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Dwyer et al.

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[54] **METHOD OF COATING HONEYCOMBED SUBSTRATES**

[75] Inventors: **Thomas J. Dwyer**, Painted Post; **George P. Pesansky**, Beaver Dams, both of N.Y.

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

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[52] **U.S. Cl.** ..... **117/95**, 117/47 H, 117/98, 117/102 R, 117/113, 117/119, 117/119.8, 117/123 A, 117/123 B, 117/169 A, 117/169 R

[51] **Int. Cl.** **B44d 1/092**

[58] **Field of Search** ..... 117/47 H, 95, 98, 101, 117/102 R, 113, 119, 119.8, 169 A, 169 R, 123 A, 123 B

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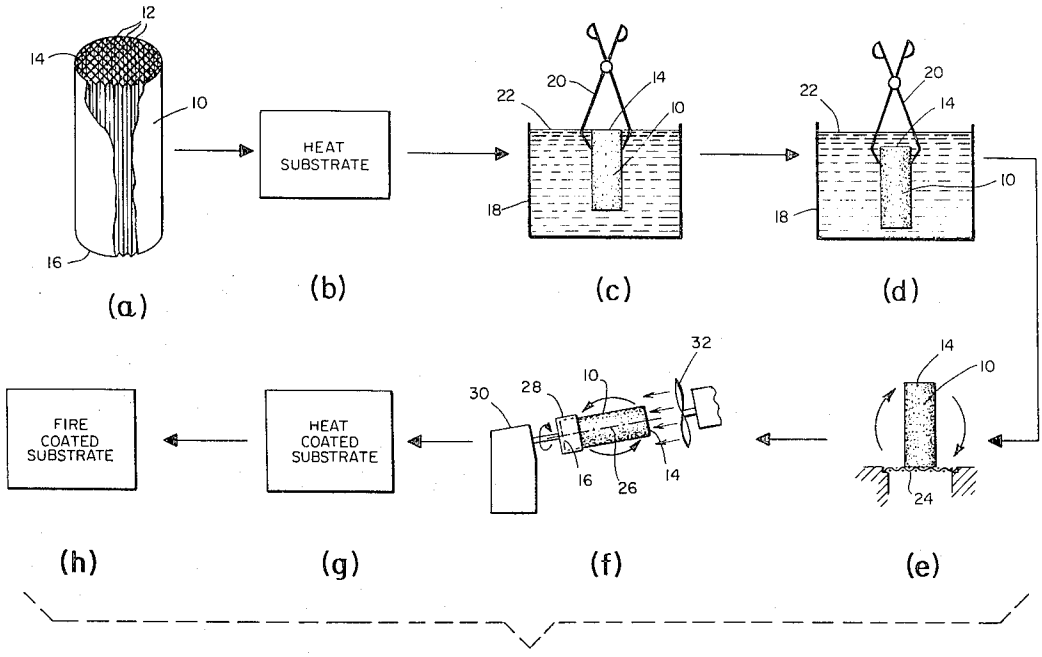
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Primary Examiner—William D. Martin
Assistant Examiner—Shrive P. Beck
Attorney, Agent, or Firm—Richard N. Wardell; Norman L. Norris; Clarence R. Patty, Jr.

[57] **ABSTRACT**

A honeycombed substrate to be coated with a slurry is first heated to a temperature in excess of the boiling point of the slurry liquid medium. The substrate is slowly dipped into the slurry with the axes of the cells extending substantially vertically while maintaining the uppermost ends of the cells above the upper surface of the slurry until the air within the cells has escaped. After the substrate has been removed from the slurry, the substrate is periodically inverted and/or subjected to a series of shakes or jerks while draining under the influence of gravity with the open cell axes extending substantially vertically after each inversion. The substrate is then rotated around a horizontal axis of rotation which extends substantially parallel with the axes of the substrate cells. Forced air is passed through the cells from alternate ends of the substrate until the slurry no longer flows within the cells. The coated substrate is then dried and fired.

