

J. Q.



Industria y Comercio
SUPERINTENDENCIA

Delegatura de Propiedad Industrial

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

05-11675

21. EXPEDIENTE No.

54. TITULO

POLVO CERAMICO PLASMA REDONDEADO

51. CLASIFICACION INTERNACIONAL

71. SOLICITANTE

SAINT-GOBAIN CERAMICS & PLASTICS, INC.

DOMICILIO

Worcester, Massachusetts, Estados Unidos de América.

74. APODERADO

EMILIO FERRERO

C.C. 438.019 de Usaquén.

22. BOGOTA, D.C.,

**Industria y Comercio**

SUPERINTENDENCIA

PETITORIO

SUPERINDUSTRIA Y COMERCIO

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Trámite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTA

- Dependencias 2020 DIVISION DE NUEVAS CREACIONES

FORMULARIO UNICO DE SOLICITUD DE PATENTE**PCT****ENTRADA EN FASE NACIONAL****SOLICITUD DE:****1**☒ Patente de Invención.☐ Patente de Modelo de Utilidad.☐ Capítulo I.☒ Capítulo II.**2****SOLICITANTE
(71)**Nombre: **SAINT-GOBAIN CERAMICS &
PLASTICS, INC.**sociedad constituida y existente bajo las
leyes del Estado de Delaware, Estados
Unidos de América.Dirección: 1 New Bond Street,
Box Number 15138,
Worcester, Massachusetts 01615-0138,
Estados Unidos de América.
Domicilio: Worcester, Massachusetts,
Estados Unidos de América**IDENTIFICACIÓN**C.C. ☐ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número _____

3**REPRESENTANTE
O APODERADO**Nombre: **EMILIO FERRERO**Dirección: **Carrera 4ª. No. 72-35**Teléfono: **347 38 11**Fax: **217 92 11**E-mail: **clientes@camyp.com**Domicilio: **Bogotá, Colombia.****IDENTIFICACIÓN**C.C. ☒ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número **438.019** T.P **31.929****4****INVENTOR (ES)
(72)****Howard WALLAR**
12 Jaimie Ann Drive,
Rutland, Massachusetts, 01543,
Estados Unidos de América.**5****PCT (86)**Solicitud Internacional No. **PCT/US2003/024541**Fecha: **4 de agosto de 2003**Publicación Internacional No. **WO 2004/015158 A1**Fecha: **19 de febrero de 2004****6****Título (54)****POLVO CERÁMICO PLASMA REDONDEADO****7****Clasificación Internacional (51) C23C 4/10****8****Prioridad**SI ☒ NO ☐

(33) País de Origen

US.

(32) Fecha

13 de agosto de 2002

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10/217.523**9****Comprobante de pago No.: 05- 7.172 Fecha: 31 de enero de 2005**

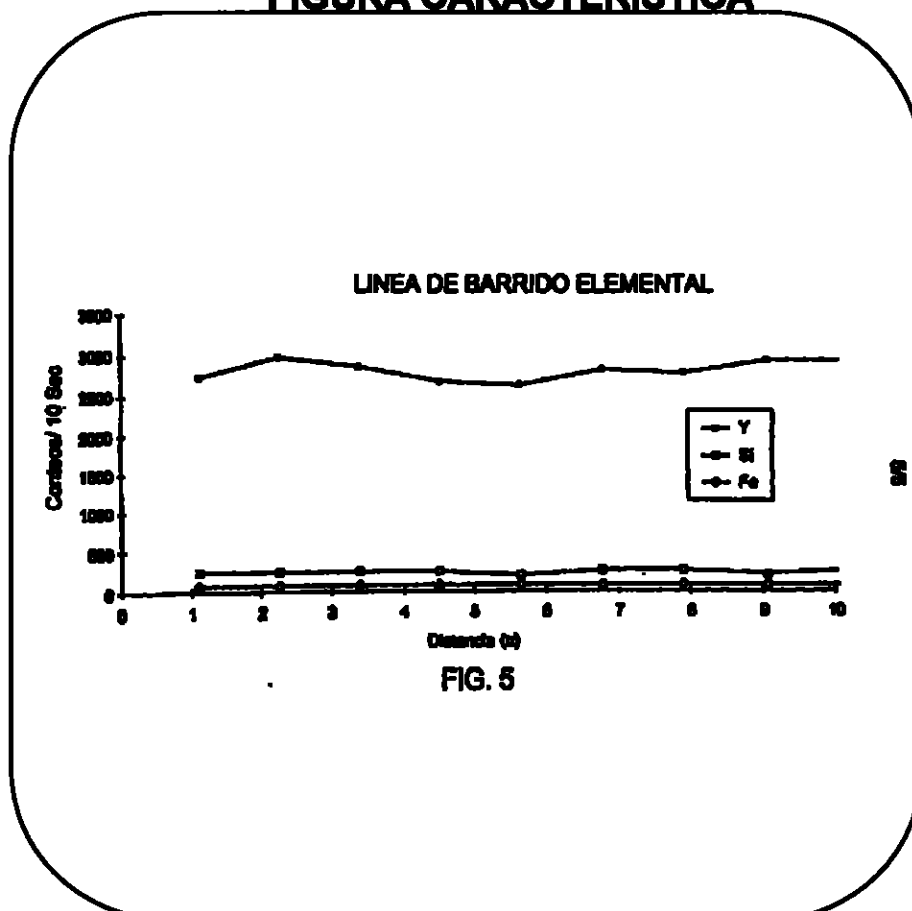
10

Anexos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por \$ 443.000.00.
- ☐ Comprobante de pago por reivindicación de prioridad.
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☒ Otros: Solicitud corrección de domicilio del inventor.

11

FIGURA CARACTERÍSTICA



12

Solicito la concesión de la patente,

NOMBRE: EMILIO FERREROFIRMA: Emilio Ferrero

C.C. 438.019 de Usaquén T.P. 31.929

The Commonwealth of Massachusetts

William Francis Galvin
Secretary of the Commonwealth

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by: Joan E. Frank

3. acting in the capacity of: Notary Public

4. bears the seal/stamp of:

the State of Massachusetts, whose commission expires on

Certified

5. at: Boston, Massachusetts

6. the: 1 November 2004

7. by: the Secretary of the Commonwealth

8. No.: 1028000

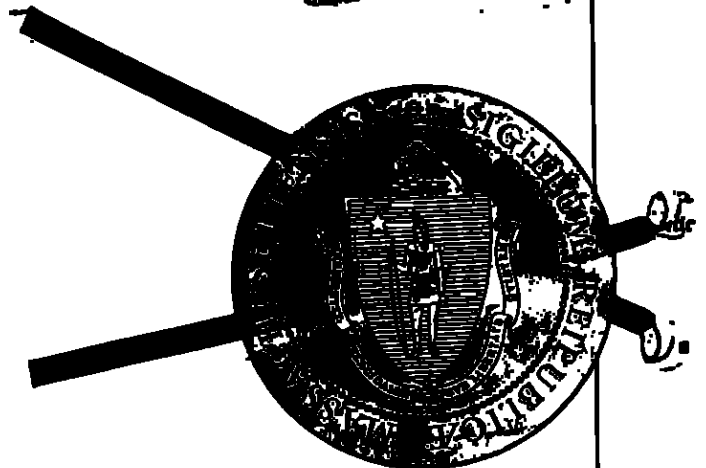
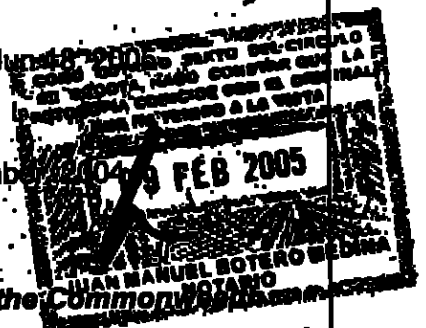
9. Seal/stamp:

10. Signature:

William Francis Galvin

William Francis Galvin
Secretary of the Commonwealth

Great Seal of the Commonwealth



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

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

REPRESENTACION Y PODER

REPRESENTATION AND POWER-OF-ATTORNEY

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

SAINT-GOBAIN CERAMICS & PLASTICS, INC.

domiciliado (s) en/of 1 New Bond Street Box No. 15138

Worcester, Massachusetts 01615-0138, United States of America

por el presente nombramos a EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555 y GERMAN CAVELIER, tpa. 832, domiciliados en la Carrera 4a N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el parágrafo 1o del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquel. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o al tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambas, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cese la ausencia o impedimento del representante principal, o de su primer o segundo suplentes, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, sumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, confiero (conferimos) poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, así como los tribunales de arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos de utilidad y diseños industriales; el registro de marcas de fábrica, colectivas, defensivas, de servicio, lemas comerciales, nombres comerciales, enseñas, nombres de dominio, variedades vegetales y denominaciones de origen; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de Marcas de uso de esos derechos; b) Las acciones de competencia desleal, protección del consumidor,

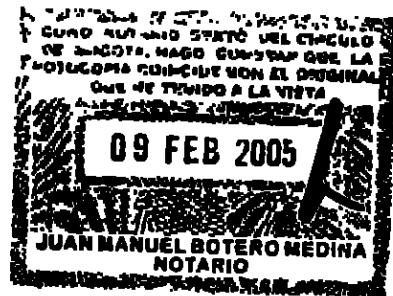
in due compliance with the terms of paragraph 1st. of article 543 of the Commercial Code, do hereby appoint EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555 and GERMAN CAVELIER, tpa. 832, domiciled at Carrera 4a N° 72-35, Bogotá, Colombia, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule will apply when the second alternate representative is to replace the first one, or when the third is to replace the first or second alternates in their turn, or both of them, second. In such cases, the principal representative, or the first or second alternates in their turn, or both of them, shall state their intention not to act as representative through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official or a Colombian Consul abroad; and in case of impediment, the appropriate certificate shall suffice. If any of appointees were to be definitely absent, the following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternates in their turn, ceases, representation can be taken again in their order, each one in turn, the first or second alternate depending on the cause of absence or impediment; and exercise will suffice. The exercise of the principal representative, or the second or third alternates in their turn shall end at such time. In a we grant a Power of Attorney in favor of the undersigned attorneys-at-law so that they may obtain the protection of my (our) industrial property and against the unfair competition, as well as (we) authorize the said attorneys to represent me (us) before the administrative, administrative contentious and judicial, as well as Arbitration Court, in all matters concerning the following: Obtainment of patents, utility models and industrial registration of trademarks, collective, defensive and service slogans, commercial names, trade emblems, domain names, varieties and denominations of origin; its renewal, assignation name or domicile, voluntary cancellation; and the registration of use of the above rights; b) Actions of unfair competition

5

oposiciones u observaciones, cancelación administrativa y judicial, nulidad, medidas cautelares, concesión de licencias, la tutela, la protección de secretos industriales, y en general los juicios civiles, penales, administrativos o contenciosos administrativos relacionados con estos derechos; acciones y procesos que promuevan o se nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir esta mandato, transigir, conciliar, admitir los hechos del proceso, desistír, cancelar, recibir, renunciar, y ratificar los actos de agentes oficiales.

the consumer, oppositions or observations, administrative or cancellation, nullity, infringement, granting of licenses, the action of mandamus, the protection of trade secrets, and in general the civil, and administrative suits relating to those rights; actions and instituted by me (m) or against me (us). And that in all the above they may substitute this Power of Attorney, compromise, conciliate the facts of the case, desist, cancel, receive, resign, and ratify acts of representatives without a power of attorney.

Dado y firmado hoy/Given and signed this October 8, 2004
en/in Worcester, Mass. U.S.A.
por/by Joseph P Sallin
Assistant Secretary
Firma [Signature] Signature



CERTIFICADO NOTARIAL (INDIVIDUO)

A las _____ días del mes de _____
de 200__ ante mí, Notario Público o Funcionario Autorizado
de _____
compareció(eron) personalmente _____

a quien(es) doy fe de conocer y me consta que es(son) la(s)
persona(s) firmante(s) del documento que preceda, y quien(es)
tiene(n) capacidad legal para otorgarlo

Notario Público o Funcionario Autorizado - Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy 8 de Octubre de 2004
Compareció(eron) ante mí
Joseph P. Sullivan, Secretario Asistente
quien(es) conozco personalmente y que firma(n) este
documento en representación de la Sociedad/compañía
denominada
SAINT-GOBAIN CERAMICS & PLASTICS, INC.

Certifico:

1. Que he visto los siguientes documentos:*

Artículos de Constitución
21 Febrero 1951

2. Que dichos documentos prueban lo siguiente:

2.1. Que Saint-Gobain Ceramics & Plastics
Inc.

es una Sociedad/Compañía legalmente constituida y existente
de acuerdo con las leyes del Estado de
Delaware

2.2. Que el domicilio de dicha Sociedad/Compañía es
1 New Bond Street, Box No. 15138, Worcester, MA
01615-0138, Estados Unidos de América

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

2.4. Que la(los) Sra.(Sras.) Joseph P. Sullivan
esté(n) autorizado(s) para otorgar el presente Poder.

Ciudad Worcester

Estado Massachusetts

Hoy 8 Oct de 2004

Notario Público o Funcionario Autorizado - Notary Public or Attesting Official

* Los documentos deben identificarse con fecha y origen

CAVELIER ABOGADOS
WFFODE01-181 (MINUTA N°12.1.1.2.6 USA)

NOTARIAL CERTIFICATE (INDIVIDUO)

On this _____ day of _____
200__ before me, a Notary Public or Attesting Official
personally appeared _____

to me known, and known to me to be the person
executed that foregoing document, and who has
capacity to execute it.

NOTARIAL CERTIFICATE (CORPORATION)

On this 8th day of October
appeared before me
Joseph P. Sullivan, Assistant Sec
who(m) I know personally and who(m) signed this document
representative(s) of the Corporation/Company named
SAINT-GOBAIN CERAMICS & PLASTICS, INC.

I certify:

1. That I have seen the following documents:*

Certificate of Incorporation dated
February 21, 1951

2. That the above documents prove the following:

2.1. That Saint-Gobain Ceramics & Plastics, Inc.

is a Corporation/Company legally existing and operating
in accordance with the laws of the State of
Delaware

2.2. That the domicile of said Corporation/Company is
1 New Bond Street, Box No. 15138, Worcester, MA
01615-0138, United States of America

2.3. That the purpose or purposes for which the present
Power of Attorney is granted are comprised within the corporate
purposes set forth in the charter of the said
Corporation/Company.

