

CONCESION



PR/E/2000/195817

195817

TITULAR(ES): INSTITUTO MEXICANO DEL PETROLEO

DOMICILIO(S): AVENIDA EJE CENTRAL LAZARO CARDENAS NORTE N°. 152,
DELEGACION GUSTAVO A. MADERO, 07730, MEXICO, D.F.

DENOMINACION: PROCESO PARA RECUBRIR MONOLITOS CERAMICOS Y PRODUCTO
RESULTANTE

CLASIF.INT⁵ : B05D7/24, B05D1/18

INVENTOR(ES): LUIS E. MIRAMONTES CARDENAS, AGUSTIN VARGAS APANGO, ANA
DE LOS ANGELES SERRANO MAGAÑA

NUMERO: 9303937

FECHA DE PRESENTACION: 30 DE JUNIO DE 1993

HORA: 13:16

PAIS:

FECHA:

NUMERO:

M. L. H. Amigo V. 29012

M. L. H. Amigo V.

20-VII-2000

IFG 24956197

3 DE ABRIL DE 2000

LIC. JORGE AMIGO CASTAÑEDA

FORMATO UNICO DE INGRESOS POR SERVICIOS

ESTE FORMATO ES DE DISTRIBUCION GRATUITA

Instituto Mexicano de la Propiedad Industrial



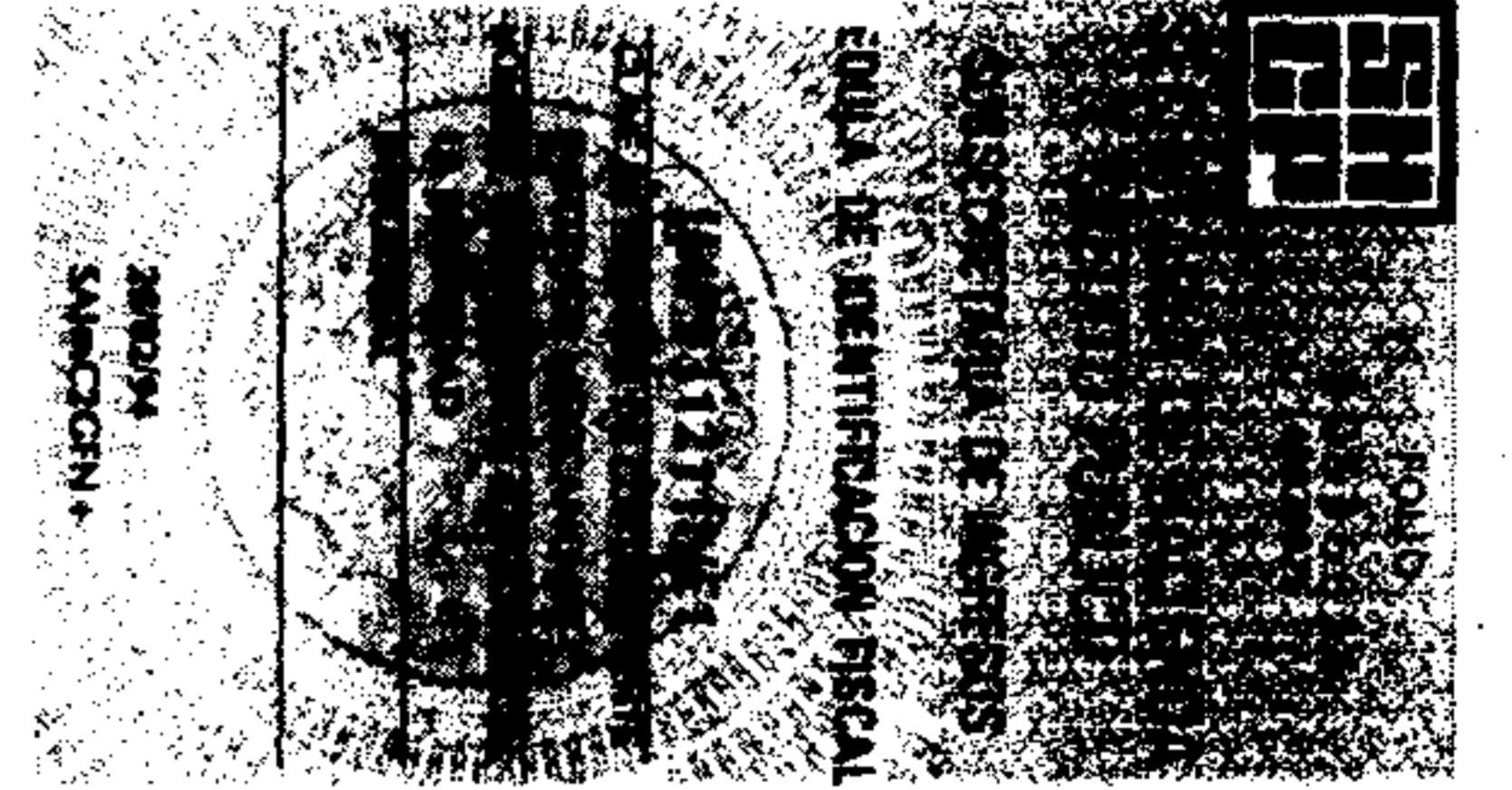
PERIFERICO SUR 3106,
COL. JARDINES DEL PEDREGAL,
DELEG. ALVARO OBREGON
01900 MEXICO, D.F.

NUMERO DE FOLIO
552167-9

NUMERO DE SOLICITUD:
9303937

Nº. PATENTE, REGISTRO O PUBLICACION:
195817

- PATENTE CERTIFICADO DE INVENCION NOMBRE COMERCIAL
- MODELO DE UTILIDAD MARCA DENOMINACION DE ORIGEN
- DISEÑO INDUSTRIAL AVISO COMERCIAL OTROS



IMPRESO POR: PRINTEX, S.A. DE C.V. IMPRESOR AUTORIZADO EN EL DIARIO OFICIAL DE LA FEDERACION DEL 10-VII-95 R.F.C. PRI-941220-PPF TEL. 582-15-00 LA REPRODUCCION NO AUTORIZADA DE ESTE COMPROBANTE CONSTITUYE UN DELITO EN LOS TERMINOS DE LAS DISPOSICIONES FISCALES.

CONCEPTO	ARTICULO TARIFA	INCISO TARIFA	IMPORTE
POR LA EXPEDICION DEL TITULO DE PATENTE POR PAGO DE ANUALIDADES DE VIGENCIA DE LA PATENTE CON No. DE EXPEDIENTE 9303937, IMP-598 8ava. a la 10ª. 11ava. a la 12ava.. FECHA LEGAL: 30 DE JUNIO DE 1993. FECHA DE CONCESIÓN: 3 DE ABRIL DE 2000.	1	e	\$ 671.17
	2	b	\$1,089.00
	2	c	\$1,092.00
50% DE DESCUENTO MICRO Y PEQUEÑA EMPRESA INSTITUCIONES DE INVESTIGACION DEL SECTOR PUBLICO INSTITUCIONES EDUCATIVAS INVENTORES INDEPENDIENTES			TOTAL TARIFAS \$ 2,852.17 RECARGOS \$ I.V.A. \$ TOTAL DEL PAGO \$ 427.83 \$ 3,280.00

195817

DIRECCION DE PATENTES
2000 ABR 3 PM 3 43

INSTITUTO MEXICANO DE LA PROPIEDAD INDUSTRIAL
013325

DATOS DEL TITULAR O SOLICITANTE

NOMBRE **INSTITUTO MEXICANO DEL PETROLEO**

DOMICILIO **EJE CENTRAL LAZARO CARDENAS NORTE No. 1**
CALLE, NUMERO, COLONIA Y CODIGO POSTAL

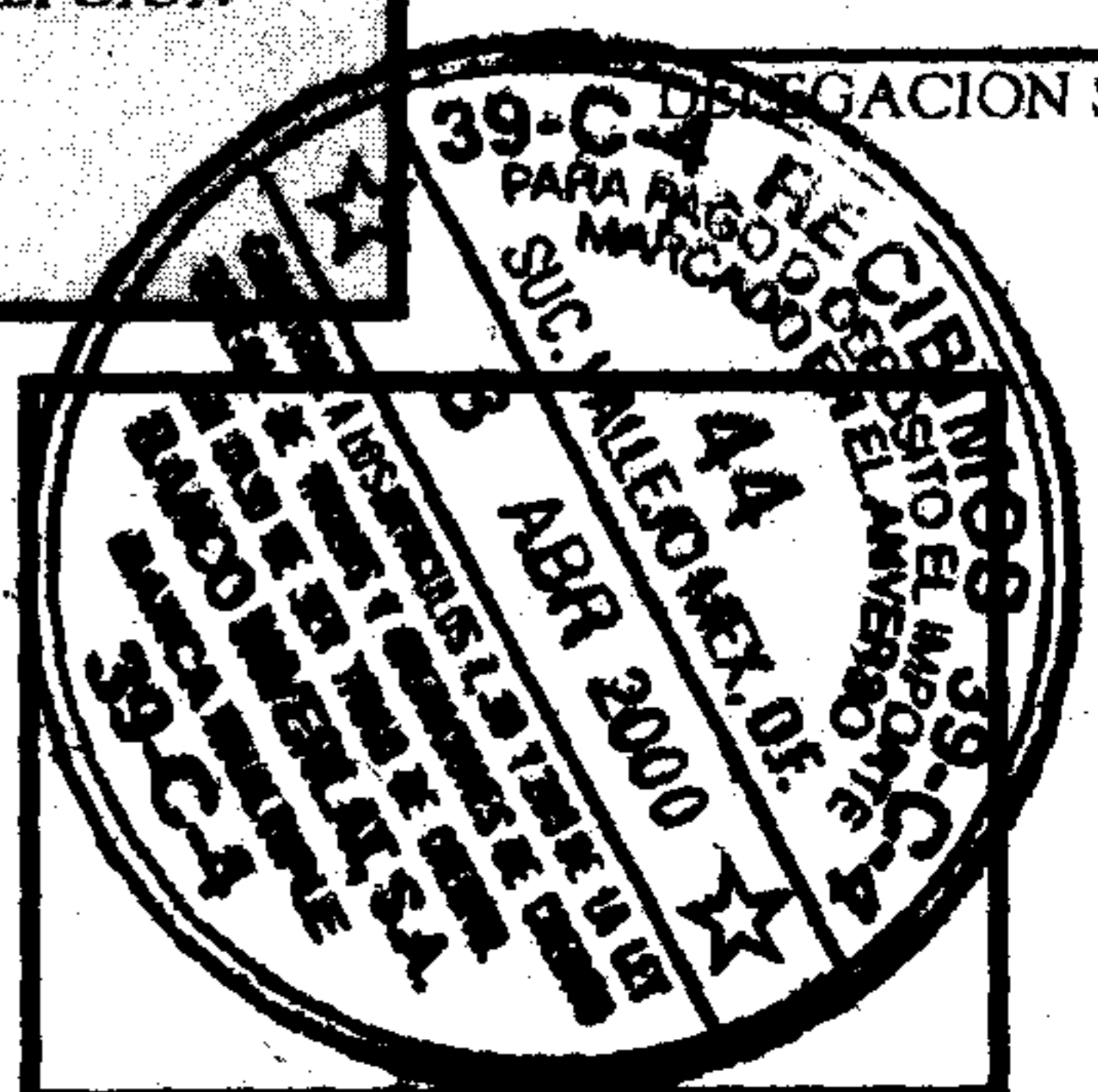
COL. **SAN BARTOLO ATEPEHUACAN, C.P. 07730, MEXICO**

POBLACION/ESTADO

R.F.C.

T M P 6 5 0 8 2 3 3 9 7

BANCO INVERLAT, S.A.
SUCURSAL VALLE DE GUADALUPE
FECHA DE RECEPCION
SALVO BUEN COPRO



[Handwritten Signature]
FIRMA DEL TITULAR O REPRESENTANTE

INSTITUTO MEXICANO DE LA PROPIEDAD INDUSTRIAL

Bajo protesta de decir verdad declaro, con respecto al beneficio establecido en la cuarta disposición general del Acuerdo por el que se da a conocer la Tarifa por los servicios que presta el Instituto Mexicano de la Propiedad Industrial, publicado en el Diario Oficial de la Federación del 23 de agosto de 1995, encontrarme en ese supuesto, por lo que solicito pagar únicamente el 50% de dicha Tarifa, aplicada a los Artículos 1e, 2b Y 2c, del mismo Acuerdo, como Apoderado del Instituto Mexicano del Petróleo, con referencia a la patente con No. de Expediente 9303937.

MARQUE CON UNA (X) EN EL RECUADRO QUE LE CORRESPONDA:

INVENTORES ()

MICRO O PEQUEÑA INDUSTRIA ()

PERSONAS FISICAS QUE NO SEAN EMPRESARIOS
O COMERCIANTES INDIVIDUALES. ()

INSTITUCIONES DE EDUCACION SUPERIOR PUBLICAS
O PRIVADAS.

INSTITUTO DE INVESTIGACION CIENTIFICA Y TECNOLOGICA
DEL SECTOR PUBLICO. (X)

ATENTAMENTE.

MEXICO, D.F., 3 DE ABRIL DEL 2000

NOMBRE: MTRO. ROBERTO RODRÍGUEZ VÉLEZ FIRMA: ROBERTO R. V.

APODERADO (X)
TITULAR ()

Solo

013325



INSTITUTO MEXICANO DE LA PROPIEDAD INDUSTRIAL

PAT. 195817

2000 ABR 3 PM 3 49

DIRECCION DE PATENTES

EXPEDIENTE No. 9303937

C. DIRECTOR GENERAL DEL INSTITUTO MEXICANO DE LA PROPIEDAD INDUSTRIAL
Presente.

He de merecer a usted se sirva aceptar el pago de las anualidades de vigencia respectivas de nuestra Patente cuyos datos se indican enseguida:

Expediente No.: 9303937

Fecha Legal: 30 de junio de 1993

Fecha de Expedición: 3 de abril de 2000

Invención: Proceso para recubrir monolitos cerámicos y producto resultante.

Anualidades: de la 8ava. a la 12ava.

Titular: Instituto Mexicano del Petróleo

Protesto a usted mi más atenta consideración.