20 Claims, 8 Drawing Figures



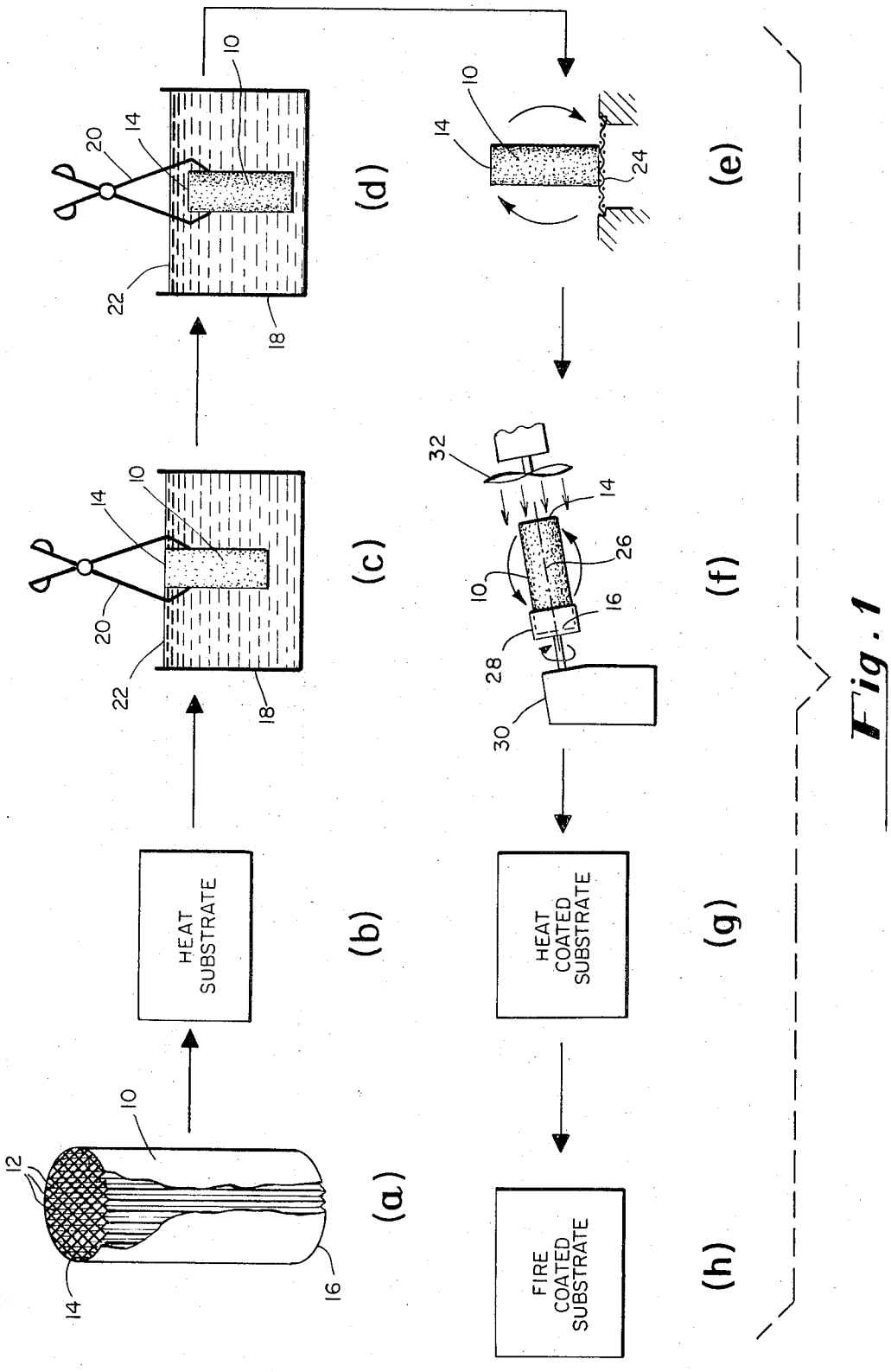

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
HEAT SUBSTRATE
HEAT COATED SUBSTRATE
FIRE COATED SUBSTRATE
10
12
14
16
18
20
22
24
26
28
30
32

Fig. 1

METHOD OF COATING HONEYCOMBED SUBSTRATES

BACKGROUND OF THE INVENTION

This invention relates to the coating of thin-walled honeycombed substrates.

Thin-walled honeycombed substrates find extensive use as catalyst supports where a honeycombed substrate is coated with a thin film comprising a high surface area, active metal oxide such as gamma alumina. Heretofore, considerable difficulty has been encountered in obtaining a thin, uniform coating of the honeycombed substrate. The difficulties involved may readily be appreciated when one considers that the honeycombed substrate is often times characterized by 200 or more cells per square inch of cross-section where the cells walls are less than 0.02 inch thick. It is of course somewhat difficult to obtain a uniform coating on the walls of these extremely small cells.

