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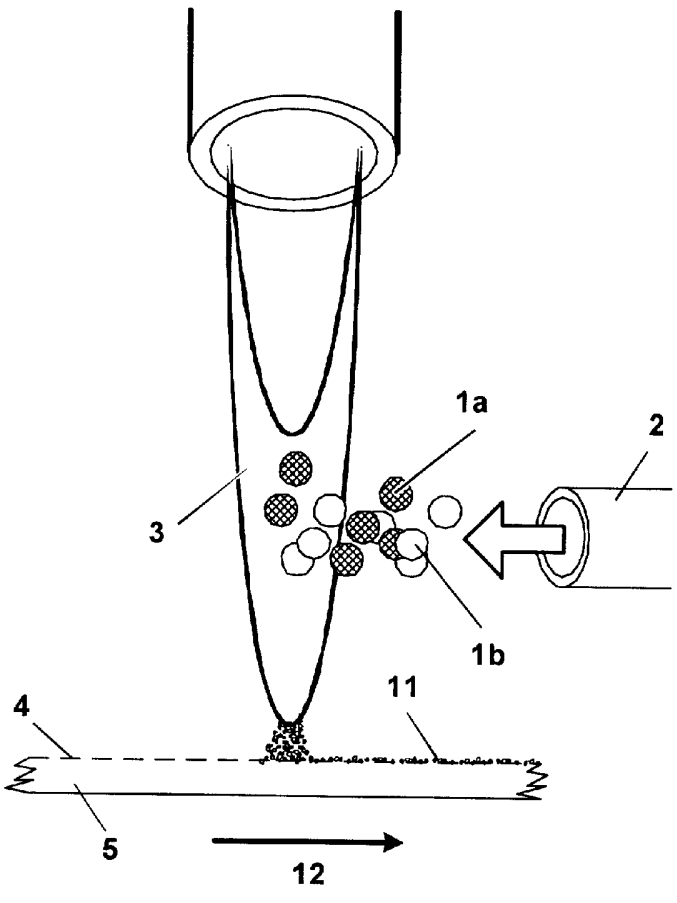
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[Continued on next page]

(54) Title: METAL OXIDE AND NOBLE METAL CATALYST COATINGS



(57) Abstract: A substrate (5) having a catalytic surface (4) having a coating (11) of metal oxide and noble metal particles (1a and 1b) in the nominal diameter size distribution range of less than three microns, preferably less than one micron is produced by thermal spraying a mixture of large size particles (1a and 1b) (greater than 10 microns in nominal size distribution range) of hydroxides, carbonates or nitrates of the metals: cerium, aluminium, tin, manganese, copper, cobalt, nickel, praseodymium or terbium particles; and hydroxides, carbonates or nitrates of the nobles metals: ruthenium, rhodium, palladium, silver, iridium, platinum and gold onto the substrate (5). The coating (11) adheres to the surface (4) and provides desirable catalyst properties.

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TITLE OF THE INVENTION

SUBSTRATES WITH SMALL PARTICLE SIZE METAL OXIDE AND NOBLE METAL CATALYST COATINGS AND THERMAL SPRAYING METHODS FOR PRODUCING THE SAME

REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending United States application for Letters Patent No. 09/742,697 filed on December 20, 2000, entitled "Method for Enhancing the Surface of a Substrate and Catalyst Products Produced Thereby," the disclosure of which is hereby incorporated by reference as if set out in full herein.

TECHNICAL FIELD TO WHICH THE INVENTION RELATES

The invention relates to a method of coating a substrate with a metal oxide (such as ceria (CeO_2)) and a noble metal catalyst (such as palladium or platinum) by thermal spraying a mixture of large size metal component precursor particles (such as cerium carbonate ($Ce_2(CO_3)_3$) mixed with large size noble metal precursor particles (such as palladium hydroxide ($Pd(OH)_x$).

BACKGROUND ART

Prior art disclosures of processes for the deposition of ceria particles on a substrate include United States Patent No. 5,063,193 to Bedford *et al.* which discloses a wash coat of high surface area ceria particles and the preparation thereof in which cerium carbonate is converted to ceria via chemical reactions and calcination; United States Patent No. 6,051,528 to Brezny which discloses a wash coat created by dissolving cerium carbonate to form cerium acetate which is then treated by spray pyrolysis to form a ceria powder; and United States Patent No. 5,989,648 to Phillips which discloses the plasma generation of supported metal

catalysts. The referenced patents do not disclose the use of large particle precursors that decompose in a plasma spray to smaller particles that form a catalyst coating on the target substrate.

In a preferred embodiment, the present invention injects a mixture of large size (approximate nominal diameter distribution range > 10 micrometers) metal component precursor particles and large size (approximate nominal diameter > 10 micrometers) noble metal component particles into a thermal spray to produce a catalyst coating of metal oxide / noble metal having a nominal particle size diameter distribution in the range of < 5 microns, particularly < 2 or 3 microns, and more preferably < 1 micron. (In the ranges stated herein, a particular distribution includes approximately 90% of the particles within the parameter stated.) The invention provides, by a thermal spray process, a porous, fine particle coating of metal oxides and noble metals, having good mechanical adhesion to a substrate surface and stability properties and surface characteristics useful for catalytic reactor applications.

My previous application describes the deposition of metal hydroxides, carbonates and nitrates on a substrate by thermal spray processes. During a line of sight spray process, the precursor materials decompose and oxides are formed that adhere in a mechanically stable manner to the surface of a thin metal substrate. For example, with hydroxide, carbonate and nitrate metal compositions, the reactions respectively occur: a) $Me(OH)_x \rightarrow MeO_x + H_2O$; b) $Me(CO_3)_x \rightarrow MeO_x + CO_2$; and c) $Me(NO_3)_x \rightarrow MeO_x + N_2$.

