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Depositing method and apparatus.

A green ceramic shape is formed by electrophoretic deposition on to a mandrel from a slurry of finely divided ceramic material in a carrier liquid. The mandrel is supported in the slurry and an electric field is applied to deposit material from the slurry on to the mandrel. The weight of the mandrel and any material deposited thereon is continuously monitored and the deposition terminated when the weight reaches a threshold. The green ceramic shape is then removed.

The present invention relates to a deposition method and apparatus, in particular, for electrophoretic deposition.

The usual method of forming an electrophoretic deposit is to suspend the object to be coated in a solid/liquid suspension and apply a voltage between the object and a counter-electrode (which may be the walls of the containing vessel). A problem often encountered in such a method is the monitoring of the thickness of the electrophoretic deposit. D.C. Cornish (J. Phys.E. Ser.2, 2, 123, 1969) describes an electrical probe device for monitoring the thickness of electrophoretic deposits but the installation of such probes and associated electrical circuitry for each deposition chamber is inconvenient, and the accuracy of the probes is somewhat limited. Whilst it is possible, with a great deal of experience, to monitor deposition thickness by monitoring the deposition time, subtle changes in rate of deposition from a batch of suspension can occur as a result of contamination, for example, by the presence of traces of water in a non-aqueous system or changes in temperature, etc. Furthermore, in practice, control of thickness by monitoring deposition time has proved difficult. It has been found that deposition thickness can vary up to $\pm 10\%$ of the intended thickness. There is thus a demand for an accurate method of monitoring deposition thickness.

Accordingly, the present invention provides a method of forming a green ceramic shape by electrophoretic deposition onto a mandrel from a slurry of finely divided ceramic material in a carrier liquid, the method comprising the steps of:

- supporting the mandrel in the slurry;
- applying an electric field to deposit material from the slurry onto the mandrel;
- continuously monitoring the weight of the mandrel and any material deposited thereon;
- terminating the deposition when said weight reaches a predetermined threshold;
- and removing the deposited green ceramic shape from the mandrel.

Preferably, the deposition is performed in repeated cycles from a single batch of the suspension, each cycle comprising depositing onto the object up to the weight threshold and then removing the deposit from the object, and wherein the predetermined weight threshold is increased for a later cycle to compensate for reduction of the specific gravity of the depleted suspension.

Preferably, the ceramic material is beta alumina and the carrier liquid is an organic liquid.

Preferably, the weight of deposit is monitored by supporting the object in the suspension by means which are sensitive to changes in weight of the object.

Preferably, the means are one or more load cells.

The present invention further provides an apparatus for electrophoretic deposition of a green

ceramic shape from a slurry of finely divided ceramic material in a carrier liquid, the apparatus comprising:

- a chamber for holding the slurry;
- a mandrel locatable in the chamber;
- means for applying an electric field to deposit material from the slurry onto the mandrel;
- means for continuously monitoring the weight of the mandrel and any material deposited thereon;
- means for indicating that said weight has reached a predetermined threshold;
- and means for terminating the deposition.

Preferably, the device further comprises an apparatus wherein the means for supporting the object are one or more load cells the output of which is sensitive to changes in the weight of the object.

A preferred embodiment of the present invention will now be described in detail, by way of example only, with reference to the accompanying drawings, of which:

Figures 1 and 2 depict the apparatus of the present invention before and after immersion in a suspension;

Figure 3 shows the circuitry for connection to the apparatus in Figures 1 and 2;

Figure 4 is a graph of measured weight variation with time.

Figures 1 and 2 depict objects 1a and 1b (in the form of mandrels) to be coated which are rigidly attached to a bar or plate 2. The objects 1a and 1b and bar 2 rest on three supporting beams 3 whose displacement is monitored by means of one or more strain gauge load cells 4. In order to provide point contact between bar 2 and beams 3, knife edges, ball bearings or other suitable means of contact 5 are used which avoid frictional effects. The objects are suspended in a solid/liquid suspension 6 within a containing vessel 7. The vessel 7 acts as a counter-electrode when a voltage is applied by means of load cell instrument 8 between the objects and the vessel 7. Before deposition is started the output of the load cells 4 is zeroed so that during deposition a deposit will build up upon the surface of the object 1 and its weight will increase such that the load cells 4 alter the resistance of the circuit and hence alter the voltage reading. Deposition can be terminated either manually or automatically once the output from the load cells 4 has reached a predetermined level. Figure 1 shows the arrangement before lowering of the objects into the suspension and Figure 2 shows the arrangement when in the suspension with a voltage applied across the object and vessel.