However, the uniform coating of these cell walls is particularly important in many applications including catalyst supports where the objective is to maximize the overall surface area at which reactions can be promoted by a catalyst such as platinum. If a coating is sufficiently non-uniform so as to plug various cells of the substrate, the surface area of the metal oxide coating is reduced. It is also desirable to provide reproducibility in the coating of a particular substrate. In other words, it is desirable to be able to coat substrate after substrate within a batch with a certain specific percentage by weight coating and to coat substrates of different batches with the same specific percentage by weight coating.

In the prior art, various techniques have been utilized in an attempt to coat substrates. In the catalyst support art, these techniques have included spraying and dipping as disclosed, for example, in U.S. Pat. No. 3,565,830 — Keith et al. However, we have found that these techniques practiced by the prior art have not produced a high degree of uniformity or reproducibility in the coating of thin-walled honeycombed substrates.

SUMMARY OF THE INVENTION

It is an overall object of this invention to provide an improved method of applying coatings to the surface of cell walls of a thin-walled, honeycombed substrate.

It is a more specific object of this invention to provide a method for uniformly coating substrates of this type.

It is also a specific object of this invention to provide a method of obtaining reproducible coatings on substrates of this type.

In accordance with one important aspect of this invention, a thin-walled honeycombed substrate is heated prior to dipping in a slurry comprising a liquid medium and solids maintained in suspension in the medium. More specifically, the substrate is heated to a temperature in excess of the boiling point of the liquid medium so as to negate the capillary action of the substrate cells on the liquid medium. The substrate is then dipped into the slurry with the axes of the cells within the substrate extending at a substantial angle with respect to the surface of the slurry so as to allow the slurry to rise in these cells as the substrate is dipped into the slurry.

In accordance with another important aspect of the invention, the excess slurry is drained from the substrate prior to drying by supporting the substrate with the axes of the cells extending substantially vertically for a period of time and then inverting and/or shaking or jerking the substrate for a period of time so as to avoid the build-up of slurry deposits within the substrate.

In accordance with another important aspect of the invention, the initially drained substrate is rotated about an axis extending from one end of the substrate to the other where the axis of rotation is substantially parallel with the cell axes and forms an angle of 0°–25° with respect to a horizontal plane. A gaseous drying medium is then forced in one direction through the cells of the substrate and then another until the slurry ceases to flow within the cells of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1(*a–h*) are illustrations of the various steps of a method which forms the preferred embodiment of the invention.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

FIG. 1(*a*) illustrates a thin-walled substrate **10** of a type which may be coated in accordance with the method of this invention. The substrate illustrated is an extruded, monolithic, ceramic structure comprising a multiplicity of open-ended cells **12** having parallel cell axes where the cells extend from one end **14** of the substrate to the other end **16.** The method of making this particular ceramic substrate is disclosed in copending application Ser. No. 196,986 filed Nov. 9, 1971, now U.S. Pat. No. 3,790,654, which is incorporated herein by reference. Substrates of this type which are sold by Corning Glass Works under the trademark W-1 are often characterized by a cordierite composition, by 200 or more cells per square inch of cross-sectional area, by cell walls having a thickness of 0.005–0.100 inch and by a porosity of 15–50%.

In accordance with one very important aspect of the invention, the substrate as depicted in FIG. 1(*b*) is now heated in preparation for dipping in a slurry, which has been previously mixed by rolling for an hour or more or by other suitable means, where the slurry comprises a liquid medium and solids maintained in suspension in the liquid medium. This heating defeats the capillary action of the cells (which have relatively small cross-sectional area perpendicular to their axes) to allow the solids of the slurry to remain uniformly mixed with the liquid medium as the slurry passes into successive portions of the cells to thereby obtain a uniform coating. In general, the substrate is heated to a temperature in excess of the boiling point of the liquid medium in the slurry and only slightly in excess of that boiling point so as to preclude rapid evaporation of the liquid medium which can cause a build-up of heavy deposits on the cell walls during the coating process. In this particular embodiment of the invention, the substrate is being coated for use as a catalyst support where the slurry comprises a metal oxide in the form of hydrated alumina (a precursor of high surface area, active gamma alumina) and a liquid medium comprising an aromatic organic solvent in the form of toluene. The heating of the substrate may be done in an air circulating oven where the temperature is maintained at 120°–130° C. which is 10°–20° C. above the toluene boiling point. In general, the temperature for drying should be maintained 2°–50° C. above the liquid medium boiling point

where the lower temperatures are used for low cell densities and higher temperatures are used for high cell densities.