The present invention provides an improved catalytic surface and an enhanced method in which the metal oxide precursors, preferably cerium

carbonate or cerium hydroxide, become a ceria coating on a metal surface and a noble metal catalyst is deposited on the surface in the same operation. Large particle cerium carbonate is oxidized to cerium oxide, $Ce_2(CO_3)_x \cdot XH_2O \rightarrow Ce_2O_3 + 3CO_2 + XH_2O$. In the presence of air or oxygen, Ce_2O_3 is oxidized to CeO_2, namely, $Ce_2O_3 + \frac{1}{2}O_2 = 2CeO_2$. After the thermal spraying, if a substantial quantity of Ce_2O_3 is present on the substrate surface, an after-treatment may be applied to achieve the correct phase of CeO_2. In the process, the large size particles decompose, the water component vaporizes and a ceria and noble metal catalyst coating on the substrate results. More particularly the invention relates to a method of thermally spraying catalyst precursor materials directly onto a substrate surface and the catalyst substrates formed thereby as a result of the pyrolysis reactions occurring in the process. The invention is particularly useful in the deposition of a catalyst material on surfaces of components used in micro-component reaction chamber assemblies.

My referenced parent application for patent describes characteristics and properties of prior art processes and coatings. In the present invention, thermal spraying of large particles produces a coating of small particle size and high surface area on a substrate.

SUMMARY OF THE INVENTION

In the invention, a thermally sprayed coating on a substrate yields a thin layer of a catalyst coating with small particle size and high surface area. In an embodiment, the method is applied to form a catalyst coating on a channel separator element used in a micro-component heat exchanger / reactor unit used in laminar flow reactors for hydrogen production devices employed in conjunction

with low power fuel cells in automotive or mobile or other equivalent applications. *See* United States application for Letters Patent No. 09/627,267 filed on July 28, 2000, entitled "Multi-purpose Micro-channel Micro-component," assigned to the assignee of the present application, the disclosure of which is hereby incorporated by reference.

The overall process of forming such a micro component includes steps from substrate preparation to substrate surface modification to the application of a final coating by thermal spraying to produce a metal oxide and noble metal catalyst on the substrate. The process begins with the formation of the substrate, such as the pre-formation of folds or corrugations in a shim precursor to a wavy plate. The substrate surface is subjected to grit blasting or like treatment before or after the formation of partial folds (or fold lines) on the wavy plate. The substrate is positioned to receive the thermal spray, preferably mounted on a heat sink to maintain a low temperature. The coating mixture of cerium and noble metal precursors is applied to the substrate by a plasma spray.

The thermal sprayed coating bonds directly with the surface of the substrate. Desirable characteristics, including high porosity, high surface profile and surface area and small particle size, are beneficially achieved in the thermally sprayed coating. A catalyst precursor material, preferably a mixture of multiple materials, in the form of a particulate, powder or granule having a large particle size, for example, in a scale greater than about 10 micrometers and up to about 200 or more micrometers, is thermally sprayed onto the substrate and forms a catalyst coating that bonds to the substrate surface. The coating is formed from decomposition products of the sprayed mixture material and is characterized as a

distribution of small size particles, namely in the order of less than approximately 5 microns in nominal diameter, preferably in the order of less than approximately 2 or 3 microns in nominal diameter, and more preferably in the order of less than approximately 1 micron in nominal diameter. Although the substrate may be coated sequentially in multiple layers beginning with a ceria foundation, followed by a further coating of a catalytic material, such as a noble metal, a mixture of both compositions is preferred to be thermally sprayed in the same operation. In a useful embodiment, the coated substrate is used as a flow separator / heat exchange media between alternate fluid flows in a micro-component reaction chamber, or heat exchanger.

The catalyst formed in the thermal spray process and subsequent treatment, if any, promotes a chemical reaction when a reagent fluid flows through the channels of the micro-component device. One or both sides of the wavy plate separator may be treated. In this aspect of the invention, the coating, and the enhanced surface properties thereof, also assist in the transfer of heat between facing channels in the micro-component device. In the invention, large size particles, or a mixture of large size particles comprising a catalyst precursor is flame sprayed or plasma sprayed onto a substrate to produce a small particle size coating by a pyrolysis process in which heat decomposes the sprayed material. Before thermal spraying, the substrate surface may be enhanced by methods such as grit blasting and/or chemical treatment to improve adhesion of the thermally sprayed coating to the substrate.

The invention is described more fully in the following description of the preferred embodiment considered in view of the drawings in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a representation of the thermal spray process (not to scale) in which a powder mixture is introduced from a single orifice into a flame or plasma directed to a substrate surface.

FIG. 1B is a representation of selected parameters incident to a plasma thermal spray process.

FIG. 2A is a representation of the thermal spray process (not to scale) in which separate powders are introduced, each from an associated separate orifice, into a flame or plasma directed to a substrate surface.

FIG. 2B is a representation of the thermal spray process (not to scale) applied to a preliminarily folded wavy plate maintained by vacuum on a supporting and complementarily shaped heat sink.

FIG. 3A is a 2000x magnified view of the surface of a metal substrate coated with a metal oxide / noble metal (ceria/palladium) catalyst.

FIG. 3B is a 4000x magnified view of the surface of a metal substrate coated with a metal oxide / noble metal (ceria/palladium) catalyst.

FIG. 4 represents in perspective a section of laminar flow micro channels in a heat exchange / reaction chamber with catalyst coatings of the invention on the opposite sides of a wavy plate separator, as used in a micro-component reactor assembly.