México, D.F., a 3 de abril de 2000

INSTITUTO MEXICANO DEL PETRÓLEO

MTR. ROBERTO RODRÍGUEZ VÉLEZ
Apoderado

MT-1-e
MT-2: bxc
3.280

El pago original se encuentra en la cta a paco
Tel 552167-9

DOMICILIO PARA NOTIFICACIONES:

Av. Eje Central Lázaro Cárdenas Norte No. 152, Col. San Bartolo Atepehuacan, Deleg. Gustavo A. Madero, C.P. 07730

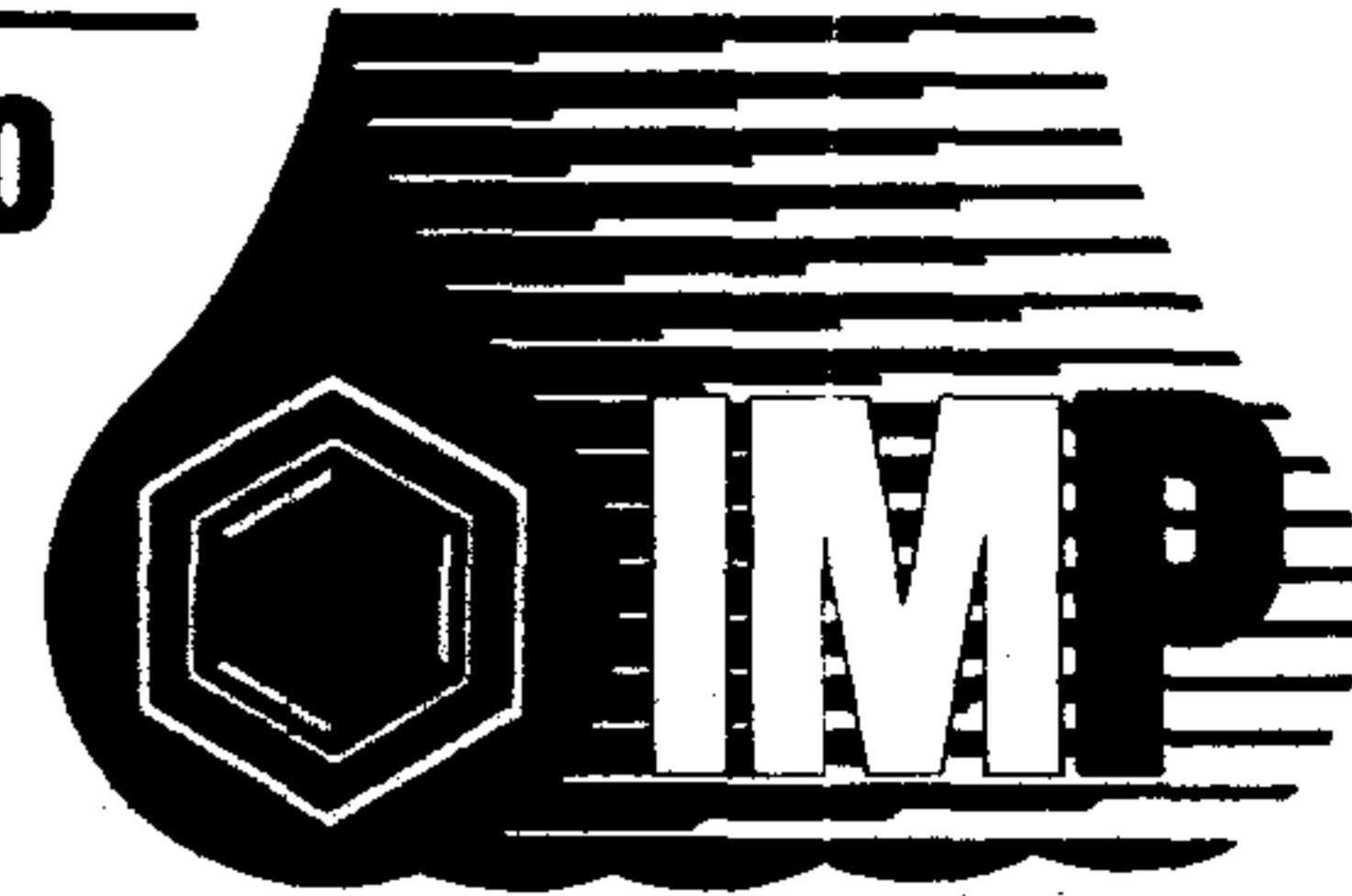
Se To

013325

INSTITUTO MEXICANO DEL PETROLEO



INSTITUTO MEXICANO
DE LA PROPIEDAD
INDUSTRIAL



29 de marzo de 2000

2000 ABR 3 PM 3 44

a su expediente

9303937

DRA. DEBORAH LAZARD SALTIEL
Directora de Patentes del Instituto Mexicano de la
Propiedad Industrial.
Presente.

DIRECCION DE
PATENTES

195817

Roberto Rodríguez Vélez, Apoderado Legal del Instituto Mexicano del Petróleo (IMP), personalidad que se acredita con la fotocopia que anexo de la solicitud de inscripción con fecha del 6 de septiembre del año en curso, con domicilio para oír y recibir notificaciones en Ave. Eje Central Lázaro Cárdenas Norte No. 152, Col. San Bartolo Atepehuacan, C.P. 07730, Deleg. Gustavo A. Madero, México, D.F., en el Registro General de Poderes de ese Instituto bajo el número de folio 07941, ante usted respetuosamente expongo:

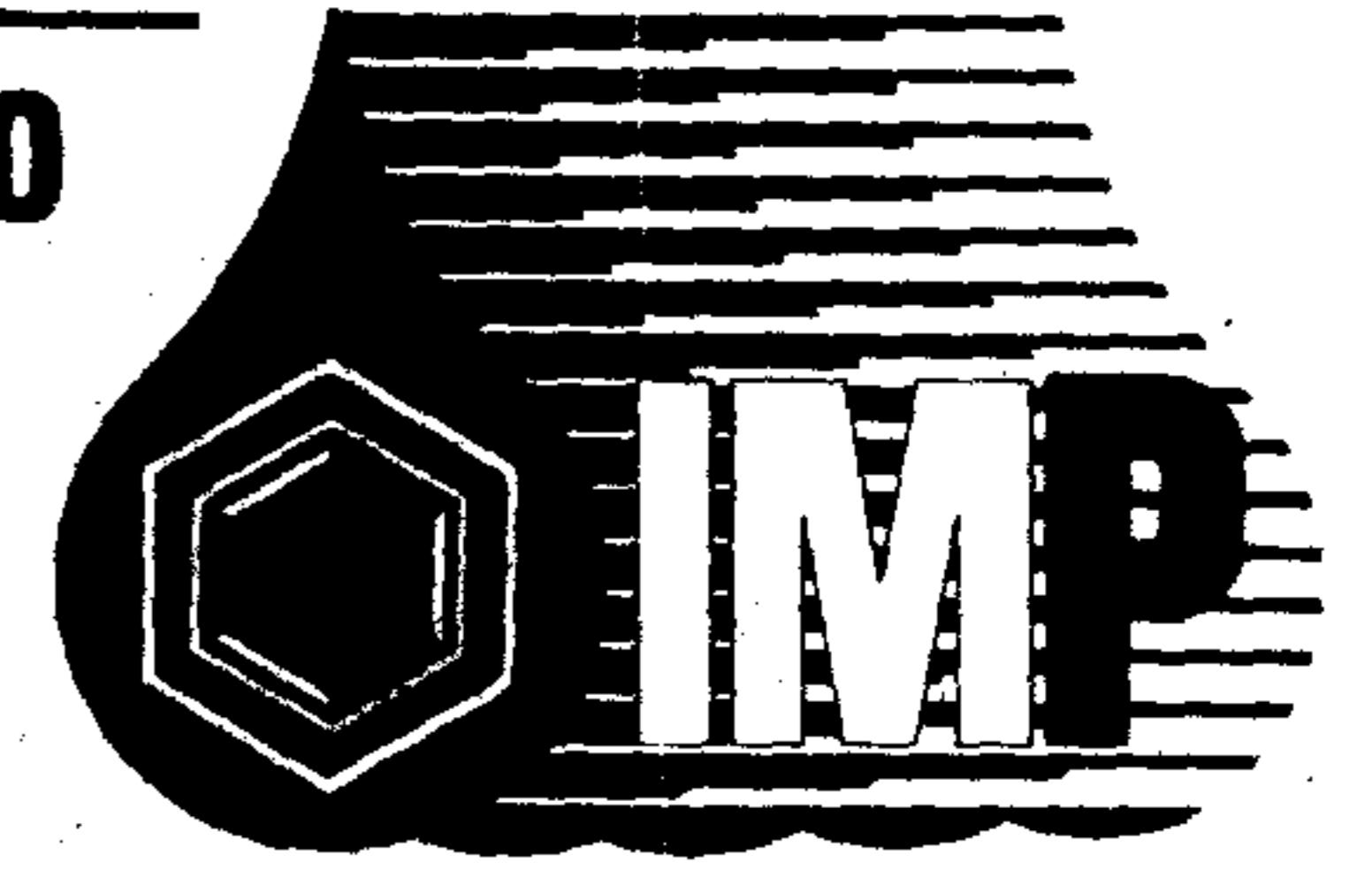
Que por medio del presente solicito se sirva tener por autorizado a los Ings. Guillermo Soto Carranza, Antonio Alberto Alcázar y Rodolfo Angeles Vázquez, para presentar y tramitar toda clase de solicitudes, recoger oficios y consultar los expedientes de solicitud de patente del IMP, en los archivos de ese Instituto. Lo anterior de conformidad con el Artículo 186 los Artículos 13 Fracción 4º. y 16, Fracción 5º. del Reglamento de la Ley de la Propiedad Industrial.

Acepto la autorización:

ING. GUILLERMO SOTO CARRANZA

ING. ALTONIO ALBERTO ALCAZAR

ING. RODOLFO ANGELES VÁZQUEZ



Por lo antes expuesto, atentamente pido se sirva:

UNICO: Tenerme por presentado en los términos de este escrito, autorizando a las Personas mencionadas en el cuerpo del presente, para que los mismos puedan consultar los expedientes de solicitud de patente del Instituto Mexicano del Petróleo.

Protesto lo necesario

MTRO. ROBERTO RODRÍGUEZ VÉLEZ
Apoderado Legal.

-Anexo: Fotocopia de la Solicitud de Inscripción bajo el número de folio 07941.

*gca.

DIRECCION DE PATENTES
SUBDIRECCION DE EXAMEN DE FONDO DE PATENTES
DEPARTAMENTO DE EXAMEN DE FONDO AREA QUIMICA
EXAMINADOR: MOR

R E S U M E N

No. DE EXPEDIENTE: 9303937 De PATENTE

PROCESO PARA RECUBRIR MONOLITOS CERAMICOS Y
PRODUCTO RESULTANTE

La presente invención se refiere a un procedimiento para recubrir monolitos cerámicos cuya etapa inicial consiste en la preparación de un gel de alúmina, vía la reacción entre cloruro de aluminio e hidróxido de amonio, bajo condiciones específicas de reacción que determinen área superficial, volumen y distribución de poros y densidad finales de recubrimiento, caracterizado por las siguientes etapas: 1) preparar un gel de alúmina constituido por hidróxido de amonio (en donde el cloruro de aluminio se prepara poniendo en contacto alúmina y ácido clorhídrico en una relación cercana a la estequiométrica; 2) preparar un gel ácido y tratando el hidróxido de aluminio obtenido en la etapa 1 con un ácido orgánico de cadena corta preferentemente ácido acético, en un medio acuoso; 3) preparar una suspensión para recubrimiento, incorporando el gel ácido obtenido en la etapa 2 a una mezcla constituida por; a) una alúmina de transición; b) una sal de un metal alcalinotérreo; c) un material surfactante, preferentemente nonoil fenol etoxilado y d) un mineral de tipo arcilloso del grupo de las monimorrillonitas; 4) acondicionar los monolitos cerámicos que van a ser recubiertos con la suspensión preparada según la etapa 3, mediante un tratamiento ácido que se efectúa por separado; 5) recubrir los monolitos cerámicos previamente acondicionados como se menciona en la etapa 4, con una solución de un alcohol polimérico insaturado; 6) recubrir los monolitos cerámicos tratados en las etapas 4 y 5 según se describe, sumergiéndolos en la suspensión de recubrimiento y sometiéndolos posteriormente a tratamiento térmico de secado y calcinación.

(12) Tipo de documento: Solicitudes

(22) Fecha de Presentación:
19/diciembre/1996

(73) Solicitante:
FUKUYO-ICHIMURA

(30) Prioridad:

(72) Inventor(es):
SHOJI ICHIMURA

(45) Fecha de Publicación:
31/junio/1998

(74) Agente(s):
JAIME DELGADO R Paseo de la Reforma 355 - 2 Piso Cuauhtémoc Cuauhtémoc
06500 D.F.

(54) Título:

CATALIZADORES DE CERAMICA PARA REFORMAR EL FLUIDO COMBUSTIBLE Y SUS METODOS DE FABRICACION.

NO ✓

(57) Resumen :

Un catalizador de cerámica reformante de combustible líquido comprendiendo un núcleo 2 hecho de una cerámica de óxido de cerámica de metales de transición, una capa intermedia 3 de una hecha de una cerámica de silicato basada en alumi na cubriendo el núcleo 2 y una capa exterior 4 hecha de una cerámica conteniend o metales nobles preparada para formar el núcleo por quemado u horneado de la ce rámica de óxido complejo de metal de transición, poniendo la capa intermedia de la cerámica de silicato basada en alumina como recubrimiento del núcleo y pon ie ndo la capa exterior de cerámica conteniendo metales nobles como cubierta de la capa intermedia, lo cual aumenta el número de octanos del combustible, mejora su eficiencia de combustión u decrece las sustancias perjudiciales en los gases d e salida.

(12) Tipo de documento: Patente

(22) Fecha de Presentación:
14/junio/1983

(73) Titular:
EUTECTIC CORPORATION

(30) Prioridad:
US 388263 1982/06/14

(72) Inventor(es):
BURTON A. KUSHNER

(45) Fecha de Concesión:
24/agosto/1989

(74) Agente(s):

(54) Título:

MEJORAS EN METODO PARA RECUBRIR UN SUBSTRATO DE METAL CON UN POLVO CERAMICO ADHERENTE ATOMIZADO A LA FLAMA

NO

(57) Resumen :

La presente invencion se refiere a mejoras en metodo para recubrir un subs trato de metal con un polvo ceramico adherente atomizado a la flama, que compren de los pasos de: atomizar a la flama un recubrimiento de aleacion adherente sob re el substrato, caracterizadas porque comprende: atomizar la flama sobre el rec ubrimiento adherente una composicion de ceramica que consiste esenc ialmente por peso de aproximadamente 10 a 50 de alumina y lo restante esencialmente zirconia .

~~US 3243769~~

~~SU 1023072~~

~~EP 0209556~~

~~EP 005147~~

CA 1059159 - US 3885977

~~US 5410204~~

US 5187142 ✓

(10) MX 185898
A

(21) Número de Solicitud: 9301182
(51) Int. CL. 5a: B01J-023/072

(12) Tipo de documento: Patente

(22) Fecha de Presentación:
03/marzo/1993

(30) Prioridad:

(73) Titular:
INSTITUTO MEXICANO DEL PETROLEO

(72) Inventor(es):
LUIS E. MIRAMONTES CARDENAS
SALVADOR CASTILLO CERVANTES
FLORENCIA MARINA MORAN PINEDA

(45) Fecha de Concesión:
09/septiembre/1997

(74) Agente(s):
ENRIQUE A. MARTINEZ-CAÑEDO.

(54) Título:

**PROCEDIMIENTO PARA LA PREPARACION DE
MONOLITOS CERAMICOS CATALITICAMENTE ACTIVOS,
PARA LA REDUCCION DE CONTAMINANTES
PROVENIENTES DE MOTORES A GASOLINA CON PLOMO
Y PRODUCTO RESULTANTE**

(57) Resumen :

La presente invención se refiere a un procedimiento para la preparación de monolitos cerámicos catalíticamente activos, para la reducción de contaminantes provenientes de motores a gasolina con plomo tetraetilo que comprende los pasos de impregnar un monolito cerámico tipo panel revestido con gamma alúmina, con una solución de óxidos y sales de metales y posteriormente someter a un tratamiento térmico el monolito impregnado, caracterizado porque la impregnación se lleva a cabo empleando una solución acuosa que contiene cromo, cobre y níquel.