The substrate **10** is now dipped in the slurry comprising the hydrated alumina and the toluene. In order to assure a thermally stable substrate coating with a large surface area and good adherence between the coating and the substrate, the slurry also comprises a binder and deflocculant in the form of an organo-silicon compound having a polysiloxane chain structure, such as a silicone or organopolysiloxane resin, containing a plurality of silanol groups. In a preferred embodiment, the slurry consists essentially of 45–70% by weight of powdered Alcoa C333 alumina trihydrate, 7–28% by weight of Dow Corning 804 silicone resin with solvent and 15–24% by weight of Baker reagent grade toluene. Since the Dow Corning 804 resin includes toluene as a solvent, the slurry consists essentially of 45–70% by weight of Alcoa C333 alumina trihydrate, 4–18% by weight of the polysiloxane resin and 18–35% by weight of toluene as described in copending application Ser. No. 333,642, filed Feb. 20, 1973 (assigned to the assignee of this invention), which is incorporated herein by reference. The slurry is mixed by rolling for about 12 hours.

In order to assure a uniform coating, the substrate **10** is dipped slowly into a vessel **18** containing the slurry utilizing a pair of tongs **20** as shown in FIG. **1**(*c*). While the substrate **10** is dipped slowly into the slurry, the axes of the cells **12** are maintained at a substantial angle with respect to the surface **22** of the slurry, preferably 90° with respect thereto or vertical, so as to allow the slurry to rise slowly in the cells **12** thereby expelling the air trapped in the cells. This assures that all cells are filled from the bottom rather than filled as overflow from the top. In order to assure expulsion of all air, the upper end **14** of the substrate **10** is maintained at or slightly above the upper level of the slurry surface **22** for a period of 10 seconds as depicted in FIG. **1**(*c*).

After all of the air has been expelled, the substrate **10** is submerged beneath the surface **22** of the slurry as depicted in FIG. **1**(*d*) and held in the submerged position for a period of approximately 2 minutes. The slurry may be continuously stirred by a magnetically driven stirrer during dipping to assist in maintaining the alumina in suspension.

In accordance with another important aspect of the invention shown in FIG. **1**(*e*), the slurry is drained from the substrate **10** by supporting the substrate **10** by a screen **24** or other suitable means with the axes of the cells extending substantially vertically. The substrate is then inverted periodically, e.g., every 20 to 100 seconds, several, e.g., 2 to 6, different times, to avoid the build-up of slurry deposits within the substrate cells. Shorter length substrates, e.g., 3 inches in length, generally require lesser periods of draining after each inversion but more inversions while longer lengths of substrate, e.g., 6 inches in length, require longer periods of draining after each inversion but fewer inversions. Shakes or jerks can be substituted for part or all of the inversions.

In accordance with still another important aspect of the invention shown in FIG. **1**(*f*), the initially drained substrate **10** is rotated about an axis **26** which extends from one end of the substrate to the other where the axis of rotation is substantially parallel with the cell axes and forms an angle of 0°–25° with respect to a horizontal plane. This is accomplished by mounting the substrate **10** in a circular chuck **28** which is driven by a motor located within a motor housing **30** and which rotates at a speed of 1–15 R.P.M. with 6 R.P.M. being preferred. This rotation achieves uniformity of coating within a cell in a plane perpendicular to the cell axes.

As also depicted in FIG. **1**(*f*), a gaseous drying medium is forced into the cells from the ends of the substrate. The drying medium may comprise air where the air is forced into the cells of the substrate by a 12 inch diameter household fan **32** located approximately 12–18 inches from the end **14** of the substrate **10.** In order to assure uniformity in coating of the cell walls along the entire length of the cells, the substrate **10** is removed from the chuck **28** after a period, e.g., 20 seconds, of forced air drying. The substrate **10** is then turned 180° so as to place the end **14** in the chuck **28.** Drying then proceeds for another period, e.g., 3 minutes, while the substrate **10** rotates after which the substrate is turned 180° again so as to place the end **16** back in the chuck **28.** This forcing of the air into the cells from alternate ends of the substrate will assure a uniform coating of the cells along the length thereof. When all traces of wetness are gone, in general about 5 minutes, the substrate **10** is removed from the chuck **28.** If further drying time is required, the substrate can again be turned 180°.