DESCRIPTION OF THE INVENTION AND THE BEST MODE

The present invention provides a catalytic substrate surface comprising a particulate coating of a) one or more than one of cerium, aluminum, tin, manganese, copper, cobalt, nickel, praseodymium or terbium oxide and b) one or

more than one of ruthenium, rhodium, palladium, silver, iridium, platinum and gold, characterized as a substantially uniform distribution over the surface of the substrate in which the coating particles are in the nominal diameter size distribution range of < 5 microns, preferably, in the nominal diameter size distribution range of < 2 or 3 microns. Most preferably, the coating particles are in the nominal diameter size distribution range of < 1 micron; namely, in the distribution 90% of the particles have a diameter less than 1 micron. Smaller particle sizes at the surface optimize the desired characteristics of the substrate achieved by the invention. The catalytic surface coating is produced by thermal spraying a mixture of large size particles (*e.g.*, in a nominal size distribution range of > 10 micrometers up to 200 micrometers or more, limited by the nozzle spray orifice of the thermal spray) of hydroxides, carbonates or nitrates of the metals, cerium, aluminum, tin, manganese, copper, cobalt, nickel, praseodymium or terbium and the hydroxides, carbonates or nitrates of the noble metals, ruthenium, rhodium, palladium, silver, iridium, platinum and gold onto the substrate.

Figure 1A shows a representation of the thermal spray process used in the invention. A large size particulate, granule or powder mixture of catalyst precursor compositions 1a and 1b, is introduced from orifice 2 into a flame or plasma 3 that is directed to the surface 4 of a substrate 5, such as a thin shim from which a wavy plate is formed. The mixture of catalyst precursor materials, for example, cerium hydroxide and a noble metal hydroxide, decompose to a small particle size coating 11 which provides a porous, or enhanced surface area, on the substrate surface. In a line of sight thermal spray, the materials in the mixture decompose and oxidize by pyrolysis and produce oxides that adhere to the substrate surface.

For example, cerium carbonate oxidizes to ceria, $Ce_2(CO_3)_3 \rightarrow 2CeO_x + XCO_2$; palladium hydroxide oxidizes to palladium oxide, $Pd(OH)_x \rightarrow PdO_x + H_2O$; and palladium oxide reduces to palladium, $PdO_x \rightarrow Pd + XO_2$. The large size particles of the catalyst precursor compositions introduced into the flame or plasma are thermally sprayed directly onto the substrate and decompose into a coating of small size particles fixed on the substrate. Arrow 12 shows the direction of relative movement of the flame/plasma spray and the substrate. The surface area and porosity properties of the substrate surface are enhanced for use as a component of a catalytic reactors micro-component assembly.

Preferred noble metals and noble metal hydroxides, carbonates, or nitrates of the invention include ruthenium (Ru), rhodium (Rh), palladium (Pd) and silver (Ag) and iridium (Ir), platinum (Pt) and gold (Au). Preferred metals forming the metal hydroxide, metal carbonate, or metal nitrate particles capable of decomposing to a metal oxide include cerium (Ce), aluminum (Al), tin (Sn), manganese (Mn), copper (Cu), cobalt (Co) and nickel (Ni), and the rare earth metals praseodymium (Pr) and terbium (Tb).

Figure 2A illustrates the thermal spray process in which separate powders are introduced, each from an associated separate orifice, into a flame or plasma 3 directed to a substrate surface 4. For example, metal hydroxide, metal carbonate, or metal nitrate particles 8 may be introduced into the thermal spray 3 from orifice 21 and noble metal, and/or noble metal hydroxide, carbonate or nitrate particles 9 may be introduced into the thermal spray 3 from orifice 22. A heat sink is shown as 15 in Figure 2A. Preferably, a heat sink, such as a copper block with a shape complementary to the substrate, whether flat or folded, is employed as a support

member for the substrate in the plasma spray to absorb heat generated during the spray process. A vacuum hold down system 25 maintains the substrate in place relative to heat sink 15. Coolant channel 26 allows the flow of a cooling fluid through the heat sink to maintain the substrate at a regulated relatively low temperature (for example, at about or less than 100° C) during the spray process.

FIG. 2B shows a thermal spray process in which the mixture of oxide 30 and noble metal 31 precursor particles are introduced through a nozzle 32 into a flame or plasma source 33. In the example, a preliminarily formed shim plate 34 having folds of approximately 60° is held by a vacuum source 35 to a complimentary copper block heat sink 36. The heat sink 36 includes channels therein for the flow in 37 and out 38 of a fluid coolant, such as water (H_2O), through the block, to maintain the substrate at a regulated low temperature in the range of about 100° C.

In a cerium/palladium example depicted in Figure 3A and Figure 3B, the thermal spray deposits on the surface a mixture of 5% by weight of ceria 30s and 95% by weight of palladium 31s, distributed as a surface of small size particles < 1 micron derived from the decomposition of the large size cerium carbonate 30 and palladium hydroxide 31 precursor particles. The relative stoiciometric proportions of the cerium carbonate and palladium hydroxide precursors introduced to the nozzle are calculated backward from the ultimate proportions of ceria/ palladium desired on the surface taking into consideration the breakdown reaction equations of the precursor particles, in the instance of cerium carbonate: $Ce_2(CO_3)_x \cdot H_2O \rightarrow Ce_2O_3 + 3CO_2 + XH_2O$ and $Ce_2O_3 + \frac{1}{2}O_2 = 2CeO_2$; in the

instance of palladium hydroxoxide: $Pd(OH)_x \rightarrow PdO_x + H_2O$ and $PdO_x \rightarrow Pd + XO_2$.

The photomicrographs of Figures 3A and 3B illustrate a metal surface coated with Ce_2O_3 and palladium particles deposited in accordance with the invention. In Figure 3A and Figure 3B a metal surface is coated with a mixture of CeO_2 and palladium particles in which 90% of the particles are less than 1 micron in size and 10% of the particles are in the size range between 1 micron and 3 microns. It is understood that the range stated is approximate and may vary, although the preferred embodiment of the invention is a substrate surface coated with particles in a size, or sizes within the range noted, the smaller the surface particles, the better. The coating adheres to the surface and provides desirable catalyst properties. As an example, the relationship of the metal oxide to the noble metal particles deposited by the thermal spray onto the substrate is in the ratio of approximately 10% noble metal to 90% metal oxide by weight. The preferred proportion of noble metal particles is in the range of 10% or less by weight and the proportion of metal oxide particles is approximately the remainder, 90% or greater by weight, and vice versa. The proportions and ratios stated are subject to design preferences, intended purpose and experimentation with regard to a particular catalyst combination and its application.

