (41-22) 338.86.75	Telephone No. (41-22) 338 8472

PATENT COOPERATION TREATY

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PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 4004)

To:

TROFFKIN, Howard, J. *1-46*
W.R. Grace & Co.-Conn.
7500 Grace Drive
Columbia, MD 21044
United States of America

Date of mailing (day/month/year) 30 April 2004 (30.04.2004)	
Applicant's or agent's file reference W9563-01	IMPORTANT NOTIFICATION
International application No. PCT/US2003/039368	International filing date (day/month/year) 12 December 2003 (12.12.2003)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 19 December 2002 (19.12.2002)
Applicant W. R. GRACE & CO.-CONN.	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR" in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, 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.
- (If applicable) 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) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as priority document, Rule 17.1(c) 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.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 Dec 2002 (19.12.2002)	10/322,614	US	23 Febr 2004 (23.02.2004)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.89.75	Authorized officer Daniel VILLARS (Fax : 338 89 75) Telephone No. (41-22) 338 8919
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The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, 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 below:

IPEA/ US

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 or agent's file reference W-9563 - 01
International application No. PCT/US03/039368	International filing date (day/month/year) 12/12/2003	(Earliest) Priority date (day/month/year) 19/12/2002
Title of invention Process for Removal of Nitrogen Containing Contaminants from Gas Oil Feedstreams		
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 20144-4098 USA		Telephone No. 410-531-4508 Facsimile No. 410-531-4195 Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality: USA		State (that is, country) of residence: USA
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) LESEMANN, Markus Friedrich Manfred 3925 Canterbury Road Baltimore, Maryland 21218 USA		
State (that is, country) of nationality: Germany		State (that is, country) of residence: USA
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) SETZER, Constanze Albanusstr 68 Mainz, Germany 55128		
State (that is, country) of nationality: Germany		State (that is, country) of residence: Germany
☐ Further applicants are indicated on a continuation sheet.		

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 designation. The address must include postal code and name of country)

TROFFKIN, Howard J.
W. R. Grace & Co. - Conn.
7500 Grace Drive
Columbia, Maryland 21044 - 4098
USA

Telephone No.

301-299-9326

Facsimile No.

301-299-4575

Teleprinter No.

Agent's registration No. with the Office
25,184

☐ 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 INTER-NATIONAL 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 the applicable time limit under Rule 69.1(d)

4. ☐ The applicant expressly wishes the international preliminary examination to start earlier than at the expiration of the applicable time limit under Rule 34 bis. 1(a).

* 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 filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the PCT

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:		For International Preliminary Examining Authority use only	
		received	not received
1. translation of international application	sheets	☐	☐
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 sheet	5. ☐ statement explaining lack of signature
2. ☐ original separate power of attorney	6. ☐ sequence listings in computer readable form
3. ☐ original general power of attorney	7. ☐ tables in computer readable form related to sequence listings
4. ☐ copy of general power of attorney; reference number, if any:	8. ☒ other (specify): <u>Post Card</u>

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).


 Howard J. Trojahn
 Attorney for Applicant
 Reg. No. 25,184

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 accordingly.	6. ☐ The date of receipt of the demand is AFTER the expiration of the time limit under Rule 54 bis. 1(a) and item 7 or 8, below, does not apply.
4. ☐ The date of receipt of the demand is WITHIN the time limit of 19 months from the priority date as extended by virtue of Rule 80.5.	7. ☐ The date of receipt of the demand is WITHIN the time limit under Rule 54 bis. 1(a) as extended by virtue of Rule 80.5.
5. 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.	8. ☐ Although the date of receipt of the demand is after the expiration of the time limit under Rule 54 bis. 1(a) the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on: _____

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/US03/039368 Applicant's or agent's file reference W-9563-01 Applicant W. R. Grace & Co. - Conn.	For International Preliminary Examining Authority use only
CALCULATION OF PRESCRIBED FEES 1. Preliminary examination fee (Fee Codes 1805 or 1808) ----- \$750 P 2. Handling fee (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.) - (Fee Code 1708 \$162) ----- (Entitled to reduction ☐) \$162 H 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box ----- \$912.00 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 (This mode of payment may not be available at all IPEAs) ☒ Authorization to charge the total fees indicated above. ☐ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above. IPEA/ USPTO Deposit Account No.: 07-1770 Date: July 19, 2004 Name: Howard J. Troffkin Signature:	

Attorney Docket No. W-9563-01

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Markus Friedrich Manfred Lesemann, et al

Applicant: W. R. Grace Co.-Conn.
International Filing Date:
December 12, 2003

International Application No.

PCT/US03/039368

For: Process for Removal of Nitrogen Containing Contaminants from Gas Oil
Feedstreams

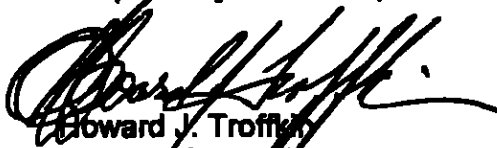
TRANSMITTAL LETTER

Mail Stop PCT
Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

Sir:

Submitted herewith is the Demand (3 pages), Fee Calculation Sheet (1 page in duplicate), Express Mail Certificate and a Return Post Card for the above-identified application.

Respectfully submitted,



Howard J. Troffey
Attorney for Applicant
Registration No. 25,184

Date: July 19, 2004

7500 Grace Drive
Columbia, MD 21044-4098

(301) 299-9326

"Express Mail" Mailing Label Number: EV 311098984 US

Date of Deposit: July 19, 2004

I hereby certify that a PCT Transmittal Letter, PCT Demand under Article 31 of the Patent Cooperation Treaty, Annex to Demand for International Preliminary Examination, a Fee Calculation Sheet (in duplicate), and a Return Post Card in PCT/US03/039368; filed December 12, 2003, for "Process for Removal of Nitrogen Containing Contaminants from Gas Oil Feedstreams"; Attorney Docket W-9563-01 and the required fees are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service on the date indicated above and is addressed to the Mail Stop PCT, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Linda L. Burton

Name

A handwritten signature in cursive script, appearing to read "Linda L. Burton", written over a horizontal line.

Signature

PROCESO PARA LA REMOCIÓN DE CONTAMINANTES QUE
CONTIENEN NITRÓGENO PROVENIENTES DE CORRIENTES
DE ALIMENTACIÓN DE GASÓLEO

CAMPO DE LA INVENCION

La presente invención está dirigida a un método mejorado para producir un combustible de petróleo, en particular un combustible diesel, sustancialmente libre de compuestos que contienen nitrógeno y azufre. Específicamente, el presente método comprende material de alimentación de hidrocarburo de petróleo tratante que tiene un punto de ebullición que varía desde aproximadamente 125 a 560°C (preferiblemente un corte de petróleo de hidrocarburo C₁₂ y mayor) con un adsorbente de óxido inorgánico que tiene una acidez Lewis alta impartida a esta antes de someter el material de alimentación a hidrodeshulfurización catalítica convencional. El pretratamiento actualmente requerido se ha encontrado que remueve fácilmente los compuestos nitrogenosos del material de alimentación y permite que tenga lugar la hidrodeshulfurización más eficientemente y más efectivamente para producir improducto de petróleo de contenido reducido de nitrógeno y azufre.

ANTECEDENTES DE LA INVENCION

Los problemas de polución ambiental, especialmente los de degradación de la calidad del aire, se han vuelto de gran preocupación en todo el mundo y especialmente en los países industriales desarrollados. Tales preocupaciones han conducido a políticas regulatorias ambientales que imponen regulaciones de mucha calidad sobre el transporte de combustible. De tales combustibles, el combustible diesel es considerado como el mayor contribuyente de los contaminantes dañinos conocidos, tales como SO_x, NO_x y materia en partículas y, por lo tanto, han sido propuestos estatuidos estándares regulatorios exigentes para reducir las emisiones de tales contaminantes por los combustibles diesel.

El contenido de azufre en los combustibles es una preocupación crítica, como es conocido por formar dióxido de azufre cuando se somete a un proceso de combustión. El dióxido de azufre, junto con la humedad atmosférica forma ácido sulfúrico en la atmósfera. Esta es la causa de la lluvia ácida, a la que se le ha atribuido la causa de daño sustancial sobre el ambiente así como también las estructuras hechas por el hombre.

Además, los óxidos de azufre generados se han encontrado que envenenan los catalizadores metálicos nobles convencionalmente utilizados como parte de los dispositivos

pos-tratamiento de emisión de los automóviles. Por ésta razón, los fabricantes de automóviles han sugerido que el contenido de azufre en los combustibles diesel sea reducido a menos de 30 partes por millón en peso (ppm) para cumplir las nuevas regulaciones de emisión de los escapes contemplados para convertirse en ley. Así, un mercado diesel con ultra-bajo azufre (ULSD) está emergiendo para reemplazar los estándares de combustible diesel con azufre convencional de 500 ppm. En varios países tales como los Estados Unidos y en un número de países europeos, las reglamentaciones han propuesto o estatuido requerir contenidos de azufre para ser reducidos a niveles de menos de 50 ppm y, en ciertos casos, a niveles menores de 15 ppm. En vista de las presiones regulatorias cada vez más crecientes, los productores refinadores y catalizadores de petróleo han invertido tiempo, dinero y esfuerzo considerable en producir productos de petróleo ambientalmente amigables.

Los procesos de hidrodeshulfurización (HDS) más comúnmente utilizados reducen el contenido de azufre en el material de alimentación de petróleo al convertir los compuestos de azufre presentes en el material de alimentación a sulfuro de hidrógeno. Desde los 60 varios procesos de HDS se han desarrollado los cuales, en general, someten el material de alimentación a hidrógeno bajo temperaturas y presiones elevadas en la presencia de un catalizador. Un modo de reducir el contenido de azufre es desarrollar mejoras

innovadoras en uno o más de los parámetros de operación de la actividad del catalizador, a temperatura de reacción, el volumen del lecho y/o la presión parcial de hidrógeno del proceso HDS.

Aunque la actividad del catalizador ha sido el doble desde que los catalizadores HDS fueron introducidos primero, se ha calculado que el factor de mejora de la actividad de 3.2 veces se requiere para cumplir el actual contenido de azufre de 500 ppm y un factor de aproximadamente 17 se requiere para alcanzar el nivel de 50 ppm más altamente deseado. Así, si uno confía en la actividad sola del catalizador, el número de reactores HDS debe ser sustancialmente incrementado y/o, la proporción de carga sustancialmente disminuida al menos que la actividad del catalizador se mejore dramáticamente.

Como se estableció anteriormente, la temperatura de reacción se puede incrementar para originar la reducción del contenido de azufre. Sin embargo, tal incremento de temperatura solo puede ser hecho en un pequeño grado debido a las limitaciones de diseño de los actuales equipos. Además, temperaturas muy altas son conocidas por originar la degradación de la corriente del producto. Similarmente, la presión incrementada ayudaría a lograr un contenido de azufre reducido pero los reactores actualmente diseñados establecen

un límite sobre este parámetro, y un nuevo equipo capaz de manejar presiones muy altas sería muy costoso.

Así, los procesos convencionales para tratar material de alimentación diesel (también conocida como gasóleo ligero, LGO) tienen limitaciones técnicas mientras que no sean producidos avances en la actividad del catalizador. Por lo tanto, los métodos, que utilizan diferentes materiales de alimentación en lugar de LGO, o que utilizan caminos de reacción novedosos, están siendo estudiados.

Por ejemplo, un proceso desarrollado por Shell Oil Company polimeriza gas natural para producir un compuesto destilado de productos C_{12} - C_{25} , similares al material de alimentación diesel. En este proceso gas natural es convertido en gas sintetizado a través de reacciones Fischer-Tropsch y el producto es polimerizado para producir destilado diesel libre de compuestos de azufre. Este proceso tiene los inconvenientes de utilizar alimentación medianamente costosa y requerir tres diferentes etapas de reacción para dar como resultado un proceso de costo alto.

La Patente U.S. 5,454,933 describe un proceso de adsorción para producir un combustible diesel libre de azufre al remover los compuestos de azufre restantes del material LGO que ya ha sufrido hidrodeshulfurización. El proceso post-

HDS descrito utiliza adsorbentes diseñados para remover directamente los compuestos de azufre residuales del material tratado post-HDS.

Se ha propuesto que la reducción o remoción de los compuestos que contienen nitrógeno de las corrientes que son alimentadas a una unidad HDS catalítica originan que el HDS tengan lugar de una manera más eficiente y, así, hacer el sistema capaz de producir un producto con un contenido de azufre muy bajo utilizando parámetros de operación operativos convencionales.