(10) MX 168257
A

(21) Número de Solicitud: 0002188
(51) Int. CL. 5a: F01N-003/024
B01D-046/000

(12) Tipo de documento: Patente

(22) Fecha de Presentación:
16/abril/1986

(30) Prioridad:
US 723984 1985/04/16

(45) Fecha de Concesión:
mayo/1993

(73) Titular:
KENNECOTT CORPORATION

(72) Inventor(es):
JOHN D. TENEYCK

(74) Agente(s):

(54) Título:

**MONTAJE DE UN CONVERTIDOR CATALITICO
MONOLITICO**

(57) Resumen :

La presente invención se refiere a montaje de un convertidor catalítico monolítico caracterizado por un dispositivo para tratamiento de gases de escape procedentes de un motor de combustión interna, que comprende: a) un alojamiento que tiene una entrada en un extremo y una salida en su otro extremo opuesto, a través del cual circulan los gases de escape; b) un monolito de cerámica frangible montado elásticamente dentro de dicho alojamiento, teniendo dicho monolito una superficie exterior y una cara extrema de entrada en un extremo, en comunicación con dicha entrada del citado alojamiento y una cara extrema de salida en su extremo opuesto, en comunicación con dicha salida del mencionado alojamiento; c) una capa de fibras cerámicas en contacto con al menos una parte de dicha superficie exterior del mencionado monolito y que la recubre; y d) una capa intumescente dispuesta entre dicho alojamiento y dicha capa de fibras cerámicas.

(10) MX A

(21) Número de Solicitud: 9303937
(51) Int. CL. 5a: C04B-035/010

(12) Tipo de documento: Solicitudes

(22) Fecha de Presentación:
30/junio/1993

(30) Prioridad:

(45) Fecha de Publicación:
31/diciembre/1994

(73) Solicitante:
INSTITUTO MEXICANO DEL PETROLEO

(72) Inventor(es):
LUIS E. MIRAMONTES CARDENAS

AGUSTIN VARGAS APANGO

ANA DE LOS ANGELES SERRANO MAGAÑA

(74) Agente(s):
JULIO BRENA TORRES Lázaro Cardenas No. 152 San Bartolo Atepehuac
Gustavo A. Madero 07730 D.F.

(54) Título:

PROCESO PARA RECUBRIR MONOLITOS CERAMICOS Y PRODUCTO RESULTANTE.

(57) Resumen :

La presente invención está relacionada con un novedoso para recubrir monolitos cerámicos y el producto resultante del proceso. Los monolitos cerámicos están generalmente constituidos por un mineral llamado cordierita y el recubrimiento se realiza mediante una técnica particular en la cual la materia prima principal es alúmina, preferiblemente gamma alúmina. El producto de este proceso, sirve para que en su superficie depositen metales de los grupos IB, VIB y VIIB de la Tabla periódica y los monolitos así impregnados se emplean como parte constitutiva de convertidores catalíticos para la oxidación y reducción simultánea de los contaminantes que contienen los gases de escape de motores a gasolina con plomo.

(10) MX A

(21) Número de Solicitud: 9301182

(51) Int. CL. 5a: B01J-029/006

(12) Tipo de documento: Solicitudes

(22) Fecha de Presentación:
03/marzo/1993

(30) Prioridad:

(45) Fecha de Publicación:
31/septiembre/1994

(73) Solicitante:
INSTITUTO MEXICANO DE PETROLEO

(72) Inventor(es):
LUIS E. MIRAMONTES CARDENAS

SALVADOR CASTILLO CERVANTES

FLORENCIA MARINA MORAN PINEDA

(74) Agente(s):
JULIO BRENA TORRES Lázaro Cardenas No. 152 San Bartolo Atepehuacan
Gustavo A. Madero 07730 D.F.

(54) Título:

PROCEDIMIENTO PARA LA PREPARACION DE MONOLITOS CERAMICOS CATALITICAMENTE ACTIVOS, PARA LA REDUCCION DE CONTAMINANTES PROVENIENTES DE MOTORES A GASOLINA CON PLOMO Y PRODUCTO RESULTANTE.

(57) Resumen :

La presente invención está relacionada con un procedimiento para la preparación de monolitos cerámicos catalíticamente activos, tipo panel, recubiertos con gamma alúmina en la cual se depositan metales de transición de los grupos IB, VIB y VIIB, de la tabla periódica, para ser utilizados en la oxidación y reducción simultánea de los contaminantes contenidos en los gases de escape de motores a gasolina con plomo tetrátilo y el producto resultante de dicho procedimiento.

(10) MX 191890
A

(21) Número de Solicitud: 9404320

(51) Int. CL. 5a: B43K-024/008

B43K-007/002

(12) Tipo de documento: Patente

(22) Fecha de Presentación:
08/junio/1994

(30) Prioridad:
US 73726 1993/06/08

(45) Fecha de Concesión:
30/abril/1999

(73) Titular:
BIC CORPORATION

(72) Inventor(es):
RONALD S. RUKAN

BARRY W. CHADWICK

(74) Agente(s):
EDUARDO CORREA ESTRADA.

(54) Título:

TAPON VENTILADO PARA CARTUCHOS DE TINTA

(57) Resumen :

La presente invención se refiere a un cartucho para un instrumento de escritura retraíble, teniendo dicho instrumento de escritura una superficie de apoyo contra la cual se apoya dicho cartucho, comprendiendo el cartucho: a) un cuerpo o tubular alargado para contener la tinta, que tiene un extremo frontal que incluye medios para aplicar la tinta; y b) un miembro de tapón que tiene una porción de cuerpo cilíndrico formada de un material esencialmente plegable dispuesto por lo menos parcialmente en un extremo trasero de dicho cuerpo tubular, incluyendo dicho miembro de tapón: i) un rebajo axial que se extiende parcialmente hacia la porción de cuerpo cilíndrico desde un extremo trasero del mismo, una porción de pared circunferencial que define un canal helicoidal alrededor de dicha porción de cuerpo, y una trayectoria que se extiende radialmente dentro de la porción de cuerpo cilíndrico que comunica el canal helicoidal con el rebajo axial; e ii) medios formados en un monolito con dicha porción de cuerpo para acojinarse el miembro tubular contra la superficie de apoyo de dicho instrumento de escritura.

(10) MX 191880

A

(21) Número de Solicitud: 9404320

(51) Int. CL. 5a: B43K-024/008

B43K-007/002

(12) Tipo de documento: **Patente**

(22) Fecha de Presentación:
08/junio/1994

(30) Prioridad:
US 73726 1993/06/08

(45) Fecha de Concesión:
Abril/1999

(73) Titular:
BIC CORPORATION

(72) Inventor(es):
RONALD S. RUKAN

BARRY W. CHADWICK

(74) Agente(s):
EDUARDO CORREA ESTRADA.

(54) Título:

TAPON VENTILADO PARA CARTUCHOS DE TINTA

(57) Resumen :

La presente invención se refiere a un cartucho para un instrumento de escritura retraíble, teniendo dicho instrumento de escritura una superficie de apoyo contra la cual se apoya dicho cartucho, comprendiendo el cartucho: a) un cuerpo o tubular alargado para contener la tinta, que tiene un extremo frontal que incluye medios para aplicar la tinta; y b) un miembro de tapón que tiene una porción de cuerpo cilíndrico formada de un material esencialmente plegable dispuesto por lo menos parcialmente en un extremo trasero de dicho cuerpo tubular, incluyendo dicho miembro de tapón: i) un rebajo axial que se extiende parcialmente hacia la porción de cuerpo cilíndrico desde un extremo trasero del mismo, una porción de pared circunferencial que define un canal helicoidal alrededor de dicha porción de cuerpo, y una trayectoria que se extiende radialmente dentro de la porción de cuerpo cilíndrico que comunica el canal helicoidal con el rebajo axial; e ii) medios formados en un monolito con dicha porción de cuerpo para acojinarse el miembro tubular contra la superficie de apoyo de dicho instrumento de escritura.

(10) MX A

(21) Número de Solicitud: 9805896

(51) Int. CL. 5a: B01J-023/000

(12) Tipo de documento: **Solicitudes**

(22) Fecha de Presentación:
22/julio/1998

(30) Prioridad:
US589387, 1996/01/22

US97/00548, 1997/01/22

(45) Fecha de Publicación:
31/febrero/1999

(73) Solicitante:
REGENTS OF THE UNIVERSITY OF MINNESOTA

(72) Inventor(es):
CHIKAFUMI YOKOYAMA

SAMEER S. BHARADWAJ

LANNY D. SCHMIDT

(74) Agente(s):
BERNARDO GOMEZ VEGA Hamburgo No. 260 Juárez Cuauhtémoc 06600 D.F.

(54) Título:

PROCESO Y CATALIZADOR DE DESHIDROGENACION CATALITICA OXIDATIVA.

(57) Resumen :

Se describe un proceso para la producción de una monoolefina a partir de un hidrocarburo parafínico gaseoso que tiene por lo menos dos átomos de carbono, o mezclas de los mismos, que comprende hacer reaccionar los hidrocarburos y el oxígeno molecular en presencia de un catalizador de paladio. El catalizador consiste esencialmente de platino modificado con Sn o Cu y soportado en un monolito cerámico.

(12) Tipo de documento: **Patente**

(22) Fecha de Presentación:
23/marzo/1984

(30) Prioridad:
US 478218 1983/03/24

(45) Fecha de Concesión:
12/abril/1993

(73) Titular:
U.S.S. ENGINEERS AND CONSULTANTS, INC.

(72) Inventor(es):
PATRICK DANA KING

(74) Agente(s):

(54) Título: **UNA PLACA ESTACIONARIA PARA UNA VALVULA DE HORNO**

(57) Resumen :

La presente invención se refiere a una placa estacionaria para una válvula de horno, caracterizada porque comprende, en asociación, un bastidor, dicho bastidor teniendo porciones de soporte subyacentes y un interior modificado para recibir un vaciado monolítico, dichas porciones de soporte incluyendo un soporte de boquilla de pozo central y soportes que blanquean al soporte de boquilla de pozo que contiene aberturas comunicando con la porción interna del bastidor, dichas aberturas siendo efectivas para servir como aberturas de bebedero de molde para suministrar material refractario monolítico vaciable a la porción interna del bastidor y aberturas golpeables para remover dicho material refractario monolítico cuando se gastan, intertrabadores asociados con dichas aberturas para intertrabar el material monolítico dentro del bastidor, separadores para separar inserto refractario de un material refractario altamente resistente a la erosión en una porción central del bastidor, y una porción recortada sobre los insertos refractarios para acoplar trabadoramente un refractario monolítico, con lo cual puede formarse una placa estacionaria que tiene un orificio refractario altamente resistente a la erosión en una porción media, y un cuerpo secundario monolítico que permite la remanufactura removiendo el monolito y el orificio refractario resistente a la erosión.

PCT

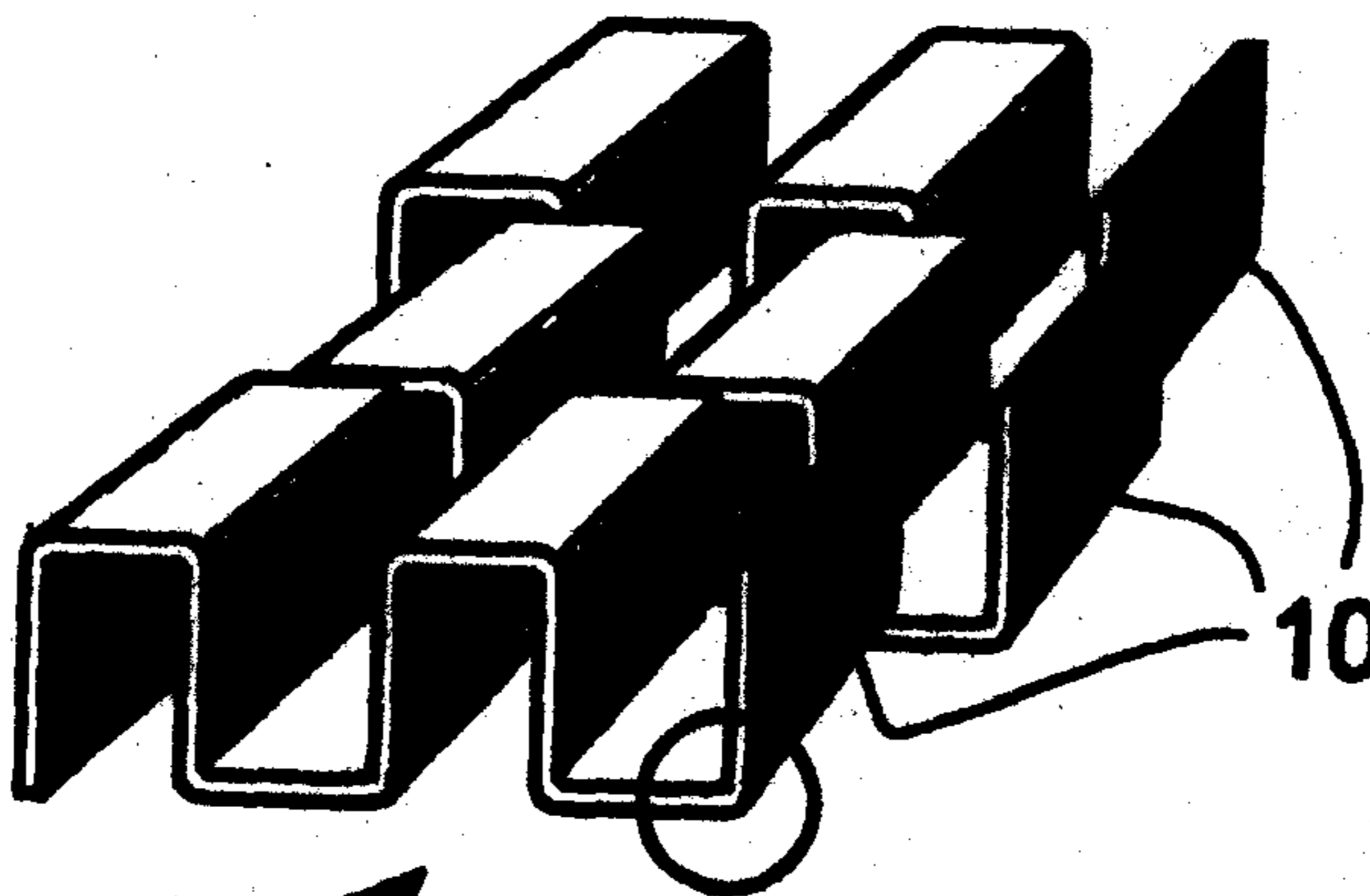
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : B01J 37/02, B01D 53/36</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/09903 (43) International Publication Date: 11 May 1994 (11.05.94)</p>
<p>(21) International Application Number: PCT/US93/10377 (22) International Filing Date: 28 October 1993 (28.10.93) (30) Priority data: 967,591 28 October 1992 (28.10.92) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245 (Law Department), Morristown, NJ 07962-2245 (US). (72) Inventors: LESTER, George, Ronald ; 209 Vine Street, 2A Park Ridge, IL 60068 (US). HOMEYER, Stephan, Thomas ; 10353 Dearlove Road, Apt. #2C, Glenview, IL 60025 (US).</p>	<p>(74) Agent: FUCHS, Gerhard, H.; Allied-Signal Inc., Law Department (C.A.McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>	

(54) Title: CATALYTIC CONVERTER WITH METAL MONOLITH HAVING AN INTEGRAL CATALYST



Air Flow

(57) Abstract

An improved catalytic converter which comprises a metal monolith made of aluminum or aluminum alloy having an anodized surface layer on which is disposed catalytic metals, particularly noble metals from Group VIII and optionally base metals. In a preferred embodiment the metal monolith employs plate fin elements defining a large plurality of fins arranged in an axial succession of offset fin rows. The catalytic converter has application in the conversion of ozone and the oxidation of atmospheric pollutants.