Figure 4 is a representation of a section of a wavy plate or separator in a micro-component reactor processed in accordance with the invention. In this embodiment, a shaped wavy plate 40 has two opposite sides 40A and 40B, respectively exposed to laminar fluid flows 45A and 45B in a heat exchanger / reactor assembly such as described in United States application for patent No.

09/627,267 referenced above. In an example, one side 40A of the wavy plate is coated in accordance with the process herein with a catalyst material of platinum 42 and ceria 43 to provide a reactor chamber, for example, to promote a steam reforming reaction in fluid flow 45A that may be generally characterized as: Hydrocarbon Fuel + $H_2O \rightarrow H_2 + CO_2 + H_2O + CO$. Maintenance of the steam reforming reaction requires a sustained 700° C temperature for the catalytic reaction that is provided by an exothermic reaction in fluid flow 45B of a mixture of combustible materials, such as fuel cell off gas and/or gasoline in a mixture with air on the opposite side 40B of the wavy plate.

The invention is useful in the production of micro-component assemblies used as heat exchangers or reaction chambers in various chemical reaction processes. Coatings produced by the invention are adaptable to separator elements used in such assemblies where separate fluid flows pass on opposite sides of a separator and different catalytically induced reactions occur on opposite sides of the separator. In examples, metal alloy substrates, such as a plate or foil shim with a thickness of approximately 60 micrometers, 100 micrometers, or more are cleaned and prepared for surface treatment, for example, by washing in trichloroethylene and ethanol and rinsing with deionized water. The surface may be grit blasted to increase roughness to a range of about 5 micrometers.

The coating is formed on the cleaned substrate by thermally spraying powders that are catalyst precursors directly onto the substrate by thermal spraying processes. In plasma spraying, for example, a temperature in the order of 30,000° C may exist in the plasma, however, the peripheral regions of the spray where pyrolysis of the introduced powder occurs involve reaction temperatures in

the range of approximately 2,000° C to approximately 2,400° C. Multiple parameters are known to affect the thermal spraying process that are apparatus dependent, such as the power input, rate of particle introduction, distance of the nozzle and the substrate from the flame or plasma, and the like. Specific temperatures that induce the pyrolytic decomposition reaction of the invention are dependent on particle size of the introduced powder, its composition, the rate of introduction, and the porosity characteristics of the substrate (*i.e.*, particle sizes on the substrate) ultimately desired after treatment. Many other factors encountered in thermal spraying differ according to the machine used. Figure 1B illustrates several process parameters associated with an example. The distance D from the plasma source P in the treatment of a flat substrate will typically be from about 3 centimeters to about 15 centimeters. The plasma temperature T1 is dependent on the plasma power which is typically up to about 50 kW or more, the gas flow rate and the type of gas. The surface temperature of the substrate during the spray process T2 should be maintained at about less than 100° C.

A further consideration of using $Ce_2(CO_3)_3$ or cerium based compositions is the phase transition during deposition and decomposition of the particles to result in a coating on the surface, from Ce_2O_3 to CeO_2. This transition prevents the formation of large crystalline clusters on the surface. Overall, by introducing $Ce_2(CO_3)_3$ particles into the thermal spray, porous CeO_2 surface coatings are produced with nominal particle size distributions in the range smaller than approximately 3 micrometers and preferably, in the range smaller than approximately 1 micrometer, as a result of the decomposition process during coating: $Ce_2 (CO_3)_3 + ½ O_2 \rightarrow 2CeO_2 + 3CO_2$.

As noted above, the flame temperature or plasma power required to achieve sufficient mechanical bonding of the catalyst precursor material to the substrate varies depending on equipment parameters, process rates, the spraying environment, and specific catalyst precursor material used. The appropriate temperature / power is process and material dependent, but should be sufficient for pyrolysis of the sprayed mixture. A catalyst coating may be formed on the substrate by using a mixture of catalyst precursors that decomposes to a metal oxide, a noble metal and/or a noble metal oxide.

The hydroxide, carbonate, or nitrate powders or particles used provide a large size precursor to produce a coating of small size particles. While useful particle or powder sizes are not limited in the invention, the normal size distributions for particles or powders sprayed in the invention are in the range of nominally greater than 10 micrometers, and range from approximately 15 micrometers up to approximately 200 micrometers. The mixture may be prepared by thorough mixing of the components. In an example, the mixture was separated into a consistent particle size less than 200 micrometers and greater than 10 micrometers by passing through an appropriately dimensioned sieve or mesh. As illustrated in the following example, a coating of catalytic material applied to a substrate will exhibit small particle size and high surface area characteristics particularly useful with micro-channel micro-component assemblies.

EXAMPLE I

The photomicrographs of Figure 3A and Figure 3B depict the following example. A substrate (a 5 centimeter by 10 centimeter shim) of a stainless steel

alloy, Iconel® 625, with a thickness of approximately 100 micrometers, was cleaned by washing with trichloroethylene for approximately 30 minutes and ethanol for another approximately 30 minutes and then soaked in deionized water for approximately 60 minutes in an ultrasonic cleaner. The surface of the cleaned shim was enhanced by grit blasting using alumina particles of approximately 220 mesh size to obtain a roughness of several micrometers. The flat surface of the shim was coated by a plasma spray of precursors that produced the mixture of ceria and palladium shown in the figures.

Having described the invention in detail, those skilled in the art will appreciate that, given the present disclosure, modifications may be made to the invention without departing from the spirit of the inventive concept herein described. Rather, it is intended that the scope of the invention be determined by the appended claims.

CLAIMS:

[C1] A catalytic surface comprising a particulate coating on a substrate of a) one or more than one of cerium, aluminum, tin, manganese, copper, cobalt, nickel, praseodymium or terbium oxide and b) one or more than one of ruthenium, rhodium, palladium, silver, iridium, platinum and gold, characterized as a substantially uniform distribution over the surface of the substrate in which the coating particles are in the nominal diameter size distribution range of < 3 microns.