Es bien conocido que los compuestos que contienen heteroátomos, en particular compuestos que contienen nitrógeno y azufre pueden ser fácilmente removidos de los cortes livianos, tales como las corrientes de C_4 - C_8 , como son obtenidas de una unidad FCC convencional o de corrientes eterizadas. Los diferentes procesos, tales como de adsorción y extracción se han propuesto para este propósito. Los compuestos contaminados con heteroátomos que se encuentran en tales corrientes de corte ligero son pocos en número, fácilmente identificados, tienen pesos moleculares bajos y puntos de ebullición bajos consistentes con los hidrocarburos ligeros que forman este tipo de corte. Como consecuencia, estos contaminantes son fácilmente removidos del material de alimentación en los cuales ellos están contenidos. Esas características no son aplicables con respecto a la mezcla

más compleja de compuestos que contienen heteroátomos encontrada en las corrientes de hidrocarburo más pesadas.

Las corrientes LGO más pesadas, compuestas principalmente de C_{12} - C_{30} y compuestos mayores obtenidos de la destilación de unidades FCC son similares, contienen una mezcla vasta de especies de heteroátomo. Estos compuestos han sido difíciles de identificar, están generalmente compuestos de alto peso molecular y tienen puntos de ebullición altos. Algunas de las especies de azufre han sido identificadas y estudiadas por Whitehurst et al. En Adv. Catal. 42,345-471 (1998). Los intentos para identificar las especies de nitrógeno de tales cortes de gasóleo han sido ilusorias y un reto debido a la concentración en la matriz de hidrocarburo y a la complejidad de la mezcla de las especies. Un grupo de científicos provenientes de la Universidad de Kyushu en Fukuoka, Japón y la Chevron Research and Technical Company de Richmond, California, han intentado identificar compuestos que contienen nitrógeno de gasóleo y fueron solo capaces de reportar clases amplias que incluyen anilina sustituida con alquilo, quinolina y sus derivados de alquilo, y, derivados de carbazol (S. Shin et al., Energy & Fuels (2000), 14(3), 539-544. Wiwel et al. En "Assessing Compositional Changes of Nitrogen Compounds of Typical Diesel Range Gasóleo. . ." (Industrial & Engineering Chemistry Research (2000), 39(2), 533-540) Reportaron que el petróleo crudo contiene generalmente desde aproximadamente 0.1 a 2% de compuestos de

nitrógeno pero el contenido de nitrógeno rápidamente se incrementa con el incremento del punto de ebullición de la fracción de petróleo. Reconociendo que los combustibles diesel son comercialmente preparados de destilados de tramo recto y productos craqueados de material de alimentación más pesado, los niveles de nitrógeno normalmente varían desde 20-1000 µgN/ml. Ellos reportaron que tales compuestos son generalmente hechos de cuatro diferentes clases químicas: aminas alifáticas, anilinas, y compuestos con sistemas de anillo piridínico de cinco y seis miembros. Ellos han identificado algunos 64 compuestos (que utilizan el método de ASTM D-4629-91) y establecieron que muchos más compuestos no identificados están contenidos en la fracción de material más pesada.

La remoción de los compuestos que contienen nitrógeno de corrientes de petróleo de corte ligero (C_4 - C_8) se han logrado por que los compuestos de nitrógeno son más pocos en número, son fácilmente identificables y tienen peso molecular más bajo. Sin embargo, en razón a que los compuestos que contienen nitrógeno en el material de fracción más pesada son difíciles de identificar y, en el mejor de los casos, son una mezcla compleja de compuestos, la remoción ha sido ilusoria.

La Patente U.S. 2,384,315 describe filtrar petróleo crudo a través de un lecho de bauxita antes de someter el petróleo a tratamiento de craqueo catalítico. Tal

procedimiento produciría un producto que tenga aún más altas cantidades de compuestos de nitrógeno con relación a los estándares requeridos hoy.

La Patente U.S. 2,744,053 describe la remoción de compuestos de nitrógeno provenientes de material de hidrocarburo de gasolina con bajo punto de ebullición al pasar el material de alimentación a través de un lecho de adsorción formado de óxido de silicio solo o una mezcla de óxido de silicio y alúmina. Es bien conocido que el óxido de silicio y otros adsorbentes convencionales no exhiben la acidez Lewis requerida por el adsorbente utilizado en la presente invención.

La Patente U.S. 4,708,786 describe un proceso de craqueo catalítico fluido en el cual el material de alimentación es tratado con una mezcla de catalizador de craqueo y óxido refractario micro poroso capaz de adsorber piridina a temperatura ambiente de cuarto y retener una porción del material adsorbido. Este adsorbente es para ser utilizado en conjunto con el catalizador en la zona FCC.

La Patente U.S. 5, 051,163 describe un proceso en donde la alimentación inicial o un reactor de craqueo catalítico es primero tratada con una cantidad pequeña de catalizador de craqueo. La referencia sugiere que el material nitrogenoso se

unirá con el catalizador de sacrificio presente en la zona de pre-craqueo para evitar así el envenenamiento del catalizador de craqueo utilizado en la zona de craqueo. No se hace ninguna sugerencia a la remoción de los compuestos nitrogenosos justo antes de la hidrodeshulfurización que disminuiría adicionalmente el contenido de azufre después del HDS, para mejorar la efectividad del HDS y para inhibir el envenenamiento del catalizador HDS.

Los documentos 5, 210,326 y U. S. 5, 378,250 están dirigidos a procesos que incluyen tratar corrientes de hidrocarburos ligeros (C_3-C_8) obtenidos de una zona de proceso FCC con alúmina superactivada para remover compuestos de nitrógeno, mercaptanos y agua antes de proceso ulterior.

Los documentos U. S. 6,107,535 y U.S. 6,118,037 también enseñan procesos, que incluyen tratamiento de corriente de hidrocarburo de bajo peso molecular (C_3-C_8) con geles de sílica para remover los compuestos contaminantes que contienen azufre, nitrógeno y/o oxígeno.

La Patente u.s. 6,248,230 describe un proceso para la elaboración de combustibles más limpios al remover los compuestos polares naturales (NPC) de material de alimentación de petróleo con punto de ebullición de rango amplio antes de someter la corriente a hidrodeshulfurización

catalítica. La referencia enseña que las corrientes de producto de hidrocarburo de petróleo obtenidas de FCC o procesos similares pueden ser contactadas con un adsorbente, tal como sílica gel, alúmina hidratada, carbón activado, alúmina activa, o arcilla. La referencia establece que la sílica o la alúmina hidratada son cada uno adsorbentes preferidos. Tales adsorbentes son conocidos por ser sustancialmente libres o tener solamente grados limitados de acidez Lewis. Aunque ésta referencia indica que grandes cantidades de NPC contenido en el material de alimentación de petróleo tratado puede ser removido, tal remoción, especialmente de una corriente LGO, requiere proporciones altas no económicas de adsorbente para la alimentación.

Las referencias anteriores ilustran el deseo de la industria de refinación petrolera de remover los compuestos que contienen heteroátomos de los productos de petróleo de corte ligeros. Desafortunadamente, el material de fracción más pesado, tal como las fracciones de combustible diesel no han sido exitosamente tratadas para remover los contaminantes que contienen nitrógeno y azufre comúnmente encontrados allí de una manera efectiva en costos, eficiente para suministrar un producto ambientalmente amigable. La remoción de nitrógeno orgánico es importante a muchos procesos de refinería diferentes y es esencialmente para suministrar unos productos de combustible diesel, que cumplen con las necesidades ambientales y las reglamentaciones asociadas que están siendo

propuestas y estipuladas en la ley. Es altamente deseable suministrar un proceso efectivo en costos para remover una mayoría o sustancialmente todos los compuestos nitrogenosos de las fracciones de combustible diesel de tal forma que el material de alimentación del combustible diesel tratado pueda ser efectiva y eficientemente tratado mediante procesos HDS convencionales para producir un material resultante que tiene menos de 50 ppm y más preferiblemente menos de 15 ppm de compuestos que contienen azufre en la corriente de producto resultante.

Un objeto del proceso presente es suministrar unos medios efectivos en costos y eficientes para remover los compuestos nitrogenosos de una fracción del combustible diesel (C_{12} y mayor, por ejemplo material de alimentación de petróleo C_{12} - C_{30}) antes del sometimiento de tratamiento HDS.

Otro objeto de la presente invención es suministrar unos medios económicos y eficientes para remover al menos aproximadamente el 75% en peso, preferiblemente al menos aproximadamente 80% en peso y más preferiblemente al menos 90% en peso de los compuestos nitrogenosos provenientes de la fracción de combustible diesel antes de someter al tratamiento HDS.

Otro objeto de la presente invención es producir efectivamente un combustible diesel, que cumpla las reglamentaciones ambientales actuales y las contempladas con respecto a la emisión de contaminantes de NO_x y SO_x.

RESUMEN DE LA INVENCION

La presente invención esta dirigida a un método mejorado de producir combustible diesel y otros productos de petróleo de peso molecular alto sustancialmente libres de contaminantes orgánicos que contienen nitrógeno y azufre. Específicamente, el presente método comprende poner en contacto primero el material de alimentación de petróleo compuesto de LGO y materiales de petróleo de peso molecular mayor obtenidos de una zona de destilación o craqueo catalítico de FCC o similar con ciertos adsorbentes inorgánicos que tienen altos niveles de sitios con ácido Lewis como se describe completamente aquí adelante, para remover los compuestos de nitrógeno de dicho LGO, y someter subsecuentemente el LGO tratado a hidrodeshulfurización catalítica profunda. El presente método ha sido encontrado por proporcionar los medios para remover los compuestos que contienen nitrógeno orgánico de corrientes de alimentación de gasóleo C₁₂ y mayores en una manera efectiva y eficiente.

La presente invención esta dirigida a un proceso mejorado y económico para producir combustibles diesel capaces de exhibir niveles muy bajos de contaminantes, especialmente productos de óxidos de nitrógeno y óxido de azufre y otros contaminantes derivados de estos, cuando se utilizan en motores de combustión.

BREVE DESCRIPCIÓN DE LAS FIGURAS

La figura 1 es una representación gráfica de la capacidad de adsorción para los compuestos que contienen nitrógeno con respecto a un adsorbente marcado "muestra I", ilustrativo de la presente invención (sílica xerogel que tiene zirconia allí para impartir una acides Lewis de 1940 $\mu\text{mol/g}$, formada de acuerdo al ejemplo 1. Este material es comparado con materiales adsorbentes de sílica gel con una área de superficie alta marcados "muestra III Si/1" y "Muestra III Si/2" formados de acuerdo al ejemplo 5. Estos adsorbentes comparativos no exhiben acides Lewis. La figura 1 muestra gráficamente que el adsorbente de la presente invención suministra una capacidad de adsorción sustancialmente mayor para moléculas que contienen nitrógeno en LGO que los materiales adsorbentes de sílica gel convencionales.

La figura 2 es una representación gráfica de la capacidad de adsorción para compuestos que contienen nitrógeno con respecto a adsorbentes ilustrativos de la presente invención (sílica xerogel que tiene alúmina en cantidades para impartir acides Lewis alta) como se describe completamente en el ejemplo 2. Estos materiales son comparados con materiales conocidos adsorbentes de sílica gel de superficie alta marcados muestra III Si/1 y muestra III Si/2 formados de acuerdo al ejemplo 5. La figura 2 muestra gráficamente que los adsorbentes de la presente invención suministran una capacidad de adsorción sustancialmente mayor para moléculas que contienen nitrógeno que los materiales adsorbentes de sílica gel convencionales. Los materiales de muestra ilustrativas sustancialmente en el área de superficie, pero cuando los datos de la sílica/alúmina gel examinados de acides Lewis alta se normaliza con respecto al área de superficie, los datos siguen una línea sencilla. Todos los ejemplos ilustrativos exhiben una capacidad de adsorción significativamente más alta que los materiales adsorbentes conocidos de sílica gel con el área de superficie alta.

La figura 3 es una representación grafica de la capacidad de adsorción de los compuestos que contienen nitrógeno con respecto a los adsorbentes ilustrativos de la presente invención (sílica xerogel que tiene alúmina en esta y en cantidades para impartir acides Lewis alta) como se

describirá completamente en el ejemplo 2. Estos materiales son comparados con adsorbentes de alúmina con área de superficie alta, conocidos formados del ejemplo 5. La figura 3 muestra gráficamente que los adsorbentes de la presente invención suministran capacidad de adsorción sustancialmente mayor para moléculas que contienen nitrógeno que tal material adsorbente de alúmina convencional.