CLAIMS:

1. A monolithic catalytic converter comprising
 - (a) a unitary aluminum or aluminum alloy support providing torturous flow paths for gases between an inlet and an outlet end and having an integral anodized surface layer at least 2 μm thick, said support comprising one or more plate fin elements having a plurality of fins arranged in an axial succession of offset fin rows between said inlet end and said outlet end;
 - (b) one or more Group VIII noble metals and optionally base metals from Groups VIII, IIIa, and VIIa disposed on and within said anodized surface layer of (a).
2. The monolithic catalytic converter of Claim 1 wherein said integral surface layer is at least 10 μm thick and has a surface area of 30 to 150 m^2/g .
3. The catalytic converter of Claim 1 wherein said anodized surface layer was formed by passing a direct current through said aluminum or aluminum alloy support as an anode in an electrolytic bath.
4. The catalytic converter of Claim 3 wherein said electrolytic bath was 5-20 wt.% aqueous sulfuric acid, said direct current provides about 9 amps/ft^2 (96.9 amps/m^2) and said direct current is provided at about 8 to 15 volts.
5. A method of destroying ozone in air comprising passing said ozone-containing air over the catalyst of Claim 1.
6. The method of Claim 5 wherein said catalyst comprises palladium as the Group VIII metal and nickel as the base metal.
7. The method of Claim 6 wherein the loading of palladium is 0.88 to 2.65 g/L of said monolith and the loading of nickel is 7.06 to 14.1 g/L of said monolith.



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 605 142 A1**

⑫

EUROPEAN PATENT APPLICATION

⑪ Application number: **93310114.9**

⑪ Int. Cl.⁵: **B01J 23/02, B01J 23/04,
B01J 27/18, B01J 37/02,
C08G 77/08**

⑫ Date of filing: **15.12.93**

⑬ Priority: **31.12.92 GB 9227152**

⑰ Applicant: **DOW CORNING LIMITED
Cardiff Road
Barry
South Glamorgan CF63 2YL Wales(GB)**

⑭ Date of publication of application:
06.07.94 Bulletin 94/27

⑱ Inventor: **Kolaczowski, Stanislaw T.
Park House,
Park Gardens
Bath(GB)**
Inventor: **Serbetcioğlu, Serpil
6 Marlborough Buildings
Bath(GB)**
Inventor: **Perera, Semail
9 Pines Way,
Radstock
Bath(GB)**

⑮ Designated Contracting States:
DE FR GB

⑲ Representative: **Vandamme, Luc Johan Roger
Dow Corning Limited
Cardiff Road
Barry South Glamorgan CF6 7YL Wales (GB)**

⑳ **Process for coating a ceramic monolith support with a catalyst.**

㉑ A process of coating or loading a ceramic monolithic catalyst support with a heterogeneous water soluble catalyst comprises making a slurry of the catalyst in a mixture of from 2 to 50% by weight of water and from 98 to 50% of a liquid organic carrier, applying the slurry onto the surface of the monolithic catalyst support and allowing the slurry to dry by evaporation of the mixture of water and liquid organic carrier.

EP 0 605 142 A1

The appearance and adhesion of the catalyst to the monolithic support was visually inspected. It was found that all the Example coatings (1 to 11) had good adhesion to the walls of the monolith tube and gave a fairly uniform slightly rough coating. All the comparative examples (C1-C6) had major flaws in the coating and peeled away from the walls.

5

Claims

1. A process of loading a ceramic monolithic catalyst support with a heterogeneous water soluble catalyst which comprises making a slurry of the catalyst, applying the slurry onto the surface of the monolithic catalyst support and allowing the slurry to dry, characterised in that the slurry is prepared by mixing the catalyst with a mixture of from 2 to 50% by weight of water and from 98 to 50% of a liquid organic carrier.
10
2. A process according to Claim 1 further characterised in that the slurry consist of 30 to 50% by weight of the catalyst and 50 to 70% by weight of the mixture of water and the liquid organic carrier.
15
3. A process according to Claim 1 or Claim 2 further characterised in that the liquid organic carrier consists of one or more of an organic hydrocarbon, alcohol, aldehyde, ether or ketone which carrier has a boiling point at standard atmospheric pressure (1000 mbar) of no more than 150 °C.
20
4. A process according to any one of the preceding claims further characterised in that the catalyst is insoluble in the liquid organic carrier.
5. A process according to any one of the preceding claims further characterised in that the mixture of water and the liquid organic carrier contains from 5 to 20% by weight of water.
25
6. A process according to any one of the preceding claims further characterised in that the liquid organic carrier is a lower alkanol having less than 6 carbon atoms.
- 30 7. A process according to any one of the preceding claims further characterised in that the slurry has the consistency of a paste at the temperature and conditions of loading the ceramic monolithic catalyst support.
- 35 8. A process according to any one of the preceding claims further characterised in that the slurry is applied to the surface of the monolithic catalyst support by dip coating, flow coating, brushing or spraying.
- 40 9. A process according to any one of the preceding claims further characterised in that drying of the slurry is effected by the evaporation of the mixture of water and the liquid organic carrier through exposure of the coated support to heat or to a gas flow.
- 45 10. A process according to any one of the preceding claims further characterised in that drying the slurry is effected by allowing the majority of the mixture of water and the liquid organic carrier to evaporate at relatively lower temperatures, followed by heating the coated monolith at higher temperatures.
50
55



US005534475A

United States Patent [19]

[11] Patent Number: 5,534,475

Miramontes Cardenas et al.

[45] Date of Patent: Jul. 9, 1996

[54] CATALYTICALLY ACTIVE CERAMIC MONOLITHS FOR THE REDUCTION OF LEADED GASOLINE FUELED ENGINE POLLUTANTS AND THE PRODUCTION THEREOF

[75] Inventors: Luis E. Miramontes Cardenas; Salvador Castillo Cervantes; Florencia M. Moran Pineda, all of Mexico City, Mexico

[73] Assignee: Instituto Mexicano Del Petroleo, Mexico

[21] Appl. No.: 204,567

[22] Filed: Mar. 2, 1994

[51] Int. Cl.⁶ B01J 21/04; B01J 23/10; B01J 23/26; B01J 23/72

[52] U.S. Cl. 502/304; 502/314; 502/315; 502/318; 502/370; 502/323; 502/331; 502/337; 502/346; 502/439; 502/527; 423/213.2; 423/213.5

[58] Field of Search 502/315, 318, 502/320, 337, 346, 314, 323, 331, 439, 527; 423/213.2, 213.5

[56] References Cited

U.S. PATENT DOCUMENTS

3,993,572	11/1976	Hindin et al.	502/302
4,199,477	4/1980	Hegedus .	
4,208,454	6/1980	Reed et al. .	
4,539,311	9/1985	Harrison et al.	502/304
4,960,574	10/1990	Bricker .	
5,106,802	4/1992	Horiuchi et al.	502/302
5,242,883	9/1993	Ichikawa et al.	502/439

FOREIGN PATENT DOCUMENTS

62-241552	10/1987	Japan .
62-266142	11/1987	Japan .
63-107751	5/1988	Japan .

OTHER PUBLICATIONS

Thomas, W. John "The Catalytic Monolith." *Chemistry and Ind. (Lond)*, N. 9 315-319 (May 4, 1987).
 "Cell Design for Ceramic Monoliths for Catalytic Converter Application", Gulati, SAE Int. Fuel Lubr. Meet. (Portland, OR Oct. 10-13, 1988 Pap. No. 881685 9P). (1988).
 Centi et al. "Role of the Nature of Copper Sites in the Activity of Copper-Based Catalysts for No Conversion." *Research on Chemical Intermediates*, vol. 17, (1992) pp. 125-135.
 Fu et al. "A Low-Temperature IR Spectroscopic Study of Selective Adsorption of NO and CO on CuO γ -Al₂O₃." *Journal of Catalysis*, vol. 132, (1991) pp. 84-91.
 Nunan et al. "Physicochemical Properties of Co-Containing Three-Way Catalysts and the Effect of Ce on Catalyst Activity." *Journal of Catalysis*, vol. 133, (1992) pp. 308-325.
 Larson et al. "The Effect of the Chemical Nature of the Wash-Coat on the Catalytic Performance of CO Oxidation Catalysts of Monolith Type." *Catalysts and Automotive Pollution Control*, (1987), pp. 332-343.
 Kubush et al. "High-Temperature Substrates and Washcoats for Auto Exhaust Emission Control." *Society of Automotive Engineers, Inc.*, (1987), pp. 1-11.
 Irandoust et al. "Monolithic Catalysts for Nonautomobile Applications." *Catal. Rev.-Sci. Eng.*, vol. 30(3), (1988), pp. 341-392.
 Williamson et al. "Performance of Copper Base Metal Catalysts in Stoichiometric Automotive Exhausts." *SAE Int. Fuel Lubr. Meet. (Toronto Nov. 2-5, 1987) PAP.* (ISSN 0148-7191) No. 872132 12, pp. 14.

Primary Examiner—Anthony McFarlane
Attorney, Agent, or Firm—Roylance, Abrams, Berdo & Goodman

[57] ABSTRACT

Catalytically active ceramic monoliths coated with gamma alumina and impregnated with chromium, copper and nickel are used in catalytic converters for reduction of pollutants resulting from exhaust gases produced by internal combustion engines fueled with leaded gasoline.

17 Claims, No Drawings

MX 170409A (NO)

0108SZ

MX 302SE

5

(CO) and nitrogen oxides (NO_x) is passed through the catalytic converter at temperatures from 300° to 500°. Reaction takes place with a conversion to carbon dioxide (CO₂), nitrogen (N₂) and water in the range of 40 to 60% without significant loss of catalyst due to the entrainment in the system. The average conversion of contaminants at the operating conditions in the converter is shown in Table 3.

TABLE 3

Temperature (°C.)	Average Percent Conversion		
	HC	CO	NO _x
300	35	49	3
400	40	60	9
500	38	52	15

Although the invention has been described with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example and that numerous changes in the details of construction and the combination and arrangement of parts may be resorted to without departing from the spirit and scope of the invention. Thus, the scope of the invention should not be limited by the foregoing specification.

What is claimed is:

1. A process for the preparation of catalytically active ceramic monoliths for the reduction of pollutants derived from leaded gasoline fueled engines comprising the steps of impregnating a gamma alumina-cerium oxide base-coated honeycomb ceramic monolith with an aqueous solution comprising chromium, copper and nickel and subsequently heating the impregnated monolith.

2. The process of claim 1, wherein said honeycomb ceramic monolith coated with gamma alumina is heated to a temperature between about 70° and about 110° C. prior to impregnation.

3. The process of claim 1, wherein said impregnation solution is an aqueous solution having a chromium concentration between about 2 and about 6 weight percent; a copper concentration between about 1 and about 3 weight percent, and a nickel concentration between about 0.5 and about 2 weight percent.

4. The process of claim 1, wherein the impregnated catalyst is subjected to thermal treatment including a drying step and a calcining step.

5. The process of claim 4, wherein said drying step is carried out at a temperature between about 70° and about 110° C., for a period from about 2 to about 6 hours.

6. The process of claim 5, wherein said calcination step is

6

carried out at a temperature in the range of from about 200° to about 600° C. for a period from about 2 to about 6 hours.

7. A catalyst for conversion of exhaust gas pollutants comprising a gamma alumina-cerium oxide base-coated honeycomb ceramic monolithic substrate in which said gamma alumina is impregnated with chromium, copper and nickel.

8. The catalyst of claim 7, wherein said substrate contains from about 2 to about 5 weight percent chromium, from about 1 to about 3 weight percent copper, and from about 0.5 to about 2 weight percent nickel.

9. The catalyst of claim 8, wherein said substrate contains from about 3 to about 5 weight percent chromium, and from about 1 to about 2 weight percent nickel.

10. The catalyst of claim 8, wherein said gamma alumina base comprises cerium oxide.

11. The catalyst of claim 9, wherein said gamma alumina base comprises cerium oxide.

12. The catalyst of claim 7, wherein said cerium oxide is present in the amount of from about 1 to about 10 weight percent.

13. The catalyst of claim 12, wherein said cerium oxide is present in the amount of from about 2 to about 5 weight percent.

14. A catalyst for conversion of exhaust gas pollutants derived from lead gasoline fueled engines consisting essentially of a gamma alumina-cerium oxide base-coated honeycomb ceramic monolithic substrate impregnated with chromium, copper and nickel.

15. The catalyst prepared by the process of claim 1.

16. The process for the preparation of catalytically active ceramic monoliths for the reduction of pollutants resulting from leaded gasoline fueled engines comprising the steps of providing a gamma alumina base-coated honeycomb ceramic monolith;

impregnating said gamma alumina base-coated honeycomb ceramic monolith with an aqueous solution comprising an aqueous salt solution of chromium, copper and nickel salts;

drying said impregnated monolith at a temperature of about 70° to about 100° C.; and

calcining said dried impregnated monolith at a temperature of from about 200° to about 600° C.

17. The process of claim 16, wherein said gamma alumina base comprises cerium oxide.

* * * * *

United States Patent [19]

Pereira et al.

[11] Patent Number: 4,771,029

[45] Date of Patent: Sep. 13, 1988

[54] MONOLITH WASHCOAT HAVING OPTIMUM PORE STRUCTURE AND OPTIMUM METHOD OF DESIGNING THE WASHCOAT

[75] Inventors: Carmo J. Pereira; Joseph E. Kubak, both of Silver Spring; Louis Hegedus, Rockville, all of Md.

[73] Assignee: W. R. Grace & Co.-Conn, New York, N.Y.

[21] Appl. No.: 52,103

[22] Filed: May 18, 1987

[51] Int. Cl.⁴ B01J 21/04; B01J 32/00

[52] U.S. Cl. 502/355; 502/439; 423/213.5

[58] Field of Search 502/439, 355; 423/213.5

[56] References Cited

U.S. PATENT DOCUMENTS

3,907,512 9/1975 Ziegenhain et al. 23/293 A
4,119,571 10/1978 Hegedus et al. 252/466 PT
4,154,812 5/1979 Sanchez et al. 423/626
4,529,718 7/1985 Dupin 502/439
4,587,231 5/1986 Sawamura et al. 502/304
4,624,940 11/1986 Wan et al. 502/303 X

FOREIGN PATENT DOCUMENTS

0119715 9/1984 European Pat. Off. .

OTHER PUBLICATIONS

Se H. Oh et al., "Design Aspects of Poison-Resistant Automobile Monolithic Catalysts", Ind. Eng. Chem. Prod. Res. Dev., vol. 22, No. 4, pp. 509-518, 1983.
L. L. Hegedus, Ind. Eng. Chem. Prod. Res. Dev., 19, 553, 1980.

Primary Examiner—W. J. Shine
Attorney, Agent, or Firm—Edward J. Cabic

[57]

ABSTRACT

An optimum washcoated ceramic monolith for treating automotive exhaust gases is made by

- (a) specifying the reactants, process conditions and desired time on stream;
- (b) determining from the parameters in step (a) the pore size distribution and thickness of the washcoat to produce the desired auto exhaust conversion;
- (c) preparing a washcoat catalyst with an alumina having the desired pore size distribution; and
- (d) applying the prepared washcoat catalyst to a ceramic or metal monolith to produce a finished automotive exhaust gas catalyst. Following this process the optimized washcoated catalyst can then be used to treat automotive exhaust gases.

4 Claims, 2 Drawing Sheets

What is claimed is:

1. An optimum washcoated monolith catalyst for treating automotive exhaust gases where the monolith is either ceramic or metal comprising a washcoat having a thickness in the range of 30-80 microns, a total pore volume in the range of 0.60-1.80 cm³/g washcoat, a micropore volume in the range of 0.35-0.60 cm³/g washcoat, a micropore radius below 60 Angstrom units, and a surface area between 125-250 m²/g washcoat.