2.4. That Mrs.(Messrs.) Joseph P. Sullivan
is(are) authorized to grant the present Power of Attorney.

City Worcester

State Massachusetts

This 8th day of October 200__

JOAN E. FRANK, NOTARY PUBLIC
Commission Expires June 18, 2006

7

APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country:

This public document

2. has been signed by

3. acting in the capacity of

4. bears the seal/stamp of

Certified

5. at 6. the

7. by

8. No.

9. Seal/stamp 10. Signature

.....



6

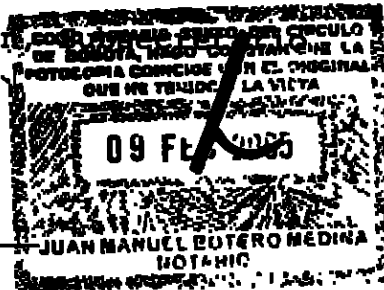
8

TRADUCCIÓN OFICIAL No. 11.22/04a realizada por Diego Vargas, Traductor Oficial, Resolución No. 0001 de 1999 del Ministerio de Justicia y registrado ante el Ministerio de Relaciones Exteriores de Colombia.

A continuación se traducen los sellos y legalizaciones de un documento mediante el cual SAINT-GOBAIN CERAMICS & PLASTICS, INC., domiciliada en 1 New Bond Street, Box No. 15138, Worcester, Massachusetts 01615-0138, Estados Unidos de América, otorga derechos de representación y poder a los Doctores EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PÁEZ, tpa. 23555 y GERMÁN CAVELIER, tpa. 832, domiciliados en la Carrera 4 No. 72-35, Bogotá 8, Colombia.

Dado y firmado hoy 8 de octubre de 2004 en Worcester, Massachusetts, Estados Unidos de América, por Joseph P. Sullivan,

Firma Firma Ilegible



CERTIFICADO NOTARIAL (SOCIEDAD) por medio de la cual se certifica la firma anterior del Señor Joseph P. Sullivan en representación de Saint-Gobain Ceramics & Plastics, Inc. y así mismo se certifica que la anterior es una sociedad legalmente existente y constituida de acuerdo a las leyes del Estado de Delaware, domiciliada en 1 New Bond Street, Box No. 15138, Worcester, Massachusetts 01615-0138, Estados Unidos de América. Adicionalmente se certifica que el Señor Joseph P. Sullivan está autorizado para otorgar el presente poder. Dado y firmado en la ciudad de Worcester, Estado de Massachusetts, el 8 de octubre de 2004.

Notario Público o Funcionario Autorizado Firma Ilegible

JOAN E. FRANK, NOTARIO PÚBLICO
Comisión Vence Junio 18 de 2005

El Estado de Massachusetts

William Francis Galvin

Secretario del Estado

APOSTILLA

(Convention de La Haye du 5 octubre 1961)

1. País: Estados Unidos de América

Este documento público

2. ha sido firmado por: Joan E. Frank

3. actuando en capacidad de: Notario Público

4. lleva el sello/estampilla de:

el Estado de Massachusetts, cuya comisión vence el 18 Jun. 2005

CERTIFICADO

5. en: Boston, Massachusetts

6. el: 1 de Noviembre de 2004

7. por: el Secretario del Estado

8. No.: 1028000

9. Sello/estampilla:

GRAN SELLO DEL ESTADO

10. Firma:

Firma ilegible

William Francis Galvin

Secretario del Estado

preparado por DGittens

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

DVZ/ID-6216/WPCL002G/COLO 14496-841-002-3

Diego F. Varela
DIEGO F. VARELA
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA 2

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2004 NOV 23 P 2:24

mas
JEFE DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.

TERMINO DE RELACIONES
EXTERNOAS

2004 NOV 23 P 2:24
mas
JEFE DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE
BOGOTA, HAGO CONSTAR QUE LA(S) FIRMA(S) DE
Diego Jaramillo
Vosgo
CON LA FIRMA REGISTRADA POR
LOS) EN ESTA NOTARIA
23 NOV 2004



COMO NOTARIO SEXTO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA CONFORME CON EL ORIGINAL
QUE SE ENVIÓ A LA VISTA
09 FEB 2005
JUAN MANUEL BOTERO MEDINA
NOTARIO

(19) World Intellectual Property
Organization
International Bureau



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(25) Filing Language: English

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(30) Priority Data:
10/217,523 13 August 2002 (13.08.2002) US

(71) Applicant (for all designated States except US): SAINT-
GOBAIN CERAMICS & PLASTICS, INC. [US/US];
1 New Bond Street, Box Number 15138, Worcester, MA
01615-0138 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): WALLAR, Howard
[US/US]; 12 Tucker Street, Worcester, MA 01606 (US).

(74) Agents: BUJOLD, Michael, J. et al.; Davis & Bujold,
P.L.L.C., Fourth Floor, 500 North Commercial Street, Man-
chester, NH 03101 (US).

(81) Designated States (national): AB, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GE, GD, GR, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KY, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN,
YU, ZA, ZM, ZW.

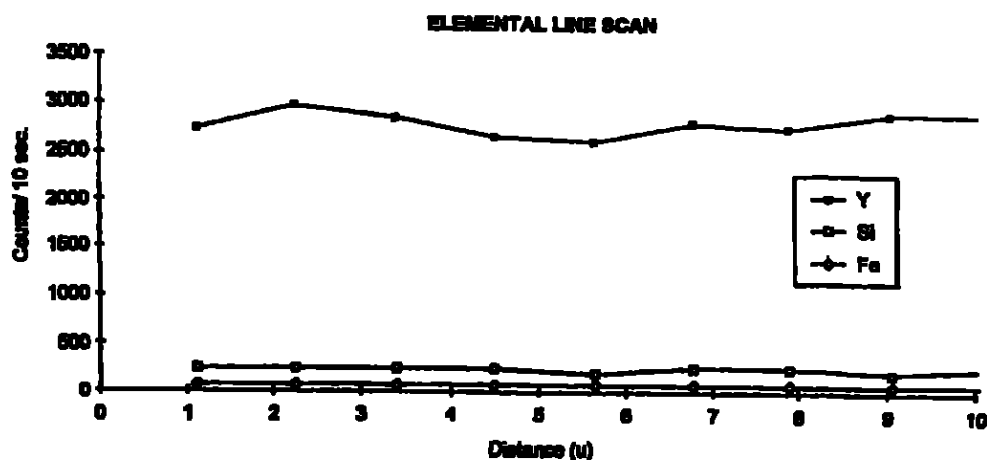
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European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
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Published:

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- before the expiration of the time limit for amending the
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amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PLASMA SPHEROIDIZED CERAMIC POWDER



(57) Abstract: Thermal spray powders suitable for application of a thermal barrier coating on a substrate can be obtained by plasma spraying a chemically homogeneous zirconia stabilized in the tetragonal form using a stabilizing oxide such as yttria to obtain a powder comprising substantially spherical hollow zirconia particles with sizes less than about 200 micrometers.

WO 2004/015158 A1

PLASMA SPHEROIDIZED CERAMIC POWDER

FIELD OF THE INVENTION

The present invention relates to ceramic powders, particularly zirconia powders, and a process for the production of ceramic powders in which the powders have a highly uniform composition.

BACKGROUND OF THE INVENTION

Stabilized zirconia powders are widely used to provide thermally stable and abrasion resistant coatings to parts that are exposed to very high temperatures during use but which are also exposed to ambient temperatures. It does, however, have a well-known drawback in that, as it cycles between high and low temperatures, it undergoes a crystal phase change from the tetragonal crystal phase structure, which is stable at elevated temperatures, to the monoclinic crystal phase structure, which is stable at room temperature. Volume changes occur as this crystal phase change takes place compromising the physical integrity of the zirconia coating. There is another phase of zirconia which is also stable at temperatures above the monoclinic/tetragonal transition temperature, (the "cubic" phase), but since little or no volume change occurs on the transition from cubic to tetragonal, this is treated for the purposes of this Description as a form of the tetragonal phase and is not distinguished therefrom.

In order to resolve the integrity problems with zirconia coatings resulting from the crystal phase changes, it is common to use stabilized zirconia in powder coatings. Stabilization can be achieved by the addition of a number of additives that have the effect of inhibiting the conversion from the tetragonal crystal phase to the monoclinic crystal phase upon cooling. Such additives include stabilizing oxides such as calcia, magnesia, yttria, ceria, hafnia, and rare earth metal oxides.

Stabilized zirconia coatings are widely used to produce an abradable protective coating on surfaces or thermal barrier coatings. They are typically applied as sprays by a flame spray or a plasma spray approach.

In the production of stabilized zirconia powders, the most common technique is described in U.S. Patent No. 4,450,184 to Longo et al., in which an aqueous slurry comprising a blend of zirconia and stabilizer materials is fed into a spray dryer to form dried porous particles. The porous particles are fused into homogenous hollow structures with a plasma or flame spray gun

which melts and fuses the components such that the particles ejected therefrom are stabilized zirconia. Thermal spraying of the hollow spheres creates a porous and abradable coating. However the Longo process does not achieve a high degree of uniformity of composition.

U.S. Patent No. 5,418,015 to Jackson et al. discloses a feed composition for thermal spray applications composed of stabilized zirconia mixed with zircon and a selected oxide to form an amorphous refractory oxide coating. Such products do not however have the required level of size and compositional uniformity that would be desirable to secure good thermal barrier coating compositions for high temperature applications. This is at least in part because there are many opportunities for variability in the resultant coating as a result of differing particle sizes in the feed, the flame or plasma gun design/shape, feed rate pressures, and the like.

Another method of forming stabilized zirconia involves sintering wherein the components are blended together as powders, sintered, and upon cooling, the sintered mass is broken up into particles. These particles may then serve as feed for a flame spray device. Unfortunately, this process does not provide for a high level of chemical homogeneity in the stabilization and results in widely varying shapes and particle sizes in the feed.

Ceramic mixtures such as stabilized zirconia may also be made by electrofusion. The fused mixtures are much more uniform than those made by the processes discussed above because they are the result of complete melting of the components. However, the components are difficult to melt and have poor flow characteristics as a result of their high density and irregular shape generated when the fused masses are crushed to provide particles. Thus, the currently available stabilized zirconia powders made by electrofusion have a high degree of un-melted material in the spray process resulting in poor efficiencies and coatings with a high content of such un-melted material particles. The un-melted particles introduce stresses into the coating due to the varying density of the coating in and around the un-melted particles. As a result, the longevity of the resultant coating is diminished, particularly under stressful conditions.

Notwithstanding the state of the technology, it would be desirable to provide a ceramic powder having a high level of chemical and morphological uniformity, which in turn, provides a durable thermal spray coating.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a zirconia powder particularly adapted for use as a thermal barrier coating which comprises morphologically and chemically uniform stabilized zirconia in the form of substantially spheroidal hollow spheres.

5 The zirconia is chemically uniform and by this meant that the zirconia is at least 90% pure and is at least about 96% by weight stabilized in a tetragonal crystal phase. The zirconia is also morphologically uniform and by this is mean that at least 95 volume % of the zirconia is in the form of spheres with a particle size of less than about 200 micrometers. The spheres may be somewhat deformed but are identifiably based on spheres rather than having random shapes.

10 The spheres are preferably at least 75% hollow spheres. In a preferred embodiment a chemically uniform stabilized zirconia is heat-treated by plasma fusion to obtain the substantially spheroidal shape. Preferably, the stabilized zirconia contains less than 1.0% by weight monoclinic zirconia.

In a preferred aspect, the present invention is directed to a thermally sprayable composition comprising hollow spheres of yttria stabilized zirconia, the hollow spheres having a
15 particle size of less than about 200 micrometers, wherein the yttria is uniformly incorporated into the zirconia by electrofusion prior to formation of the hollow spheres. Preferably, the zirconia contains less than 2.0% by weight monoclinic zirconia. The hollow spheres are preferably formed by plasma fusion.

In yet another aspect, the present invention is directed to a process for producing
20 spheroidized ceramic powder comprising the steps of: providing a chemically uniform, stabilized zirconia; and heat treating the zirconia to form substantially hollow spheres thereof of morphological uniformity. Preferably, the stabilized ceramic material comprises zirconia stabilized in a tetragonal crystal phase and contains less than about 2.0% by weight monoclinic zirconia. The stabilized zirconia is preferably formed by electrofusion of zirconia and a stabilizing
25 oxide. Preferably, heat treating occurs in a plasma spray gun or a flame spray gun. The process may further include the step of comminuting the stabilized ceramic materials prior to heat treating.

In still yet another aspect, the present invention is directed to a process of forming a thermal sprayable powder coating comprising the steps of: providing a zirconia feedstock wherein the zirconia is at least 96% by weight stabilized in a tetragonal crystal phase; and plasma fusing
30 the zirconia feedstock to form substantially hollow spheres thereof. Preferably, the stabilized zirconia is formed by electrofusion.

The invention also comprises a process for the application of a thermal barrier coating to a substrate which comprises thermal spray coating the substrate using a sprayable composition comprising zirconia, of which at least 96% is stabilized in the tetragonal form, having a substantially uniform spherical morphology with particle sizes smaller than 200, and more preferably smaller than 100, micrometers. In referring to particle sizes it is understood that the reference is to volume average particle sizes unless otherwise apparent from the context.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 through 4 are elemental line scans of well sintered particles from commercially available stabilized zirconia powders.

Figure 5 is an elemental line scan of a hollow spheroidized zirconia particle made in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is directed to a thermal sprayable zirconia powder having a very uniform chemical composition and morphology. The thermal sprayable ceramic powder preferably has a spheroidized shape, and even more preferably, the spheroidized particles are substantially hollow so that the particles melt more rapidly forming either dense coatings or coatings with uniform porosity depending on the spray conditions. In a most preferred embodiment, the thermal sprayable zirconia powder of the present invention comprises at least 90 volume % zirconia, and the zirconia is at least about 96% by weight stabilized in the tetragonal form by a stabilizing oxide. More preferably, the zirconia is at least 98% by weight stabilized in the tetragonal form, and most preferably, at least about 99% by weight stabilized in the tetragonal form.