DESCRIPCIÓN DETALLADA

El petróleo refinado convencionalmente trata crudo de petróleo en un proceso, tal como un proceso catalítico de craqueo de fluido (FCC), en donde el crudo es puesto en contacto con un catalizador FCC bajo temperatura y presión elevada y/o un proceso de destilación, para producir una pluralidad de corrientes de producto de petróleo de diferentes compuestos de peso molecular y rangos relacionados de puntos de ebullición. Por ejemplo, la corrientes de producto pueden ser definidas como material de corte ligero compuesto de hidrocarburos C_4-C_8 que tiene normalmente un rango de punto de ebullición desde aproximadamente $0^{\circ}C$ a $115^{\circ}C$; gasóleos ligeros (LGO) o corrientes de producto de combustible diesel compuesta de hidrocarburos $C_{12}-C_{30}$ (por ejemplo $C_{12}-C_{25}$) que normalmente tienen un rango de punto de ebullición de desde aproximadamente 200 a aproximadamente $550^{\circ}C$, tales como desde aproximadamente 225 a aproximadamente $460^{\circ}C$. La corriente de producto de fondo pesada de la unidad

FCC (residuos) esta compuesta de material de peso molecular alto. Los residuos no son convencionalmente utilizados como combustible para motores de combustión aunque ellos se pueden utilizar para tal propósito en ciertas aplicaciones.

La corriente de producto compuesta de LGO o combustible diesel es el material objetivo con la cual se relaciona la presente invención aunque corrientes de alimentación de petróleo aun mayores pueden ser similarmente tratadas para remover los contaminantes de nitrógenos que se encuentran allí. Esto no tiene importancia el modo exacto de formar este material aunque ellos son formados comúnmente mediante destilación o procesamiento FCC de petróleo crudo. Como se estableció anteriormente, una de las preocupaciones con las corrientes LGO es que ellas normalmente contienen grandes cantidades y muchos diferentes compuestos complejos que contienen nitrógeno que, en general, no son fácilmente identificados pero se cree que reducen la efectividad en el procesamiento HDS del material de alimentación. La cantidad exacta y la composición de estos compuestos dependen de la fuente de petróleo crudo que esta siendo procesada.

La remoción de los compuestos que contienen nitrógeno de la corriente de alimentación de petróleo antes de una unidad de hidrosulfurización (HDS) se cree que origina que el proceso HDS tenga lugar de una manera más eficiente para producir un combustible diesel deseado más ambientalmente

amigable. Se cree, aunque no se establezca como una limitación de la presente invención, que los compuestos que contienen nitrógeno se combinan con los sitios activos del catalizador HDS y, por lo tanto, la remoción de tales compuestos ayudan a originar que los catalizadores suministren un procesamiento HDS mejorado. Al utilizar material con contenido de nitrógeno bajo como la alimentación para una unidad HDS convencional, se mejora la efectividad del proceso HDS al posibilitarle al proceso ser conducido a temperaturas de procesamiento más bajas o a proporciones de flujo más altas aunque extendiendo la vida del catalizador de desulfurización CONVENCIONAL utilizado. El producto de la unidad HDS se ha encontrado que tiene muy bajo contenido de azufre, tal como menos de 50 ppm o aún menos de 30 ppm y aún menos de 15 ppm de contenido de azufre.

Los presentes inventores han descubierto que las corrientes LGO (combustible diesel) de composición C_{12} y mayor puede ser fácilmente tratado de una manera efectiva en costos y eficiente para remover los contaminantes de nitrógeno provenientes de corrientes LGO antes de su introducción a la zona HDS. El presente proceso utiliza ciertos adsorbentes de óxido inorgánico mejorado con ácido Lewis completamente descrito aquí adelante. Estos adsorbentes se ha encontrado que logran remover efectivamente los contaminantes de nitrógeno comúnmente contenidos en los materiales de alimentación LGO sin la necesidad de requerir múltiples

pasadas. El uso de proporciones de proporciones de flujo económicamente indeseables (velocidad de espacio de líquido horaria), o proporciones económicamente indeseables de alimentación al adsorbente (antes de que la regeneración del adsorbente se vuelva necesaria), cuando se trata la corriente.

En general, el presente proceso puede ser logrado al poner en contacto un material de alimentación LGO con el adsorbente actualmente requerido antes de introducir el material de alimentación a la zona HDS de una refinería. El contacto puede ser hecho mediante cualquier método conocido de poner en contacto un material sólido y un líquido tal como mediante la utilización de una zona de adsorción compuesta de una (adecuadamente para un proceso de tanda) o dos o más (adecuadamente para un proceso continuo) columnas de lechos fijos (lecho empacado), columna de lecho fluidizado, o una zona de lecho abullante. La zona de adsorción preferida es un sistema de lecho fijo o empacado.

La presente invención debe ser descrita utilizando el sistema de lecho fijo o empacado preferido, aunque otros sistema de zona de adsorción puede ser fácilmente sustituidos por tales sistemas por aquellos expertos en la técnica. Normalmente, las columnas son empacadas con el adsorbente presente que se le permite poner en contacto la corriente de alimentación de petróleo y originar la adsorción de los

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compuestos contaminantes de nitrógeno allí. El adsorbente, en un punto de agotamiento de su capacidad adsorbente o antes de esta, es sometido a desorción para remover los contaminantes de nitrógeno de estos y finalmente la regeneración con el fin de reestablecer la capacidad adsorbente del adsorbente. Un proceso continuo puede ser fácilmente logrado al utilizar una pluralidad de columnas en la cual al menos una columna esta en modo de adsorción aunque el adsorbente de al menos otra columna esta siendo desasorbida del contaminante de nitrógeno y siendo regenerada.

El contaminante de nitrógeno se inmoviliza sobre el adsorbente. El termino "inmovilizada" y "adsorbida" como se utiliza aquí y en las reivindicaciones finales se refiere a la adsorción física y/o química (adhesión del compuesto de nitrógeno a la superficie del adsorbente) y/o la adsorción física (penetración en la estructura interior del adsorbente. Sin desear estar ligado por ninguna teoría particular, se cree que los contaminantes de nitrógeno forman algún tipo de unión débil con el adsorbente presente. La estructura de tal unión puede ser simplemente física o iónica o dativa o una mezcla de estos.

El adsorbente requerido por la presente invención es un material de matriz de óxido inorgánico poroso que tiene una acidez Lewis alta impartida a esta. Más específicamente, el adsorbente utilizado en la presente invención está en la

forma de adsorbente en partículas formado de (a) al menos un componente de óxido inorgánico seleccionado de una matriz tridimensional o formas similares a enrejado de sílica, titanio, alúmina, zirconio o estania. El término "material de matriz de óxido inorgánico", como se utiliza aquí y en las reivindicaciones finales, se refiere a un material formado de una estructura tridimensional de átomos que comprenden átomos M (seleccionados de átomos de silicio, titanio, aluminio, zirconio o estaño) y átomos de oxígeno. Los átomos de oxígeno forman un puente entre los átomos M. El enrejado puede tener adicionalmente pequeñas cantidades de otros grupos químicos, tales como grupos hidroxilo o alcóxido y similares. El componente (a) es preferiblemente seleccionado de sílica, alúmina o zirconio o titania. La matriz formada puede ser compuesta de material similar a rejilla o amorfo o a una mezcla de ambos (el grado de la estructura similar a rejilla cristalina puede ser determinada mediante técnicas de espectroscopia de difracción de rayos X convencional o similares).

El material de matriz de óxido inorgánico tridimensional (en la forma de un gel o similar) (a) que forma el presente adsorbente, antes del tratamiento con el componente (b) descrito adelante, usualmente exhibe grados muy bajos de acidez Lewis de menos de 300, generalmente menos de 200 y, en la mayoría de los casos, menos de aproximadamente 100 $\mu\text{mol/gm}$.

El sujeto adsorbente contiene además átomos de metal diferentes de M (de un material adsorbente particular) como parte de la estructura de matriz. Tales átomos de metal pueden ser impartidos a la matriz al poner en contacto un material de matriz (a) con al menos una cantidad suficiente de un metal que contiene compuesto precursor (b) capaz de impartir acidez Lewis al componente de matriz de óxido inorgánico (a) del adsorbente resultante, como se describe aquí adelante.

La acidez Lewis de un grado alto, como se requiere actualmente, se puede impartir al material de matriz (a) mediante la inserción o sustitución de átomos de metal en la matriz de óxido inorgánico para establecer sitios pobres en electrones dentro de la matriz. Los átomos que imparten acidez Lewis pueden ser seleccionados de átomos de metales del grupo IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA, U VIIIA, de la tabla Periódica (formato IUPAC). Por ejemplo, los metales se pueden seleccionar de Mg, Ca, Sr, Ba, B, Al, Ga, Zn, Cd, Sc, Y La, Ti, Zr, Hf, V, Nb, Mo, W, Fe, Co, Ni, o mezclas de estos con Mg, Ca, Zn, La, Ti, Zr, Fe, Co, Ga, y Al y mezclas de estos que son preferidas y Mg, Zn, La, Ti, Zr, Fe, y Al y mezclas de estos que son más preferidas, y Zr, Al, Fe, y Ti que son más preferidas, siempre y cuando dicho metal sea diferente de los átomos que forman el componente de matriz original (a). Por ejemplo, una porción de los átomos Zr de un

gel de zirconio puede ser sustituida por uno de los átomos de metal anteriores descritos o mezclas de estos, tales como átomos de calcio para impartir sitios pobres en electrón para ácido Lewis. Similarmente, una porción de los átomos Al de un gel de alúmina puede ser sustituida por uno de los átomos de metal descritos anteriormente o mezclas de estos, como se describe más completamente aquí adelante.

Los átomos de metal del precursor (b) se puede introducir en un componente (a) mediante cualquier método y en cantidades por medio de las cuales el adsorbente resultante tiene acidez Lewis impartida con al menos el grado citado aquí adelante. Por ejemplo, el metal puede ser introducido en la forma de un material precursor, tal como un metal u otro precursor de metal que sea soluble en el medio seleccionado para poner en contacto la matriz con el precursor (b) o mezclas de estos. Se cree, aunque no signifique ser una limitación de la presente invención, que cuando los componentes (a) y (b) son puestos en contacto para formar el adsorbente cuando el adsorbente formado inicialmente es adicionalmente procesado y/o activado, como se describe aquí adelante, una porción de óxido de metal del metal del precursor (b) se forma como parte de la matriz.

La acidez Lewis del presente adsorbente debe ser al menos 500 $\mu\text{mol/gm}$ (por ejemplo 600/ $\mu\text{mol/gm}$), 700 $\mu\text{mol/gm}$ 800

$\mu\text{mol/gm}$), preferiblemente de 600 a 3000 y más preferiblemente de 700 a 2500 (por ejemplo 750-2000) $\mu\text{mol/gm}$ de adsorbente.

El término "acidez Lewis" como se utiliza aquí y en las reivindicaciones finales se refiere a la capacidad de una sustancia a aceptar los electrones de una sustancia rica en electrones o átomos de tal sustancia. La presencia y los valores cuantitativos de la acidez Lewis se puede determinar de acuerdo con el método descrito por E. Rakiewicz et al., J. Phys. Chem. B, 102, 2890-2896 (1998) titulada "Characterization of Acid Sites in zeolita and Other Inorganic Systems Using Solid State ^{31}P NMR of the Probe Molecule Trimethylphosphine Oxide" La enseñanza de esta referencia se incorpora aquí en su totalidad como referencia. El método descrito suministra un procedimiento analítico para determinar cuantitativamente la acidez Lewis de una sustancia inorgánica para discriminar entre la población de sitios de ácido Lewis y Bronsted allí.

El material de matriz (a) del adsorbente es preferiblemente una alúmina, zirconio, titania o sílica gel (por ejemplo hidrogel, aerogel, o xerogel). Los geles de esos óxidos inorgánicos son materiales sólidos conocidos que tienen estructuras tridimensionales formadas por una pluralidad de metales y átomos O. En el caso de sílica, este puede ser en la forma de un hidrogel, también conocido como un acuagel, el cual es un gel formado en agua que tiene sus



poros llenados con agua. Un xerogel es un hidrogel con el agua removida. Un aerogel es un tipo de xerogel del cual se ha removido el líquido de tal forma que minimice cualquier colapso o cambio en la estructura en la medida en que el agua es removida. Los otros óxidos inorgánicos también pueden estar en estas formas.

La matriz que forma el óxido inorgánico [componente (a)] del ácido Lewis adsorbente utilizado en la presente invención se puede formar mediante métodos conocidos. Por ejemplo, una sílica gel puede ser preparada mediante medios convencionales, tales como al mezclar una solución acuosa de un silicato de metal alcalino (por ejemplo silicato de sodio) con ácido fuerte tal como ácido nítrico o sulfúrico (preferido), siendo la mezcla hecha bajo condiciones adecuadas y agitación para formar un sol de sílica claro el cual se establezca en un hidrogel en menos de aproximadamente media hora. La concentración de SiO_2 en el hidrogel que es formado es está usualmente en el rango de típicamente entre aproximadamente 15 y aproximadamente 40, preferiblemente entre aproximadamente 20 y aproximadamente 35, y más preferiblemente entre aproximadamente 30, y más preferiblemente entre aproximadamente 30 y aproximadamente 35% en peso, con el pH del gel siendo de aproximadamente 1 a aproximadamente 9, preferiblemente 1 a aproximadamente 4. Un rango amplio de temperaturas de mezcla se puede emplear, este

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rango siendo típicamente desde aproximadamente 20 a aproximadamente 50°C.