2. A washcoated monolith catalyst according to claim 1 wherein the micropore radius is above 30 Angstrom units.

3. A washcoated monolith catalyst according to claim 1, having optimum thickness between lines A and B in FIG. 2 depending on the desired service length of the converter where lines A and B are based on the following data points

Service Length Optimal Washcoat Thickness (accumulated miles) (microns)
50,000 40-50
100,000 70-80

4. Process for making a washcoated ceramic or metal monolith for treating automotive exhaust gases comprising the steps: (a) specifying (i) the reactant of CO, HC and NO_x and poisons so that the effective diffusion coefficient and mass transfer coefficients can be determined, (ii) the process conditions including the volumetric flow rate, the temperature, and concentration of poisons, and (iii) desired time on stream in terms of desired catalyst life in hours; (b) determining from the parameters in step (a) the optimum pore size distribution and thickness of the washcoat to maximize alpha in the equation $\alpha = \frac{1}{1 + \frac{C_{p,g}}{C_{p,inf}} \left(\frac{4x}{b} \right) \left(\frac{Q}{4R} \right) \left(\frac{w}{a} \right) \left(\frac{1}{k_{m,p}} \right) \left(\frac{1}{D_{e,p}} \right) \left(\frac{1}{y} \right)}$ where y is obtained from the following equations $y = \frac{1}{1 + \frac{C_{p,g}}{C_{p,inf}} \left(\frac{4x}{b} \right) \left(\frac{Q}{4R} \right) \left(\frac{w}{a} \right) \left(\frac{1}{k_{m,p}} \right) \left(\frac{1}{D_{e,p}} \right) \left(\frac{1}{y} \right)}$ where C_{p,g} is the gas phase poison concentration, x is the axial distance down the monolith, t is the time of operation of the catalyst, k_{m,p} is the mass transfer coefficient for the poison, D_{e,p} is the effective diffusion coefficient of the poison into the washcoat layer, y is the thickness of the poisoned layer within the washcoat, b is the size of the cross-section of the square honeycomb, w is the washcoat thickness, C_{p,inf} is the saturation concentration of the poison on the support, Q is the volumetric flow rate of the inlet gas at reaction conditions, R is the radius of the monolith catalyst, and a is the thickness of the walls separating the channels; (c) preparing a washcoat catalyst with an alumina washcoat having the desired pore size distribution; and (d) applying the prepared alumina washcoat catalyst to the ceramic or metal monolith to produce a finished automotive exhaust gas catalyst where the washcoat on the catalyst has a thickness in the range of 30-80 microns, a total pore volume in the range of 0.60-1.80 cm³/g washcoat, a micropore volume in the range of 0.35-0.60 cm³/g washcoat, a micropore radius below 60 Angstrom units, and a surface area between 125-250 m²/g washcoat.

[54] METHOD FOR COATING CATALYST SUPPORTS

[75] Inventors: James R. Reed; Terrance Way; Richard A. Leal, all of Flint, Mich.

[73] Assignee: General Motors Corporation, Detroit, Mich.

[21] Appl. No.: 870,613

[22] Filed: Jan. 19, 1978

[51] Int. Cl.² B05D 7/22

[52] U.S. Cl. 427/238; 118/50; 427/243; 427/443.2

[58] Field of Search 427/243, 294, 238, 350, 427/430 B; 118/50, 50.1; 252/466 PT, 477 R

[56] References Cited

U.S. PATENT DOCUMENTS

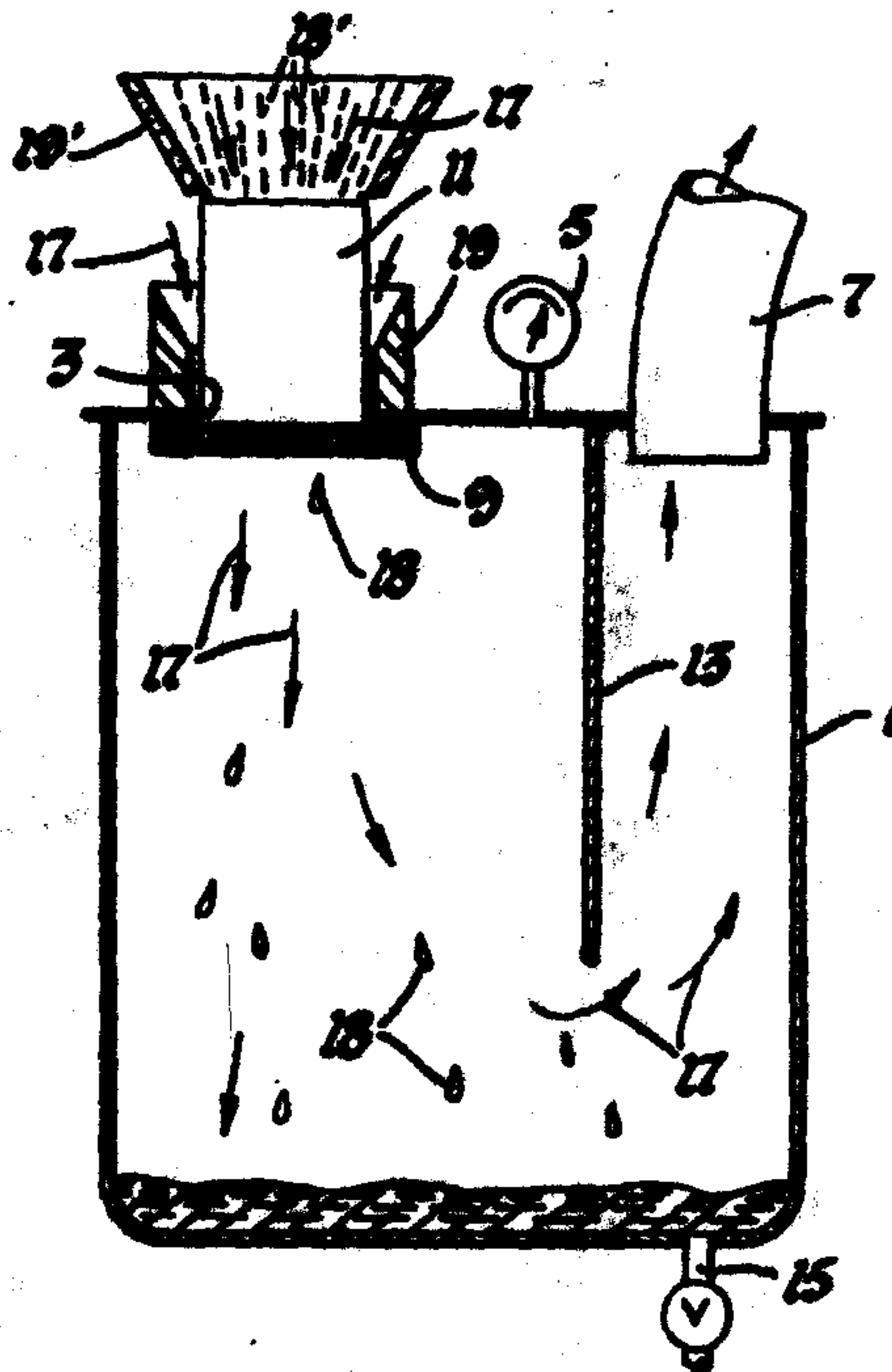
2,612,443	9/1952	Goetzel et al.	118/50 X
2,867,544	1/1959	Hall, Jr.	427/294 X
3,022,187	2/1962	Eyraud et al.	118/50
3,948,213	4/1976	Hoyer et al.	118/50

Primary Examiner—Evan K. Lawrence
Attorney, Agent, or Firm—Sidney Carter

[57] ABSTRACT

A method for controlling the coating with alumina of ceramic monolithic catalyst supports on a production basis to achieve repeatability of coating utilizing a vacuum system to distribute a coating slurry of alumina over the interior surfaces of and purge the excess coating slurry from the support at the same time that plugged tubular passageways through the support are unplugged, comprising the steps of applying the coating slurry to the support which has at least about 100 axially aligned tubular passageways to the square inch and subjecting the support to a vacuum to draw the slurry through the passageways and remove plugging and excess slurry to form a coating of alumina on the passageway surfaces. The support is dried and calcined to fix the alumina coating on the passageway surfaces.

5 Claims, 3 Drawing Figures



plugging of passageways though even more than half of the tubular channels in the support are unplugged. We have also found it to be advantageous after the support has been purged from one end, to invert the support and continue the purge from the opposite end. This has been found to improve the uniformity of coating distribution on the passageway walls.

Having reference to FIG. 2, there is shown a perspective view of a production line of the preferred type for coating monolith supports in accordance with our invention. In this embodiment, the monolith supports 20 are shown being passed along a linear conveyor system through a series of stations to the point where the coated monolith support is packed in bins for either subsequent assembly in a catalytic converter or for impregnation with the catalytically active materials where co-impregnation with the high surface area alumina slurry was not accomplished.

More particularly, the monolith supports 20 from the extruding and calcining operations are loaded onto a conveyor for movement to a weigh station 22 where the initial weight of each support is taken and recorded for the purpose of coating control, each part being marked for identification. The support then moves to the coating and purging station 24 where the support is positioned, by any suitable means such as a movable clamp or calipers which comes in to grip the part and move it into the desired position, in vertical alignment between a charge tube connected to a slurry tank 26 above the top end of support 20 and the inlet 3 to the purge tank 1 below the bottom end of the support. The clamp holding the support then cooperates with a conduit connected to inlet 3 to enable the establishment of either a sealed or an open supporting connection between the conduit and the bottom end of the monolith support. Where a sealed connection is desired, it is established preferably about the outer peripheral surface or edge of the support 20 using a resilient sealing ring to minimize breaking stress. Alternatively, but not preferred, the seal may be established on the end surface of the support radially inward from but closely adjacent to the periphery, the outermost passageways being blocked. A preferred form of construction of such sealing mechanism is shown in FIG. 3 and is described in greater detail hereinafter. A similar sealing arrangement is provided at the top end of the monolith support with the feed tube from the slurry tank 26.

The coating and purging operation comprises releasing a measured amount, approximately one liter for the cylindrical parts previously described, of, preferably, catalyzed slurry from tank 26 into a tube having a sealed connection with the top end of the monolith support as previously described. The tank 26 is then closed off from the tube which is open to atmosphere at a point above the surface of the charge of coating slurry and the monolith support is subjected to the subatmospheric pressure in tank 1 by the opening of dampers or valves in the conduit 7, or at any other suitable position in the air flow stream, such as at the inlet 3. The vacuum pressure is then effective on the monolith to draw the slurry through the passageways of the support. As a preferred example, we have found that a total of at least about 30 seconds is sufficient time to remove the excess slurry and coat uniformly and repeatably the monoliths previously described when using a centrifugal blower giving a static pressure of about 6 inches of water as described.

It should be understood that the various actions into and within the coating and purging station 24 are timed and sequenced as desired. By way of example, it is preferred that the monolith support be subjected to the subatmospheric pressure in tank 1 a short time, less than about one second, prior to the release of slurry to the support in order that any leakage between the seal at the upper end of the support 20 be of air into the support passageways to prevent loss of slurry to the outer surface of the support. Also, the sequencing may be timed to break the seal at the upper end of the support 20 after drawing the coating slurry charge, this coating taking a period of about 5 seconds out of a total of 15 seconds in the preferred example given, through the tubular passageways, to supplement the air being drawn there-through from the opening in the feed tube previously described.

Similarly, the through-put on the equipment may be increased by reducing the time the support 20 remains in the coating-purging fixture 30 and moving each support ahead to one or more additional purging fixtures 30' which are identical to the coating-purging fixture 30, including connection to a purge tank 1, except that the slurry tank 26 and connection thereto is omitted. As shown in FIG. 2, we prefer the multiple purge fixture system and show the use of a first purge fixture 30' connected to a first purge tank 1 together with the coating and purging fixture 30. A second pair of purge fixtures 30' are shown connected to a second purge tank 1'. Turnover means 32 is provided between the two pairs of fixtures to turn the monolith support end-for-end in order to achieve more uniform coating of the passageway surfaces. Such turnover fixture may be of any design well known in the art. In the arrangement described, the monolith support 20 is resident in each fixture for a period of 15 seconds, thus producing a coated support every 15 seconds.

The coated and purged monolith is then moved to a monolith support rotating machine 34 where the supports are rotated at a rate of about 4 RPM for a period of about 2 to 6 minutes, preferably about 4 minutes. This is an optional step in the processing of the monolith support but is preferred in our system since the rotation appears to prevent the slurry from sagging and improve distribution on the support. As shown, each part is automatically loaded into a rotatable holder on wheel 36 by a pusher device 38, similar mechanization being provided on the opposite side to unload the support from the wheel. Alternate rotating systems may be readily devised by those skilled in the art, e.g., a conveyer system in which each support is held on a rotatable spindle with sprocket at one end, separate chain means being used to rotate the sprocket and spindle, and such systems form no part of our invention. The support is then passed through a dryer-calciner oven 40 in which the free water in the support is first dried in a flowing stream of air at about 200° F. to an amount of about 0.5% by weight. We have found that drying may be conveniently accomplished in a dielectric oven over a period of about two minutes. The support is then calcined at a temperature of about 800° F. to remove combined water, this over a period of about 4 minutes. The removal of water prevents catalyst migration via water transport thus keeping the catalyst on the surface of the support. The part is then cooled and conveyed to a second scale 42 where it is weighed, recorded and coating weight determined for control purposes. After visual inspection for plugged passages and chips and the

like, acceptable supports are packed for assembly in the catalytic converter or for impregnation with catalytically active material where co-impregnation in the slurry is not practiced. It should be understood that the viscosity of the coating slurry may be adjusted as necessary to achieve the desired coating, a viscosity of from about 60 to about 400 centipoises being used for the catalyzed slurry described herein, though viscosities as high as about 3,000 centipoises may be used as described in assignee's copending application Ser. No. 783,188 in the name of A. V. Somers, now abandoned the coating slurry being compounded as described in Ser. No. 783,188. In measuring viscosity, a #2 spindle was used at 60 rpm using an L.V.T. viscosimeter. Typical properties of catalyzed platinum-palladium-alumina slurry are

Range	Preferred	
about 3.6-4.7	pH	- about 4
30-45	% solids	- about 37
60-3,000	viscosity cpa.	- about 400
at least 100	surface area m ² /g	- about 190
ratio of Pt:Pd = 5:2; weight as desired for performance	% platinum - % palladium-	about 0.9 of dry solids about 0.36 of dry solids
		about 25 grams ft ³

In Table I there is shown the results of tests coating a large number of the above described monolith supports to determine the effectiveness of our method for flow coating monoliths of the kind described hereinbefore. In this series the flow coating with vacuum was started before the slurry charge was loaded at the top of the support.