The zirconia feedstock used in the present invention is stabilized with a stabilizing oxide such as, but not limited to, yttria, calcia, ceria, hafnia, magnesia, a rare earth metal oxide, and combinations thereof. To achieve a high chemical uniformity in the stabilized zirconia feedstock, the stabilizing oxide is preferably electrofused with the zirconia. The amount of stabilizing oxide used may vary depending on the result desired. A sufficient amount of the stabilizing oxide is an amount which substantially stabilizes the zirconia in the tetragonal crystal phase. The stabilizing oxide is desirably fully reacted with and incorporated into the zirconia crystal structure such that X-ray analysis cannot detect a

significant amount, (no more than 4%), of the monoclinic zirconia. The amount of the stabilizing oxide present can be up to about 10% by weight but some stabilizers are effective at lower levels. For example, in the case of zirconia stabilized using yttria, an effective amount may be about 1% but can be as high as 20% by weight; for magnesia, about 2% to about 20% by weight is effective; for calcia, about 3% to about 5% by weight may be used; and for a rare earth metal oxide, about 1% to about 60% by weight. A mixture of stabilizing oxides may be used.

The stabilizing oxide, preferably yttria, is arc fused with the zirconia at a temperature range of about 2750°C to about 2950°C such that components are completely molten and, since this is above the transition temperature, the zirconia is substantially completely in the tetragonal crystal phase. Upon cooling to room temperature, the stabilizing oxide maintains this tetragonal state even below the normal transition temperature. To enhance this effect, the molten material is preferably rapidly cooled with water or air such that the melt flow is broken up into a flow of droplets and cooled to provide fine particles of stabilized zirconia with a very homogenous chemical composition. A method of quenching the molten zirconia and stabilizing oxide, where the rapid solidification tends to stabilize the tetragonal form of zirconia, is disclosed in U.S. Patent No. 5,851,926, the entirety which is herein incorporated by reference. Preferably, the resulting fine particles of stabilized zirconia are further comminuted. Typically, the fine particles are milled to a size of less than about 5 microns, preferably less than about 2 microns, more preferably about 0.5 microns. The fine particles of stabilized zirconia are then preferably spray dried and collected as agglomerated particles. Although the agglomeration step is not essential to the practice of the invention, it does provide a more useable size for further heat treatment of the stabilized zirconia as discussed below.

The agglomerated particles are further heat treated to form substantially hollow spheres thereof having uniform morphology. A particularly preferred form of heat treatment is a plasma fusion process where the particles are melted together in a plasma flame and collected as a fine powder having a high level of chemical and morphological uniformity. Substantially hollow spheres of the stabilized zirconia are formed which preferably contain less than about 4% by weight, more preferably less than about 2% by weight, and more preferably less than about 1% by weight, monoclinic zirconia. Preferably, the substantially hollow spheres have a particle size of less than about 200

microns, more preferably less than about 100 microns, and most preferably, less than about 75 microns.

Unexpectedly, the substantially hollow spheres of the stabilized zirconia feedstock have a high level of chemical and morphological uniformity wherein the zirconia is at least about 96% by weight stabilized in the tetragonal crystal phase, preferably at least about 98% by weight stabilized in the tetragonal crystal phase, and more preferably at least about 99% by weight in the tetragonal crystal phase. Thus, thermal sprayable spheroidized powders of the present invention form more stable and durable coatings due to the high level of chemical uniformity due to the electrofusion of the zirconia and stabilizing oxide which substantially stabilizes the zirconia. The spheroidized particles of the stabilized zirconia melt more readily because of the hollow sphere morphology and complete reaction of the stabilizer with the zirconia. The coatings sprayed have very predictable density from high density to controlled porosity depending on the spray conditions.

To obtain durable zirconia thermal sprayable coatings, a uniform stabilization of the tetragonal crystal phase of the zirconia is crucial. It has now been shown that in comparison to commercially available zirconia powders stabilized with yttria, the spheroidized zirconia powder of the present invention shows substantial incorporation of the yttria into the zirconia. Table I illustrates an example of a zirconia powder of the present invention in comparison with commercially available stabilized zirconia powders with regard to volume percent of each crystal phase through X-ray Diffraction data (XRD).

TABLE I

Ex.	Tet * ZrO ₂ (vol %)	Mono ZrO ₂ (vol %)	Y ₂ O ₃ (vol %)
PF	100	0.0	--
PX	98.3	11.7	--
ST	98.9	1.1	--
M1	95.6	4.4	--
M2	99.4	10.6	--

* Includes cubic zirconia as well as tetragonal

PF = zirconia powder of the present invention.

PX = PRAXAIR ZRO™ available from Praxair, Inc., Danbury, Connecticut.

ST = STARK YZ available from H.O. Stark GmbH.

5 M1 = METCO ZD4NS-G available from Sulzer Metco, The Coatings Co., Westbury, NY.

M2 = METCO Z04 available from Sulzer Metco.

Although the concentration of yttria was not detected by X-ray diffraction (XRD) in all samples, it is the concentration of the monoclinic zirconia which determines whether the zirconia has been substantially stabilized in the tetragonal crystal phase. Elemental line scans of particles of Examples PX, ST, M1, and M2 are illustrated in Figures 1 through 4 to determine the composition of the particles. In Figure 1, the elemental line scan, edge to edge, of a well-sintered particle of Example PX shows that the particle analyzed did not have a uniform composition given the non-linear line representing yttrium. Therefore, although XRD did not detect yttrium, the elemental line scan shows that the yttria did not completely co-fuse with the zirconia, and as such, the composition is not sufficiently chemically uniform. The spike in the silicon line further attests that the particle is also not chemically or morphologically uniform. In Figure 2, the elemental line scan of a well-sintered particle of Example ST, edge to edge, also shows variations in the yttrium concentration, and thus, the particle is not chemically uniform. In Figure 3, the elemental line scan of a well-sintered particle of Example M1, again shows variation in the yttrium concentration, and thus, the particle is not chemically uniform. In Figure 4, the elemental line scan of a well-sintered particle of Example M2 again show variations in the yttrium concentration, and thus, the particle is not chemically uniform.

25 By electrofusing the stabilizing oxide, yttria, with the zirconia, the stabilized zirconia is relatively uniform in composition. Further heat treatment such as plasma fusion provides the morphological uniformity of the substantially hollow spheres. The unexpected chemical and morphological uniformity is clearly illustrated in the elemental line scan shown in Figure 5 of a hollow sphere of Example PF. The substantially linear yttrium line illustrates that a complete melt and re-solidification had occurred to provide a chemically uniform sphere. Also, the substantially flat silicon and iron element lines illustrate the morphological uniformity of the sphere.

Therefore, although the commercially available stabilized zirconia powders appear to be similar on their face, the spheroidized zirconia powder of the present invention provide a more chemically and morphologically uniform particle for thermal spray applications. The chemical and morphological uniformity in turn produces thermal spray coatings of exceptional durability.

Other variations and modifications of the basic invention can be conceived without departing from the concepts described above. It is intended that all such variations and modifications be included within the broad understanding of this invention.

CLAIMS

1. Zirconia thermal spray powder comprising a chemically uniform stabilized zirconia wherein the zirconia is at least about 96% by weight stabilized in the tetragonal crystal phase, said powder being in the form of substantially spherical particles having a particle size of less than 200 micrometers, at least the majority of said particles being hollow.
2. The zirconia powder of claim 1 wherein said hollow particles have a particle size of less than about 100 microns.
3. The zirconia powder of claim 1 wherein the zirconia is stabilized with an oxide selected from the group consisting of yttria, magnesia, calcia, ceria, hafnia, a rare earth oxide, and combinations thereof.
4. The zirconia powder of claim 1 which contains less than 1.0% by weight monoclinic zirconia.
5. A process for the production of a chemically uniform thermal spray powder which comprises the steps of:
 - a) electrofusing zirconia with up to 60% by weight of an oxide effective to stabilize the zirconia in the tetragonal phase;
 - b) quenching the electrofused stabilized zirconia to obtain particulate stabilized zirconia with at least 96% of the zirconia in the tetragonal phase;
 - c) heat treating the stabilized zirconia to form substantially spherical hollow particles of stabilized zirconia with particle sizes of 200 micrometers or less.
6. A process according to Claim 5 in which the zirconia is stabilized in the tetragonal form using up to 60% by weight of a stabilizing oxide selected from the group consisting of yttria, rare earth metal oxide, calcium oxide and magnesium oxide.
7. A process according to Claim 5 in which the stabilizing oxide is yttria in an amount of from 1 to 25% by weight.
8. A process according to Claim 5 in which the quenched stabilized zirconia is at least 98% in the tetragonal phase.
9. A process according to Claim 5 in which particulate stabilized zirconia is plasma sprayed to yield substantially spherical particles at least the majority of which are hollow with particle sizes below 100 micrometers.

[Handwritten signature]

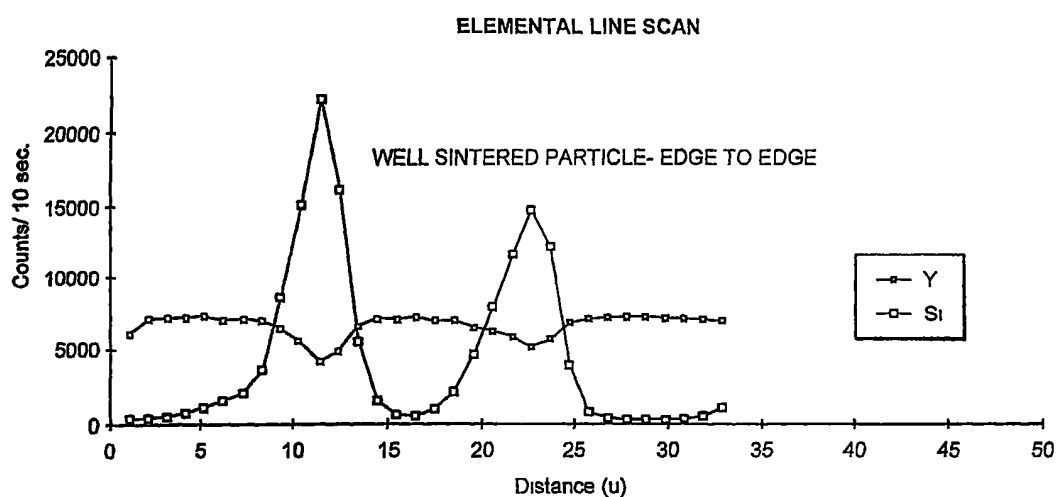


FIG 1
PRIOR ART

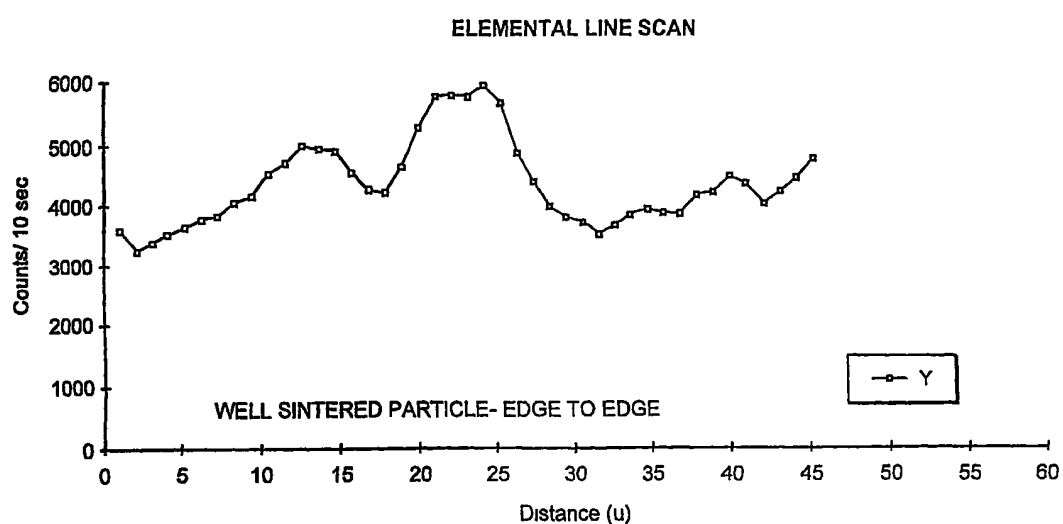


FIG 2
PRIOR ART

SB

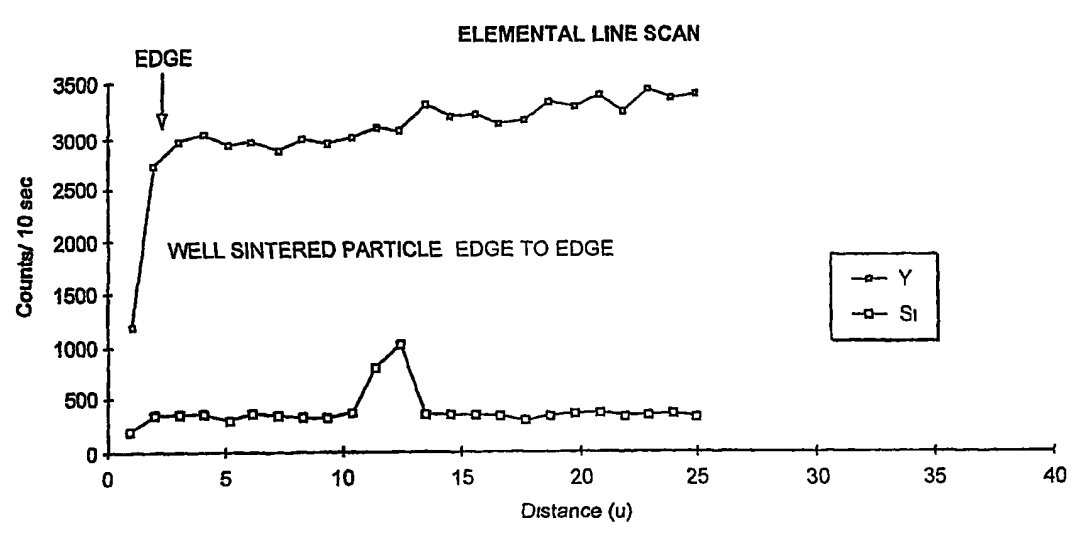


FIG 3
PRIOR ART

[Handwritten signature]