Similarmente, los soles de alúmina y los geles de alúmina se pueden formar mediante medios convencionales, tales como mediante hidrólisis de las sales de aluminio. Por ejemplo, un sol de alúmina se forma al introducir metal de aluminio a una solución ácida (por ejemplo ácido clorhídrico, ácido nítrico y similares) a temperatura elevada. El sol resultante es entonces envejecido a temperaturas elevadas desde aproximadamente 100 a 360°C. Durante un periodo de tiempo desde 0.5 a 24 horas seguido por secado por rociado para formar un producto de polvo sólido. Los geles de alúmina (bohemitas gelatinosas) se forman mediante hidrólisis controlada de alcóxido de aluminio en una solución acuosa o alcohólica.

Similarmente, los métodos conocidos para formar partículas de titania incluyen hidrólisis de alcóxido de titanio, tales como etóxido de titanio (TEOT) con agua a temperatura elevada.

La escogencia del metal adecuado para impartir la acidez Lewis a una matriz particular dependerá de la configuración de electrónica de los átomos M de la matriz y de aquella del ácido Lewis que le imparte metal del precursor (b). Esto se

puede determinar mediante un ensayo menor con la ayuda de las técnicas de Tanabe et al., infra. Los métodos adicionales para formar materiales de matriz de óxido inorgánicos encontrados útiles en la presente invención son descritos Por J-E. Otterstedt and D. Brandreth in "Small Particle Technology, Chapter 3, 85-155 (1998); por K. Tanabe et al. en "studies in Surface Science and Catalysis" 51, 108-113 (1998); and By-C. J. Brinker, G.W. Scherer, in "Sol-Gel Science The physics and Chemistry of Sol-Gel Processing", Academic Press, (1990). Las enseñanzas de esta referencia se incorporan aquí en su totalidad como referencia.

El material formado es entonces lavado. El lavado es logrado simplemente al sumergir el hidrogel recientemente formado en una corriente de agua que se mueve continuamente, que lava las sales indeseables que lixivian las sales indeseables, dejando un polímero de óxido inorgánico sustancialmente puro detrás. El pH, la temperatura, y la duración del agua de lavado influenciarán las propiedades físicas de la matriz formada, tal como el área de superficie (SA) y el volumen de poro (PV). Por ejemplo, la sílica gel lavada a 65-90°C a pH de 8-9 durante 28-36 horas usualmente tendrá los SA de 290-350 m²/g y forma xerogeles con PV de 1.4 a 1.7 cc/gm. El sílica gel. El sílica gel lavado a pH de 3-5 a 50-65°C durante 15-25 horas tendrá los SA de 700-850 m²/g y forma xerogeles con PV de 0.3-0.6 cc/g.

El presente adsorbente se puede formar al poner en contacto el material formador de matriz de óxido inorgánico con un material precursor de un metal capaz de impartir acidez Lewis al producto resultante al grado requerido aquí. El átomo metálico que contiene material precursor puede ser puesto en contacto con el material formador de matriz de oxido inorgánico o durante la formación de gel o subsecuente a dicha formación. Por ejemplo, el componente de precursor de metal formador de ácido Lewis (b) puede ser cogelificado con el componente formador de matriz de óxido inorgánica (a) o, alternativamente, el material de matriz de oxido inorgánico ya formado puede ser tratado con un precursor de metal de ácido Lewis de manera de impartir acidez Lewis a la matriz.

Los metales formadores de ácido Lewis de los componentes precursores que imparten ácido Lewis (por ejemplo sales metálicas, oxido de metal y similares que tienen solubilidad en el medio utilizadas para formar el presente adsorbente y mezclas de estos) se pueden incorporar como parte de la matriz de óxido inorgánica mediante varias técnicas, a saber (1) al ser íntimamente incorporados dentro de la estructura de gel luego de la formación, por ejemplo, mediante la formación del material de matriz inorgánica en la presencia de uno o más materiales precursores de metal de ácido Lewis; (2) al mezclar el material precursor de metal de ácido Lewis con las partículas de gel inicialmente formadas del material de matriz de oxido inorgánico antes de moler o después de

moler en forma de lechada justo antes de secado por rociado para originar la aglomeración de los componentes, como se describe aquí adelante; (3) mediante la adición de un material precursor de metal de ácido Lewis a una matriz de óxido inorgánica ya formada o material de gel por medio de impregnación o similar; o (4) al poner en contacto el material precursor de metal de ácido Lewis con partículas de matriz de óxido inorgánica formadas durante el procedimiento post-tratamiento, tal como durante envejecimiento a temperatura elevada.

Así, los materiales que representan la primer categoría son geles mezclados tales como por ejemplo, alúmina-zirconia, alúmina-titania, titania-zirconia, Titania-sílica, zirconio-sílica, alúmina-sílica, sílica-alúmina, sílica-zirconia, sílica-titania, sílica-titania-alúmina, sílica-alúmina-zirconia, sílica-hierro, titania-óxido de cobre, titania-alúmina, titania-óxido de hierro, zirconio-óxido de cadmio, alúmina-magnesia y cogeles similares. Tales cogeles muestran una distribución sustancialmente homogénea del metal que imparte ácido Lewis a través de la masa y sobre la superficie del adsorbente resultante. La proporción en peso del óxido inorgánico primario al metal que imparte ácido Lewis puede variar desde aproximadamente 100: 1 a aproximadamente 1: 3. La proporción de peso preferida dependerá de la identidad del metal que imparte ácido Lewis y el grado de acidez Lewis deseada.



En la segunda categoría, el componente (b) se puede mezclar, usualmente en proporciones ligeras, con un material de matriz de óxido inorgánico, antes de moler y/o justo antes de aglomeración. Este método es más adecuado cuando se contempla para formar el adsorbente resultante del material de gel que va a sufrir mezcla, molienda y/o aglomeración física para preparar el adsorbente en partículas resultantes para utilizar el presente proceso mejorado.

En la tercer categoría, el material precursor de metal otro material utilizado por impartir acidez Lewis se puede contactar con el material de matriz de óxido inorgánico ya formado mediante técnicas conocidas, tales como aquella de impregnación de humedad incipiente en donde el material de matriz de óxido inorgánico es puesto en contacto con una solución (solvente orgánico acuoso o de bajo peso molecular) de un precursor de metal soluble (con respecto al solvente de la solución) seguido por la remoción del solvente. El material tratado es normalmente sometido a temperatura elevada para ayudar a que el átomo de metal que imparte el ácido Lewis sea oxidado para volverse parte de la configuración de matriz. Cuando se emplea este método, los sitios de ácido Lewis que imparten los iones de metal están localizados casi completamente sobre el área de superficie del adsorbente.

En la cuarta categoría, el material de matriz de óxido inorgánico puede ser un gel, tal como un gel de alúmina o un gel de titania, el cual, luego de la etapa de impregnación, es sometido a un procedimiento de envejecimiento. El envejecimiento de los geles se puede conducir a temperaturas elevadas tales como, por ejemplo una temperatura desde aproximadamente 50 a 200°C (por ejemplo 65-90°C) y pH elevado de desde aproximadamente 7.5 a 10 (por ejemplo pH de 8-9) durante 4-12 horas. En este caso, el producto resultante muestra un enriquecimiento de superficie en los sitios de ácido Lewis con una concentración disminuyente de tales sitios en la masa de la matriz.

En cada uno de los adsorbentes resultantes anteriores, el metal que imparte el ácido Lewis puede estar presente (como un óxido de metal) en desde 1 a 80% en peso del adsorbente resultante con, preferiblemente, desde 1 a 30 y desde 1 a 20 por ciento en peso siendo el más preferido.

El adsorbente preferido es un material de matriz de óxido inorgánico altamente poroso que tiene poros de un diámetro mayor. El diámetro de poro mayor debe preferiblemente ser desde aproximadamente 40 a aproximadamente 400, más preferiblemente desde aproximadamente 45 a aproximadamente 100 y más preferiblemente desde 45 a 75 Ångstrom.

Los adsorbentes preferidos son formados al producir una sílica gel con una alúmina para suministrar una sílica gel que tiene una acidez Lewis impartida por los átomos de aluminio al grado descrito aquí anteriormente; o mediante cogelificación de un silicato de metal alcalino en la presencia de una sal de zirconio; o al tratar un sol de sílica con dióxido de carbono, envejeciendo a temperatura elevada y luego agregando aluminato al sol para originar la formación de gel para suministrar la acidez Lewis deseada. Las combinaciones de lo anterior son también materiales preferidos, tales como, por ejemplo, sílica gel que tiene átomos de zirconio y átomos de aluminio presentes.

Otros constituyentes que pueden estar presentes, incluyen aquellos constituyentes no afectados adversamente por agua, secado por rociado o calcinación, como apropiado con respecto al método para formar el particulado adsorbente, tal como óxido solamente divididos o compuestos químicos. Similarmente, es posible agregar polvos o partículas de otros constituyentes a las partículas de gel para impartir propiedades adicionales al adsorbente resultante. De acuerdo con esto, se pueden agregar materiales que poseen propiedades adsorbentes adicionales, tales como zeolitas sintéticas. En adición, se pueden agregar materiales que actúen como un ligador para ayudar en la resistencia al desgaste de las partículas resultantes. Tales ligadores pueden ser seleccionados de arcillas, tales como, por ejemplo,

atapulgita, bentonita, sepiolita y similares y mezclas de estos usualmente en forma coloidal o de polvo. El experto apreciará que las cantidades de tales componentes adicionales deben estar restringidas con el fin de evitar comprometer las propiedades de adsorción deseadas descritas aquí.

También, es factible agregar constituyentes al material de matriz de óxido inorgánico que se puede eliminar después de la aglomeración con el fin de controlar la porosidad dentro de un rango deseado; tales agentes como celulosa, grafito, carbón de madera, y similares siendo particularmente útiles para este propósito. Cuando tales materiales son empleados, ellos se pueden agregar de maneras convencionales antes de la formación de gel o antes de la aglomeración. Sin embargo, cuando se utiliza la molienda y la aglomeración en la formación del adsorbente en partículas resultantes, es preferible que ellos estén presentes en el gel durante o antes de la molienda como se describió en razón a que es mucho menos probable afectar la morfología del aglomerado deseada después del secado por rociado cuando ellos son sometidos a molienda.

En vista de lo anterior el término "gel" (por ejemplo "gel de alúmina", "gel de titania" y similares) como se utilizan aquí en las reivindicaciones finales, pretenden incluir la inclusión opcional de los constituyentes sin gel

anteriormente mencionados permitidos por estar presentes en el adsorbente de óxido inorgánico.

El presente adsorbente tiene un área de superficie (técnica BET descrita por S. Brunauer, P. Emmett and E. Teller in J.A.C.S. 60, 209-319 (1939)) de más de aproximadamente 200 m²/g, preferiblemente de 300 a 1000, más preferiblemente de 400 a 600 y más preferiblemente de 400 a 550 m²/g. Además el presente adsorbente tiene un volumen de poro de nitrógeno (BET) de al menos 0.5, preferiblemente desde 0.5 a 1.8, más preferiblemente desde 0.6 a 1.5 y más preferiblemente desde 0.6 a 01.2 cc/g. Aún adicionalmente, el diámetro de poro promedio del adsorbente debe ser preferiblemente de aproximadamente 40 a 400, tal como desde 45 a 200, más preferiblemente de 45 a 100 y más preferiblemente de 45 a 75 Ångstrom.

El material precursor de metal u otro material utilizado para impartir acides Lewis se puede agregar a los materiales de materia prima inorgánicos que forman la matriz como parte de la formación de hidrogel o xerogel o aerogel o se pueden agregar al hidrogel o xerogel formado o al aerogel antes de la molienda, secado por rociado o extrusión para suministrar el adsorbente en partículas resultantes de la presente invención. Se prefiere incorporar el material de precursor metálico u otro material para impartir la acidez Lewis en un

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sol de óxido inorgánico como parte de la formación de hidrogel o xerogel o aerogel.

El adsorbente objeto se puede formar en un material de partículas de acuerdo con métodos bien conocidos en la técnica, tales como mediante secado por rociado, molienda o tamizado de partículas mayores de material gelificado, paletizado, extrusión, o formación en glóbulos y en un tambor de recubrimiento rotatorio, y similares así como también mediante la técnica de nodulizar por medio de la cual las partículas compuestas que tienen un diámetro no mayor de aproximadamente 0.05 mm se aglomeran en partículas con un diámetro de al menos 1 mm por medio de granulación. También puede ser empleado un líquido.