[C2] The surface of claim 1 in which and the coating particles are in the nominal diameter size distribution range of < 1 micron.

[C3] A method for depositing a catalyst coating of small size metal oxide and noble metal particles onto the surface of a substrate comprising thermally spraying a particulate mixture principally comprising 1) metal hydroxide, metal carbonate, or metal nitrate particles and 2) a noble metal, noble metal hydroxide, noble metal carbonate, or noble metal nitrate directly onto the surface of the substrate.

[C4] A method for depositing a catalyst coating of metal oxide / noble metal particles in the nominal diameter size distribution range of < 3 microns onto the surface of a substrate comprising thermally spraying a particulate mixture principally comprising 1) metal hydroxide, metal carbonate, or metal nitrate particles capable of decomposing to a metal oxide and 2) a noble metal, noble

metal hydroxide, noble metal carbonate, or noble metal nitrate capable of decomposing to a metal or metal oxide directly onto the surface of the substrate.

[C5] A method for depositing a metal oxide / noble metal catalyst onto the surface of a substrate comprising thermally spraying a particulate mixture of large size particles in a nominal diameter size distribution range of > 10 micrometers and principally comprising 1) one or more than one composition selected from the group of metal hydroxides, metal carbonates, and metal nitrates capable of decomposing to a metal oxide and 2) one or more than one composition selected from the group of noble metals, noble metal hydroxides, noble metal carbonates, and noble metal nitrates capable of decomposing to a metal directly onto the surface of the substrate.

[C6] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a cerium composition.

[C7] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is an aluminum composition.

[C8] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a tin composition.

[C9] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a manganese composition.

[C10] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a copper composition.

[C11] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a cobalt composition.

[C12] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a nickel composition.

[C13] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a praseodymium composition.

[C14] The method of claim 4 or claim 5 in which the metal hydroxide, metal carbonate, or metal nitrate particle capable of decomposing to a metal oxide is a terbium composition.

[C15] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a palladium composition.

[C16] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a platinum composition.

[C17] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a ruthenium composition.

[C18] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a rhodium composition.

[C19] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a silver composition.

[C20] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a iridium composition.

[C21] The method of claim 4 or claim 5 in which the noble metal hydroxide, carbonate, or nitrate particle capable of decomposing to a metal is a gold composition.

[C22] The method of claim 3 or claim 4 or claim 5 in which the particles are flame sprayed onto the surface of the substrate.

[C23] The method of claim 3 or claim 4 or claim 5 in which the particles are plasma sprayed onto the surface of the substrate.