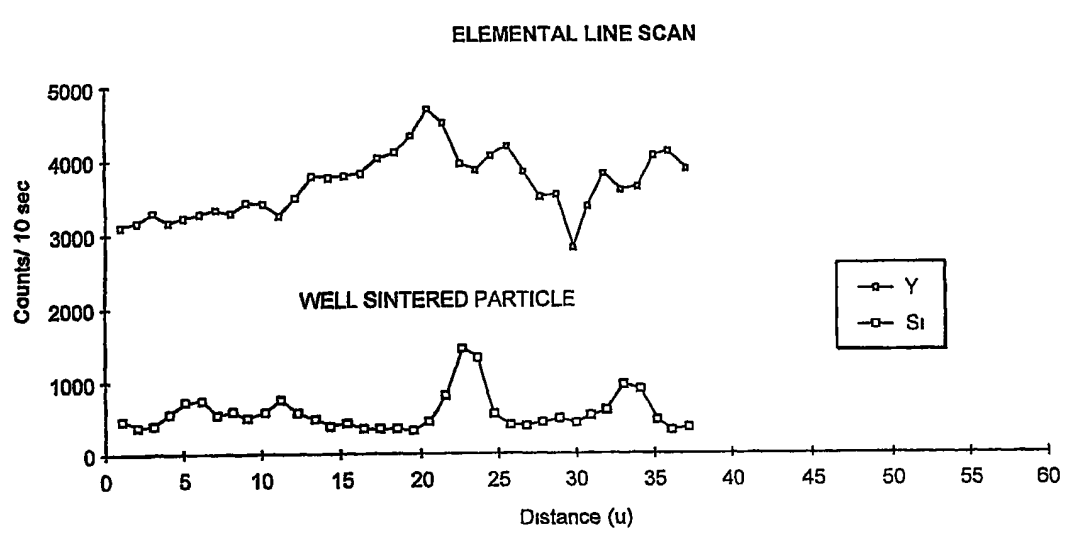


FIG 4
PRIOR ART

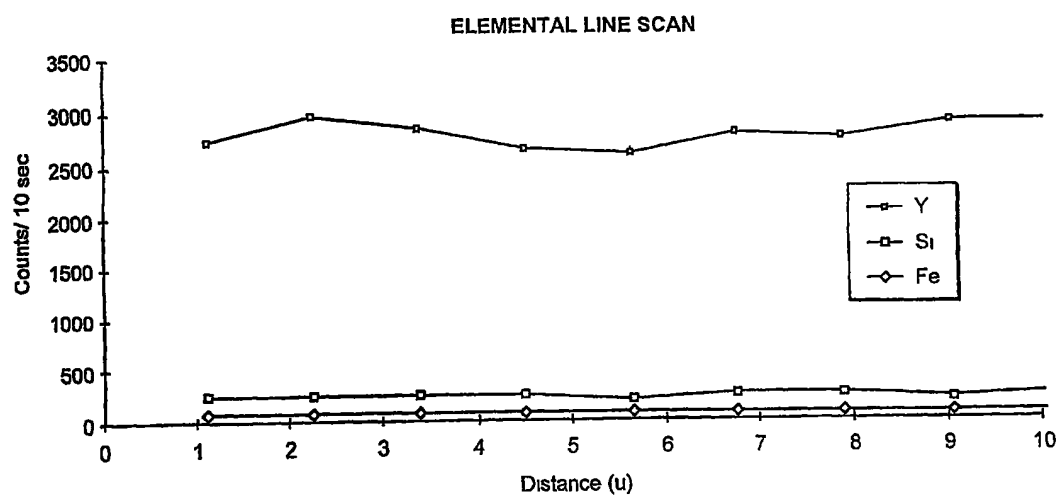


FIG 5

INTERNATIONAL SEARCH REPORT

Intern. application No.

PCT/US 03/24541

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C4/10

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

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

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

CHEM ABS Data, PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YANO, TOYOHICO ET AL: "Effects of spray pyrolysis conditions on the character of yttria-partially stabilized zirconia powders" retrieved from STN Database accession no. 106:89058 CA XP002265437 abstract & YOGYO KYOKAISHI (1987), 95(1), 111-16 , 1987, -- -/-	1-4

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

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Date of the actual completion of the International search

17 December 2003

Date of mailing of the International search report

14/01/2004

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 03/24541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KATO, AKIO ET AL: "Sinterability of calcia-stabilized zirconia powders prepared by spray-pyrolysis technique" retrieved from STN Database accession no. 99:199472 CA XP002265438 abstract & NIPPON KAGAKU KAISHI (1983), (10), 1544-6 , 1983,	1-4
Y	K.A. KHOR: "rapidly solidified neodymia-stabilised zirconia coatings prepared by dc plasma spraying" ELSEVIER, vol. 96, 1997, pages 313-322, XP002265436 page 316 -page 317, column 1 abstract	1-9
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A	US 4 450 184 A (FRANK N. LONGO) 22 May 1984 (1984-05-22) cited in the application column 3, line 36 - line 68; claims 1-3,5	1-9
A	WO 02 45931 A (SULZER METCO) 13 June 2002 (2002-06-13) page 3, line 7 - line 8 , sentence 21 - sentence 25; claims 1-7	1-9
A	US 4 590 090 A (PAUL A. SIEMERS) 20 May 1986 (1986-05-20) column 2, line 40 - line 52 column 3, line 25 - line 47; claims 1,2	1-9
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	-/-	

INTERNATIONAL SEARCH REPORT

22

International Application No.
PCT/us 03/24541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 549 (C-662), 7 December 1989 (1989-12-07) & JP 01 226732 A (NKK CORP), 11 September 1989 (1989-09-11) abstract	1,3,5,6
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internet Application No
PCT/us 03/24541

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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JP 11335804	A	07-12-1999	NONE	
JP 01226732	A	11-09-1989	NONE	
JP 02064016	A	05-03-1990	JP 2705133 B2	26-01-1998
US 6022594	A	08-02-2000	NONE	
GB 833107	A	21-04-1960	NONE	

PCT REQUEST

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

For receiving Office use only	
International Application No.	
International Filing Date	
Name of receiving Office and "PCT" International Application	
Applicant's or agent's file reference (if desired) (12 characters maximum)	NOR A-3363PC

Box No. I TITLE OF INVENTION PLASMA SPHEROIDIZED CERAMIC POWDER	
Box No. II APPLICANT	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)</i> SAINT-GOBAIN CERAMICS & PLASTICS, INC. 1 New Bond Street Box Number 15138 Worcester, MA 01615-0138 US	☐ This person is also inventor. Telephone No. 508-795-5712 Facsimile No. 508-795-2653 Teleprinter No.
State (i.e. country) of nationality: US	State (i.e. country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the U.S.A. ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
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United States of America

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- | | |
|---|---|
| ☐ AE United Arab Emirates | ☐ LR Liberia |
| ☐ AG Antigua and Barbuda | ☐ LS Lesotho |
| ☐ AL Albania | ☐ LT Lithuania |
| ☐ AM Armenia | ☐ LU Luxembourg |
| ☐ AT Austria | ☐ LV Latvia |
| ☐ AU Australia | ☐ MA Morocco |
| ☐ AZ Azerbaijan | ☐ MD Republic of Moldova |
| ☐ BA Bosnia and Herzegovina | ☐ MG Madagascar |
| ☐ BB Barbados | ☐ MK The former Yugoslav Republic of Macedonia |
| ☐ BG Bulgaria | ☐ MN Mongolia |
| ☐ BR Brazil | ☐ MW Malawi |
| ☐ BY Belarus | ☐ MX Mexico |
| ☐ BZ Belize | ☐ MZ Mozambique |
| ☐ CA Canada | ☐ NO Norway |
| ☐ CH and LI Switzerland and Liechtenstein | ☐ NZ New Zealand |
| ☐ CN China | ☐ OM Oman |
| ☐ CO Colombia | ☐ PH Philippines |
| ☐ CR Costa Rica | ☐ PL Poland |
| ☐ CU Cuba | ☐ PT Portugal |
| ☐ CZ Czech Republic | ☐ RO Romania |
| ☐ DE Germany | ☐ RU Russian Federation |
| ☐ DK Denmark | ☐ SD Sudan |
| ☐ DM Dominica | ☐ SE Sweden |
| ☐ DZ Algeria | ☐ SG Singapore |
| ☐ EC Ecuador | ☐ SI Slovenia |
| ☐ EE Estonia | ☐ SK Slovakia |
| ☐ ES Spain | ☐ SL Sierra Leone |
| ☐ FI Finland | ☐ TJ Tajikistan |
| ☐ GB United Kingdom | ☐ TM Turkmenistan |
| ☐ GD Grenada | ☐ TN Tunisia |
| ☐ GE Georgia | ☐ TR Turkey |
| ☐ GH Ghana | ☐ TT Trinidad and Tobago |
| ☐ GM Gambia | ☐ TZ United Republic of Tanzania |
| ☐ HR Croatia | ☐ UA Ukraine |
| ☐ HU Hungary | ☐ UG Uganda |
| ☐ ID Indonesia | ☐ US United States of America |
| ☐ IL Israel | ☐ UZ Uzbekistan |
| ☐ IN India | ☐ VN Viet Nam |
| ☐ IS Iceland | ☐ YU Yugoslavia |
| ☐ JP Japan | ☐ ZA South Africa |
| ☐ KE Kenya | ☐ ZM Zambia |
| ☐ KG Kyrgyzstan | ☐ ZW Zimbabwe |
| ☐ KP Democratic People's Republic of Korea | |
| ☐ KR Republic of Korea | |
| ☐ KZ Kazakhstan | |
| ☐ LC Saint Lucia | |
| ☐ LK Sri Lanka | |

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- ☐ Any newly added PCT country
- ☐

In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that these additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving office with in the 15-month time limit.)

Box No. VI	PRIORITY CLAIM	Further priority claims are indicated in the Supplemental Box ☐
-------------------	-----------------------	--

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

Country (in which, or for which, the applicant was filed)	Filing Date (Day/month/year)	Application No.	Office of filing (only for regional or international application)
Item (1) US	13 August 2002	10/217,523	
Item (2)			
Item (3)			

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

☒ The receiving Office is hereby requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s): (1) one

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

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

Earlier search Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search, to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request:
Country (or regional Office): _____ Date (day/month/year): _____ Number: _____

Box No. VIII CHECK LIST

This international application contains the following number of sheets:

1. request	:	4	sheets
2. description	:	8	sheets
3. claims	:	1	sheets
4. abstract	:	1	sheets
5. drawings	:	5	sheets
Total	:	19	sheets

This international application is accompanied by the item(s) marked below:

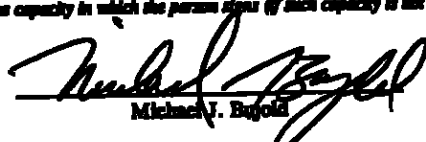
- | | |
|--|--|
| 1. ☐ signed power of attorney | 5. ☒ fee calculation sheet |
| 2. ☐ copy of general power of attorney | 6. ☐ separate indications concerning deposited microorganisms |
| 3. ☐ statement explaining lack of signature | 7. ☐ nucleotide and/or amino acid sequence listing (diskette) |
| 4. ☐ priority document(s) | 8. ☒ other (specify): 1) Return Postcard, 2) Transmittal Letter - 1 page; 3) a further signed power of attorney. |

Identified in Box No. VI as item(s):

Figure No. 5 of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

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


Michael J. Buford

For receiving Office use only

1. Date of actual receipt of the purported international application: 3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application: 4. Date of timely receipt of the required corrections under PCT Article 11(2): 5. International Searching Authority specified by the applicant: <u>ISA/</u>	2. Drawings: ☐ received: ☐ not received: 6. ☐ Transmittal of search copy delayed until search fee is paid
---	--

For International Bureau use only

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

RECEIVED

APR 12 2004

DAVIS AND BUJOLD

PATENT COOPERATION TREATY

22

PCT

From the INTERNATIONAL BUREAU

To:

BUJOLD, Michael, J.
Davis & Bujold, P.L.L.C.
Fourth Floor
500 North Commercial Street
Manchester, NH 03101
United States of America

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

TAC

Date of mailing (day/month/year) 30 March 2004 (30.03.2004)		
Applicant's or agent's file reference NOR A-3363PC		IMPORTANT INFORMATION
International application No. PCT/US2003/024541	International filing date (day/month/year) 04 August 2003 (04.08.2003)	Priority date (day/month/year) 13 August 2002 (13.08.2002)
Applicant SAINT-GOBAIN CERAMICS & PLASTICS, INC. et al		

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR
National : BG, CA, CN, DE, GB, IL, JP, KP, KR, MN, NO, PL, RO, RU, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National : AE, AG, AL, AM, AT, AU, AZ, BA, BB, BR, BY, BZ, CH, CO, CR, CU, CZ, DK, DM, DZ, EC,
EE, ES, FI, GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MW, MX, MZ, NZ, OM, PH, PT, SD, SE, SG, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU,
ZA, ZM, ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 38(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: Anita ZANDRINI
Facsimile No. (41-22) 338.89.65	Telephone No. (41-22) 338 8989

PATENT COOPERATION TREATY

28

PCT TAC

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

BUJOLD, Michael, J.
Davis & Bujold, P.L.L.C.
Fourth Floor
500 North Commercial Street
Manchester, NH 03101
United States of America

Date of mailing (day/month/year) 24 September 2003 (24.09.03)	
Applicant's or agent's file reference NOR A-3363PC	IMPORTANT NOTIFICATION
International application No. PCT/US03/24541	International filing date (day/month/year) 04 August 2003 (04.08.03)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 13 August 2002 (13.08.02)
Applicant SAINT-GOBAIN CERAMICS & PLASTICS, INC. et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
13 Augu 2002 (13.08.02)	10/217,523	US	15 Sept 2003 (15.09.03)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.88.85	Authorized officer Sylvie SOBEZYNSKI Telephone No. (41-22) 338 8087
--	---