El tamaño de partícula del adsorbente dependerá del modo contemplado de contacto del adsorbente y del material de alimentación de petróleo para un sistema de proceso particular. Por ejemplo, cuando el adsorbente se contempla para uso en una columna de lecho empacado o similar, el tamaño de partícula del adsorbente debe ser de aproximadamente 0.2 a aproximadamente 20, tal como desde aproximadamente 0.5 a 5 mm, con desde aproximadamente 0.6 a 1.5 mm siendo la preferida. Las partículas de tamaño de partícula más pequeño o más grande se pueden utilizar y dependerán del diseño de la columna particular utilizada. El tamaño de partícula exacto se puede determinar mediante

métodos conocidos por aquellos expertos en la técnica. Similarmente, cuando se ponen en contacto el material de alimentación adsorbente y de petróleo van a ser hechos en un lecho fluidizado, el tamaño de partícula del adsorbente debe ser de aproximadamente 10 a aproximadamente 100 micrómetros.

Un adsorbente preferido se forma al cogelificar un silicato de metal alcalino con ácido inorgánico (por ejemplo ácido sulfúrico) (el sol se forma después de que los dos materiales de materia prima han sido contactados) Que contiene sal de zirconio, titanio o aluminio disueltas o mezclas de estos, tales como sal de zirconio, titanio o aluminio en ácido sulfúrico. El material cogelificado resultante contendrá un ácido Lewis elegido que imparte átomos de metal (por ejemplo átomos de zirconio) tal como sustituto para algunos de los átomos de silicio en la matriz de gel formada para impartir así acidez Lewis al material formado. Otro adsorbente preferido se forma mediante gelificación de un silicato de metal alcalino que utiliza dióxido de carbono en la presencia de sulfato de aluminio. El gel resultante es luego macerado o molido para reducir el tamaño d partícula promedio del material a aproximadamente 0.2 a aproximadamente 20 (por ejemplo 0.2 a aproximadamente 10), preferiblemente desde aproximadamente 0.5 a aproximadamente 5 mm, con desde 0.6 a aproximadamente 1,5 mm siendo aun más preferidos y desde 0.7 a aproximadamente 1.2 mm siendo más preferidos.

Alternativamente, el presente adsorbente puede ser hecho al secar, preferiblemente secar por rociado, una lechada de material precursor de metal de ácido Lewis y un óxido inorgánico que produce una matriz (por ejemplo gel de alúmina) o de un metal de ácido Lewis ya formado que contiene gel de alúmina seguido por aglomeración. Más específicamente, en esta modalidad, el adsorbente se forma en una lechada, preferiblemente una lechada acuosa, que comprende típicamente al menos 50, preferiblemente al menos 75 (por ejemplo al menos 80), y más preferiblemente al menos 85 (por ejemplo al menos 90) por ciento en peso basado en agua sobre el peso de la lechada. Sin embargo, los solventes orgánicos, tales como los alcanos C_3 a C_{12} , los alcoholes (por ejemplo isopropil alcohol), también se pueden emplear aunque ellos representen un riesgo de fuego con relación al agua y a menudo hagan aglomerados demasiado frágiles para utilizar como adsorbente objeto.

Para hacer un gel adecuado para formación de aglomerado (partículas), por ejemplo, mediante secado por rociado, varios procedimientos de molienda son empleados típicamente (aunque no se requieren). La meta de un procedimiento de molienda es para suministrar finalmente material de gel con un tamaño de partícula promedio de típicamente desde aproximadamente 0.2 a aproximadamente 10 (por ejemplo 2 a aproximadamente 10) preferiblemente desde aproximadamente 4 a

aproximadamente 9 y más preferiblemente de 4 a 8 micrómetros. Además, para ayudar en la formación de material de partícula aglomerado, el gel puede contener un material ligador, tal como un sol de sílica que tiene propiedades de unión conocidas o material adicional que tiene un diámetro de partícula en el rango coloidal de típicamente menos de aproximadamente 1, preferiblemente menos de aproximadamente 0.5, y típicamente desde aproximadamente 0.4 a aproximadamente 1 micrómetro. Todos los tamaños de partícula y las mediciones de distribución y tamaño de partícula descrita aquí son determinadas mediante infracción de luz láser y es conocida por aquellos familiarizados en la técnica de análisis de partícula pequeña.

Una vez que el tamaño de partícula promedio objetivo se imparte al material de matriz de óxido inorgánico, una lechada, preferiblemente una lechada acuosa, se prepara para la aglomeración, preferiblemente mediante secado por rociado. Las partículas aglomeradas formadas en la manera anterior son de un tamaño normalmente adecuado para la lechada de aplicación de lecho fluidizado para contactar adsorbente objeto con un material de alimentación De petróleo LGO.

Otro método adecuado para elaborar el presente adsorbente es mediante la aglomeración extrusión de gel de óxido inorgánico de un metal de ácido Lewis ya formado que contiene material de matriz de óxido inorgánica. Más

específicamente, en este proceso el material de gel con un tamaño de partícula promedio de 3 a aproximadamente 100 preferiblemente desde aproximadamente 4 a aproximadamente 30, y más preferiblemente desde 4 a 10 micrómetros se aglomera o extruye en la presencia de un ligador. Tales ligadores se pueden seleccionar de arcillas o arcillas coloidales tales como, por ejemplo, atapulgita, bentonita, sepiolita, y similares y mezclas de estos, sílica coloidal o submicrométrica, hidrogeles de sílica, alúminas y similares y mezclas de estas. La extrusión y aglomeración puede ser llevada a cabo mediante métodos conocidos que incluyen, pero no están limitados a, extrusores de tornillos simples y gemelo, peletizadores, diferentes tipos de mezcladores de impacto de corte, tales como mezclador de tornillo o mezclador peletizante. Por ejemplo, la mezcla de ligador de gel es procesada a una pasta que utiliza un solvente (por ejemplo agua) y luego extruida. En el caso de aglomeración, la mezcla unidora de gel es formada en glóbulo en la presencia de un líquido, tal como agua, ácido cítrico diluido o sol de sílica.

El material de partícula resultante es normalmente secado para remover el líquido de procesamiento (agua o solvente inorgánico). El secador normalmente conducido a temperaturas elevadas desde aproximadamente 50 a 250°C, aunque temperaturas inferiores son mayores se pueden utilizar. El secado es normalmente conducido a una presión

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atmosférica aunque se puede emplear presión reducida. El material en partícula seco es entonces activado mediante la calcinación del material. Así, el material es sometido a temperatura elevada, tal como, por ejemplo, desde aproximadamente 200 a 600, preferiblemente desde 400 a 600°C, bajo una atmósfera vaciada de oxígeno tal como aire.

De acuerdo con esto, se utiliza cualquier proceso total, la formación de partículas es controlada para impartir preferiblemente las siguientes propiedades al adsorbente:

- (1) Un área de superficie (BET) de típicamente al menos de aproximadamente 200, preferiblemente al menos aproximadamente 300, y más preferiblemente de al menos aproximadamente 450 m²/g, cuya área de superficie puede variar típicamente desde aproximadamente 300 a aproximadamente 1000, preferiblemente desde aproximadamente 400 a aproximadamente 600, y más preferiblemente desde aproximadamente 400 a aproximadamente 550 m²/g.
- (2) Un diámetro de poro promedio (BET) de desde aproximadamente 40 a aproximadamente 400, preferiblemente desde aproximadamente 45 a 200, más preferiblemente desde aproximadamente 45 a 100, y más preferiblemente desde aproximadamente 45 a aproximadamente 75 Ångstrom (en casos donde las partículas están

en la forma de glóbulos o extruido, las partículas también pueden contener poros mayores de 100 Ångstrom que pueden ser detectados y medidos al utilizar un método de difusión de mercurio de medición);

- (3) Un volumen de poro total de al menos 0.5 con desde 0.5 a aproximadamente 1.8, preferiblemente desde aproximadamente 0.6 a 1.5, y más preferiblemente desde aproximadamente 0.6 a aproximadamente 1.2 cc/g; y
- (4) Una densidad de masa de las partículas adsorbentes de típicamente al menos aproximadamente 0.2, preferiblemente al menos aproximadamente 0.3, y más preferiblemente al menos aproximadamente 0.4 g/ml, cuya densidad de masa puede variar típicamente desde aproximadamente 0.2 a aproximadamente 1, preferiblemente desde aproximadamente 0.3 a aproximadamente 0.8, y más preferiblemente desde aproximadamente 0.4 a aproximadamente 0.7 g/ml.
- (5) La resistencia al desgaste que suministra suficiente resistencia para permitirle al adsorbente sufrir múltiples ciclos de adsorción/desorción (por ejemplo 50 1000).

El tamaño de partícula y la distribución del tamaño de partícula prevista para ser impartida a las partículas adsorbentes es dictada y controlada por el modo contemplado de contacto por medio del cual el adsorbente y el material de alimentación de petróleo será empleado así como también los parámetros de diseño específico de la operación de contacto (por ejemplo caída de presión dentro de una columna). Por ejemplo, cuando se emplea o va a ser empleada una columna empacada, las partículas deben tener una distribución de tamaño de partícula en donde la mayoría de las partículas (> 95%) son menos de 2, preferiblemente menos de 1.6 y más preferiblemente menos de 1.4 mm aunque solo una minoría de las partículas (< 10%, preferiblemente <7%, más preferiblemente <5%) son menores de 0.6 milímetros de diámetro en promedio.

El material de alimentación de petróleo se puede poner en contacto con el adsorbente bajo condiciones de temperatura y presión que mantengan la materia del material de alimentación de petróleo en un estado líquido durante la operación de adsorción. Por ejemplo, las condiciones de temperatura pueden variar desde aproximadamente 0 a 100 °C, preferiblemente desde aproximadamente 20 a 60°C y con presiones de desde aproximadamente 1 a 15 bar, preferiblemente desde aproximadamente 1 a 5 bar. Las condiciones de presión dependen del diseño específico de la columna, el tamaño de partícula adsorbente y la viscosidad de

alimentación, de tal forma que aún presiones mayores de aquellas mencionadas aquí se pueden aplicar bajo condiciones bien conocidas por el experto. Preferiblemente, el material de alimentación se puede poner en contacto con el adsorbente objeto bajo condiciones de presión atmosférica y a una temperatura dictada por el material de alimentación de petróleo obtenido del procesamiento anterior. La temperatura y la presión particular para la optimización de la adsorción se pueden determinar fácilmente mediante simple experimentación.

El presente adsorbente se ha encontrado que remueve efectivamente los compuestos de nitrógeno provenientes de C_{12} y de materiales de alimentación de petróleos mayores. Tales corrientes de alimentación son conocidas por contener una mezcla variada y compleja de compuestos de nitrógeno normalmente que se consideran difíciles de remover de una manera eficiente.

El presente adsorbente se puede poner en contacto con el material de alimentación al utilizar cualquier medios convencionales para poner en contacto el material sólido y líquido, tal como utilizando una columna empacada, una columna de lecho fluidizada o una columna de lecho ebulida. Se prefiere utilizar el presente adsorbente al utilizarlo como el empaque de una columna empacada. El tamaño y el tiempo de residencia del diseño de columna se pueden

determinar por la naturaleza del material de alimentación contemplado para el tratamiento. Normalmente, cuando se desea un sistema continuo, se utiliza una prioridad de columnas en paralelo de tal forma que al menos una columna esté en modo de adsorción aunque el resto de las columnas estén en un modo de desorción o regeneración para el tratamiento continuo de un material de alimentación de petróleo.

Cuando se gasta el adsorbente objeto (esto es, tiene una reducción en la proporción de adsorción por debajo de un cierto nivel de diseño predeterminado), el adsorbente se remueve del servicio para adsorción de los compuestos de nitrógeno, y se regeneran para regresar al servicio como un adsorbente. En un sistema continuo, cuando una columna que contiene adsorbentes gastados, se remueve el servicio, una segunda columna que tiene un adsorbente regenerado se ubica el servicio. Se ha encontrado que el presente adsorbente se puede notar para adsorción, desorción y regeneración en una manera de ciclo durante periodos extendidos (ciclos múltiples) antes de la necesidad de removerla del servicio.