In order to expeditiously complete the drying of the slurry coated substrate, it is beneficial to heat the substrate **10** by placing it in a furnace which is maintained at approximately 100° C. as depicted by FIG. **1**(*g*). The coated substrate is then allowed to remain in the furnace at this temperature until thoroughly free of volatile liquid, e.g., for approximately 2 hours. The temperature of the furnace is then raised approximately 100° C. per hour until the 600° C. firing temperature is reached. This temperature calcines the alumina trihydrate to form a high surface area, active alumina, i.e., gamma alumina, while also converting the silicone or polysiloxane resin to a silica which serves to bind the coating to the ceramic substrate.

By coating a honeycombed substrate with the foregoing method, it has been found that substantial uniformity in the coating from area to area within a given substrate is achieved. In this connection, substrates measuring 3 inches in length and 1 inch in diameter were coated with the method described and subsequently cut into designated pieces. These pieces were then crushed to −12 mesh particles and submitted for standard B.E.T. nitrogen-absorption surface area measurements. The surface areas were then compiled by location in the substrate to statistically determine the uniformity of the coating. The following table indicates the surface area measurements for various locations within the coated substrate where the first letter represents a selected partial cross-sectional area of the sample at any selected axial position on the sample, the middle digit represents an axial position on the sample and the second and last letter represents the particular half of the selected partial area under consideration.

Table 1

Alumina Coating Distribution	
Sample Designation	Surface Area, M^2/gr
C2A	56

Table 1-Continued

Alumina Coating Distribution Sample Designation	Surface Area, M^2/gr	
C4A	52	
C6A	43	50.8 ave.
C2B	54	
C4B	54	
C6B	45	
E2A	46	
E4A	49	
E6A	43	48.7 ave.
E2B	53	
E4B	46	
E6B	55	
H2C	57	
H4C	48	
H6C	42	50.1 ave.
H2D	64	
H4D	48	
H6D	42	
Tops	61	
Bottoms	53	

It will be noted that the surface area measurements vary from 42–64 square meters/gram which represents a fairly uniform coating of ±22% of the average surface area of approximately $50M^2$/gram where the error in surface area measurements was ±10%. Similar results were achieved when 6 inch lengths of substrate were coated.

In addition to the uniformity of the coating, it has been found that the foregoing method achieves fairly reproducible results from slurry batch to slurry batch. Different slurry batches containing the same percent by weight of toluene produce coatings to within ±10% of the coating weight. Good reproducibility for coated substrates prepared from the same batch is achieved if the liquid medium plus resin is replenished after each coating to maintain a relatively constant specific gravity for the slurry.

Finally, it has been found that substrates coated in accordance with the foregoing method are characterized by good coating adherence to the substrate. As a test of this adherence, the coated substrates were placed in an ultrasonic bath and the percent weight loss of coating was recorded as function of time. It was found that W-1 substrates coated utilizing the 2:1 ratio of Alcoa C333 alumina to Dow Corning 804 silicone resin and 22% added toluene resulted in a coating which showed less than 1% weight loss after 30 minutes in an ultrasonic bath.

In the foregoing, a specific slurry has been described for use in coating the substrate **10** so as to produce a catalyst support. It will of course be appreciated that other slurries may be utilized. Some examples of such other slurries are those disclosed in the aforesaid copending application Ser. No. 333,642, filed Feb. 20, 1973, and in U.S. Pat. No. 3,565,830. Also, the alumina may be replaced, in whole or in part, by one or more high surface area oxides of metals from the Groups II, III and IV having an atomic number of 40 or less. It may also be replaced in whole or in part of by a precursor of such a metal oxide, which precursor becomes the desired oxide upon firing of the coated substrate. Moreover, the method described in the foregoing may be utilized in the manufacture of coated honeycombed structures for use other than as catalyst where the slurry differs considerably from those previously described.

It will also be understood that the substrate **10** need not be a Corning W-1 ceramic substrate but may comprise any thin-walled honeycombed structure having open-ended cells wherein it is desirable to achieve a uniform and reproducible coating. For example, the substrate may comprise a metal or plastic material. Also, the cells may be square and hexagonal in cross-section with 900 or more cells per square inch or as few as 20 or less cells per square inch of cross-section.