From the INTERNATIONAL BUREAU

PCT

CMP

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

(PCT Rule 47.1(c), first sentence)

To:

BUJOLD, Michael, J.
Davis & Bujold, P.L.L.C.
Fourth Floor
500 North Commercial Street
Manchester, NH 03101
ETATS-UNIS D'AMERIQUE

RECEIVED

MAR - 1 2004

DAVIS AND BUJOLD

Date of mailing (day/month/year) 19 February 2004 (19.02.2004)		
Applicant's or agent's file reference NOR A-3363PC		IMPORTANT NOTICE
International application No. PCT/US2003/024541	International filing date (day/month/year) 04 August 2003 (04.08.2003)	Priority date (day/month/year) 13 August 2002 (13.08.2002)
Applicant SAINT-GOBAIN CERAMICS & PLASTICS, INC. et al		

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

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

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

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

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

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

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on 19 February 2004 (19.02.2004) under No. WO 2004/015158

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

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

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

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

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

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

Authorized officer

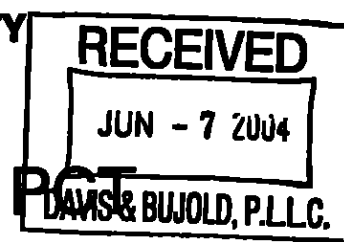
Gijsbertus Beijer - Carlos Roy

Facsimile No.(41-22) 740.14.35

Telephone No.(41-22) 338.91.11

Form PCT/IB/308 (April 2002)

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY



To:

Bujold, Michael J.
DAVIS & BUJOLD P.L.L.C.
500 N. Commercial Street,
4th floor
MANCHESTER, New Hampshire 03101
ETATS-UNIS D'AMERIQUE

3
TAC

WRITTEN OPINION
(PCT Rule 66)

Aug 18, 04

Applicant's or agent's file reference NOR A-3363PC		REPLY DUE within 3 month(s) from the above date of mailing	
International application No. PCT/US 03/24541	International filing date (day/month/year) 04.08.2003	Priority date (day/month/year) 13.08.2002	
International Patent Classification (IPC) or both national classification and IPC C23C4/10			
Applicant SAINT-GOBAIN CERAMICS & PLASTICS, INC.			

- This written opinion is the first drawn up by this International Preliminary Examining Authority.
- This opinion contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application
- The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
- The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 13.12.2004

Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tlx 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Eisen, D Formalities officer (incl. extension of time limits) Delmon, G Telephone No. +31 70 340-2525	
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WRITTEN OPINION

International application No. **PCT/US 03/24541**

I. Basis of the opinion

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*):

Description, Pages

1-8 as originally filed

Claims, Numbers

1-9 as originally filed

Drawings, Sheets

15-55 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

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

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

6. Additional observations, if necessary:

WRITTEN OPINION

International application No. **PCT/US 03/24541**

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1
Inventive step (IS)	Claims	1-9
Industrial applicability (IA)	Claims	1-9

2. Citations and explanations

see separate sheet

**WRITTEN OPINION
SEPARATE SHEET**

International application No. PCT/US03/24541

Re Item V**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

1. D1: Chemical Abstracts Service, Columbus, Ohio, US

Yano, Toyohiko: " Effects of spray pyrolysis conditions on the character of yttria-partial stabilized zirconia powders".

retrieved from STN

database accession no.: 106:89058

XP002265437

& Yogyo Kyokaishi (1987), 95(1), 111-16

D2: Chemical Abstracts Service, Columbus, Ohio, US

Kato, Akio: " Sinterability of calcia-stabilized zirconia powders prepared by spray-pyrolysis technique".

retrieved from STN

database accession no.: 99:199472

XP002265438

& Nippon Kagaku Kaishi (1983), (10), 1544-6

D3: Surface and Coatings Technology 96 (1997) 313-322

K.A.Khor: "Rapidly solidified neodymium-stabilized zirconia coatings prepared by DC plasma spraying".

D4: US-A-2535526**D5: US-A-4450184****D6: WO-A-0245931****D7: JP-A-11335804****2. D1 discloses a fine Y₂O₃-partially stabilized ZrO₂ powder. The powder crystal phase is tetragonal. The particle size is 0.2-5 μ m and is hollow.****Hence independent claim 1 doesn't fulfill the criterion of Art.33(2) and (3) with respect of novelty and inventive step.**

3. D2 discloses a CaO-stabilized tetragonal hollow ZrO₂ powder (1-5 μ m.)

Hence independent claim 1 doesn't fulfill the criterion of Art.33(2) and (3) with respect of novelty and inventive step.

4. D3 discloses a method for preparing neodymia-stabilized zirconia powders and their coatings by plasma spraying by combination of mechanical milling, thermal plasma melting, solidifying, heat treating and spraying. The spheroidised powders have a particle size from 5 microm. to 70 microm. and consist of the cubic phase (97,43% with 10% Nd₂O₃) (see page 314, point 2- 317, point3.2).

The difference between D3 and the present application is the non-specification of the electrofusing step and that the powders are hollow .

5. D4 discloses a process for making of stabilized zirconia (cubic zirconia is 75% to 90% or even more), ready for manufacture into bricks or other shapes, comprising fusing in an electric arc furnace a stabilized zirconia charge, cooling and calcining it (see col.4, lin. 46- col.6, lin.2; col.6, lin. 52-55; claims1-3).

6. D5 discloses a process for producing a coating by spraying hollow stabilized zirconium oxide particles. The hollow sphere particles are made by feeding and fusing the particles into a plasma spray gun (see col.3, lin. 56-63; claims 1-5).

The skilled person would therefore combine the teachings of D3,D4 and D5 to arrive at the same solution of claim 5.

Hence independent claim 5 doesn't fulfill the criterion of Art.33(3) with respect of inventive step.

7. D6 discloses a method of producing a prealloyed stabilized zirconia powder comprising the steps of mixing and alloying yttria and zirconia powders using an induction arc process, powderizing the alloyed cubic/tetragonal yttria-zirconia material, spray-drying the stabilized zirconia powder suitable for use in spray coating applications. The powder has an average particle size of no more than about 10 microns or between about 11 and 150 microns.

8. D7 discloses the plasma spray coating of yttria-stabilized zirconia, comprising

**WRITTEN OPINION
SEPARATE SHEET**

International application No. PCT/US03/24541

plasma spraying of raw powder, wich is obtained by mixing 5 to 20 vol. % yttria and zirconia powder into an hollow shape , wich is obtained by gas atomization into yttria-stabilized zirconia powder, wich is obtained by melting and pulverizing.

9. Dependent claims 2-4, 6-9 do not appear to contain any additional feature wich, in combination with the features of any claim to wich they refer, meet the requirements of the PCT with respect of inventive step. The reasons are as follows: said features are known from D1,D2,D3,D4,D5,D6 and /or D7.

PATENT COOPERATION TREATY

Applicant(s): Saint-Gobain Ceramics and Plastics, Inc.

International App. No.: PCT/US03/24541

International filing date: August 4, 2003

Officer: D. Elsen

Priority Date: August 13, 2002

Applicant or Agent's Ref.: NOR A-3363PC

EUROPEAN PATENT OFFICE

ATTN: IPEA

P.B. 5818 Palentlaan 2

NL-2280 HV Rijswijk-Pays Bas

Fax No.: 011-31-70-340-3016

RESPONSE TO WRITTEN OPINION

Sir:

In response to the Written Opinion dated June 1, 2004, reconsideration of the reasoned statements contained in the Written Opinion is respectfully requested for the reasons outlined below.

1. Independent claim 1 was rejected as lacking to fulfill the criterion under Article 33(2) and Article 33(3) with respect to novelty and inventive step. The EPO has cited D1 and D2 to support its position.

By way of background, the claimed invention is drawn to a zirconia thermal spray powder having at least about 96% by weight stabilized in the tetragonal crystal phase and being in the form substantially spherical particles having a particle size less than 200 microns, the majority of the particles being hollow. Of particular significance, the zirconia thermal spray powder is chemically uniform.

The claimed invention was developed after recognition that state of the art thermally sprayed hollow zirconia particles are chemically non-uniform. A discussion is provided in the section entitled "Background of the Invention" in the present specification, which describes state

of the art processing in which untreated raw materials are fed to a flame spray apparatus to effect hollow zirconia particles. Upon characterization, these particles were found to be chemically non-uniform, as shown by the largely irregular and non-linear edge-to-edge data plots of elemental yttrium shown in Figs. 3 and 4 in the present application. In contrast, as described in the present specification, page 6, lines 7-10 and unequivocally shown by the edge-to-edge data plot shown in Fig. 5, the present invention has a high degree of chemical uniformity. As described, this high degree of chemical uniformity is at least partly due to treating the raw materials prior to heat treating (e.g., flame spraying) to form hollow particles. More particularly, the raw material is formed through an electrofusion technique, where the material is electrofused prior to heat-treating to form spherical hollow particles.

Applicant respectfully submits that D1 and D2 fail to disclose or even remotely suggest such features that contribute to chemical uniformity, and further, that D1 and D2 fails to teach any other processing characteristics to achieve chemical uniformity. Indeed, the references D1 and D2 expressly disclose that the materials are chemically non-uniform. As described in D1, processing the feedstock material (salts) by pyrolysis was found to be incomplete. This incomplete pyrolysis of the feedstock materials results in chemically non-uniform end product. Applicant submits that this processing pathway results in even less chemically uniform zirconia powder than the state of the art described in the Background, which at least provides for complete processing by thermal spraying (albeit still non-uniform). Accordingly, the claimed invention is clearly distinguished of the D1 and D2.

Since D1 and D2 fail to disclose or even remotely suggest chemically uniform zirconia thermal spray powder as required by the claimed invention, reconsideration of the positions taken by the EPO are respectfully requested.

2. The Written Opinion goes on to state that independent claim 5 does not fulfill the criterion of Article 33(3) with respect to inventive step. Reconsideration of this position is respectfully requested as well.

It appears that the EPO has combined the teachings of D3, D4 and D5 in an attempt to meet all features of the claimed invention. D3 and D5 have been relied upon by the EPO to show that spheroidal, hollow zirconia powders may be formed by thermal spraying. Since

references D3 and D5 fail to disclose or suggest preliminarily electrofusing and quenching the material prior to heat treatment (e.g., thermal spraying) to form spherical, hollow powder, the EPO has relied upon D4. However, Applicant submits that D4 merely teaches a well known, art-recognized technique for forming zirconia raw material by an electrofusion process. In this context, the resulting material is then used in a typical molding process, followed by heat treatment to form end products. Nowhere do the references alone or in combination suggest combining electrofusion with heat treatment (e.g., thermal spraying) to form chemically uniform, spherical and hollow zirconia powder. It appears that in the stated combination of D3, D4, and D5, individual features of various references have been chosen without any sound technical basis in an attempt to recreate the invention. The references nowhere suggest combining electrofusion with thermal spraying, let alone such a combination to achieve chemical uniformity as claimed. Absent Applicant's own disclosure, the disclosed electrofusion technique would be interpreted to be merely a traditional alternative to formation of zirconia powder by thermal spraying. The combination of features is clearly nowhere suggested by the art of record.

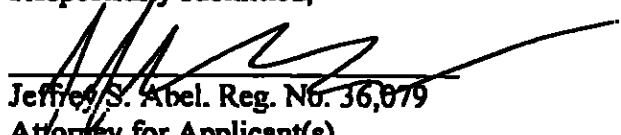
For at least the foregoing reasons, Applicant respectfully requests reconsideration of the reasoned statement with respect to claim 5.

3. The remaining references D6 and D7 have been further relied upon by the EPO in an attempt to meet the additional features of the dependent claims. Applicant respectfully submits that the additional references fail to overcome the deficiencies discussed above. Accordingly, reconsideration of the positions with respect to the dependent claims is respectfully requested as well.

For at least the foregoing reasons, Applicant respectfully requests issuance of a favorable International Preliminary Examination Report.

8/17/04
Date/

Respectfully submitted,


Jeffrey S. Abel. Reg. No. 36,079
Attorney for Applicant(s)
TOLER, LARSON & ABEL, L.L.P.
5000 Plaza On The Lake, Suite 265
Austin, TX 78746
(512) 327-5515 (phone)
(512) 327-5452 (fax)

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

IPEA/_____

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty.

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference NOR A-3363PC
International application No. PCT/US03/24541	International filing date (day/month/year) August 04, 2003	(Earliest) Priority date (day/month/year) 13 August 2002
Title of invention PLASMA SPHEROIDIZED CERAMIC POWDER		
Box No. II APPLICANT(S) Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) SAINT-GOBAIN CERAMICS & PLASTICS, INC. 1 New Bond Street Box Number 15138 Worcester, MA 01615-0138 US		Telephone No.: 508-795-5712 Facsimile No.: 508-795-2653 Teleprinter No.:
State (i.e. country) of nationality: US		State (i.e. country) of residence: US
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) WALLAR, Howard 12 Jaimie Ann Drive Rutland, MA 01543 US		
State (i.e. country) of nationality: US		State (i.e. country) of residence: US
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)		
State (i.e. country) of nationality:		State (i.e. country) of residence:
☐ Further applicants are indicated on a continuation sheet.		

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is ☒ agent ☐ common representative

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

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

Michael J. Bujold
 Customer No. 020210
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 US
 E-mail: patent@davisandbujold.com

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603 624-9220

Facsimile No.:

603 624-9229

Teleprinter No.:

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

Box No. IV STATEMENT CONCERNING AMENDMENTS

The applicant wishes the International Preliminary Examining Authority*

- (i) ☒ to start the international preliminary examination on the basis of the international application as originally filed.
 (ii) ☐ to take into account the amendments under Article 34 of
☐ the description (amendments attached).
☐ the claims (amendments attached).
☐ the drawings (amendments attached).
 (iii) ☐ to take into account any amendments of the claims under Article 19 filed with the International Bureau (a copy is attached).
 (iv) ☐ to disregard any amendments of the claims made under Article 19 and to consider them as reversed.
 (v) ☐ to postpone the start of the international preliminary examination until the expiration of 20 months from the priority date unless that Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). (This check-box may be marked only where the time limit under Article 19 has not yet expired.)