El proceso continuo se puede describir como alimentar primero una alimentación de petróleo obtenida de una unidad de destilación o FCC o su equivalente en una de al menos dos columnas de adsorción empacadas con el adsorbente actualmente descrito. Las columnas de adsorción están localizadas antes (normalmente justo antes) de las unidades HDS de un diagrama

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de flujo del proceso de petróleo total que está siendo utilizado. La corriente es alimentada en la columna durante un tiempo predeterminado para utilizar sustancialmente toda la capacidad de adsorción del adsorbente objeto. Tal tiempo se puede determinar durante o para una unidad de columna particular mediante experimentación convencional. Una vez sustancialmente toda la capacidad de adsorción se utiliza, el material de alimentación está dirigido a otra columna de adsorción aunque tomando la primer unidad del modo de adsorción.

La primer columna de adsorción es entonces sometida a descripción para remover los compuestos contaminados de nitrógeno reconectados del adsorbente allí. Se cree, aunque no se considera limitación sobre la invención reivindicada, que, en razón a que los compuestos contaminantes de nitrógeno son simplemente adsorbidos y/o adsorbidos bien sea físicamente o a través de unión iónica o dativa o similar y no, en general, unida al adsorbente mediante uniones covalentes, los contaminantes de nitrógeno pueden ser fácilmente removidos al utilizar un solvente orgánico polar u otro compuesto que sea solvente para la mayoría o, preferiblemente, sustancialmente todos los compuestos de nitrógeno. El solvente requiere ser inerte, esto es inerte con respecto al material de alimentación de petróleo residual adsorbente y otros compuestos en el adsorbente y no originará la formación de un precipitado sólido con los compuestos

nitrogenosos. En general, el adsorbente es tratado con un líquido inerte, de bajo punto de ebullición que se selecciona preferiblemente de un líquido orgánico polar, aunque los líquidos no polares también son utilizados. El líquido de desorción es usualmente seleccionado de alcoholes C_1-C_6 tales como alcanoles de cadena recta y ramificada como, por ejemplo, metanol, etanol, propanol (todos los isómeros), butanol (todos los isómeros), pentanol (todos los isómeros), hexanol (todos los isómeros), mezclas de estos y similares, éteres C_1-C_6 tales como dialquil éteres y alquil cicloalquil éteres como, por ejemplo, dimetil éter, dietil éter, dipropil éter, metil t-butil éter, metil ciclopropil éter, metil ciclobutil éter, etil ciclobutil éter, mezclas de estos y similares; aldehídos C_1-C_6 tales como aldehídos que contienen alquilo y cicloalquilo, como acetaldehído, propionaldehído, butiraldehído, malonaldehído, mezclas de estos y similares; cetonas C_1-C_6 tales como dialquil cetonas como por ejemplo, acetona, metil etil cetona, metil propil cetona, metil butil cetona, etil propil cetona, metil ciclopropil cetona, metil ciclobutil cetona, mezclas de estos y similares. Los líquidos de desorción con peso molecular mayor se pueden utilizar aunque su punto de ebullición creciente requiere más energía para pelar el líquido del material de nitrógeno y, por lo tanto, es menos preferido.

El solvente de adsorción es puesto en contacto con el adsorbente vaciado de compuesto de nitrógeno usualmente al

pasar simplemente el solvente a través de una columna empacada durante un tiempo predeterminado para remover sustancialmente todos los compuestos nitrogenosos de estos. Tal tiempo puede ser fácilmente determinado mediante simple experimentación y puede ser hecho en coordinación con la determinación del tiempo de adsorción adecuado para el adsorbente, como se describió anteriormente. El solvente resultante que contiene los contaminantes nitrogenosos es entonces removido. Opcionalmente, el solvente es separado de los contaminantes de nitrógeno y reciclados para una desorción adicional.

La determinación de ambos tiempos de adsorción y desorción para adsorber efectivamente los compuestos nitrogenosos dependerán del diseño de la columna, el material de alimentación de petróleo que está siendo tratado, la temperatura del material de alimentación así como también otros factores conocidos.

La columna desasorbida puede ser directamente regresada a la función de adsorción o puede, opcionalmente, ser adicionalmente tratada para remover cualquier solvente restante, residuo de petróleo capaz de ensusamiento de la columna, o similar antes de ser regresado al servicio como una columna de adsorción.

La corriente del producto de petróleo con alto punto de ebullición obtenida del proceso de adsorción descrito anteriormente es subsecuentemente tratada con un proceso de hidrodesulfurización (HDS). En general, tales procesos implican poner en contacto el material de petróleo obtenido con un catalizador HDS convencional a temperaturas (por ejemplo 250 a 450°C) y presiones (por ejemplo 10 a 150 bares) elevadas con una proporción de hidrógeno a petróleo de 36 a 620 m³/m³. Los catalizadores HDS en general tienen sitios ácidos, que son ubicados por la presencia de compuestos que contienen nitrógeno. Así, el proceso presente, donde estos compuestos de nitrógeno son removidos antes del procesamiento HDS suministra una manera eficiente para remover el nitrógeno y los contaminantes de azufre de los cortes de punto de ebullición altos obtenidos del material de alimentación de petróleo.

Todas las referencias aquí a elementos o metales que pertenecen a ciertos Grupos se refieren ala Tabla Periódica de Elementos en el Hawleys Condensed Chemical Dictionary, 12aba edición. También, cualquier referencia al Grupo o los Grupos deben ser al Grupo o a los Grupos según se refleja en esta Tabla Periódica de Elementos que utilizan sistemas de notación IUPAC para grupos de numeración.

Los siguientes ejemplos son dados como ilustraciones específicas de la invención reivindicada. Se debe entender,

sin embargo, que la invención no está limitada a los detalles específicos establecidos en los ejemplos. Todas las partes y porcentajes en los ejemplos, así como también en el resto de la especificación, son en peso a menos que se especifique otra cosa.

Adicionalmente, cualquier rango de números citados en la especificación o reivindicaciones, tales como aquel que representa un conjunto particular de propiedades, unidades de medición, condiciones, estados o porcentajes físicos, pretende incorporar literalmente expresamente aquí como referencia o de otra manera, cualquier número que caiga dentro de tal rango, incluyendo tal subconjunto de números dentro de cualquier rango así citado.

EJEMPLO 1

Formación de Adsorbente de Sílica-Zirconia

Un cogel de sílica-zirconia se formó utilizando una boquilla de mezcla que tiene la capacidad para introducción concurrente de dos corrientes de líquido seguido por el paso de líquidos introducidos a través de una senda tortuosa capaz de suministrar la mezcla rápida de las corrientes. Una solución acuosa de silicato de sodio (análisis: 24.2% de SiO_2 , 7.5% de Na_2O) se introdujo en la boquilla de mezcla en

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la proporción de 29.5 l/hr aunque introduciendo simultáneamente, a una proporción de 10.5 l/hr, una solución de ácido sulfúrico que tiene ortosulfato de zirconio disuelto allí (análisis: 30.7% H_2SO_4 ; 3.2% de ZrO_2). Luego de la salida del aparato de mezcla, se formó un hidrogel de sílica que tiene metal de zirconio como promotor de ácido Lewis formado en 11 minutos. 2500 partes del hidrogel resultante fueron lavadas al pasar 2100 partes de agua mantenida a 60°C a través de un producto de hidrogel sobre durante un periodo de 1 hora. Esta etapa de lavado fue repetida 3 veces adicionales. Después del lavado final, el hidrogel resultante fue secuencialmente tratado.

- (a) con una primer solución de 2100 partes de agua que contienen 103 partes de una solución de amonio acuosa al 12.5% durante 4 horas a 90°C ;
- (b) repetir el tratamiento (a) anterior;
- (c) repetir el tratamiento (a) anterior excepto que solamente 5 partes de la solución de amonio acuoso fue introducida con el agua y la duración fue de 2 horas;
- (d) poner en contacto el hidrogel con 2100 partes de agua que contienen 24 partes de una solución de ácido sulfúrico acuoso 45% durante 2 horas a 60°C; y

- (e) lavar 4 veces, cada una con 2100 partes de agua durante 1 hora a 60°C.

El hidrogel lavado fue secado durante 15 horas a 200°C seguido por el calentamiento a 200°C durante 2 horas. El aerogel de sílica-zirconia activador resultante fue enfriado a condiciones ambiente y bajo una atmósfera seca.

El gel resultante contenía 3.2 por ciento en peso de zirconio (como ZrO_2) (MUESTRA 1). Las acideces Lewis y Bronsted fueron medidas mediante el procedimiento de E. Bakiewicz et al, descrito en J. Phys. Chem. B 102 2890-2896 (1998). Las propiedades físicas del área de superficie BET el volumen de poro y el diámetro del poro fueron medidos utilizando metodología convencional para estas propiedades. La Tabla 1 de adelante muestra la acidez Lewis y Bronsted así como también las propiedades físicas del adsorbente resultante.

Tabla 1

Propiedades físicas del adsorbente de gel $\text{SiO}_2\text{-ZrO}_2$.

	Acidez Lewis $\mu\text{mol/gel}$	Acidez Bronsted $\mu\text{mol/gel}$	Área de Superficie m^2/g	Volumen de Poro cc/g	Diámetro Promedio de Poro $\text{\AA}$
SiO_2 con 3.2% de	1940	0	467	0.78	67

Zr (como ZrO ₂)					
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EJEMPLO 2:

Formación de Adsorbentes de Sílica modificada con Alúmina

Cuatro muestras de sílica gel secada por rociado que tienen átomos de alúmina en la matriz para impartir la acidez Lewis fueron formadas como sigue.

IIA. Un sol de sílica acuoso se formó al disolver inicialmente silicato de sodio (análisis: 24.2% SiO₂, 7.5% Na₂O) en agua calentada a 85°C en una proporción de silicato/H₂O de 0.15 para producir un sol de sílica acuoso. El sol de sílica fue mezclado con dióxido de carbono en una proporción tal que el tiempo del gel del sol de sílica fue de entre 10 y 30 segundos. La mezcla se desarrolló utilizando un reactor de tubo para posibilitar la mezcla íntima de los materiales. El gel se mezcló adicionalmente en el agua del reactante durante aproximadamente 140 minutos para permitir que el desarrollo de la estructura de gel se completará. El gel fue entonces bombeado a través de un mezclador estático aunque agregando una solución de sulfato de aluminio en la proporción de sílica aluminio 28/5. Debido al cambio en el pH, el gas de dióxido de carbono se expelió de la mezcla de gel. El hidrogel de alúmina-sílica resultante se desaguó a

200°C durante 15 horas y se secó por rociado para formar las partículas esféricas (1100 psi). El producto de polvo resultante fue entonces lechado en agua y lavado con una solución de sulfato de amonio para intercambiar soda de la misma manera como se describió en el ejemplo 1 anterior. El material resultante fue secado por destello a 182°C. Las partículas esféricas secadas (aproximadamente de 60 µm de diámetro) fueron entonces molidas a aproximadamente un tamaño de partícula de 8 µm utilizando una molienda de chorro. El polvo fue entonces formado en glóbulos de aproximadamente 1 mm de diámetro de acuerdo con el procedimiento descrito adelante.

IIB. El proceso IIA descrito anteriormente fue repetido exceptuando que el sol fue inicialmente formado a aproximadamente 35°C en lugar de 85°C; utilizando una proporción de silicato/H₂O de 0.24 en lugar de 0.15; y envejeciendo el gel durante 60 minutos en lugar de 140 minutos.

IIC. Se preparó una muestra de la misma manera como se describió en la muestra IIB, excepto que se agregó aluminato de sodio adicional (10% de Al₂O₃) después de la etapa de envejecimiento para producir un producto que tenía un contenido de alúmina de 25 por ciento en peso.

IID. Esta muestra se formó de la misma manera como se describió en la muestra IIB excepto que el material

resultante fue utilizado en forma de polvo con un tamaño de partícula de entre 20 y 70 micrómetros. El material no fue formado en glóbulos como se describe adelante.

Ejemplo 3

Formación de Adsorbente de Alumina-Titanio

El isopropóxido de aluminio es hidrolizado al introducirlo en agua que es mantenida a 85°C durante un periodo de 10 minutos para producir una solución que tiene 15% en peso de aluminio en agua. La suspensión resultante es mantenida a 85°C durante 20 minutos. El material es luego peptizado mediante la adición de una solución de tetracloruro de titanio en isopropanol. El material resultante es secado al calentar a 200° C durante 20 horas para producir un cogel de alúmina-titania.

Ejemplo 4

Formación de glóbulos de polvos de sílica modificados con alúmina:

800 partes de cada una de las muestras anteriores del ejemplo II (excepto II E) fueron mezcladas separadamente con 200 partes del ligador (muestra II A) con bohemita; muestras II B y II C con arcilla atapulgita) en un mezclador Eirich

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durante media hora. Las mezclas de polvos resultantes fueron cada una aglomeradas al agregar una cantidad apropiada de agua para observar la formación de glóbulo. El contenido de agua difirió dependiendo del polvo de sílica-alúmina y del sistema ligador utilizado. El tamaño de partícula de los glóbulos estaba entre 0.6 y 1.4 mm.