In use, the objects 1a and 1b will be secured to the plate 2 and then arranged on the load cells 4. The objects will then be partially submerged in the suspension 6. A pumping sequence will be started and after a short delay the load cell instrument 8 will be tared off and the deposition of material onto the objects started by applying a voltage across the objects and the

vessel. When the weight of material on the objects has reached a set point on the instrument 8 the pumps and voltage will be switched off and the objects raised out of the vessel to be unloaded. The sequence will then be repeated with other objects until the maximum time limit for a deposition is exceeded. At this point, the solids content of the suspension will have lowered so much that the rate of deposition of the material on an object will be too low and impractical.

The circuitry required to measure the signal produced is depicted in Figure 3. Three load cells 4 are connected in parallel. Each load cell 4 is formed as a bridge of a strain gauge. An excitation current is applied across the bridge by two wires and two further wires taken from each other bridge to monitor the balance of the bridge.

An electronic scales 5 (P.W.S 90) receives the six wires from the parallel connected load cells 4 and determines the average weight. The scales is programmed from process controller PLC (programmable logic controller) to have a given number of set points, for example, eight. The scales outputs a signal when the measured weight reaches the set point for the current cycle. The controller then switches off the deposition current to terminate the cycle.

For one batch of slurry used for electrophoretic deposition, successive cycles take longer as the concentration of slurry is depleted. More significantly, the specific gravity of slurry reduces thereby reducing the buoyancy of the deposition on the objects. For the same thickness of deposition, the weight of the plate 2 with the objects 1a and 1b with deposit is greater when immersed in a slurry of lower specific gravity. Thus, on successive cycles in the same batch of slurry, the target weight indicated by a corresponding set point must be higher to ensure the same thickness of deposit, and therefore there is a need for several set points as the deposition proceeds. The weight of the plate and objects before deposition at the beginning of the first cycle for a new slurry batch is "backed-off" by resetting the scales to show zero.

The scales also outputs a signal W_{min} when the measured weight reaches 80% of the target weight W_{tar} for the cycle (see Figure 4). This is ignored by the controller unless the time of the cycle exceeds T_{warn} before the minimum weight is made. In this case, the controller indicates that this is the last cycle for the batch. Gradients 1, 2 and 3 in Figure 4 are ignored by the controller whereas gradients 4 and 5 will be the last cycle for the batch.

The controller will automatically terminate a cycle if T_{max} is exceeded before the target weight is reached. It is still possible to use the batch provided that the minimum weight made signal is received.

Typically, T_{max} is set at 20 mins and T_{warn} sufficiently earlier to enable (empirically) the last cycle to reach the target weight.

The advantage of the present invention is that the

accuracy of the deposition thickness is independent of the deposition rate. The only parameter that affects the thickness is the specific gravity of the liquid or the concentration of powder in the suspension. If the specific gravity of the liquid or the concentration of powder in the suspension are maintained constant so that buoyancy effects do not vary, consistent deposition thicknesses can be obtained. Small changes in ambient temperature can affect liquid density but the effect is very small compared to, for example, the effect of temperature on deposition rate. Since the output signal from the load cells 4 is sensitive to mechanical disturbances caused, for example, by agitation of a liquid or by mechanical vibrations or resonances, measures may need to be taken to provide the load cell circuit with effective signal filtering and damping.

It is possible to obtain repeated deposits from the same batch of suspension provided that the change in specific gravity of the suspension caused by the progressive depletion of the powder concentration in the suspension is taken into account when setting the voltage at which deposition is terminated. It is advisable and advantageous to be able to programme a series of set points at which successive depositions should be terminated. In Example 2 which follows most of the deposits were controlled in this way.

EXAMPLES

Example 1

The first example was carried out for the purposes of comparison only. Suspensions of beta/beta"-alumina powder in amyl alcohol were prepared for the purposes of forming green ceramic shapes by electrophoretic deposition as disclosed in US patent 3881661. Deposition thickness was controlled by switching off the electric field after a pre-set elapsed time which could be reset by the operator if necessary. The accuracy of achieving a target deposition weight was monitored over a period of 50 production runs operated by experienced operators. There were approximately 40 deposits in each production run and it was found that the standard deviation of deposition weights within a run was approximately 4.32% and the standard deviation of the mean deposit weight from run to run was approximately 3.78%.

Example 2

Electrophoretic deposition of beta/beta"-alumina suspensions in amyl alcohol was carried out as in Example 1 except that the deposition thickness was controlled by switching off the electric field once the signal from the average reading of a parallel arrangement of three load cells had reached a preset value.

The accuracy of achieving the target deposition weight was monitored over a period of 12 production runs each of 12 deposits. The standard deviation of deposition weights within a run was approximately 2.83% and the standard deviation of the mean deposition weight from run to run was approximately 0.98%.