TABLE I

Monolith Coating Test (Flow Coat)				
Slurry Charge cc	Static Pressure inches H ₂ O/time	Support Dry Wt. - gms.	Coating Dry Wt. - gms.	Coating Pick-up %
500	5.9/30/30	921.4	98.4	10.7
500	6.0/25/25	915.1	107.5	11.7
500	5.9/25/25	906.6	108.4	12.0
500	6.1/25/25	916.2	105.9	11.6
500	5.9/25/25	925.3	101.7	11.0
500	5.8/25/25	889.5	110.5	12.4
500	5.9/25/25	938.5	100.7	10.7
500	5.5/30/30	929.2	92.6	10.0
500	5.9/30/30	910.3	108.2	11.9
500	6.0/30/30	932.5	95.5	10.2
500	6.1/30/30	927.1	99.2	10.7
500	6.1/30/30	925.0	107.0	11.6
500	6.0/30/30	919.1	95.8	10.4
500	6.5/25/25	915.3	107.9	11.8
500	6.7/25/25	914.2	105.6	11.6
500	6.8/25/25	916.9	104.8	11.4
500	6.8/25/25	914.5	106.3	11.6
500	6.9/25/25	929.8	99.4	10.7
500	6.8/25/25	904.2	103.7	11.5
Average			103.1 gms.	11.2%

In conducting these tests, a slurry charge of 500 cc was applied at the upper end of the support and a static pressure of from 5.5 to 6.9 inches of water was drawn on the purge tank, each support being subjected to this vacuum pressure for a period of 25 or 30 seconds on each end, i.e., after being subjected to the vacuum for a period of time indicated, the support is reversed to place the upper end at the lower end position. In this manner we find we achieve a more uniform coating than when drawing the vacuum from one end only. The slurry is

drawn through the monolith support passageways during the first 5 seconds, approximately, and the remaining time is used to purge the excess slurry from their surfaces and to unplug those passageways which are blocked by slurry.

As can be seen from the data, about 84% of the pieces coated had the average coating weight of 103.1 grams $\pm 5\%$, the remaining pieces being within a 10% limit. Control of this character enables the use of a lower over-all loading with the high surface area alumina and catalytically active materials while still being assured of sufficient catalytic materials to achieve the desired level of activity and life for each monolith support coated.

Table II shows the results of tests coating a large number of the above-described monolith supports using dip coating for applying coating slurry to the monolith surfaces. As indicated, after dipping the monolith in the coating slurry and keeping it submerged therein for 30 seconds, the supports were removed and cleared of excess slurry by draining and application of blow-off air stream over the support for a period varying from 4 to 39 seconds. The parts were then subjected to vacuum pressure to purge excess slurry from and clear plugged passageways in the support. As noted, the supports were subjected to purge vacuum of 9.5 inches of water for a period of 30 seconds from each end. The average coating weight is 99.4 and all parts but two are within $\pm 5\%$ of the average.

TABLE II

Monolith Dip Coating Test				
Support	Dry Wt. g.	Blow-off time-sec.	Coating Dry Wt. g.	Coating Pick-up %
1	943.0	18	101.3	10.7
2	930.8	39	96.0	10.3
3	936.4	24	101.9	10.9
4	934.6	34	97.5	10.4
5	944.0	29	101.6	10.8
6	944.4	36	99.1	10.5
7	944.9	28	99.8	10.6
8	946.0	31	100.3	10.6
9	943.6	28	97.8	10.4
10	949.1	29	100.0	10.5
11	941.9	27	95.6	10.1
12	941.8	24	99.3	10.5
13	932.1	21	100.8	10.8
14	928.2	21	98.6	10.6
15	938.0	20	100.8	10.7
16	941.7	19	97.9	10.4
17	944.1	16	98.0	10.4
18	934.0	16	101.8	10.9
19	945.4	18	96.1	10.2
20	945.1	14	98.5	10.4
21	944.7	12	96.5	10.2
22	929.0	14	99.8	10.7
23	935.1	9	100.0	10.7
24	943.5	6	96.5	10.2
25	949.4	4	100.6	10.6
26	940.7	7	94.9	10.1
27	944.1	5	87.1	9.2
28	927.8	6	122.1	13.1
29	942.8	5	103.1	11.0
30	950.1	10	100.0	10.6
Average			99.4 gms.	10.6%

As shown in FIG. 3, a suitable coating and purging fixture comprises a pair of tubular connecting members 50 and 52 adapted to be brought in contact with the lower and upper ends of the monolith support when the support is brought within the treating station for coating and purging. The lower end 51 of lower connecting member 50 has an interconnection with the vacuum purge tank 1, shown as being telescopically sleeved

within the inlet 3. Other interconnections such as described for member 52 may also be used. The upper end 53 of upper connecting member 52 has a sealed interconnection through a bellows member 54 with a slurry metering member 56 connected to the slurry feed tank 26. As shown with respect to lower connecting member 50, the various interconnections may be made by telescoping pieces. Open type interconnections may be used in practicing the method of our invention since the vacuum purge system has sufficient capacity to clear plugged passageways in the monolith support even though such passageways decrease and open passageways increase during the purge period of treatment. As shown in FIG. 3, the wall of upper connecting member 52 has a plurality of vents 58 to assure availability of sufficient air at least of atmospheric pressure to accomplish the purging action through the monolith. The vents 58 are positioned above the level of the coating slurry charge metered into connecting member 52, the vents serving to permit the vacuum to draw the slurry through the support. It is to be noted that in lieu of vents to atmosphere, the venting may be accomplished by recirculating the moist air from the outlet side of the vacuum pump, pressure of recirculated air being controlled by suitable means forming no part of our invention.

The ends of connecting members 50 and 52 spaced from their corresponding ends 51 and 53 are similarly designed to enable the members to form a sealed connection with the upper end of the monolith support and an unsealed connection with the lower end of the support. More particularly, each connecting member is provided with an annular plastic sealing ring 60 formed of a plastic material such as rigid polyurethane having resilience without being so soft as to fold down and block outer passageways of the support when the seal is established in the manner hereinafter described. A durometer reading of 70 has been found acceptable with the polyurethane seals described. The inner peripheral wall surface of the ring 60 is formed with a conical face 61 opening outwardly from the center thereof so as to enable convenient sealing of monolith supports of varying diameters. As shown, the sealing rings 60 are retained on the ends of the connecting members 50 and 52 by clamp rings 63 which are secured to the connecting members by screws 64 spaced around the clamp rings. To achieve the unsealed connection with the lower end of the monolith support, a plurality of support tabs 66 are provided on the sealing rings 60 so as to project radially inward to serve as supports for the end of the monolith support 20. These support tabs are preferably thinner than the width of a passageway to prevent blocking and may be formed as an integral part of the ring 60 or may be formed of stainless steel and inserted into receiving slots formed in the ring 60. Stainless steel support tabs are preferred to reduce the cost of manufacture of the rings 60. Also, stainless steel is used to avoid interaction between the noble metal catalysts in the slurry and other metals which are lower in the Electromotive Series of Metals. It is here to be noted that this concern for interaction requires that the materials used in the coating and purging stations be either made of non-reacting materials such as teflon and polyurethane, or that metal surfaces be coated with such materials to prevent interaction. It should also be noted that the sealing ring 60 on the lower connecting member 50 is provided with a radially extending drain groove 68 which cooperates with an annular drip pan 70 clamped

between the end of member 50 and sealing ring 60. Drip pan 70 serves to collect any dripping coating slurry from the slurry tank 26 and from the described structural members positioned above the monolith support being treated.

As noted above, in our preferred design of the coating and purging fixture 30, a slurry metering member 56 provides a measured amount of slurry for application to the upper end of the monolith support held in sealed contact with the conical face 61 of the sealing ring 60 on upper connecting member 52. As shown in FIG. 3, the metering is accomplished by providing a pair of spaced apart butterfly valves 57 and 57', the space between the valve centers forming the metered volume of slurry. In operation, valve 57' is shut while valve 57 is opened to fill the valve block with slurry. Upon closing valve 57 the metering member is prepared for actuation upon positioning a monolith support between connecting members 50 and 52. When so positioned, the valve 57' is opened and the measured volume of slurry is applied to the upper end of the support 20 and coating and purging vacuum is applied, all in timed sequence as desired and by means well known in the art. Alternative metering members may be used as is well known, i.e., a single timed valve may be operated to secure the desired slurry charge.

In our preferred embodiment, the monolith support 20 is positioned in the coating and purging fixture 30, in axial alignment between connecting members 50 and 52 which are actuated to contact the ends of the support 20. As noted, in our preferred embodiment this establishes a sealed connection with the upper end of the support 20 and an open connection with the lower end of the support. It should be understood that the bottom end of the support 20 may also have a sealed connection with its sealing ring 60 or the top of the support 20 may have an open connection as described. This latter open connection is not preferred since coating slurry may then leak around onto the outer surface of the support 20, it being possible to minimize such leakage by drawing the vacuum through the monolith just prior to applying the slurry charge to the monolith.

While alternative mechanizations are possible within the skill of the art, we prefer to use a pair of clamping arms or grips to pick-up the monolith support 20 from the moving belt by clamping the support between its ends, the support being rotated into position between connecting members 50 and 52 and there held by the arms. At least one of the connecting members is then actuated by any suitable means such as a linear or caliper type actuator to establish contact between the connecting members and the ends of the support 20 as described. FIG. 3 shows a fluid actuated piston-cylinder actuator 74 for establishing contact. It should be understood that the timing and actuating mechanisms form no part of our invention and may be selected as desired by those skilled in the art.

As described, about the first 5 seconds of the vacuum treatment serves to draw the coating slurry through the support, the remaining period, about 10 seconds, serving to draw down excess slurry from the open passageway surfaces and to start unplugging blocked passageways. As described and as shown in FIG. 3, the support 20 is then picked up by a second pair of clamping arms 72 and is positioned in a purge fixture 30' which is identical with the first fixture 30 except for the omission of the bellows 54, the metering member 56, and the slurry feed tank 26. The vacuum purge treatment is repeated in

this fixture 30' for a period of 15 seconds. The support is then again picked-up as before and rotated end-for-end and positioned in a second purge fixture 30' for addition vacuum treatment and this may be repeated with vacuum applied at the same rotated end. As noted above, the use of multiple treating fixtures enables a higher through put on the same production line.

Our invention in providing a simplified method and means for achieving repeatable controlled coating of the many small size passageways in a monolith support has been described in the foregoing specification and drawings. Additional advantages of our system to those described hereinbefore will be apparent to those skilled in the art, such advantages including the economy and reliability resulting from use of coating and purging stations which are open to atmosphere and unencapsulated rather than using sealed chambers, and the fact that applicants vacuum system contains the coating slurry for ready reuse as opposed to a blow-off system which scatters the slurry. Alternative and equivalent steps and structure will occur to those skilled in the art and, to the extent covered by the attached claims are intended to be within the scope of our invention.

We claim:

1. A method for coating with alumina porous ceramic monolith catalyst supports having at least about 100 axially aligned tubular passageways to the square inch extending from one end of the support to the other so as to produce repeatable results on a production basis and utilizing vacuum pressure to continuously draw air through the passageways to cause the coating slurry to flow over the porous ceramic wall surfaces of the tubular passageways of the monolith support, comprising the steps of applying the coating slurry containing high surface area alumina in suspension to the support, subjecting one end of the support to a vacuum to draw the slurry through and form an alumina coating on the passageways, continuing the application of vacuum pressure to unplug blocked passageways and to form a uniform coating and purge excess coating slurry by the continuing drawing of air through the open passageways, drying the support, and calcining the support to fix the alumina coating on the passageway surfaces, the vacuum static pressure on the support being from about 5 up to about 16 inches water and being applied for a total period of at least about 30 seconds to achieve the desired coating and to remove plugging and excess slurry from the passageways even though the number of open passageways continually increases during the period of vacuum treatment,

2. A method as in claim 1 wherein the coating slurry is applied by dipping the support in the coating slurry.

3. A method as in claim 1 wherein the coating slurry is applied by positioning the coating slurry on the upper end of the support, the lower end of the support being subjected to vacuum.

4. A method for controlling the coating with alumina of porous ceramic monolith catalyst supports having at

least about 100 axially aligned passageways to the square inch extending from one end of the support to the other to achieve repeatable results on a production basis and utilizing vacuum pressure to form a uniform coating by the continuous drawing of air through the passageways to distribute the coating slurry over the surfaces of and unplug blocked tubular passageways of the monolith support, comprising the steps of positioning said support between a pair of connecting members with one member in contact with the upper end of said support and the other member in contact with the lower end of said support, the outer surface of said support being unencapsulated and open to atmosphere, feeding said coating slurry to the connecting member at the upper end of said support, subjecting the lower end of said support to a vacuum to draw the slurry through the passageways, continuing the application of vacuum to unplug blocked passageways and to form a uniform coating and purge excess coating slurry by the continuing drawing of air through the open passageways, removing the vacuum from said support, drying the support, and calcining the support, the vacuum static pressure on the support being from about 5 up to about 16 inches water and being applied for a total period of at least about 30 seconds to achieve the desired coating and remove excess slurry from the open passageways and to unplug blocked passageways despite the increasing number of open passageways during the period of vacuum treatment.

5. A method for coating with alumina porous ceramic monolith catalyst supports having at least about 100 axially aligned passageways to the square inch extending from end to end thereof to achieve repeatable results on a production basis and utilizing vacuum pressure to distribute the coating slurry over the surfaces of and unplug blocked tubular passageways of the monolith support, comprising the steps of positioning said support between a pair of connecting members with one member in contact with the upper end of said support and the other member in contact with the lower end of said support, feeding said coating slurry to the connecting member at the upper end of said support, subjecting the lower end of said support to a vacuum to draw the slurry through the passageways, continuing the application of vacuum to unplug blocked passageways, removing the vacuum from said support, drying the support, and calcining the support, the vacuum static pressure at the lower end of said support being from about 5 up to about 16 inches water and such pressure is applied for a total period of at least about 30 seconds for coating the passageway surfaces, to remove excess slurry from the open passageways and to unplug blocked passageways despite the increasing number of open passageways during the period of vacuum treatment, vacuum being applied first at one end of said support followed by reversal by said support end-for-end with vacuum applied at the other end.

* * * * *

Pasarela Pasadizo
Disconnector
burne & desautour
(Composite no. 10050)

US 4771029

NO

12

EUROPEAN PATENT APPLICATION

13 Application number: 87302347.7

14 Int. Cl. 4: G01N 29/04

15 Date of filing: 18.03.87

16 Priority: 10.04.86 US 850042
14.05.86 US 853146

17 Date of publication of application:
21.10.87 Bulletin 87/43

18 Designated Contracting States:
DE FR GB

19 Applicant: GENERAL MOTORS CORPORATION
General Motors Building 3044 West Grand
Boulevard
Detroit Michigan 48202(US)

20 Inventor: Varterasian, John H.
29518 Bentley
Livonia Michigan 48154(US)
Inventor: Blaser, Dwight Allen
32362 Hampton Court
Fraser Michigan 48026(US)

21 Representative: Breakwell, John Neil Bower et
al
GM Patent Section Vauxhall Motors Limited
Luton Office (F6) P.O. Box No. 3 Kington
Road
Luton Bedfordshire LU2 0SY(GB)

22 Acoustic inspection method for ceramic coatings of catalytic converter monolith substrates.

23 An acoustic inspection method for ceramic coatings of catalytic converter monolith substrates includes mounting the substrate (22) in an acoustically sealed structure (32) so as to form a throat communicating a loudspeaker (34) at an entrance end of the coated passages with an empty resonator cavity (36) at an exit end of the coated passages, so forming a Helmholtz resonator.

The speaker is then driven to produce a continuous sound wave through the coated passages into the resonator cavity at a predetermined frequency of approximately the natural frequency of the resonator, whereafter the substrate is reversely mounted and the previous step is repeated.

The phase angles of the sound waves at the entrance and exit ends of the coated substrate passages are compared with those obtained for a reference substrate, to ascertain whether or not the ceramic coating was applied in a predetermined amount and uniformly to the surface of the exhaust gas passages and whether the ceramic coating is blocking any of the passages.