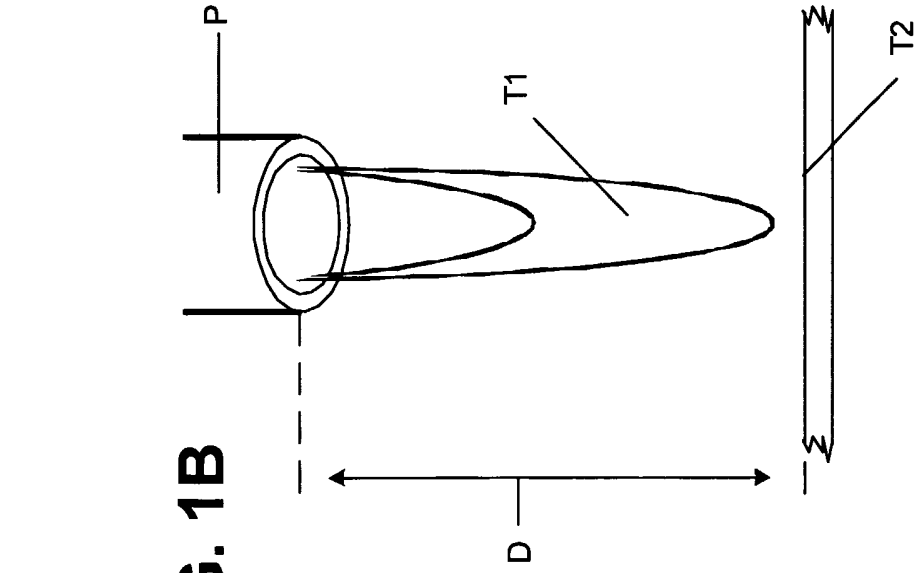


FIG. 1B

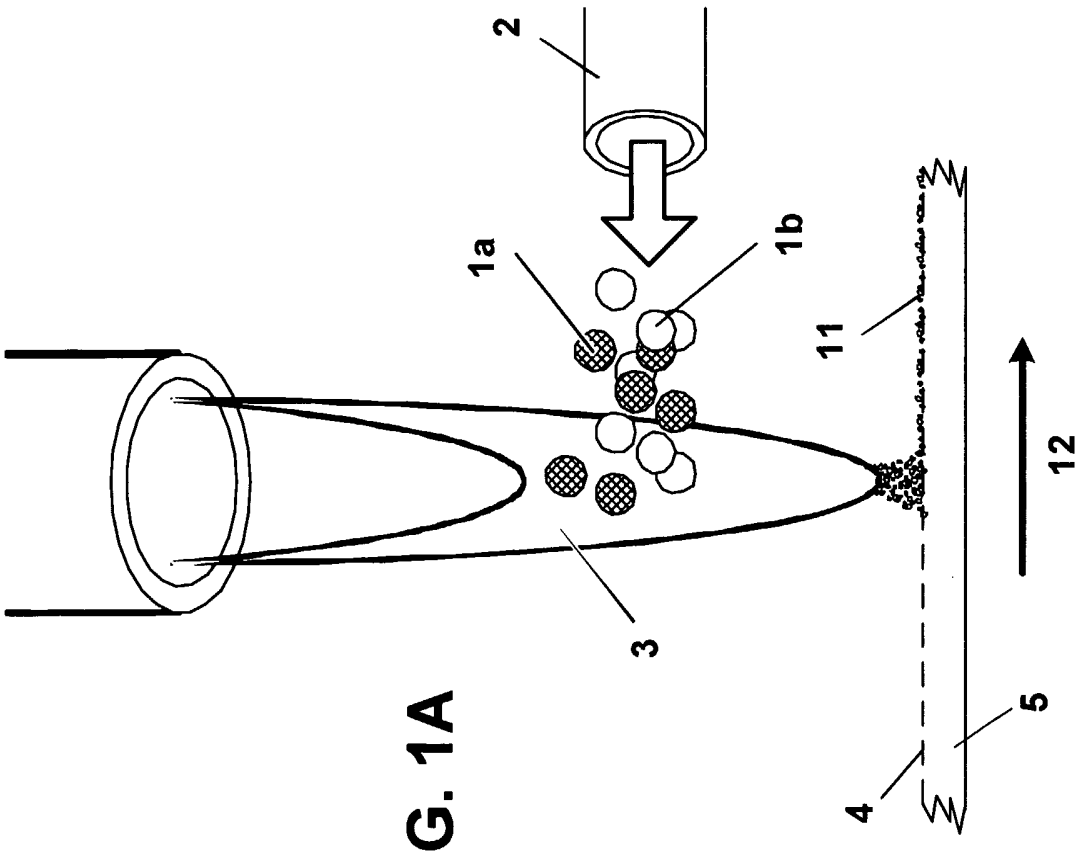


FIG. 1A

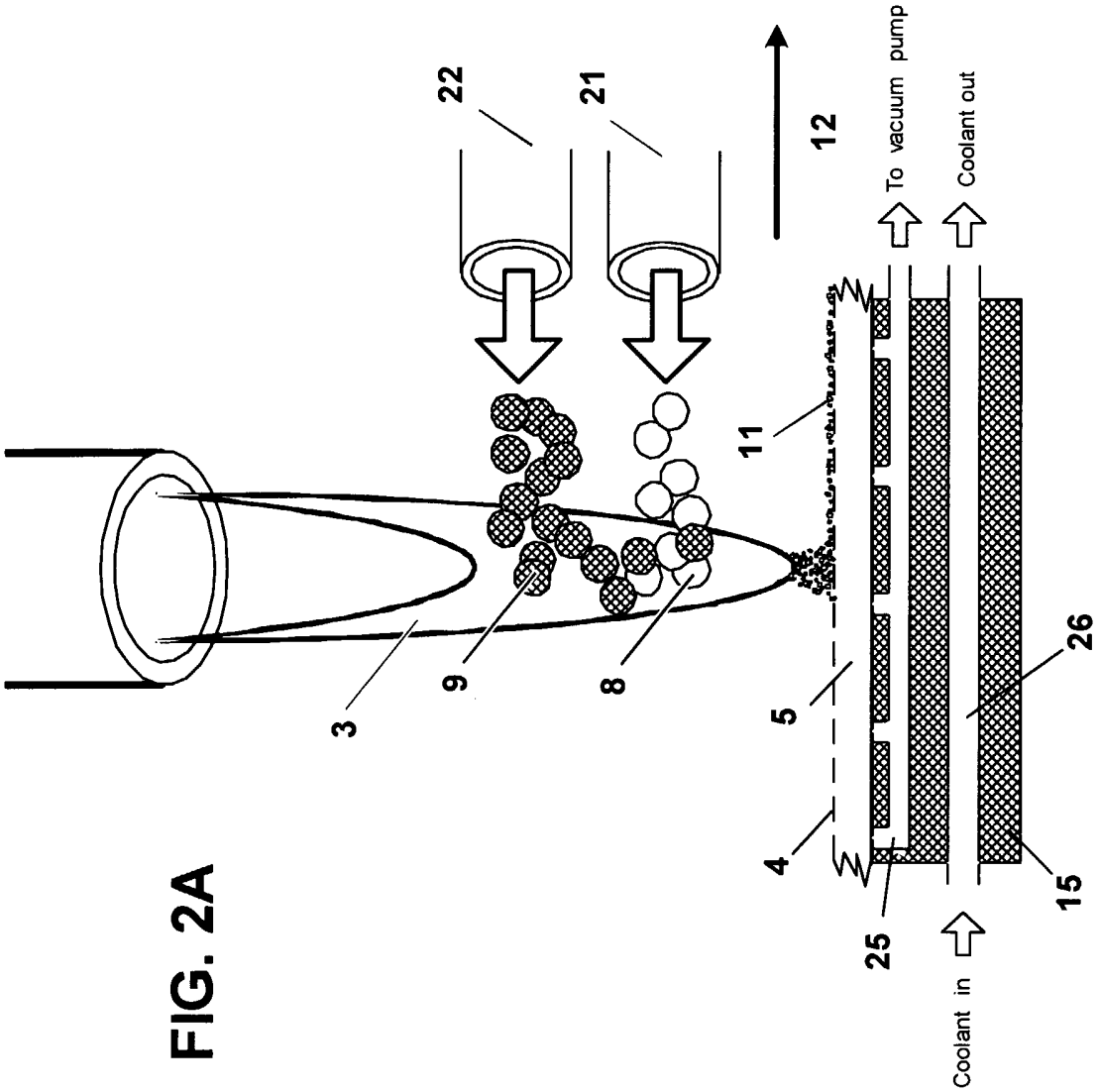

22
21
12
To vacuum pump
Coolant out
11
3
9
8
5
26
4
25
15
Coolant in