Las muestras resultantes fueron secadas durante 15 horas a 120°C y luego activadas a 550°C durante 2 horas. Las acideces Lewis y Bronsted fueron medidas mediante el procedimiento de E, Bakiewicz et al, descrito en J. Phys. Chem. B 102 2890-2896 (1998). Las propiedades físicas del área de superficie BET, el volumen de poro y el diámetro de poro fueron medidas utilizando metodología convencional para estas propiedades. Los adsorbentes en partículas resultantes fueron analizados teniendo las propiedades mostradas en la Tabla 2 de adelante.

Tabla II

Muestra	Acidez Lewis ($\mu\text{mol/g}$)	Acidez Bronsted ($\mu\text{mol/g}$)	Contenido de Al (como Al_2O_3) (Peso.%)	Área Superficial (m^2/g)	Volumen de Poro (cc/g)	Diámetro Promedio de Poro (Å)
II A	1050	270	13.1	338	0.69	81
II B	1000	30	13.3	267	0.93	140
II C	1240	100	25.0	364	0.64	70
II D	1100	260	13.1	329	1.1	134

El cogel de alúmina-titania del ejemplo III es tratado (utilizando atapulgita como ligador) de la misma manera que anteriormente para formar glóbulos de ese material. El material resultante tiene una acidez Lewis alta de aproximadamente 1000 $\mu\text{mol/gel}$ y un diámetro de poro alto de aproximadamente 75.

Ejemplo 5

Formación de Sílica Gel (Comparativa)

Dos xerogeles de sílica (Muestras III-Si/1 y III-Si/2) fueron formadas de la misma manera como se describió en el Ejemplo 1 anterior excepto que la solución de ácido sulfúrico inicial no contenía zirconio u otro agente precursor de metal de ácido Lewis. Las condiciones de lavado y envejecimiento fueron alteradas para cada muestra con el fin de ajustar la estructura a la estructura de poro deseada.

Muestra II-Si/1:

2500 partes del hidrogel resultante fueron lavadas al pasar 2100 partes de agua mantenida a 60°C a través del producto de hidrogel durante un periodo de 1 hora. Esta etapa de lavado fue repetida 3 veces adicionales. Después del lavado final, el hidrogel resultante fue secuencialmente tratado.

- (a) con una primer solución de 2100 partes de agua que contienen 103 partes de una solución de amonio acuoso al 12.5% durante 4 horas a 60°C;
- (b) poner en contacto el hidrogel con 3100 partes de agua que contienen 24 partes de una solución de ácido sulfúrico acuoso al 45% durante 2 horas a 60°C; y
- (c) lavar 3 veces, cada una con 2100 partes de agua durante 1 hora a 60°C.

Muestra III-Si/2

2500 partes del hidrogel resultante fueron lavadas al pasar 2100 partes de agua mantenida a 60°C a través del producto de hidrogel durante un periodo de 1 hora. Esta etapa de lavado fue repetida 3 veces adicionales. Después del lavado final, el hidrogel resultante fue secuencialmente tratado

- (a) con una primer solución de 2100 partes de agua que contienen 103 partes de una solución de amonio acuoso al 12.5% durante 4 horas a 60°C;
- (b) poner en contacto el hidrogel con 3100 partes de agua que contienen 24 partes de una solución de ácido sulfúrico acuoso al 45% durante 2 horas a 60°C; y
- (c) lavar 3 veces, cada una con 2100 partes de agua durante 1 hora a 60°C.

Muestra III-Si/2

2500 partes del hidrogel resultante fueron lavadas al pasar 2100 partes de agua mantenida a 60°C a través del producto de hidrogel durante un periodo de 1 hora. Esta etapa de lavado fue repetida 3 veces adicionales. Después del lavado final, el hidrogel resultante fue secuencialmente tratado

- (a) Con una primer solución de 2100 partes de agua que contiene 103 partes de una solución de amonio acuoso al 12.5% durante 4 horas a 60°C;
- (b) Poner en contacto el hidrogel con 2100 partes de agua que contienen 24 partes de una solución de ácido sulfúrico acuosos al 45% durante 2 horas a 60°C,
- (c) Lavar dos veces, cada una con 2100 partes de agua durante 1 hora a 60°C; Y
- (d) Lavar con una solución de 2100 partes de agua que contienen 103 partes de una solución de amonio acuosos al 12.5% durante 3 horas a 90°C

Adsorbente de Alúmina (Comparativo)

Un producto adsorbente de alúmina comercialmente disponible, Hi Q 30 vendido por Alcoa World Chemicals, fue marcado muestra III-Al/1 y comparado con el adsorbente objeto

de la presente invención. La muestra estaba en forma de polvo con tamaños de partícula entre 20 y 70 micrómetros.

Cada una de las muestras comparativas descritas anteriormente fue secada a 200°C durante 15 horas y luego calentadas a 400°C durante 2 horas. A Las muestras se les permitió entonces enfriarse hasta temperatura ambiente bajo una atmósfera seca. Las acideces Lewis y Bronsted para cada muestra fueron medidas mediante el procedimiento de E, Bakiewicz et al, descrito en J. Phys. Chem. B 102 2890-2896 (1998). Las propiedades físicas del área de superficie BET volumen de poro y diámetro de poro fueron medidas utilizando metodología convencional para estas propiedades.

La Tabla III de adelante muestra la acidez Lewis y Bronsted así como también las propiedades físicas de los adsorbentes comparativos.

Tabla III

Propiedades Físicas de SiO₂ y de Geles de Alúmina

Muestra	Acidez Lewis μmol/g	Acidez Bronsted μmol/g	Área de Superficie m ² /g	Volumen de Poro Cc/g	diámetro Promedio de Poro Å
III-Si/1	0	0	498	0.88	71

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III-Si/2	0	0	275	1.16	168
III-Al/10	80	60	116	0.50	172

Ejemplo 6

Cada uno de los adsorbentes de sílica-zirconia formado de acuerdo al Ejemplo I, los adsorbentes de sílica-alúmina formados de acuerdo al Ejemplo II; y los adsorbentes comparativos del Ejemplo III fueron calentados en un horno mufla durante 15 horas a 200°C seguido por calentamiento 750°F (400°C) durante 2 horas. A las muestras entonces se les permitió enfriarse hasta temperatura ambiente bajo una atmósfera seca.

Cada una de las muestras fue ensayada de acuerdo con el siguiente procedimiento:

Varias cantidades de cada adsorbente fueron cargadas en columnas de ensayo separadas seguidas por ciertas cantidades de material de alimentación de petróleo LGO (B. P. rango de 164 a 458°C; nitrógeno total de aproximadamente 220 ppm, azufre total 1.56% en peso). Para detalles de las proporciones de alimentación adsorbente ver Tablas de adelante. El contenido de nitrógeno total de la materia de material de alimentación de petróleo LGO fue analizada mediante espectrometría fotométrica utilizando un analizador de nitrógeno comercial (analizador ANTEK).

Cada una de las columnas de ensayo fue mantenida mediante agitación durante 4 horas a 40°C para permitir que ocurriera el equilibrio de adsorción. El material de petróleo restante fue removido de cada columna al centrifugar y analizado para el contenido de hidrógeno total de la misma manera como se hizo con el material de materia prima de petróleo LGO. La capacidad de adsorción de nitrógeno lograda por el adsorbente de cada columna de ensayo fue calculada de acuerdo con la formula:

$$C = (C_0 - c) \, m \, (\text{alimentación}) / m \, (\text{adsorción})$$

Donde: C es la capacidad de adsorción de nitrógeno en equilibrio mg/g; C_0 es la concentración de nitrógeno de alimentación, c es la concentración de nitrógeno del producto de alimentación después de equilibrio en contacto con adsorbente; m (alimentación) en mas de petróleo LGO ensayada; y m (adsorbente) es la masa de adsorbente en columna.

Para cada ensayo la capacidad de absorción calculada se normalizó con respecto al área de superficie (BET) del adsorbente. Los resultados son reportados en las Tablas IV hasta XI de adelante como capacidad de adsorción (mg/m²).

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Tabla IV

Muestra I				
m(ads.) (g)	m(alimen.) (g)	c (ppm)	c/co	Capacidad (mg/m2)
0.67	20	103	0.46	0.0078
1.33	20	67	0.30	0.0051
2.66	20	38	0.17	0.0030
4.00	10	10	0.04	0.0012

Tabla V

Muestra II A				
m(ads.) (g)	m(alimen.) (g)	C (ppm)	c/co	Capacidad (mg/m2)
0.17	10	151	0.66	0.0138
0.33	10	108	0.47	0.0110
0.37	10	70	0.30	0.0071
1.34	10	42	0.18	0.0042
4.00	10	10	0.04	0.0016

Tabla VI

Muestra II B				
m(ads.) (g)	m(alimen.) (g)	c (ppm)	c/co	Capacidad (mg/m2)
0.67	20	125	0.55	0.0113
1.33	20	86	0.38	0.0079
2.66	20	52	0.23	0.0049
4.00	10	16	0.07	0.0020

Tabla VII

Muestra II C				
m(ads.)	m(alimen.)	c		Capacidad

(g)	(g)	(ppm)	c/co	(mg/m ²)
0.35	20	137	0.59	0.0149
0.37	20	108	0.46	0.0102
1.33	20	71	0.31	0.0066
2.66	20	45	0.19	0.0039
8.00	20	14	0.061	0.0015

Tabla VIII

Muestra II D				
m(ads.) (g)	m(alimen.) (g)	C (ppm)	c/co	Capacidad (mg/m ²)
0.18	10	140	0.58	0.0169
0.35	10	101	0.42	0.0121
0.67	10	70	0.29	0.0077
1.33	10	43	0.18	0.0045
4.00	10	13	0.05	0.0017

Tabla IX

Muestra III-Si/2				
m(ads.) (g)	m(alimen.) (g)	C (ppm)	c/co	Capacidad (mg/m ²)
0.66	20	129	0.62	0.0048
1.33	20	86	0.42	0.0037
2.66	20	55	0.26	0.0023
4.00	10	16	0.08	0.0010

Tabla X

Muestra III-Si/2				
m(ads.) (g)	m(alimen.) (g)	c (ppm)	c/co	Capacidad (mg/m ²)
0.66	20	128	0.62	0.0087
1.33	20	100	0.48	0.0059
2.66	20	70	0.34	0.0038

4.00.	10	27	0.13	0.0016
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Tabla XI

Muestra III-A1 2				
m(ads.) (g)	m(alimen.) (g)	c (ppm)	c/co	Capacidad (mg/m ²)
0.18	10	205	0.85	0.0172
0.35	10	189	0.78	0.0128
0.37	10	161	0.67	0.0102
1.33	10	119	0.50	0.0079
4.00	10	43	0.18	0.0043

Las principales modalidades preferidas y los modos de operación de la invención han sido descritos en la especificación anterior. La invención que pretende ser protegida aquí, sin embargo, no debe ser considerada como limitada a las formas particulares descritas, en razón a que estas son consideradas como ilustrativas en lugar de receptivas. Las variaciones y cambios pueden ser hechos por aquellos expertos en la técnica, sin apartarse del espíritu de la invención.

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REIVINDICACIONES

1. Un método para elaborar combustible de hidrocarburo C_{12} y mayores que tienen contenido de nitrógeno y azufre reducido que comprende (a) poner en contacto, antes de la hidrodeshulfurización, una corriente de alimentación de petróleo C_{12} o mayor que tiene un compuesto que contienen nitrógeno y azufre allí con un adsorbente poroso, en partículas que comprende un material de matriz de óxido de metal (M) inorgánico en donde M se selecciona de Ti, Al, Zr, Si, Sn, o mezclas de estos que tienen acidez Lewis de al menos aproximadamente 500 $\mu\text{mol/g}$; y (b) subsecuentemente reatar un producto de corriente derivado de (a) hidrodeshulfurización catalítica para producir incombustible de hidrocarburo.
2. El método de la reivindicación 1 en donde el adsorbente tiene un área de superficie de al menos 200 m^2/gm ; un volumen de poro N_2 de al menos aproximadamente 0.5 cc/gm ; y un diámetro promedio de poro de 40 a 400 Å y una cantidad efectiva de átomos de metal del Grupo IB, IIA, IIB, IIIA, IIIB, IVA, VA, VIA, u VIIIA de la Tabla Periódica diferente de M para originar una acidez Lewis de al menos 500 $\mu\text{mol/g}$ al adsorbente.