EP 0 242 060 A2

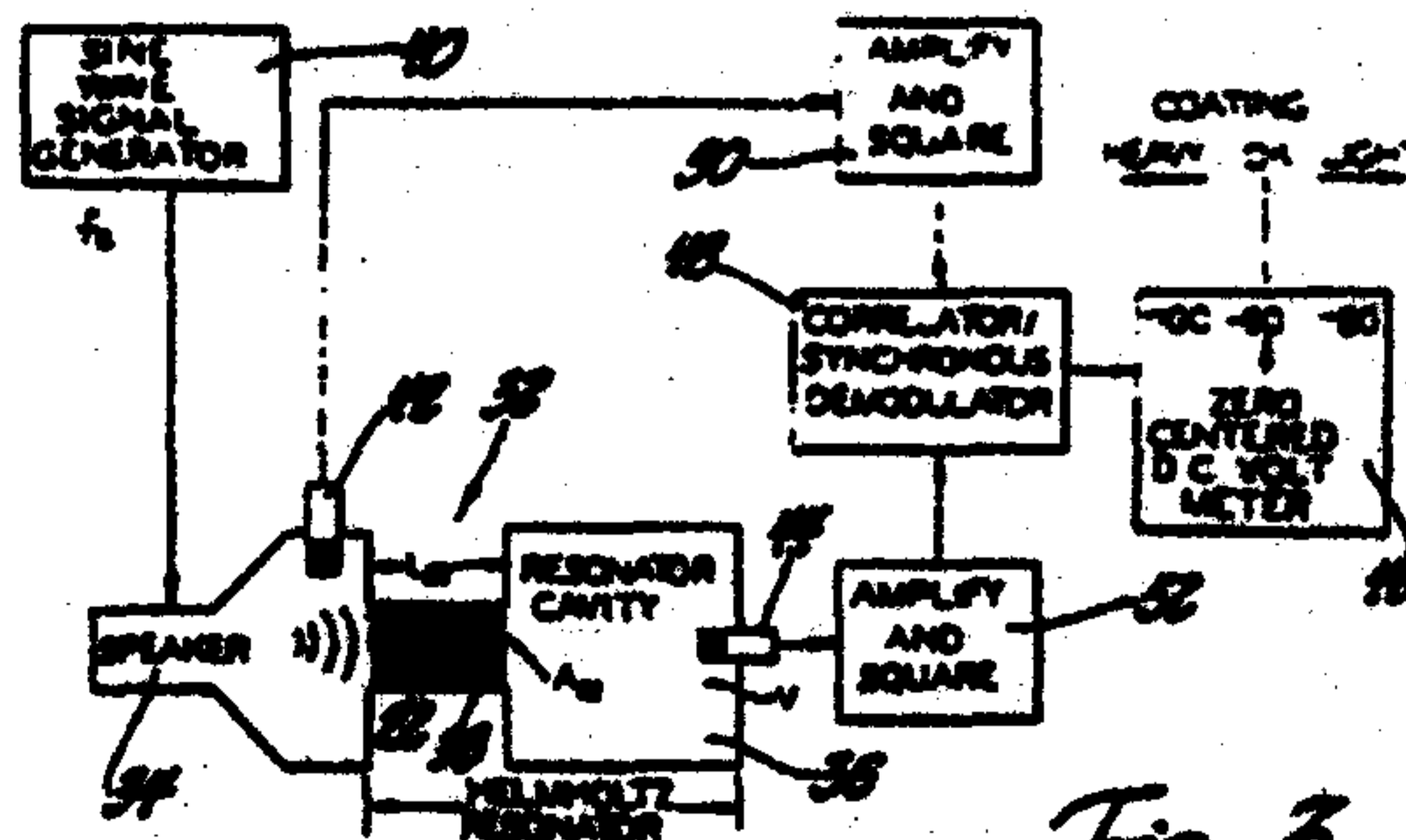


Fig. 3

Moreover, Equation (2) can be used to show that the inspection system's phase angle limits such as those given above as -80° and -100° correspond to an area increase of 7.1% and an area decrease of 6.6% respectively.

In the description thus far, it has been assumed that the speed of sound is the same during each inspection. However, the speed of sound does vary with temperature, and this will therefore affect the relationship between the acoustic phase angle and the flow area of the substrate. In this situation, the speed of sound in air varies as the square root of the absolute temperature, as given by the equation:

$$c = c_0 \sqrt{1 + T/273} \quad (13)$$

where

c_0 = speed of sound at 0°C = 331.1 m/s,

and

T = temperature, $^\circ\text{C}$.

From Equation (1), therefore, the natural frequency of the Helmholtz resonator and the resulting phase angles used in the present method also vary with temperature. Accordingly, for consistent inspection results, the system needs to be recalibrated to compensate for any substantial temperature change, as will now be demonstrated.

By substituting Equation (13) into Equation (1), the natural frequency of a Helmholtz resonator at a temperature T is given by the equation:

$$f_n = c_{air} \sqrt{(1 + T/273)(A_{eff}/V_{eff})} \quad (14)$$

Therefore, the ratio of the natural frequencies for air temperatures T_1 and T_2 respectively is given by the equation:

$$f_1/f_2 = \sqrt{(273 + T_1)/(273 + T_2)} \quad (15)$$

In Equation (15), f_1 corresponds to the natural frequency of a coated substrate at temperature T_1 , whereas f_2 corresponds to the natural frequency of the same substrate at temperature T_2 .

For instance, for a reference substrate having an oval cross-section as shown and for which the natural frequency was found to be 138.9 Hz at a temperature of 22°C , the resulting natural frequency at any other temperature, T , is given by the equation:

$$f_n = 8.1 \sqrt{273 + T} \quad (16)$$

and the natural frequency sensitivity to temperature is given by the equation:

$$\Delta f_n / \Delta T = 0.235 \text{ Hz}/^\circ\text{C} \quad (17)$$

When measured values of natural frequency versus temperature for this reference substrate were compared with the theoretical, it was found that there was good actual correlation for these values.

With such correlation found, the phase angle for this reference substrate as a function of temperature is then obtained by substituting Equation (15) into Equation (5), with the reference damping factor $\zeta = 0.195$.

As a result:

$$\phi = -\tan^{-1}[8.7 \sqrt{(273 + T)/(T-22)}] \quad (18)$$

and the phase angle sensitivity to temperature given by the derivative is:

$$\Delta\phi/\Delta T = 0.498 \text{ }^\circ/\text{C} \quad (19)$$

Thus the combined effects of excitation frequency and temperature on phase angle can be predicted and compensated for accordingly.

For instance, when the above-described system was initially calibrated with $\phi = -90^\circ$, using a substrate with a normal and uniform coating as the reference, the excitation frequency was 138.9 Hz with the temperature at 22°C . However, if the temperature were to increase for example to 25°C , the resulting phase angle would change to -88.5° , according to Equation (18). As a result, for consistent inspection results, it would be necessary to recalibrate the system by increasing the excitation frequency to 139.6 Hz, at which the phase angle is again -90° .

The temperature of the reference substrate should of course itself be representative of the temperature of the substrates being inspected.

Claims

1. An acoustic inspection method for determining, in a catalytic converter monolith substrate, whether a ceramic coating has been applied in a predetermined amount to the surface of exhaust gas passages extending therethrough, and whether the ceramic coating is blocking any of the passages, comprising the steps of:

a) mounting a catalytic converter monolith substrate (22) with ceramic-coated exhaust gas passages extending therethrough in an acoustically sealed structure (32) so as to form a throat (38) communicating a loudspeaker (34) at an entrance end of the coated passages with an empty resonator cavity (36) at an exit end of the coated passages and thereby form a Helmholtz resonator,

5 b) driving the speaker (34) to produce a continuous sound wave through the coated passages into the resonator cavity (36) at a predetermined frequency and thereby produce oscillatory sound waves through the coated passages at the same frequency,

10 c) comparing the phase angles (42,44,48,50,52) of the sound waves at the entrance and exit ends of the coated substrate passages with respect to those of a reference sound wave of the same frequency passed in like manner through a reference substrate known to have the desired quantity of coating on the passages and no blockage, and

15 d) detecting whether or not the passages of the substrate (22) being inspected have the prescribed quantity of coating and any blockage, on the basis that the occurrence of a prescribed difference in the phase angles (42,44,48,50,52) implies a deviation in the total flow area of the passages and thereby a deviation from the desired quantity of coating on the passages and lack of blockage thereof.

2. An acoustic inspection method according to claim 1, characterised in that the predetermined frequency at which the speaker (34) is driven is substantially the natural frequency of the resonator.

20 3. An acoustic inspection method according to claim 1 or 2, characterised by, for determining whether the ceramic coating has been applied uniformly to the surface of the exhaust gas passages, the following additional steps:

e) subsequent to step b), reversing the mounting of the substrate (22) so that the entrance end of the substrate (22) is then near the resonator cavity (36) and the exit end is near the speaker (34),

f) repeating step b),

25 g) comparing the phase angles (42,44,48,50,52) of the sound waves at the entrance and exit ends of the coated substrate passages with respect to those of a reference sound wave of the same frequency passed in like manner through a reference substrate known to have the desired quantity and uniformity of coating on the passages and no blockage, and

30 h) detecting whether or not the passages of the substrate (22) being inspected have the prescribed uniformity of coating, on the basis that a prescribed difference in the phase angles following reversal of the substrate mounting implies a deviation in the total flow areas at the entrance and exit ends and thereby a deviation from the desired uniformity of coating along the length of the passages.

35 4. An acoustic inspection method according to claim 1 or 2, characterised in that, for determining in the catalytic converter monolith substrate whether the ceramic coating has been applied in a predetermined amount and uniformly to the surface of the exhaust gas passages extending therethrough and whether the ceramic coating is blocking any of the passages:

subsequent to step b) the mounting of the substrate is reversed so that the entrance end is then near the resonator cavity and the exit end is near the speaker,

step b) is then repeated,

40 in step c) the comparison of the phase angles of the sound waves at the entrance and exit ends of the coated substrate passages is effected with respect to those of a reference sound wave of the same frequency passed in like manner through a reference substrate known to have the desired quantity and uniformity of coating on the passages and no blockage, and

45 step d) comprises detecting whether or not the passages of the substrate (22) being inspected have the prescribed quantity and uniformity of coating and any blockage, on the basis that the occurrence of a prescribed difference in the phase angles (42,44,48,50,52) without reversal of the substrate mounting implies a deviation in the total flow area of the passages and thereby a deviation from the desired quantity of coating on the passages and lack of blockage thereof, and that the occurrence of a prescribed difference in the phase angles (42,44,48,50,52) with reversal of the substrate mounting implies a deviation in the total flow areas at the entrance and exit ends and thereby a deviation from the desired uniformity of coating
50 along the length of the passages.



US PATENT & TRADEMARK OFFICE

PATENT FULL TEXT AND IMAGE DATABASE

NO



(1 of 1)

United States Patent
Richmond, et al.

5,187,142
February 16, 1993

Catalytic converter metal monolith

Abstract

A metal foil substrate catalytic converter for use in the exhaust system of an internal combustion engine, having corrugated metal foil sheets secured together in a stack so that a plurality of axially extending fluid flow paths are defined therebetween. Disposed at predetermined intervals throughout the stack are foil retainer sheets having integral foil tabs extending outwardly from the side edges and folded about the outer side surface of the substrate to form a segmented foil skin thereabout. The segmented foil skin may be welded continuously along its length to secure the foil sheets in a unitary catalyst substrate and to provide a weld surface for attachment of the catalyst substrate directly to the converter canister wall.

Inventors: **Richmond; Russell P. (North Branch, MI); Foster; Michael R. (Columbiaville, MI)**
 Assignee: **General Motors Corporation (Detroit, MI)**
 Appl. No.: **754514**
 Filed: **September 3, 1991**

U.S. Class: **502/439; 502/527; 428/593**
 Intern'l Class: **B01J 032/00; B01J 035/04**
 Field of Search: **502/439,527 428/593**

References Cited [Referenced By]

U.S. Patent Documents

3183963	May., 1965	Mondt	165/10.
3911675	Oct., 1975	Mondt	60/283.
3929419	Dec., 1975	Chapman	23/288.
3962869	Jun., 1976	Wossner	60/298.
4152302	May., 1979	Nonnenmann et al.	502/527.
4324701	Apr., 1982	Honda et al.	252/477.
4382323	May., 1983	Chapman et al.	29/157.
4559205	Dec., 1985	Hood	422/180.
4576800	Mar., 1986	Retallick	422/180.
4619912	Oct., 1986	Jalbing et al.	502/439.
4673553	Jun., 1987	Retallick	422/180.
4731229	Mar., 1988	Sperandio	422/188.
4814146	Mar., 1989	Brand et al.	422/179.
4849185	Jul., 1989	Wittig	422/171.
4942020	Jul., 1990	Whittenberger et al.	422/180.
4987034	Jan., 1991	Hitachi et al.	502/527.

Primary Examiner: Shine; W. J.

Attorney, Agent or Firm: Barr, Jr.; Karl F.

Claims

1. A catalyst support substrate for use in a catalytic converter comprising a plurality of corrugated metal foil sheets stacked together to form a plurality of axially extending fluid flow paths therebetween, foil retainer sheets disposed at intervals in said stack of corrugated sheets, said retainer sheets having tabs extending outwardly from the side edges thereof and folded to contact the sides of the substrate stack formed by the edges of said stack of corrugated metal foil sheets to form a segmented foil skin about a portion of said stack, said foil skin welded along its length and forming a unitary skin about said substrate.
2. A catalyst support substrate for use in a catalytic converter, as defined in claim 1, said retainer sheet having a predetermined thickness greater than that of said corrugated foil sheets wherein a desired rigidity is obtained from said foil skin.
3. A catalyst support substrate for use in a catalytic converter, as defined in claim 1, said stack of corrugated metal foil sheets and foil retainer sheets fixed together by capacitive discharge welding at the contact points between said sheets.
4. A catalyst support substrate for use in a catalytic converter comprising a plurality of corrugated metal foil sheets stacked together to form a plurality of axially extending fluid flow paths therebetween, foil retainer sheets disposed at intervals in said stack of corrugated foil sheets, said sheets having retainer tabs extending outwardly from the side edges thereof and folded to contact the sides of the substrate stack formed by the edges of said metal foil sheets to form a segmented foil skin about a portion of said stack, and a substrate supporting plate welded to said segmented foil skin.

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present application is directed to a catalytic converter for use in the exhaust system of an internal combustion engine and, more particularly, to a metal foil substrate catalytic converter having retaining means integral with the foil sheets of the converter substrate, for mounting the substrate within the converter assembly.

Description of the Relevant Art

Typical automotive vehicle exhaust systems, and an increasing number of non-automotive applications incorporating internal combustion engines, use catalytic converters for reducing the quantity of regulated exhaust constituents emitted therefrom. A common converter configuration consists of a catalyst coated ceramic substrate packaged within a stainless steel canister having openings at each end for the passage of exhaust gas. The ceramic substrate generally is extruded and has axially extending passages or bores through which the exhaust gas passes.

An alternative to the ceramic substrate converter is a metal foil substrate converter. This converter uses a stack of catalyst coated corrugated foil sheets which are fixed together to form a substrate having axially extending passages which may then be mounted in a rigid canister in much the same way as the ceramic substrate. The metal foil converter is durable and is resistant to damage from high temperatures which may occur following an engine malfunction.

Both of the catalyst substrates described above may be mounted within the converter canister using an appropriate insulative or flexible material to separate the substrate therefrom. In the case of the ceramic substrate, a ceramic mat material may be used to protect the substrate from breakage caused by vibration and differing coefficients of thermal expansion between the canister and the substrate. In some cases, the metal monolith utilizes an insulative material to reduce external noise which is generated by contact between the substrate and the canister and to assist in adequately sealing the space between the monolith and the canister wall thereby preventing exhaust gas from bypassing the substrate and reducing canister skin temperature.