It is clear from the Examples that a significant improvement was seen in Example 2 which demonstrates how the use of load cells lead to a more accurate control of deposition thickness.

Claims

1. A method of forming a green ceramic shape by electrophoretic deposition onto a mandrel from a slurry of finely divided ceramic material in a carrier liquid, the method comprising the steps of:
 - supporting the mandrel in the slurry;
 - applying an electric field to deposit material from the slurry onto the mandrel;
 - continuously monitoring the weight of the mandrel and any material deposited thereon;
 - terminating the deposition when said weight reaches a predetermined threshold;
 - and removing the deposited green ceramic shape from the mandrel.
2. A method according to Claim 1 performed in repeated cycles from a single batch of suspension, each cycle comprising the steps of depositing material onto the mandrel until said weight reaches said predetermined threshold and removing the deposited green ceramic shape from the mandrel wherein said predetermined threshold is increased for a later cycle to compensate for reduction of the specific gravity of the used suspension.
3. A method according to Claims 1 or 2 wherein the ceramic material is alumina and the carrier liquid is an organic liquid.
4. A method according to any one of the preceding claims wherein the weight of the mandrel and any deposit is monitored by supporting the mandrel in the slurry by force-sensitive means.
5. A method according to Claim 4 wherein said force-sensitive means comprises at least one load cell.
6. An apparatus for electrophoretic deposition of a green ceramic shape from a slurry of finely divided ceramic material in a carrier liquid, the apparatus comprising:
 - a chamber for holding the slurry;
 - a mandrel locatable in the chamber;

means for applying an electric field to deposit material from the slurry onto the mandrel;

means for continuously monitoring the weight of the mandrel and any material deposited thereon;

means for indicating that said weight has reached a predetermined threshold;

and means for terminating the deposition.

7. An apparatus to Claim 6 wherein said means for terminating the deposition are responsive to said means for indicating that said weight has reached a predetermined threshold to terminate the deposition when said weight reaches said predetermined threshold.
8. An apparatus according to Claims 6 or 7 wherein said indicating means is adapted to indicate different predetermined thresholds dependent on the buoyancy of the slurry.
9. An apparatus according to any one of Claims 6 to 8 wherein said means for continuously monitoring the weight of the mandrel and any material deposited thereon includes force-sensitive means for supporting the mandrel in the chamber.
10. An apparatus according to Claim 9 wherein said force-sensitive means comprises at least one load cell.

FIG. 1.

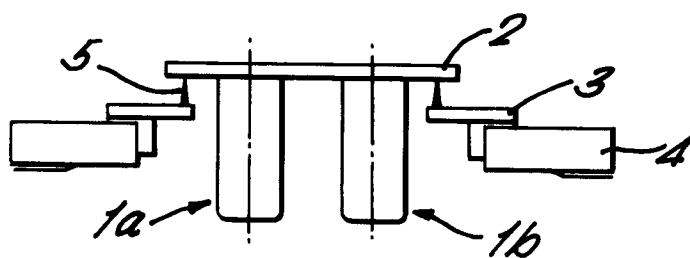


FIG. 2.

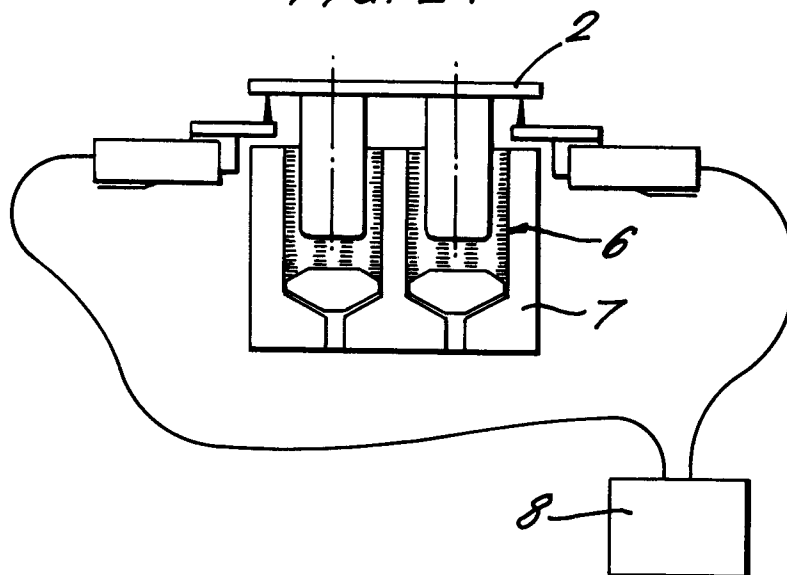


FIG. 3.