3. El método de la reivindicación 1 en donde el material de alimentación de petróleo comprende hidrocarburos $C_{12}-C_{30}$ antes formados por craqueo catalítico fluido o mediante destilación de alimentación de petróleo.
4. El método de la reivindicación 1 en donde el material de alimentación de petróleo es puesto en contacto con un adsorbente en una zona de lecho empacada que comprende al menos una columna de adsorción de lecho empacada.
5. El método de la reivindicación 2 en donde el material de alimentación de petróleo es puesto en contacto con un adsorbente en una zona de lecho empacada que comprende al menos una columna de adsorción de lecho empacada.
6. El método de la reivindicación 3 en donde el material de alimentación de petróleo es puesto en contacto con el adsorbente en una zona de lecho empacada que comprende al menos una columna de adsorción de lecho empacada.
7. El método de la reivindicación 1 en donde dicho material de alimentación de petróleo es puesto en contacto con un adsorbente en una zona de adsorción

seleccionada de una zona de adsorción de lecho fluidizada o una zona de adsorción de lecho embullante.

8. El método de la reivindicación 2 en donde dicho material de alimentación de petróleo es puesto en contacto con un adsorbente en una zona de adsorción seleccionada de una zona de adsorción de lecho fluidizada o una zona de adsorción de lecho embullante.

9. El método de la reivindicación 3 en donde dicho material de alimentación de petróleo es puesta en contacto con un adsorbente en una zona de adsorción seleccionada de una zona de adsorción de lecho fluidizada o una zona de adsorción de lecho embullante.

10. El método de la reivindicación 4 en donde la zona de adsorción de lecho empacada comprende al menos dos columnas de adsorción.

11. El método de la reivindicación 5 en donde la zona de adsorción de lecho empacada comprende al menos dos columnas de adsorción.

12. El método de la reivindicación 6 en donde la zona de adsorción de lecho empacada comprende al menos dos columnas de adsorción.
13. El método de la reivindicación 7 en donde la zona de adsorción comprende al menos dos columnas de adsorción.
14. El método de la reivindicación 8 en donde la zona de adsorción comprende al menos dos columnas de adsorción.
15. El método de la reivindicación 9 en donde la zona de adsorción comprende al menos dos columnas de adsorción.
16. El método de la reivindicación 10 en donde el material de alimentación de petróleo es puesto en contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción para remover los compuesto que contienen nitrógeno adsorbido de esta.

17. El método de la reivindicación 11 en donde el material de alimentación de petróleo es puesto en contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción para remover los compuestos que contienen nitrógeno adsorbidos de estos.

18. El método de la reivindicación 12 en donde el material de alimentación de petróleo es puesto en contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción al remover los compuestos que contienen nitrógeno adsorbido anteriormente de estos.

19. El método de la reivindicación 13 en donde el material de alimentación de petróleo es puesto en contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción para remover los compuestos que contienen nitrógeno adsorbidos previamente de estos.

20. El método de la reivindicación 14 en donde el material de alimentación de petróleo es puesto en

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contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción al remover los compuestos que contienen nitrógeno adsorbidos previamente de estos.

21. El método de la reivindicación 15 en donde el material de alimentación de petróleo es puesto en contacto con dicho adsorbente en al menos una primer columna de adsorción y el adsorbente gastado en al menos una segunda columna de adsorción es sometido a desorción para remover los compuestos que contienen nitrógeno adsorbido previamente de estos.

22. El método de la reivindicación 16 en donde la desorción comprende poner en contacto el compuesto de nitrógeno que contiene adsorbente con un compuesto líquido que es un solvente para los compuestos de nitrógeno seleccionados de alquilo C_1-C_6 y alcoholes de cicloalquilo, alquilo C_1-C_6 y éteres de cicloalquilo, alquilo C_1-C_6 y aldehídos de cicloalquilo y dialquilcetona C_1-C_6 .

23. El método de la reivindicación 19 en donde la desorción comprende poner en contacto el compuesto de nitrógeno que contiene adsorbente con un compuesto

líquido que es un solvente para los compuestos de nitrógeno seleccionados de alquilo C_1-C_6 y alcoholes de cicloalquilo, alquilo C_1-C_6 y éteres de cicloalquilo, alquilo C_1-C_6 y aldehídos de cicloalquilo y alquil cetona C_1-C_6 .

24. El método de la reivindicación 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, o 23 en donde el adsorbente comprende un compuesto formado a poner en contacto (a) una sílica seleccionada de un material formador de matriz de sílica o un material formado de matriz de sílica o mezclas de estos, (b) un compuesto precursor de ácido Lewis en una cantidad efectiva para impartir al menos una acidez Lewis de 500 $\mu\text{mol/g}$ al adsorbente resultante.

25. El método de la reivindicación 24 en donde el componente (b) comprende un compuesto precursor que tiene átomos de metal del Grupo IB, IIA, IIB, IIA, IIIB, IVA, VA, VÍA, o VIIIA de la Tabla Periódico y el adsorbente tiene una acidez Lewis de al menos 600 $\mu\text{mol/g}$.

26. El método de la reivindicación 24 en donde el metal que imparte el ácido Lewis se selecciona de Mg, Ca,

Sr, Ba, B, Al, Ga Zn, SC, y, La, Ti, Zr, Hf, V, Nb, Mo, W, Fe, Co, Ni, y mezclas de estos.

27. El método de la reivindicación 24 en donde el metal que imparte ácido Lewis es seleccionado de Mg, Zn, La, Ti, Zr, Fe, y Al, y mezclas de estos.

28. El método de la reivindicación 24 en donde el metal que imparte ácido Lewis se selecciona de Ti, Zr, Fe, Al y mezclas de estos.

29. El método de la reivindicación 24 en donde el componente (a) del adsorbente se selecciona del hidrogel de sílica, aerogel de sílica o xerogel de sílica o mezclas de estos.

30. El método de la reivindicación 26 en donde el componente (a) del adsorbente se selecciona de hidrogel de sílica, aerogel de sílica o xerogel de sílica o mezclas de estos.

31. El método de la reivindicación 27 en donde el componente (a) del adsorbente se selecciona de hidrogel de sílica, aerogel de sílica o xerogel de sílica o mezclas de estos.

32. El método de la reivindicación 28 en donde el componente (a) del adsorbente se selecciona de sílica hidrogel, de sílica aerogel o sílica xerogel o mezclas de estos.

33. El método de la reivindicación 24 en donde el adsorbente tiene una acidez Lewis desde aproximadamente 500 a 2500 $\mu\text{mol/g}$.

35. El método de la reivindicación 32 en donde el adsorbente es seleccionado de un hidrogel de sílica, un aerogel de sílica o un xerogel de sílica que tiene átomos de aluminio allí en cantidad suficiente para impartir acidez Lewis desde 500 a 2500 $\mu\text{mol/g}$.

36. El método de la reivindicación 32 en donde el adsorbente es seleccionado de un hidrogel de sílica, un aerogel de sílica o un xerogel de sílica que tiene átomos de zirconio allí en cantidad suficiente para impartir acidez Lewis de 500 a 2500 $\mu\text{mol/g}$.

37. El método de la reivindicación 24 en donde el adsorbente tiene un área de superficie desde 400 a 550 m^2/gm ; un volumen de poro N_2 desde 0.6 a 0.9

cc/gm; y un diámetro promedio de poro desde 45 a 75 Å.

38. El método de la reivindicación 32 en donde el adsorbente tiene un área de superficie desde 400 a 550 m²/gm; un diámetro de poro N₂ de desde 0.6 a 0.9 cc/gm; y un diámetro de poro promedio de desde 45 a 75 Å.

39. El método de la reivindicación 16 en donde el adsorbente es formado de una lechada de sílica y un compuesto precursor de metal para ácido Lewis en una proporción en peso de sílica a metal (como óxido de metal) de desde 0.25:1 a 99:1.

40. El método de la reivindicación 18 en donde el adsorbente comprende material en partículas que tiene una distribución de tamaño de partícula tal que en menos de 5% en peso tienen un diámetro de menos de 0.6 mm y al menos aproximadamente 95% en peso tienen diámetro de menos de 2 mm.

41. El método de la reivindicación 32 en donde el adsorbente comprende material en partículas que tiene una distribución en tamaño de partículas tal que menos de 5% en peso tienen un diámetro de menos de

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0.6 mm y al menos aproximadamente 95% en peso tienen un diámetro de menos de 2 mm.

42. Un método para elaboración de combustibles de hidrocarburo que comprende formar un material de alimentación que comprende compuestos de hidrocarburos C₁₂ y mayores en donde dicho material de alimentación comprende además compuestos que obtienen nitrógeno y azufre, introduciendo dicho material de alimentación a una zona de adsorción que comprende al menos dos columnas de adsorción empacadas seguidas mediante la introducción de dicho material de alimentación a una zona de hidrodesulfurización catalítica, en donde dicho material de alimentación es introducido a al menos una columna de la zona de adsorción que tiene adsorbente que comprende partículas porosas seleccionadas de hidrogel de sílica, aerogel de sílica o xerogel de sílica o mezclas de estos que tienen desde aproximadamente 1 a 80% en peso de átomos (como óxido de metal) de al menos unos metales que imparten ácido Lewis seleccionados de átomos de metal del grupo IB, IIA, IIB, IIIB, IVA, VA, VÍA, U VIIIA de la Tabla Periódica y que tienen la acidez Lewis de al menos aproximadamente 500 $\mu\text{mol/g}$; área de superficie de al menos 200 m^2/g ; volumen de poro N₂ de

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al menos aproximadamente 0.5 cc/gm; y diámetro de poro promedio de al menos 40 Å.

43. el proceso de la reivindicación 42 en donde el metal que le imparte ácido Lewis es seleccionado de Ti, Zr, Fe, Al, o mezclas de estos; y el adsorbente tiene una acidez Lewis de desde 600 a 3000 $\mu\text{mol/g}$; y un diámetro promedio de poro desde 40 a 400 Å.

44. El proceso de la reivindicación 42 en donde el metal que le imparte ácido Lewis se selecciona de aluminio o zirconio o mezclas de estos; y el adsorbentes tiene una acidez Lewis de desde 750 a 2500 $\mu\text{mol/g}$; y un diámetro de poro promedio de desde 40 a 400 Å.

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

SUPERINDUSTRIA Y COMERCIO
Radicación : 65069068 00000000
Fecha (HUB): 2005-07-13 17:57:44
Trámite : R11 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 162

RECIBO OFICIAL DE CAJA : 05 - 46,091
FECHA : JUNIO 21 DE 2005

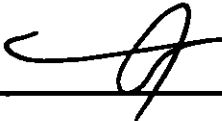
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	40117916	21/06/2005	62,639,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	443,000.00
		TOTAL :	\$ 443,000.00

SON: CUATROCIENTOS CUARENTA Y TRES MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

060 06032- 841-003-4

SUPERINDUSTRIA Y COMERCIO
 Radicacion : 05069008 00000000 Folios 162
 Fecha (ANO) 2005-07-13 17:57:44
 Trámite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
 Dependencia 2020 DIVISION DE NUEVAS CREACIONES

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION ☒	()	()
- Indicación de que se solicita la concesión de una patente	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud	()	()
- Descripción de la invención	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas	()	()
COMPLETA ()	INCOMPLETA ()	()
DISEÑO INDUSTRIAL ()		
- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud	()	()
- Representación gráfica o fotografíca del Diseño Industrial o muestra del Material que incorpora el diseño	()	()
- Comprobante de pago de las tasas establecidas	()	()
COMPLETA ()	INCOMPLETA ()	()
ESQUEMA DE TRAZADO ()		
- Indicación de que solicita el registro de un Esquema de trazado	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud	()	()
- Representación gráfica del esquema de trazado	()	()
- Comprobante de pago de las tasas establecidas	()	()
COMPLETA ()	INCOMPLETA ()	()

Firma Responsable

Fecha

[Handwritten Signature]
 13 de 2005

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
FERRERO EMILIO
Apoderado(a) y/o Representante de
W R. GRACE & CO CONN

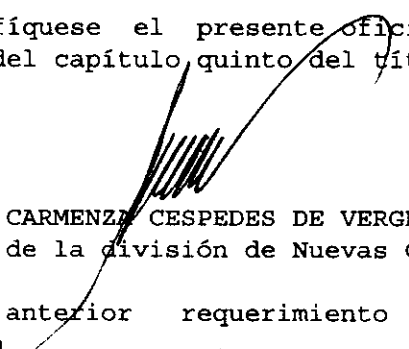
REFERENCIA	Radicación No.	5 69088
	Solicitud internacional	US2003/039368
	Fecha inicio fase nacional	19/07/2005
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	U - 8460

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 Única de la Superintendencia de Industria y Comercio, se le comunica que

1 Si fuere el caso, el solicitante debe adjuntar la traducción de los anexos del reporte de examen preliminar internacional (Art. 36.2.b) del tratado PCT

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 Única No 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 _____
adpall

16 SET. 2005

16
10/27/91

[Signature]