FIG. 2A

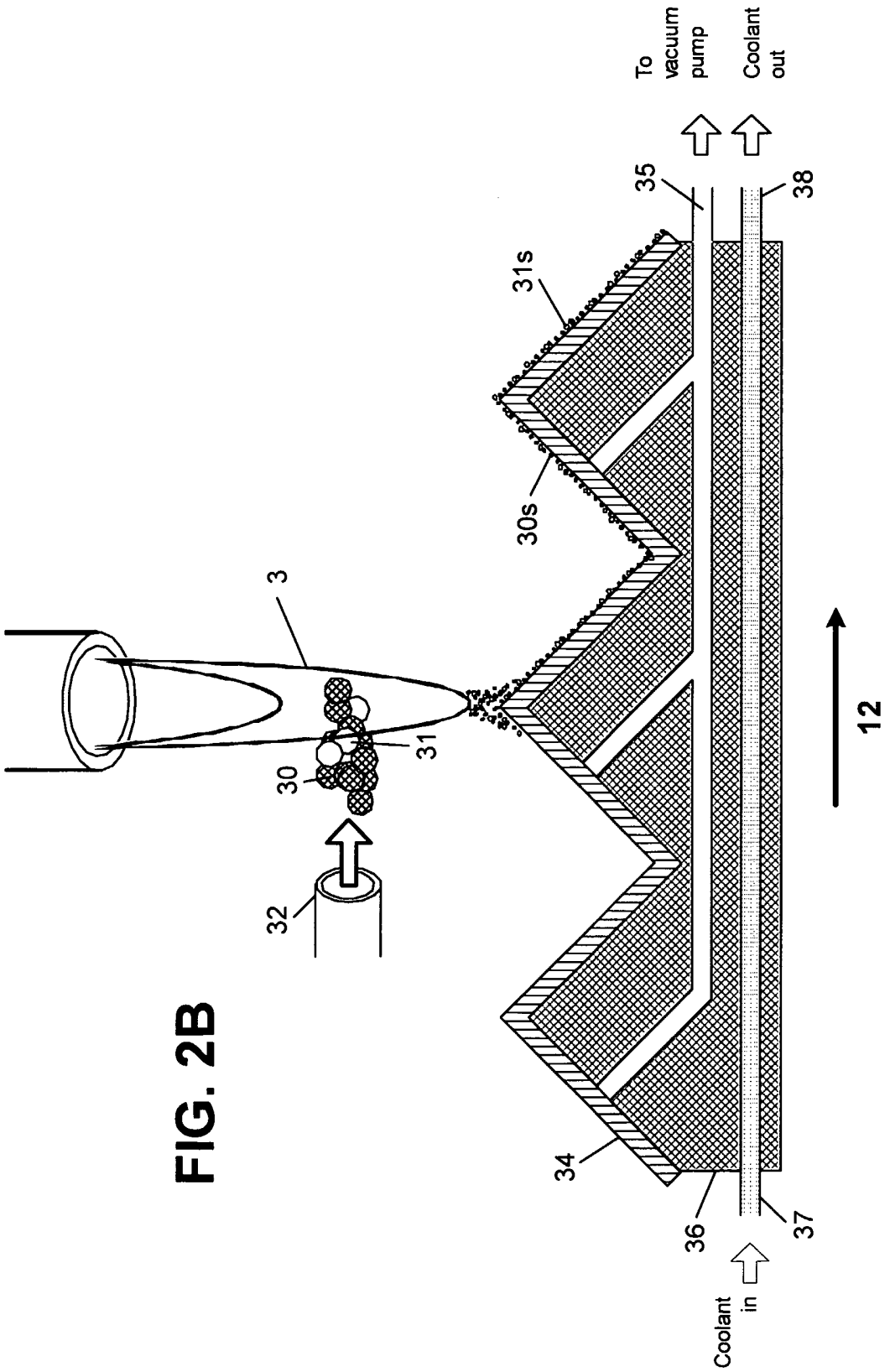

To vacuum pump
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30s
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31
30
32
34
36
37
Coolant in
12