Although a preferred embodiment of the invention has been shown and described and alternative embodiments and modifications have been suggested, it will be understood that the appended claims are intended to cover all embodiments and modifications which fall within the true spirit and scope of the invention.

What is claimed is:

1. A method of uniformly coating relatively thin porous walls of a ceramic honeycombed substrate forming a multiplicity of elongated open-ended cells extending longitudinally from one end of the substrate to the other, said cells having substantially parallel cell axes with a cell density in excess of 20 cells per square inch of cross-sectional area transverse to the cell axes, said method comprising:

mixing a slurry comprising a liquid medium and solids maintained in substantially uniform suspension in said liquid medium;

heating said substrate to a temperature in excess of the boiling point of said liquid medium; and

dipping one end of said heated substrate in said slurry while maintaining a substantial angle between the axes of said cells and the surface of said liquid medium as said substrate is lowered in said slurry so as to substantially preclude said slurry from entering said cells from said other end of said substrate while the air is escaping from said other end as said slurry rises in said cells;

said heating of said slurry substantially negating the capillary action within said cells as said substrate is lowered in said slurry so as to allow the solids of said slurry to remain uniformly suspended in said liquid medium as said slurry coats the cell walls thereby achieving a substantially uniform coating of said solids on said cell walls.

2. The method of claim **1** wherein the axes of said cells extend substantially vertically with respect to the surface of said slurry during dipping.

3. The method of claim **1** further comprising:

rotating said dipped substrate around an axis of rotation extending from said one end to said other end of said substrate and substantially parallel with the axes of said cells so as to flow said slurry on said walls of said cells, said axis of rotation forming an angle of 0°–25° with respect to a horizontal plane.

4. The method of claim **3** further comprising:

forcing a gaseous drying medium into said cells from alternate ends of said substrate while rotating said substrate to dry said slurry until the slurry no longer flows on the walls of said cells.

5. The method of claim **4** wherein said gaseous drying medium is also forced over the exterior of said substrate.

6. The method of claim **1** further comprising:

draining excess slurry from said substrate by supporting said substrate with said cell axes extending substantially vertically and periodically inverting said

substrate so as to allow excess slurry to drain from both ends of said substrate.

7. The method of claim **1** wherein said substrate is heated to a temperature of 2°–50°C. in excess of the boiling point of said liquid medium.

8. The method of claim **1** wherein said solids comprise a high surface area oxide of a metal.

9. The method of claim **1** wherein said solids comprise a precursor of a high surface area oxide of a metal and including the step of firing the dried coating on the substrate so as to convert said precursor to said oxide.

10. The method of claim **9** wherein said precursor comprises hydrated alumina.

11. The method of claim **10** wherein said slurry further comprises an organo-silicon compound having a polysiloxane chain structure containing a plurality of silanol groups and said liquid medium comprises an organic solvent.

12. The method of claim **1** further comprising:

rotating the coated substrate around an axis of rotation extending from said one end to said other end of said substrate so as to flow said slurry on the walls of said cells, said axis of rotation forming an angle of 0°–25° with respect to a horizontal plane; and

forcing a gaseous drying medium into said cells while rotating said substrate to dry said slurry.

13. The method of claim **12** wherein said gaseous drying medium is forced into said cells from alternate ends of said substrate and over the exterior of said substrate while rotating said substrate to dry said slurry until said slurry no longer flows on said cell walls.

14. The method of claim **12** wherein said substrate is rotated at 1–15 revolutions per minute.

15. The method of claim **12** wherein said gaseous drying medium comprises air.

16. The method of claim **12** further comprising:

draining excess slurry from said substrate after coating and before rotating said substrate by supporting said substrate with said cell axes extending substantially vertically and periodically inverting said substrate so as to allow excess slurry to drain from both ends of said substrate.

17. The method of claim **12** wherein said solids comprise at least one substance selected from the group consisting of (1) high surface area oxides of metals, and (2) precursors of said metal oxides.

18. The method of claim **17** wherein said substance is a said precursor and including the step of firing the dried coating on the substrate so as to convert said precursor to said oxide.

19. The method of claim **18** wherein the precursor comprises hydrated alumina and the metal oxide comprises gamma alumina.

20. The method of claim **19** wherein said slurry further comprises an organo-silicon compound having a polysiloxane chain structure containing a plurality of silanol groups and said liquid medium of said slurry comprises an organic solvent.

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