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

Box No. V ELECTION OF STATES

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

 (If the applicant does not wish to elect certain eligible States, the name(s) or country code(s) of those States must be indicated above.)

Box No. VI CHECKLIST

The demand is accompanied by the following documents for the purposes of international preliminary examination:

1. amendments under Article 34
 - description : sheets
 - claims : sheets
 - drawings : sheets
2. letter accompanying amendments under Article 34 : sheets
3. copy of amendments under Article 19 : sheets
4. copy of statement under Article 19 : sheets
- 5 other (specify): : sheets

For International Preliminary Examining Authority use only

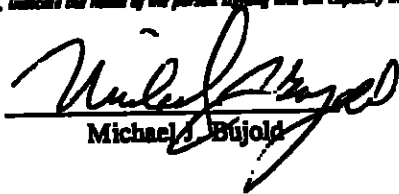
received	not received
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐

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

- | | | | |
|-----------------------------|--|--|----------------------------------|
| 1. ☐ | separate signed power of attorney | 4. ☒ | fee calculation sheet |
| 2. ☐ | copy of general power of attorney | 5. ☒ | other (specify): Check EUR 1,659 |
| 3. ☐ | statement explaining lack of signature | | |

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

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


Michael J. Bujold

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. ☐ The applicant has been informed accordingly.
4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PATENT COOPERATION TREATY

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RECEIVED

NOV 19 2004

DAVIS AND BUJOLD

PCT

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Bujold, Michael J.
DAVIS & BUJOLD P.L.L.C.
500 N. Commercial Street,
4th floor
MANCHESTER, New Hampshire 03101
ETATS-UNIS D'AMERIQUE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

16.11.2004

Applicant's or agent's file reference
NOR A-3363PC

IMPORTANT NOTIFICATION

International application No.
PCT/US 03/24541

International filing date (day/month/year)
04.08.2003

Priority date (day/month/year)
13.08.2002

Applicant
SAINT-GOBAIN CERAMICS & PLASTICS, INC.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international
preliminary examining authority:



European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
Fax: +31 70 340 - 3018

Authorized Officer

Delmon, G

Tel. +31 70 340-2525



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)

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Applicant's or agent's file reference NOR A-3383PC		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/16)	
International application No. PCT/US 03/24541	International filing date (day/month/year) 04.08.2003	Priority date (day/month/year) 13.08.2002	
International Patent Classification (IPC) or both national classification and IPC C23C4/10			
Applicant SAINT-GOBAIN CERAMICS & PLASTICS, INC.			
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 6 sheets, including this cover sheet. ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of sheets.			
3. This report contains indications relating to the following items: - I ☒ Basis of the opinion - II ☐ Priority - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability - IV ☐ Lack of unity of invention - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement - VI ☐ Certain documents cited - VII ☐ Certain defects in the international application - VIII ☐ Certain observations on the international application			
Date of submission of the demand 27.01.2004		Date of completion of this report 16.11.2004	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer Elsen, D Telephone No. +31 70 340-2005 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/US 03/24541**

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-8 as originally filed

Claims, Numbers

1-9 as originally filed

Drawings, Sheets

1/5-5/5 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

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

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/US 03/24541**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	1-4
Inventive step (IS)	Yes: Claims	
	No: Claims	1-9
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US 03/24541

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: Chemical Abstracts Service, Columbus, Ohio, US

Yano, Toyohiko: " Effects of spray pyrolysis conditions on the character of Yttria-partial stabilized Zirconia powders".

retrieved from STN

database accession no.: 106:89058

XP002265437

& Yogyo Kyokaishi (1987), 95(1), 111-116.

D2: Chemical Abstracts Service, Columbus, Ohio, US

Kato, Akio: "Sinterability of calcia-stabilized zirconia powders prepared by spray-pyrolysis technique".

retrieved from STN

database accession no.: 99:199472

XP002265436

& Nippon Kagaku Kaishi (1983), (10), 1544-6.

D3: Surface and Coatings Technology 96 (1997) 313-322

K.A.Khor: " Rapidly solidified neodyma-stabilised zirconia coatings prepared by DC plasma spraying".

D4: US-A-2535526

D5: US-A-4450184

D6: WO-A-0245931

2. The Applicant's arguments and explanation (letter of 08.07.04) have been carefully considered.

3. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-4 is not new in the sense of Article 33(2) PCT.

3.1. The document D1 discloses (the references in parentheses applying to this document): a fine Y₂O₃-partially stabilised "ZrO₂ powder". The powder crystal phase is tetragonal. The particle size is 0.2-5 μ m and is hollow.

3.2. The document D2 discloses a CaO-stabilized tetragonal hollow "ZrO₂ powder"

(1-5mu.m).

4. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 5 does not involve an inventive step in the sense of Article 33(3) PCT.

4.1. Document D3 discloses a method for preparing neodymia-stabilized zirconia "powders" and "their coatings by plasma spraying" by combination of mechanical milling, thermal plasma melting, solidifying, heat treating and spraying. The spheroidised powders have a particle size from 5 microm. to 70 microm. and consist of the cubic phase (97,43% with 10% Nd₂O₃) (see page 314, point 2-3; page 316; page 317, l.h.col.).

The difference between D3 and the present application is the non-specification of the electrofusing step and that the powders are hollow.

4.2. Document D6 discloses a method of producing a prealloyed stabilized "zirconia powder" comprising the steps of mixing and alloying yttria and zirconia powders using an induction arc process, powderizing the alloyed cubic/tetragonal yttria-zirconia material, spray-drying the stabilized zirconia powder suitable for use in " spray coating applications". The powder has an average particle size of no more than about 10 microns or between 11 and 150 microns (see claims 1,2,3,6,7,13). The spray dried powder is homogeneous (see page 4, lin. 16-17).

4.3. Document D5 discloses a process for producing a coating by "spraying" hollow stabilized zirconium oxide particles. The hollow sphere particles are made by spray-drying the powders and then by feeding and fusing them into a plasma spray gun (see col. 2, lin. 53- col.3, lin. 6; col. 3, lin. 56-67; col.4, lin. 51-66).

4.4. Document D4 discloses a process for making a stabilized relatively pure zirconia product (crystalline zirconia in the form of cubic crystals rather than monoclinic crystals) (see col. 1, lin. 23-37), ready for manufacture into bricks or other shapes, comprising fusing in an electric arc furnace a stabilized zirconia charge, cooling and crushing it and calcining it at a temperature of 1400°C to 1450°C (see col. 4, lin. 46- col.6, lin. 2; Col. 6, lin. 52-54 ; claims 1-3).

The skilled person would therefore combine the teachings of D3,D4,D5 and D6 to arrive at the same solution of claim 5.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US 03/24541

5. Dependent claims 6-9 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, see documents D1,D2,D3,D4,D5 and D6 and the corresponding passages cited in the search report.

POLVO CERÁMICO PLASMA REDONDEADO

CAMPO DE LA INVENCION

La presente invención se relaciona con los polvos cerámicos, particularmente los polvos de zirconio, y un proceso para la producción de polvos cerámicos por el cual los polvos tienen una composición altamente uniforme.

ANTECEDENTES DE LA INVENCION

Los polvos de zirconio estabilizado son ampliamente utilizados para obtener recubrimientos térmicamente estables y resistentes a la abrasión de piezas que son expuestas a muy altas temperaturas durante su uso pero que son también expuestas a temperatura ambiente. Ello tiene, sin embargo, una bien conocida limitación en cuanto que a medida que oscila entre altas y bajas, sufre un cambio de fase cristalina de una estructural cristalina tetragonal, que es estable a elevadas temperaturas, a una estructural cristalina monoclinica, que es estable a temperatura ambiente. Los cambios de volumen que ocurren a medida que estos cambios de fase cristalina tienen lugar comprometen la integridad física de los recubrimientos de zirconio.

Hay otra fase del zirconio que es también estable a temperaturas superiores de la temperatura de transición monoclinica/tetragonal, (la fase "cúbica"), pero puesto que son muy pequeños o ninguno los cambios de volumen que ocurren en la transición de cúbica a tetragonal, esta es tratada para los propósitos de esta descripción como una forma de la fase tetragonal y en consecuencia no se le hace distinción.

Para resolver los problemas de integridad con los recubrimientos de zirconio resultantes de los cambios de fase cristalina, es usual usar zirconio estabilizado en los recubrimientos de polvo. La estabilización puede ser lograda por la adición de un número de aditivos que tienen el efecto de inhibir la conversión de la fase cristalina tetragonal a la fase cristalina monoclinica durante el enfriamiento. Tales aditivos incluyen óxidos estabilizantes tales como calcia, magnesia, yttria, ceria, hafnia y óxidos de metales de tierras raras.

Los recubrimientos de zirconio estabilizado son ampliamente utilizados para producir un recubrimiento protector desgastable sobre superficies o como recubrimientos térmicos. Ellos son típicamente aplicados como sprays con un spray de llama o con un spray de plasma.

En la producción de polvos de zirconio estabilizados, la técnica más común es descrita en la patente U.S No 4,450,184 a Longo et al, en la cual una lechada acuosa de una mezcla de zirconio y materiales estabilizantes es alimentada a un secador de rociado (spray) para formar partículas porosas secas. Las partículas porosas son fundidas en estructuras huecas homogéneas con pistolas de rociado de llama o de plasma que derriten y fusionan los componentes de tal manera que las partículas lanzadas de allí son zirconio estabilizado. El termo rociado de la esferas huecas crean un recubrimiento poroso y desgastable. Sin embargo, el proceso Longo no alcanza un alto grado de uniformidad en su composición.

La patente U.S No 5,418,015 a Jackson et al, desarrolla una composición de alimentación para aplicaciones de termo-rociadores constituida por zirconio estabilizado mezclado con zircón y un óxido seleccionado para formar un recubrimiento de óxido refractario amorfo. Tales productos sin embargo, no tienen el nivel requerido de tamaño y uniformidad composicional que se sería deseable para asegurar una buena barrera térmica de recubrimiento para utilización a altas temperaturas. Esto es al menos en parte porque hay muchas oportunidades para variabilidad en el recubrimiento resultante, como consecuencia de los diferentes tamaños de partículas en la alimentación, el diseño/forma de las pistolas de llama plasma, las presiones de las tasas de alimentación y similares.

Otro método para preparar zirconio estabilizado envuelve sinterización donde los componentes son mezclados como polvos, sinterizados, y una vez enfriados, la masa sinterizada es triturada en partículas. Estas partículas pueden luego servir como alimento para un spray de flama. Desafortunadamente, este proceso no proporciona un alto nivel de homogeneidad química en la estabilización y resulta en formas y tamaños que varían ampliamente en la alimentación.

Las mezclas cerámicas de zirconio estabilizado pueden también ser hechas por electrofusión. Las mezclas fundidas son mucho mas uniformes que aquellas preparadas por los métodos discutidos anteriormente porque ellas son el resultado de un derretido completo de los componentes. Sin embargo, los componentes son difíciles de derretir y tiene pobres características de flujo como consecuencia de su

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alta densidad y forma irregular generada cuando las masas fundidas son trituradas para obtener partículas. Así, los polvos de zirconio estabilizado actualmente disponibles hechos por electrofusión tienen un alto grado de material no derretido en el proceso de rociado resultando en pobres eficiencias y recubrimientos con un alto contenido de partículas de material no derretido. Las partículas no derretidas introducen esfuerzos en el recubrimiento debido a las densidades cambiantes del recubrimiento en y alrededor de las partículas no derretidas. Como resultado, la longevidad del recubrimiento obtenido es disminuida particularmente bajo condiciones estresantes.

No obstante el estado de la tecnología, sería deseable obtener un polvo cerámico con un alto nivel de uniformidad química y morfológica, que a su vez, provea un durable recubrimiento de termo rociado.

RESUMEN DEL INVENTO

En el primer aspecto, esta invención esta dirigida a un polvo de zirconio particularmente adaptable para ser usado como un recubrimiento térmico, el cual esta comprende zirconio estabilizado morfológica y químicamente uniforme, esencialmente en la forma de esferas huecas.

El zirconio es químicamente uniforme, y por esto se indica que el zirconio es al menos 90% puro y que al menos el 96 % en peso, esta estabilizado en la fase cristalina tetragonal. El zirconio es morfológicamente uniforme, y por esto se significa que al menos el 95 % del volumen del zirconio esta en la forma de esferas con un tamaño de partícula menor a los 200 micrómetros. Las esferas pueden ser algo deformadas pero son identificables como esferas mas que como formas aleatorias.

Al menos el 75 % de las esferas son preferiblemente huecas. En una incorporación principal un zirconio estabilizado químicamente uniforme es tratado con calor a través de plasma fusión para obtener una forma substancialmente esferoidal. Preferiblemente, el zirconio estabilizado contiene menos del 1.0 % en peso de zirconio monoclinico.

En un aspecto principal, la presente invención esta dirigida a un compuesto termo rociable constituido por esferas huecas de zirconio estabilizado de yttria. Las partículas esféricas con un tamaño de partícula menor a los 200 micrómetros,

donde el yttria esta uniformemente incorporado dentro del zirconio por electrofusión antes de la formación de las partículas huecas. Preferiblemente, el zirconio contiene menos del 2% en peso de zirconio monoclinico. Las esferas huecas son preferiblemente formadas por plasma fusión.

En todavía otro aspecto, la invención presente esta dirigida a un proceso para producir polvo cerámico de forma esferoidal que comprende los pasos de: proveer un zirconio estabilizado químicamente uniforme y el tratamiento por calor del zirconio para formar substancialmente esferas huecas en consecuencia de uniformidad morfológica. Preferiblemente, el material cerámico estabilizado comprende zirconio estabilizado en la fase cristalina tetragonal, que contiene menos del 2 % en peso de zirconio monoclinico. El zirconio estabilizado esta preferiblemente preparado por electrofusión del zirconio y un óxido estabilizante. Preferiblemente, el tratamiento por calor ocurre en una pistola de rociado (spray) de plasma o en una pistola de rociado de llama. El proceso puede incluir además el paso de desmenuzar el material cerámico estabilizado antes del tratamiento por calor.