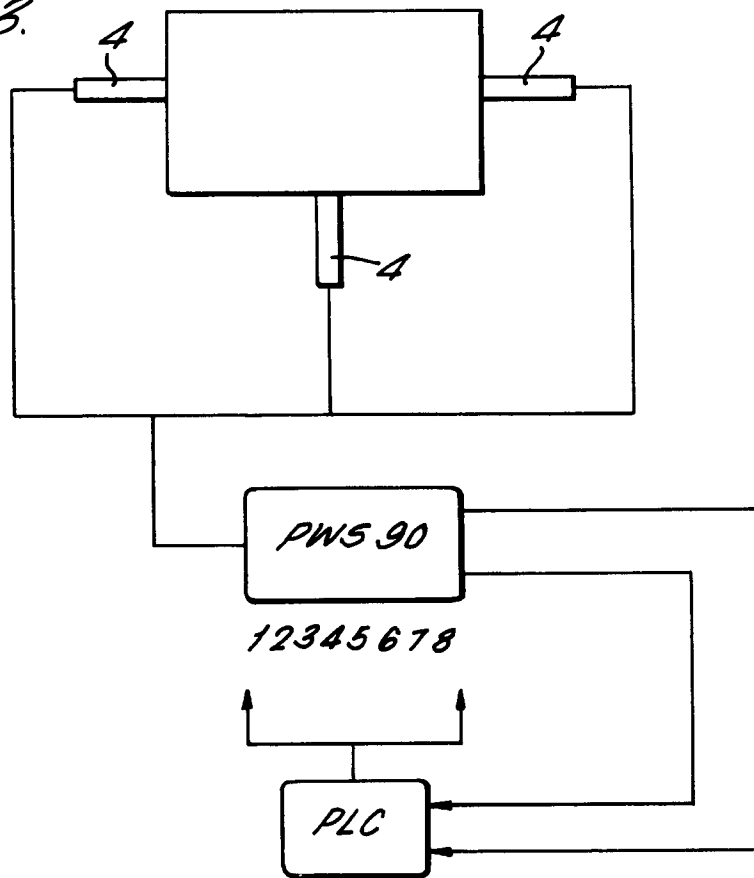
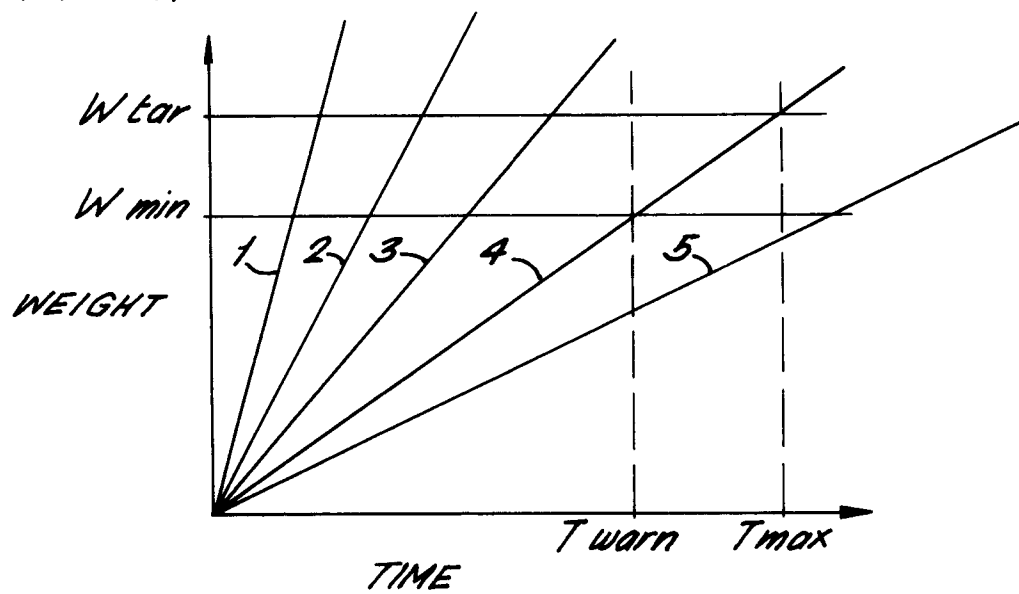


FIG. 4.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1559

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 056 262 (FERNSTENERGERÄTE ZACHARIA-OELSCH-MEIER) * page 4, line 17 - line 28 * ---	1, 2	C25D1/14 C25D21/12
A	US-A-1 856 409 (BRYCE) ---		
A	US-A-1 712 284 (TURNOCK) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 MAY 1992	Examiner NGUYEN THE NGHIEP N.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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