SUMMARY OF THE INVENTION

In accordance with the present invention, a metal foil substrate catalytic converter for use in the exhaust system of an internal combustion engine is disclosed. The catalytic converter has a metal foil catalyst substrate comprising corrugated foil sheets secured together in a stack so that a plurality of axially extending fluid flow paths are defined between the sheets. Disposed at predetermined intervals in the stack of corrugated foil sheets are corrugated retainer sheets which have tabs extending outwardly from the side edges. The tabs are folded to contact the sides of the substrate stack. In one embodiment, the tabs overlap one another to form a generally segmented foil skin about the exterior side surface of the substrate stack. The foil skin formed by the overlapping retainer tabs may be welded continuously along its length to the underlying side surface of the substrate stack, thereby aiding in the retention of the stacked foil sheets in a unitary catalyst substrate brick.

The assembled metal foil substrate is coated with a catalyst material and is placed into a rigid canister having an inlet and an outlet for conducting exhaust gas through the converter. The sides of the canister may be welded directly to the foil tabs thereby forming a rigid, unitary converter assembly.

The present invention discloses a metal monolith catalytic converter substrate having integral means for aiding in the retention of the foil sheets which form the substrate into a rigid unit. Additionally, the same integral means may be used to attach the monolith to the converter canister thereby providing a means of mounting the substrate within the converter canister which reduces the need for insulating mats and seals.

Other objects and features of the invention will become apparent by reference to the following description and to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a corrugated metal foil sheet used to assemble the catalytic converter of the present invention;

FIG. 2 illustrates a corrugated retainer sheet used to assemble the catalytic converter of the present invention;

FIG. 3 is a partial side view of a metal foil catalyst substrate embodying the present invention;

FIG. 4 is a partial side view of a metal foil catalyst substrate showing a second embodiment of the present invention;

FIG. 5 is a perspective view, partially in section, of a catalytic converter assembly embodying the present invention;

FIG. 6 is a perspective view, partially in section, of a second embodiment of a catalytic converter assembly embodying the present invention;

FIG. 7 is a partial section taken along line 7--7 of FIG. 3; and

FIG. 8 is a partial section taken along line 8--8 of FIG. 4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1 there is illustrated a corrugated metal foil sheet 10 having a series of corrugations 12 formed thereon. These sheets are of the type described in prior patents, as for example U.S. Pat. No. 3,183,963 and U.S. Pat. No. 4,619,912, such that it is not deemed necessary to describe them in detail herein. The corrugations 12 may be of any desired configuration which will allow multiple sheets to be stacked one upon the other, without the corrugations nesting, to form a series of axially extending fluid flow paths 14, shown in FIGS. 7 and 8. In the preferred embodiment, the corrugations 12 have a herringbone, or alternating chevron pattern.

The corrugated metal foil sheets 10 are stacked together as described above with foil retainer sheets 16, shown in FIG. 2, disposed at predetermined intervals therebetween. The retainer sheets 16 are dimensionally similar to the foil sheets 10 and have tabs 18 which extend outwardly from the side edges 20. The foil retainer sheets 16 may or may not have a corrugated surface. A preferred embodiment for sheet 16 is that shown in FIG. 2 where a straight corrugation 21 extends in the axial direction. The use of the straight corrugation 21 simplifies the manufacturing of the foil sheet by eliminating material stress at the boundary of the corrugations 21 and the tabs 18 which may be caused by the use of a herringbone corrugation such as that used on sheets 10.

FIG. 3 illustrates a catalyst support substrate 22 constructed from a stack of corrugated metal foil sheets 10 and foil retainer sheets 16, described above. Upon stacking of the sheets, the tabs 18 contact the sides of the substrate 22, as shown in FIG. 7, formed by the edges of the individual sheets 10. In a preferred embodiment, the retainer sheets 16 are spaced to allow overlap of the tabs 18 resulting in the formation of segmented foil skin 24 which extends about a portion of the substrate 22. The skin 24 may be welded along its length to the underlying side surface of the substrate stack, as at 26, to transform the segmented skin 24 into a unitary skin which aids in the retention of the foil sheets 10 and 16 in the desired substrate configuration. Welding of the segmented skin 24 may be used to augment other methods typically used to secure the foil sheets together, such as brazing or capacitive discharge welding which attaches the sheets to one another at their points of contact.

The configuration of the tabs 18 may vary depending on the particular application. It is contemplated that the tabs may extend the entire length of each sheet, resulting in an outer foil skin which extends over the entire side surface of the substrate. It is also contemplated that the retainer sheets 16 are of a thickness greater than that of the foil sheets 10. With such a configuration, tabs 18 may be spaced from one another, rather than overlapping due to interference problems caused by the increase in sheet thickness. The retainer sheets 16 of this design act to structurally augment the converter canister to reduce vibration and noise emitted therefrom.

FIG. 5 illustrates an assembled catalytic converter 28 which has been constructed using the substrate 22 disclosed above. The converter assembly 28 comprises a rigid canister 30 which may be constructed of stainless steel or other suitable material. The canister 30 has an inlet 32 and an outlet 34 for conducting exhaust gas through the converter. Integral with inlet 32 and

outlet 34 are mounting means, well known in the art, for coupling the converter 28 to the exhaust system (not shown) of an internal combustion engine. The catalyst support 22 described above, having a suitable catalyst applied, is mounted within canister 30 so that exhaust gas entering the converter is conducted through the fluid flow passages 14 where the undesirable constituents of the exhaust gas are reacted prior to their exit therefrom. The substrate is rigidly mounted within the converter by welding the foil skin 24 to the walls of the canister, as at 35. By welding the substrate 22 to the converter canister 30, relative movement between the components is minimized as are problems with noise and destruction of the substrate caused by vibration. Retention of substrate 22 may rely solely on the welded foil tabs 18 or skin 24. Alternatively, this means of retention may be augmented by other types of well known mounting means such as clamping or pinning.

A second embodiment of catalyst substrate 22 is illustrated in FIGS. 4 and 8, where similar features as those described above are denoted by like numerals. To strengthen the weld bonds between both the individual retainer tabs and the stacked foil sheets 10, 16 and also the substrate 22 and the sides of canister 30, substrate support plates or strips 34 are welded to the foil skin 24, as at 36. The support plates 34 contribute to the rigidity of the substrate assembly and provide additional material for welding, thereby contributing to a superior retention of substrate 22 within canister 30. In a similar manner as that described above, the catalyst coated substrate of this embodiment is mounted in the canister 30 by welding the canister walls to the substrate assembly 22 at the locations of the substrate support plates 34. As an alternative to support plate 34, it is contemplated to increase the thickness of the foil retainer sheets 16, as described above, relative to corrugated foil sheets 10 thereby increasing the thickness of tabs 18 and foil skin 24.

Although the catalyst support unit 22 described above has been illustrated as a rectangular unit, the scope of the present invention should not be limited to this configuration. It is contemplated that any suitable substrate configuration, such as the standard oval illustrated in FIG. 6 in which similar features as those described above are denoted by like numerals with an "A" suffix, may be constructed using the present invention. In the case of an oval substrate 22A, the segmented foil skin 24A may extend about the entire circumference of the substrate providing a weld surface about the entire unit.

In addition, in each of the above embodiments, it is contemplated to extend the tabs 18, 18A beyond the axial ends of the retainer sheets 16, 16A thereby extending the segmented foil skin 24, 24A beyond the inlet or outlet face of the catalyst support substrate 22, 22A. The resulting extension of the foil skin achieves greater surface area for attachment of the substrate 22, 22A to the walls of canister 30, 30A and defines inlet and outlet cylinders extending about the inlet and outlet faces of the substrate. The cylinders act as integral end cones on the substrate 22, 22A which are flush with the canister sides and channel or direct the exhaust gasses approaching and departing the frontal and end faces through the substrate thereby minimizing the quantity of exhaust which bypasses the substrate 22, 22A at the interface with the canister 30, 30A.

The catalyst support unit of the present invention contributes to a catalytic converter assembly which is simplified in its construction by eliminating the insulation package which is typically required for support of the substrate within the canister. The metal foil substrate incorporates integral retainer tabs within the assembly which may be used for retaining the metal foil sheets as an integral substrate unit and also for mounting the substrate within the canister by providing a weld surface for attachment of the substrate to the canister walls.

While certain embodiments of the invention have been described in detail above in relation to a catalytic converter assembly, it would be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary, rather than limiting, and the true scope of the invention is that described in the following claims. privilege is claimed are defined as follows:



United States Patent [19]

Lachman et al.

[11] 3,885,977

[45] May 27, 1975

NO

[54] ANISOTROPIC CORDIERITE MONOLITH

[75] Inventors: Irwin M. Lachman; Ronald M. Lewis, both of Corning, N.Y.

[73] Assignee: Corning Glass Works, Corning, N.Y.

[22] Filed: Nov. 5, 1973

[21] Appl. No.: 412,862

[52] U.S. Cl. 106/62; 106/73.33; 106/73.4; 106/73.5

[51] Int. Cl. C04b 35/18; C04b 35/20

[58] Field of Search 106/62, 73.4, 73.5, 73.33

[56] References Cited

UNITED STATES PATENTS

2,731,355	1/1956	Skinner.....	106/62
2,864,919	12/1958	Stringfellow	106/62
3,473,999	10/1969	Muchow	106/62

Primary Examiner—J. Poer

Attorney, Agent, or Firm—Barry S. Bissell; Richard N. Wardell; Clarence R. Patty, Jr.

[57] ABSTRACT

An extruded, honeycombed, monolithic fired ceramic whose primary crystal phase is cordierite and whose microstructure is characterized by a greater than random orientation of the anisotropic cordierite crystallites with their low expansion direction aligned substantially parallel to the plane of the webs of the monolith. The axial expansion coefficient of the honeycomb, with composition near that of stoichiometric cordierite, may be as low as 5.5×10^{-7} in./in./°C. or lower in the range of 25°–1000°C.

The product is particularly adapted to use as a catalytic support matrix for emissions control.

29 Claims, 6 Drawing Figures

The experimental data in Table 9 for the compressed matrix is plotted in FIG. 5 to dramatize the apparent linear relationship of the CTE in axial, radial and transverse directions and the I-ratio determined by x-ray reflections from slices cut normal to those directions. Reliance on the I-ratio to detect preferred orientation of cordierite crystallites and hence the CTE is clearly warranted as evidenced graphically in FIG. 5.

EXAMPLE 6

Effective orientation of cordierite crystals is possible when the cordierite phase is only 67.5 volume percent of the body. Body L, prepared as in Example 3 with platelet clay, consisted essentially of 41.9% SiO₂, 48.7% Al₂O₃ and 9.4% MgO. Principal phases present in the body fired to 1345°C. were 67.5% cordierite, 29.2% mullite and 3.3% sapphire, on the volume basis. Theoretical CTE for a random body with the above phases was calculated to be 24.5–28.0 × 10⁻⁷/°C. over the 25°–1000°C. range using conservatively low values for the expansions of mullite and sapphire (48–56 and 50–75 × 10⁻⁷/°C., respectively). The experimental CTE in the axial direction, however, was 23.3 × 10⁻⁷/°C. over 25°–1000°C. and the I-ratio for the cordierite peaks was 0.52, significantly below the random range of 0.61–0.69. These results are evidence that cordierite crystals may be reproducibly oriented even when substantial volumes of other phases are present. Additionally, the effect of the orientation is not masked by the other phases and the body remains anisotropic with respect to the CTE.

EXAMPLE 7

As a demonstration that stacked clay may be (and calcined clay may not be) initially selected for the raw batch and subsequently delaminated by proper processing and oriented in the forming, the inventors made a full substitution of calcined clay (Glomax LL) for the stacked clay of body composition D. The raw material batches were mixed thoroughly and pre-extruded under the same conditions. Samples were prepared by extrusion from each batch, fired, and tested for coefficient of thermal expansion and I-ratio. Body M (calcined clay) had a CTE of 16.4 and an I-ratio of 0.65. Body D on the other hand had a CTE of 10.0 and an I-ratio of 0.48.

Clearly the calcined clay could not be delaminated during processing and therefore showed no cordierite orientation in the fired body. The stacked clay in body D, however, was broken to platelets during processing of the plastic batch and therefore showed preferred orientation in the formed, fired body.

We claim:

1. An anisotropic, polycrystalline sintered ceramic product having cordierite as its primary phase and consisting essentially on an analytical oxide basis of 11.5–16.5% RO, 33–41% Al₂O₃ and 46.6–53% SiO₂ and having a coefficient of thermal expansion in at least one direction of less than 11.0 × 10⁻⁷ in./in./°C. over the range of 25°–1000°C., and wherein RO consists essentially of one member selected from the group consisting of NiO, CoO, FeO, MnO and TiO₂,

the NiO when selected being less than 25% by weight of the RO,
the CoO when selected being less than 15% by weight of the RO,

the FeO when selected being less than 40% by weight of the RO,
the MnO when selected being less than 98% by weight of the RO,
the TiO₂ when selected being less than 15% by weight of the RO,
and the balance of the RO being substantially all MgO.

2. An anisotropic, polycrystalline sintered ceramic product having cordierite as its primary crystal phase and consisting essentially of, by weight on an analytical oxide basis, 11.5–16.5% MgO, 33–41% Al₂O₃, 46.6–53.0% SiO₂, and having a coefficient of thermal expansion, in at least one direction, of less than 11.0 × 10⁻⁷ in./in./°C. over the range of 25°–1000°C.

3. A ceramic product as recited in claim 2 which contains less than, by weight, 0.1% CaO and 0.4% Na₂O plus K₂O.

4. A ceramic product as recited in claim 2 wherein the product comprises an extruded honeycomb, having a matrix of thin walls forming a multiplicity of open ended cells extending from one end to another end of the honeycomb and the thin walls having a substantially smaller coefficient of thermal expansion in the direction parallel to the axes of the open ended cells than transverse to the thin walls.

5. A ceramic product as recited in claim 4 which consists essentially, on the analytical oxide basis, of 12.5–15.5% MgO, 34.2–39.5% Al₂O₃ and 48.0–51.6% SiO₂.

6. A ceramic product as recited in claim 5 wherein the total weight of MgO, Al₂O₃, and SiO₂ is at least 97% of the entire weight of the ceramic product.

7. A ceramic product as recited in claim 2 wherein the coefficient of thermal expansion is between 4.0 × 10⁻⁷ in./in./°C. and 9.0 × 10⁻⁷ in./in./°C. over the range 25°–1000°C.

8. A ceramic product as recited in claim 7 wherein the product comprises an extruded honeycomb, having a matrix of thin walls forming a multiplicity of open ended cells extending from one end to another end of the honeycomb and the thin walls having a substantially smaller coefficient of thermal expansion in the direction parallel to the axes of the open ended cells than transverse to the thin walls.

9. A ceramic product as recited in claim 8 which consists essentially, on the analytical oxide basis, of 12.5–15.5% MgO, 34.2–39.5% Al₂O₃ and 48.0–51.6% SiO₂.

10. A ceramic product as recited in claim 9 wherein the total weight percent of MgO, Al₂O₃, and SiO₂ is at least 97% of the entire weight of the ceramic product.

11. An anisotropic sintered ceramic product consisting of substantially all crystalline cordierite phase and having a chemical oxide analysis by weight, 9–20% MgO, 30–50% Al₂O₃, and 41–56.5% SiO₂, and having an I-ratio, defined as:

$$\frac{I_{1100}}{I_{1100} + I_{040}}$$

in at least one direction of less than 0.61.

12. The product as recited in claim 11 wherein the chemical oxide analysis by weight is 11.5–16.5% MgO, 33–41% Al₂O₃, and 46.6–53% SiO₂ and the I-ratio in at least one direction is 0.43–0.55.