En todavía otro aspecto, la presente invención esta dirigida al proceso de preparar un recubrimiento de polvo termo rociable, que comprende los siguientes pasos: proveer una alimentación de zirconio donde al menos el 96 % en peso este estabilizado en una fase cristalina tetragonal; y plasma fusión de la alimentación de zirconio para formar esferas huecas a partir de él. Preferiblemente, el zirconio estabilizado es formado por electrofusión.

La invención también comprende un proceso de aplicación de un recubrimiento térmico a un sustrato el cual comprende. recubrir por termo rociado el sustrato utilizando un compuesto rociable constituido por zirconio, del cual al menos el 90 % esta estabilizado en la forma tetragonal y tiene substancialmente una morfología esférica uniforme con tamaños de partículas mas pequeños que 200 y preferiblemente menores a 100 micrómetros. Al referirse a los tamaños de partículas, se entiende que la referencia es al volumen del tamaño promedio de las partículas a menos que otra forma sea aparente del contexto.

BREVE DESCRIPCION DE LOS DIBUJOS

Las Figuras 1 a 4 son líneas de barridos de elementos de partículas sinterizadas de polvos de zirconio estabilizados comercialmente disponibles.

La Figura 5 es una línea de barrido de elementos de partículas esferoidales y huecas de zirconio hechas con la presente invención.

DESCRIPCION DETALLADA DE LA INCORPORACION PREFERIDA

La presente invención esta dirigida a un polvo de zirconio termo rociable con una composición química y morfología muy uniforme. El polvo cerámico termo rociable tiene preferencialmente una forma esférica y aún mas, las partículas esferoidales son substancialmente huecas, así que las partículas se demiten mas rápidamente formando así o recubrimientos densos o recubrimientos con porosidad uniforme dependiendo de las condiciones de rociado. En una incorporación muy preferida, el polvo de zirconio termo rociable de la presente invención comprende al menos 90 % de volumen de zirconio, y el zirconio esta al menos en el 96 % en peso estabilizado en la forma tetragonal por un óxido estabilizante. Mas preferiblemente, el zirconio esta al menos en el 98 % en peso estabilizado en la forma tetragonal, y mas preferiblemente, al menos el 99 % en peso estabilizado en la forma tetragonal.

La provisión de zirconio utilizada para la presente invención es estabilizada con un óxido estabilizante tal como, pero no limitado a, yttria, calcia, ceria, hafnia, magnesia, un óxido de metales de tierras raras y combinaciones de estos. Para alcanzar un alta uniformidad química en la alimentación de zirconio estabilizado, el óxido estabilizante es electrofusionado con el zirconio. La cantidad de óxido estabilizante usado puede variar dependiendo de los resultados deseados. Una cantidad suficiente de óxido estabilizante es una cantidad que substancialmente estabiliza el zirconio en la fase cristalina tetragonal. El óxido estabilizante está deseablemente completamente reaccionado e incorporado dentro de la estructura cristalina del zirconio, así que los análisis de rayos X no pueden detectar cantidades significativas (no mas del 4%) de zirconio monoclinico. La cantidad del óxido estabilizante presente puede ser hasta el 10 % en peso pero algunos estabilizadores son efectivos a niveles más bajos. Por ejemplo, en el caso de zirconio estabilizado utilizando yttria, una cantidad efectiva puede ser cerca de 1 % pero puede ser tan alta como 20 % en peso, para magnesia, de 2 % a cerca del

20% en peso es efectiva; para calcia de cerca de 3 % a cerca de 5 % en peso puede ser usada, y para un óxido de metales de tierras raras cerca de 1% al 60% en peso. Una mezcla de óxidos estabilizantes pueden ser usados.

El óxido estabilizante, preferiblemente yttria, es arco fusionado con el zirconio en un rango de temperatura de 2750° C a cerca de 2950° C , así que los componentes están completamente derretidos y, puesto que esto está por encima de la temperatura de transición, la totalidad del zirconio está substancialmente en la fase cristalina tetragonal. Una vez enfriado a temperatura ambiente, el óxido estabilizante mantiene el estado tetragonal aún por debajo la temperatura normal de transición. Para incrementar este efecto, el material derretido es preferiblemente enfriado rápidamente con agua o aire así que el flujo derretido es transformado en un flujo de gotas y enfriado para obtener partículas finas de zirconio estabilizado con una composición química muy homogénea. Un método de apagar el zirconio derretido y el óxido estabilizante, donde la rápida solidificación tiende a estabilizar la forma tetragonal del zirconio , es desarrollado en la patente U.S No 5,651,925 cuya integridad es incorporada aquí por referencia. Preferiblemente, las finas partículas resultantes de zirconio estabilizado son trituradas aún mas. Típicamente, las partículas finas son molidas a un tamaño de menos de cerca de 5 micrones, preferiblemente de 2 micrones y mas preferiblemente a cerca de 0.5 micrones. Las finas partículas de zirconio estabilizado son luego preferiblemente secadas por rociado y recolectadas como partículas aglomeradas. Aunque el paso de aglomeración no es esencial a la práctica de la invención, si proporciona un tamaño mas utilizable para adicionales tratamientos por calor del zirconio estabilizado como se discute abajo.

Las partículas aglomeradas son además tratadas por calor para formar esencialmente esferas huecas con una morfología uniforme. Una forma particularmente preferida de tratamiento por calor es un proceso de plasma fusión donde las partículas son derretidas en una llama de plasma y recolectadas como un polvo fino con una alto nivel de uniformidad química y morfológica. Substancialmente, las esferas huecas de zirconio estabilizado que se forman contienen preferiblemente menos del 4 % en peso y mas preferiblemente menos del 2 % en peso y lo mas preferible menos del 1 % en peso de zirconio monoclinico.

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Preferiblemente, las substancialmente esferas huecas tienen un tamaño de partícula menor de 200 micrones, mas preferiblemente menor de 100 micrones y lo mas preferible, menor de 75 micrones.

Inesperadamente, las substancialmente esferas huecas de la alimentación de zirconio estabilizado tienen un alto nivel de uniformidad química y morfológica donde el zirconio en al menos el 96 % en peso esta estabilizado en la fase cristalina tetragonal, y mas preferiblemente en al menos el 98% y la mas preferible en al menos en el 99%. Así, los polvos esferoidales termo rociables de la presente invención forman recubrimientos mas estables y durables debido al alto nivel de uniformidad química debida a la electrofusión del zirconio y los óxidos estabilizantes que estabilizan substancialmente el zirconio. Las partículas esferoidales del zirconio estabilizado se derriten mas inmediatamente por la morfología de esfera hueca y la reacción completa del estabilizador con el zirconio. Los recubrimiento rociados tienen una densidad muy predecible de alta densidad a porosidad controlada dependiendo de las condiciones de spray.

Para obtener recubrimientos termo rociables durables de zirconio, una estabilización uniforme de la fase cristalina tetragonal del zirconio es crucial. Ha sido mostrado que en comparación con polvos de zirconio estabilizados con yttria disponible comercialmente, el polvo de zirconio de forma esferoidal de la presente invención muestra un incorporación substancial del yttria dentro del zirconio. La Tabla I ilustra un ejemplo de un polvo de zirconio de la presente invención en comparación con polvos de zirconio estabilizados disponibles comercialmente en relación con el porcentaje en volumen de cada fase cristalina a través de datos de difracción de rayos-X (XRD)

Tabla I

Ex.	Tet [*] ZrO ₂ (vol. %)	Mono.ZrO ₂ (vol. %)	Y ₂ O ₃ (vol. %)
PF	100	0.0	--
PX	88.3	11.7	--
ST	98.9	1.1	--
M1	95.6	4.4	--
M2	89.4	10.6	--

* Incluye zirconio cúbico y tetragonal
PF= Polvo de zirconio de la presente invención

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PX= PRAXAIR ZRO™ disponible de Praxair, Inc., Danbury Connecticut

ST= STARK YZ disponible de HLC Stara GMBH.

M1= METCO 204NS-G disponible de Suizer Melco, The Coating Co. Westbury, NY.

M2= METCO 204 disponible de Suizer Melco.

Aunque la concentración de yttria no fue detectada por la difracción de rayos X (XRD) en todas las muestras, es la concentración de zirconio monoclinico la que determina si el zirconio ha sido substancialmente estabilizado en la fase cristalina tetragonal. Líneas de barrido elementales de las partículas de los ejemplos PX, ST, M1 y M2 son mostrados en las Figuras 1 a 4 para determinar la composición de las partículas. En la Figura 1, la línea de barrido línea elemental, borde a borde, de una partícula bien sinterizada del ejemplo PX muestra que la partícula analizada no tenía una composición uniforme dada la línea no derecha que representa el yttrium. En consecuencia, aunque el XRD no detectó yttrium, la línea de barrido elemental muestra que el yttria no se co-fusiono completamente con el zirconio, y como tal, el compuesto no suficientemente químicamente uniforme. El pico en la línea de silicón atestigua además que la partícula no es ni química, ni morfológicamente uniforme. En la Figura 2, la línea de barrido elemental de una bien sinterizada partícula del ejemplo ST, borde a borde, también muestra variación en la concentración de yttrium, y así, la partícula no es químicamente uniforme. En la Figura 3, la línea de barrido elemental de una bien sinterizada partícula del ejemplo M1, una vez mas muestra variaciones en la concentración de yttrium, y así, la partícula no es químicamente uniforme. En la Figura 4, la línea de barrido elemental de una bien sinterizada partícula del ejemplo M1, una vez mas muestra variaciones en la concentración de yttrium, y así, la partícula no es químicamente uniforme .

Por electrofusión del óxido estabilizante, yttria, con el zirconio, el zirconio estabilizado es relativamente uniforme en composición. El tratamiento de calor adicional, tal como plasma fusión, provee la uniformidad morfológica de las substancialmente esferas huecas. La inesperada uniformidad química y morfológica es claramente ilustrada en la línea de barrido elemental mostrada en la Figura 5 de una esfera hueca del ejemplo PF. La substancialmente derecha línea de yttrium ilustra que un completo derretido y una re-solidificación ha ocurrido para obtener una esfera químicamente uniforme. También, las líneas substancialmente planas de silicón y hierro ilustran la morfolología uniforme de las esferas.

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En consecuencia, aunque los polvos de zirconio estabilizado comercialmente disponibles parecan ser similares en su apariencia, el polvo de zirconio de forma esferoidal de la presente invención provee una partícula química y morfológicamente mas uniforme para aplicaciones de termo rociado. La uniformidad química y morfológica a su turno produce recubrimientos térmicos de excepcional durabilidad.

Otras variaciones y modificaciones de la invención básica pueden ser concebidas sin apartarse de los conceptos descritos atrás. Se pretende que todos esas variaciones y modificaciones sean incluidas en un interpretación amplia de esta invención.

REIVINDICACIONES

1. Polvo de zirconio para termo rociado comprendiendo un zirconio estabilizado químicamente uniforme, donde el zirconio es al menos el 96 % en peso está estabilizado en la fase cristalina tetragonal, dicho polvo está en la forma de partículas esféricas substancialmente, teniendo un tamaño de partícula de menos de 200 micrómetros y la mayoría de las partículas mencionadas son huecas.
2. El polvo de zirconio de la reivindicación 1 donde las partículas huecas mencionadas tienen tamaños de partícula de menos de 100 micrones.
3. El polvo de zirconio de la reivindicación 1 donde el zirconio es estabilizado con un óxido seleccionado del grupo constituido de yttria, magnesia, calcia, ceria, hafnia y óxidos de tierras raras y combinaciones de estos.
4. El polvo de zirconio de la reivindicación 1 el cual contiene menos del 1% en peso de zirconio monoclinico.
5. Un proceso para la producción un polvo de termo rociado químicamente uniforme, incorporando los siguientes pasos:
 - a. Electrofusion del zirconio con hasta el 60% en peso de un óxido efectivo para estabilizar el zirconio en su fase tetragonal.
 - b. Apegado el zirconio estabilizado electrofusionado para obtener zirconio estabilizado particulado con al menos el 96 % de zirconio en la fase tetragonal.;
 - c. Tratamiento con calor del zirconio estabilizado para formar substancialmente partículas esféricas huecas de zirconio estabilizado con tamaños de partículas de 200 micrómetros o menos.
6. Un proceso de acuerdo a la reivindicación 5 en el cual el zirconio es estabilizado en la forma tetragonal usando hasta el 60% en peso de un óxido estabilizante seleccionado de un grupo consistente de yttria, óxidos de metales de tierras raras, óxido de calcio y óxido de magnesio.

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7. Un proceso de acuerdo con la reivindicación 5 en la cual el óxido estabilizante es yttria en una cantidad de 1 al 25 % en peso.
8. Un proceso de acuerdo con la reivindicación 5 en el cual el zirconio estabilizado apagado está al menos el 98 % en fase tetragonal.
9. Un proceso de acuerdo con la reivindicación 5 en la cual el zirconio estabilizado particulado es plasma rociado para obtener substancialmente partículas esféricas, la mayoría de las cuales son huecas y con tamaños por debajo de los 100 micrómetros.