FIG. 2B

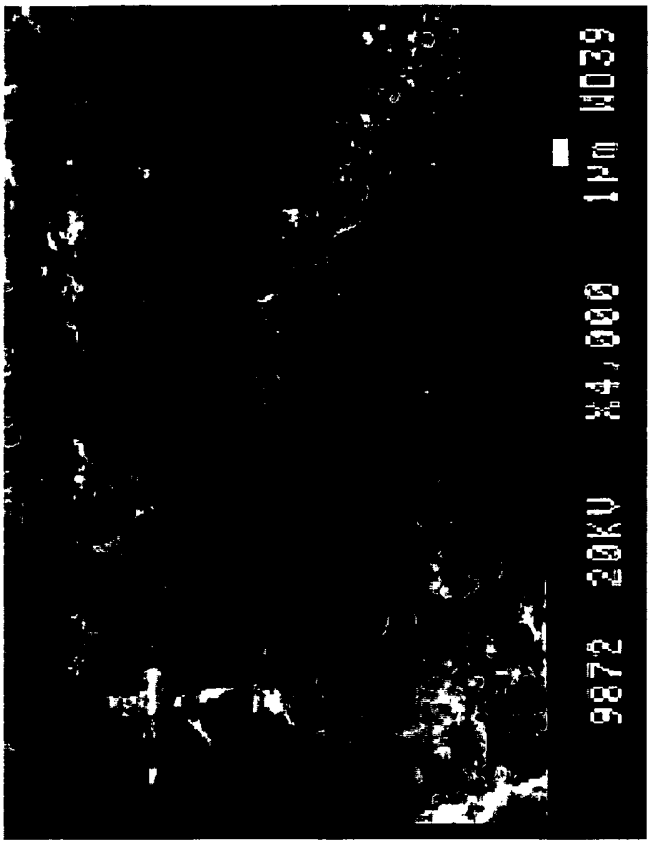


FIG. 3B

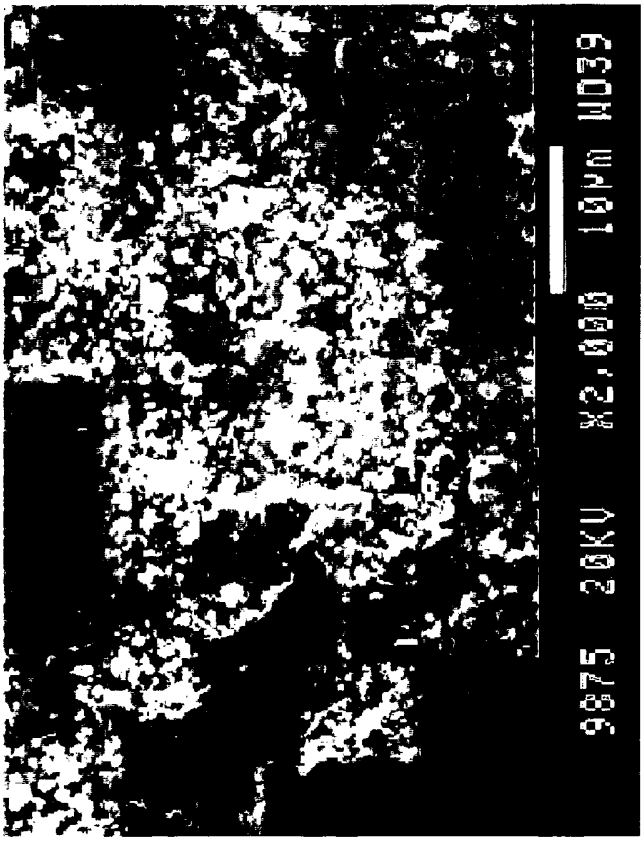


FIG. 3A

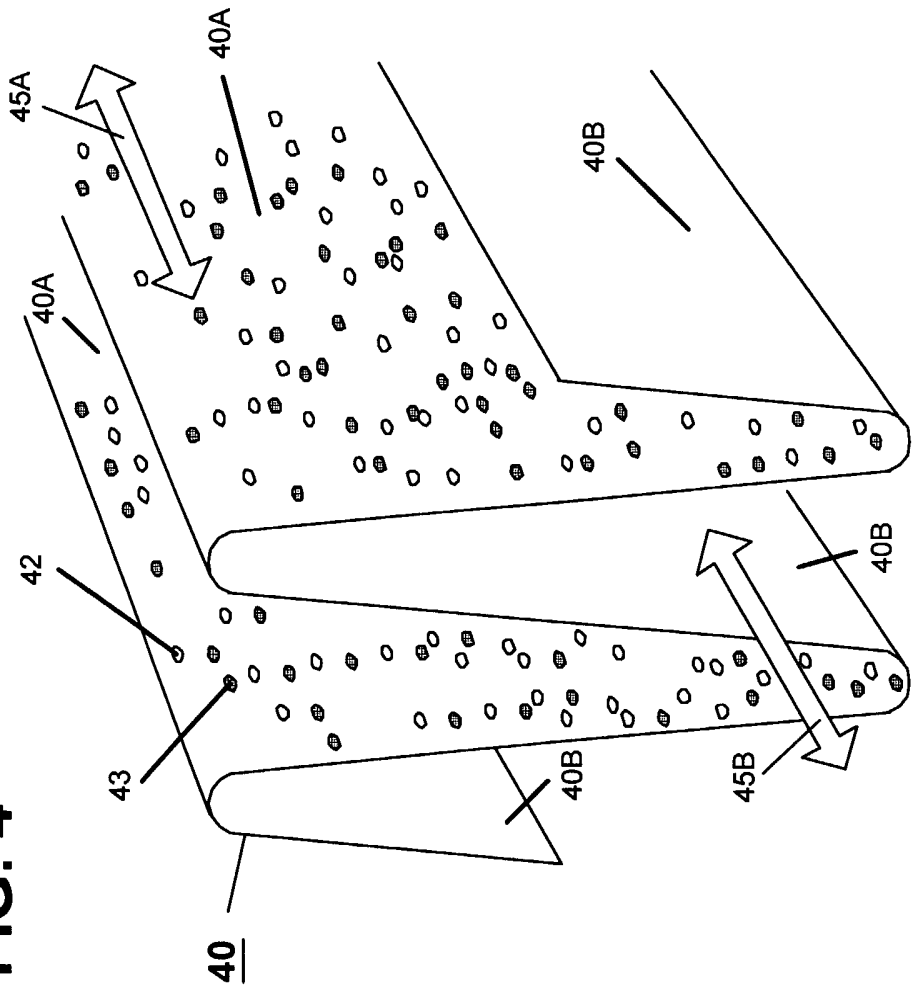


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/23267

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 21/04, 23/00, 23/10, 23/14, 23/16, 23/32, 23/38, 23/40, 23/42, 23/44, 23/46, 23/50, 23/52, 23/48, 23/62, 23/63, 23/64, 23/656, 23/66, 23/68, 23/70, 23/72, 23/755, 23/76, 23/83, 23/835, 23/84, 23/889, 23/89; C23C 4/04, 4/06, 4/10

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Continuation Sheet

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,063,192 A (MURAKAMI et al) 05 November 1991 (05.11.1991), see column 3, line 60 through column 4, line 45 and column 5, lines 35-60.	1-2 --- 3-23
X --- Y	US 4,731,261 A (TSUCHITANI et al) 15 March 1988 (15.03.1988), see column 2, lines 1-20 and column 2, line 65 through column 3, line 25.	1-2 --- 3-23
Y	US 6,228,801 B1 (Hums et al) 08 May 2001 (08.05.2001), see column 2, lines 20-30, column 3, lines 40-55, and column 4, lines 10-65.	3-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

29 October 2002 (29.10.2002)

Date of mailing of the international search report

12 DEC 2002

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
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Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

PCT/US02/23267

Continuation of Item 4 of the first sheet:
The existing title is more than 17 words.

NEW TITLE:
METAL OXIDE AND NOBLE METAL CATALYST COATINGS

Continuation of B. FIELDS SEARCHED Item 1:
502/300, 302, 304, 324, 325, 326, 327, 330, 331, 332, 333, 334, 335, 337, 339, 344, 345, 346, 347, 348, 349, 352, 355; 427/450, 451, 453, 455

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/23267

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

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

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.