LINEA DE BARRIDO ELEMENTAL

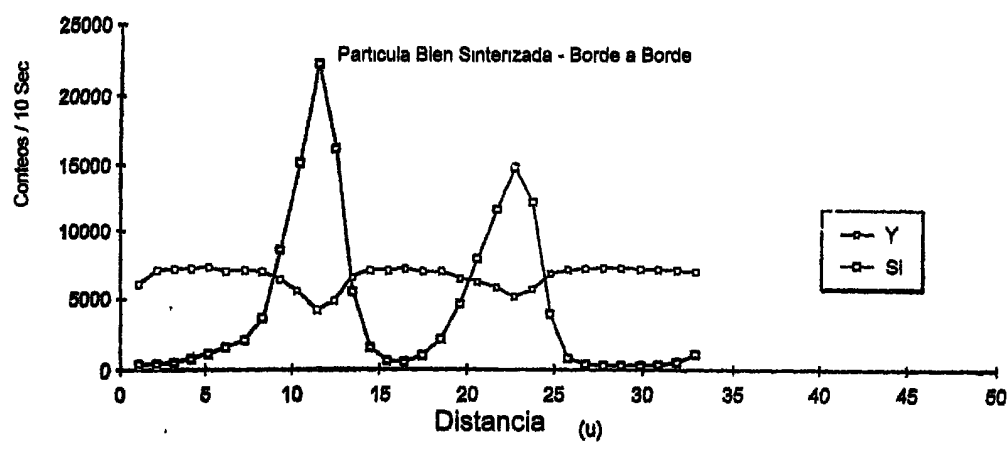
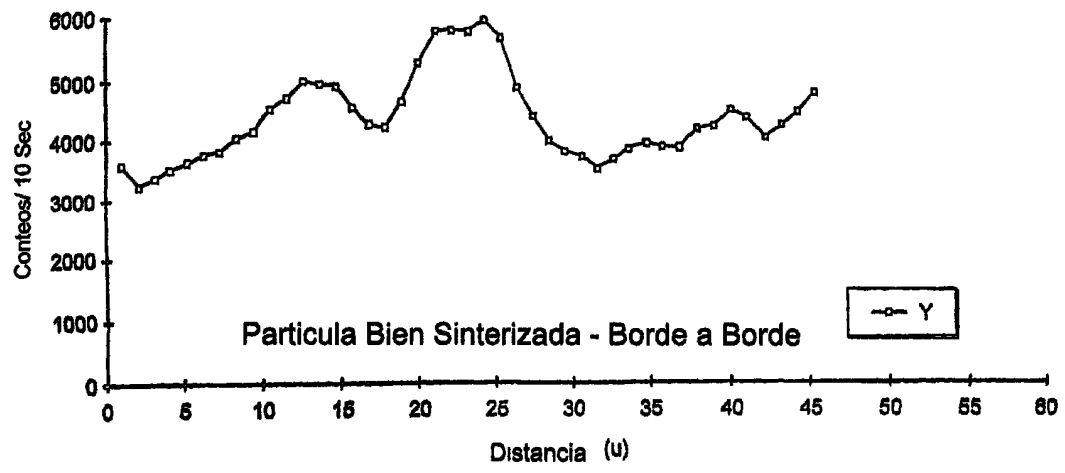


FIG. 1

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LINEA DE BARRIDO ELEMENTAL



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FIG. 2

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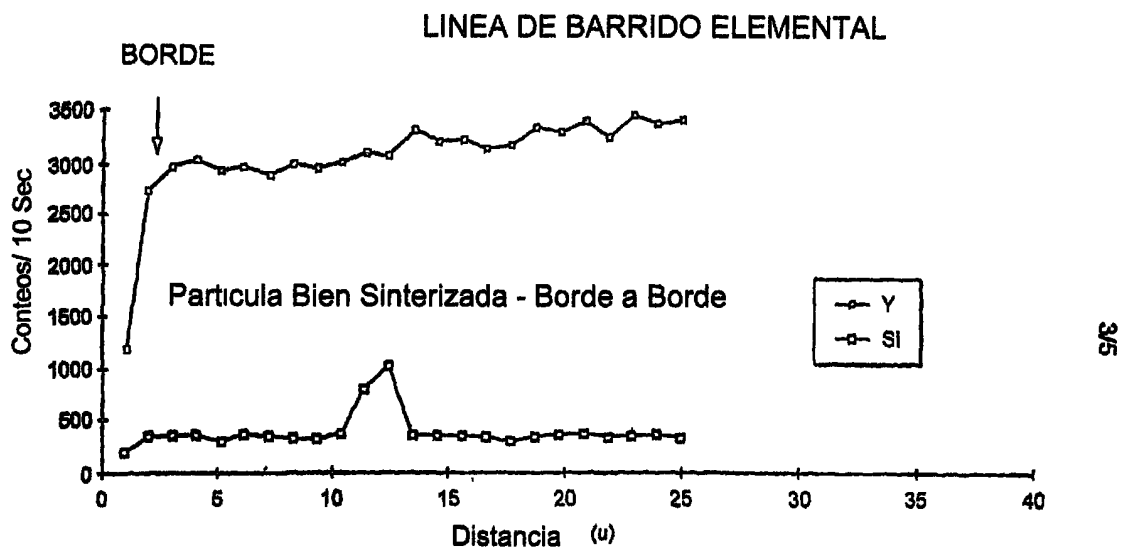


FIG. 3
ARTE ANTERIOR

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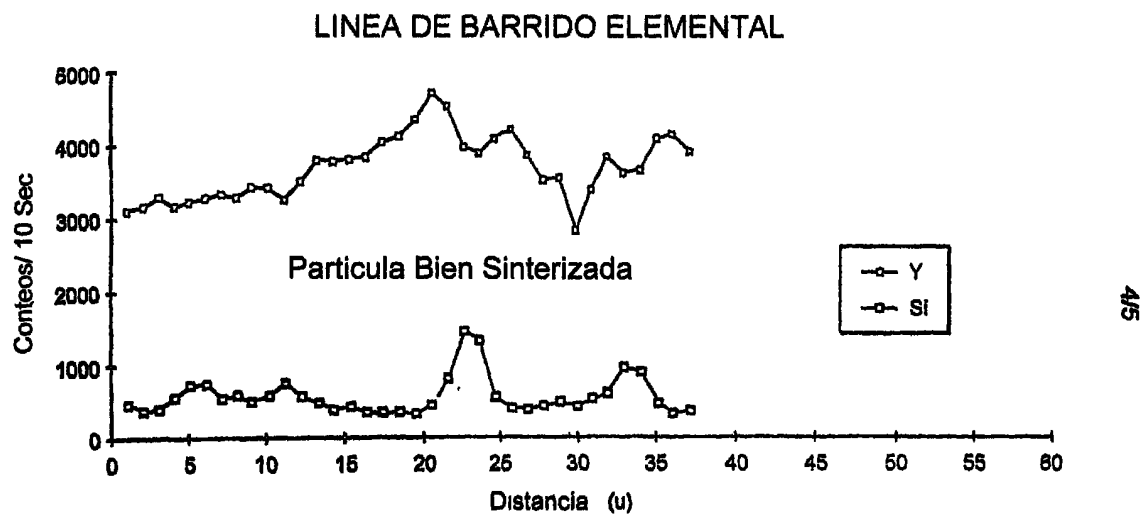


FIG. 4

ARTE ANTERIOR

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LINEA DE BARRIDO ELEMENTAL

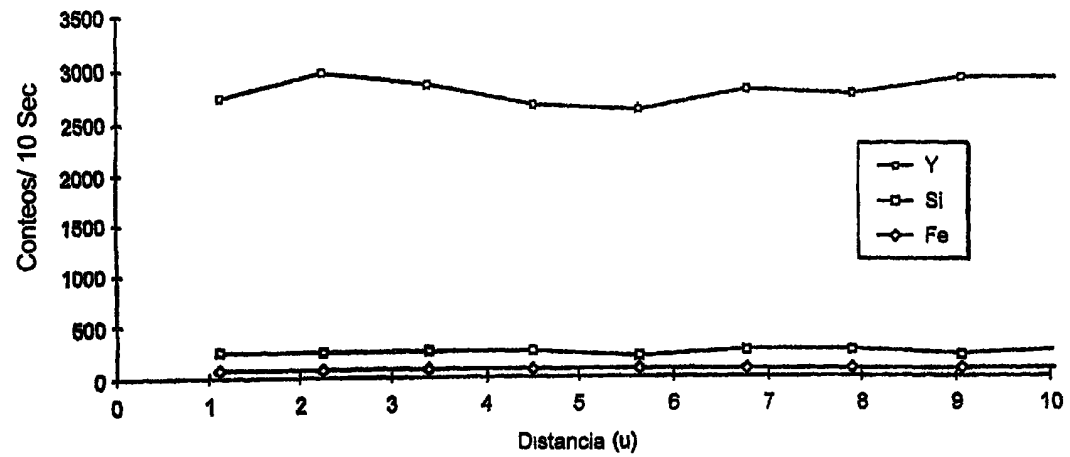


FIG. 5

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19 January 2005

PATENT

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THE INTERNATIONAL BUREAU OF WIPO

In re Application of
Serial no
Filed
For
Docket

SAINT-GOBAIN CERAMICS & PLASTICS INC
PCT/US03/24541
August 04 2003
PLASMA SPHEROIDIZED CERAMIC POWDER
NOR A-3363PC

REQUEST FOR CHANGE IN INVENTOR'S
ADDRESS ACCORDING TO RULE 92 ^{bis}

Dear Sir

The Applicant respectfully requests that the International Bureau of WIPO enter the following necessary correction to the address of the Inventor namely the Inventor Howard Wallar's address should be ' 12 Jaimie Ann Drive, Rutland MA 01543, US ' instead of ' 12 Tucker Street Worcester MA 01606, US '

It is the understanding of the Applicant that the above requested correction(s) is to be made under Rule 92 ^{bis} without submission of any further documentation In the event that the Applicant's understanding is incorrect or if further documentation is required please advise the undersigned as soon as possible In the event that there are any fee deficiencies or additional fees are payable please immediately contact the undersigned

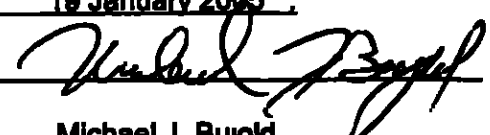
In the event that there are any fee deficiencies or additional fees are payable please charge the same or credit any overpayment to our Deposit Account (Account No 04-0213)

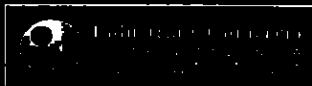
Respectfully submitted


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Telephone 603-624-9220
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CERTIFICATE OF TRANSMISSION

I hereby certify that this correspondence is being transmitted via facsimile to The International Bureau of WIPO on 19 January 2005


Michael J. Bujold
Type name of person signing certificate



FORMATO DE DIGITALIZACION
RELACION DE ANEXOS



Royal
Technologies S.A.
Calle 100 No. 100-100

67

Expediente No		05011 645	No de Folia
Item		No de unidades	
1	CD		
2	DVD		
3	REVISTA		
4	LIBRO		
5	PERIODICO		
6	DISQUETES		
7	SOBRE DE MANILA		
8	SOBRE BLANCO TAMAÑO CARTA	X 1	✓
9	SOBRE BLANCO TAMAÑO OFICIO		
10	OTROS:		

Observaciones:

contiene Atte final

68

SUPERINDUSTRIA Y COMERCIO
Radicación : 05011645, 00000000 Folios: 66
Fecha (GMD): 2005-02-09 16:46:17
Trámite : 011 PCT-PATENT 379 FASE INCI 411 PRESENTAC
Destinatario: 2026 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 7,172
FECHA : ENERO 31 DE 2005

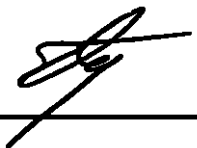
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	33236109	31/01/2005	38,751,000.

***** CONCEPTO *****

CANT. CONTABILITICO	CONCEPTO	TOTAL CONCEPTO
1 30003-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	443,000.00
	TOTAL :	\$ 443,000.00

SON: CUATROCIENTOS CUARENTA Y TRES MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Colo 14496-891-003-1

64

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

PATENTE DE INVENCION

MODELO DE UTILIDAD

- Indicacion de que se solicita la concesion de una patente
- Datos de identificación del solicitante o de la persona que presenta la solicitud
- Descripción de la invención
- Dibujos de ser estos pertinentes
- Comprobante de Pago de las tasas establecidas

USUARIO	RADICADOR
()	()
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COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicación de que se solicita el registro de Diseño Industrial
- Datos de identificación del solicitante o de la persona que presenta la solicitud
- Representación gráfica o fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño
- Comprobante de pago de las tasas establecidas

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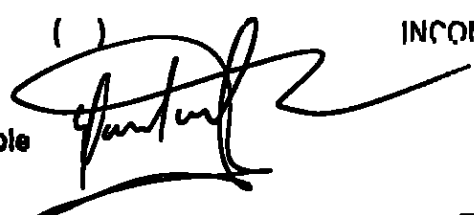
ESQUEMA DE TRAZADO ()

- Indicación de que solicita el registro de un Esquema de Trazado
- Datos de identificación del solicitante o de la persona que presenta la solicitud
- Representación grafica del esquema de trazado
- Comprobante de pago de las tasas establecidas

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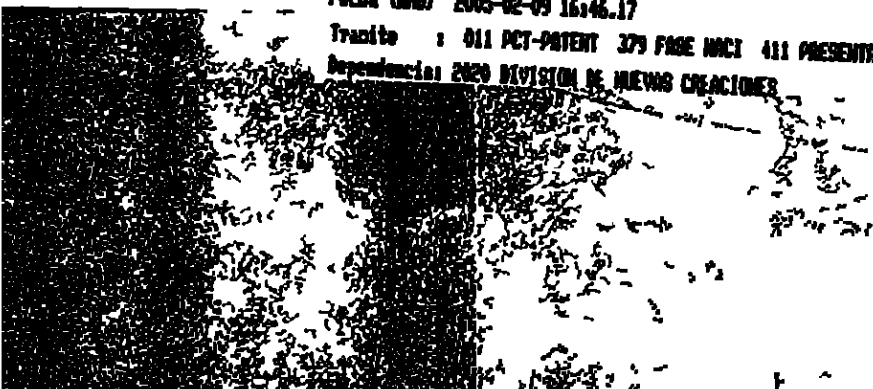
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Firma Responsable



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SEPEXINDUSTRIA Y COMERCIO
Radicación 05011645 00000000 Folios: 68
Fecha (AMD) 2005-02-09 16:46:17
Trámite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES



2020
Bogotá, D.C.,

Doctor:
EMILIO FERRERO
Apoderado
SAINT-GOBAIN CERAMICS & PLASTICS, INC.

Oficio N° 12379

ASUNTO:	Radicación N°	05-11645
	Solicitud internacional	PCT/US2003/024541
	Fecha inicio fase nacional	14/03/2005
	Trámite	011
	Evento	379
	Actuación	430
	Folios	001

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

- La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k Decisión 486).

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

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


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

El anterior requerimiento fue notificado por fijación en lista de fecha, 11 MAR 2005

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