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Szabo

[11] **3,850,733**

[45] **Nov. 26, 1974**

[54] **METHOD OF FORMING FOUNDRY MOULDS**

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Nov. 26, 1971 Canada 128672

[52] **U.S. Cl.** **204/181**

[51] **Int. Cl.** **B01k 5/02**

[58] **Field of Search** 204/181

[56] **References Cited**

UNITED STATES PATENTS

3,484,357	12/1969	Plankenhorn	204/181
3,575,838	4/1971	Hughes	204/181
3,718,564	2/1973	Ebrey	204/181

FOREIGN PATENTS OR APPLICATIONS

691,859	5/1953	Great Britain	204/181

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Attorney, Agent, or Firm—Francis W. Lemon

[57] **ABSTRACT**

A method of forming foundry moulds by the electrophoretic deposition of refractory particles from a suspension, wherein refractory particles which are substantially free from ionic contamination are initially treated, for example by milling or vacuum heat treatment to expose fresh uncontaminated surfaces of the particles to render them electrophoretically mobile when in suspension. A mould former with an electrically conductive surface, for example, a wax or plastic mould with a conductive surface, is dipped into a suspension of the treated particles containing a metal sol binder, and which is substantially free from ionic contamination, and a direct potential is applied between the mould former and the suspension to electrophoretically deposit refractory particles from the suspension as a coating on the electrically conductive surface.

6 Claims, 5 Drawing Figures

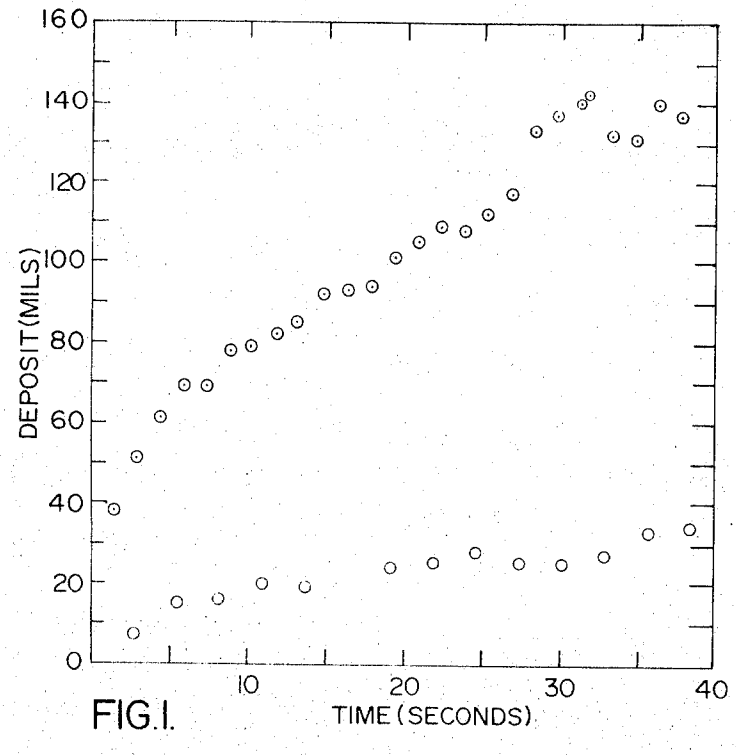

160
140
120
100
80
60
40
20
0
DEPOSIT (MILS)
10
20
30
40
TIME (SECONDS)

FIG. 1.

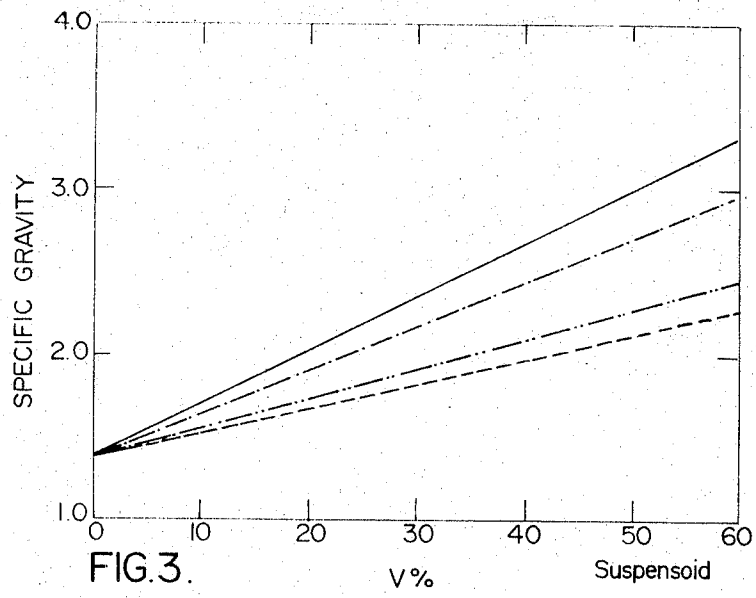

4.0
3.0
2.0
1.0
SPECIFIC GRAVITY
0
10
20
30
40
50
60
V%
Suspensoid

FIG. 3.

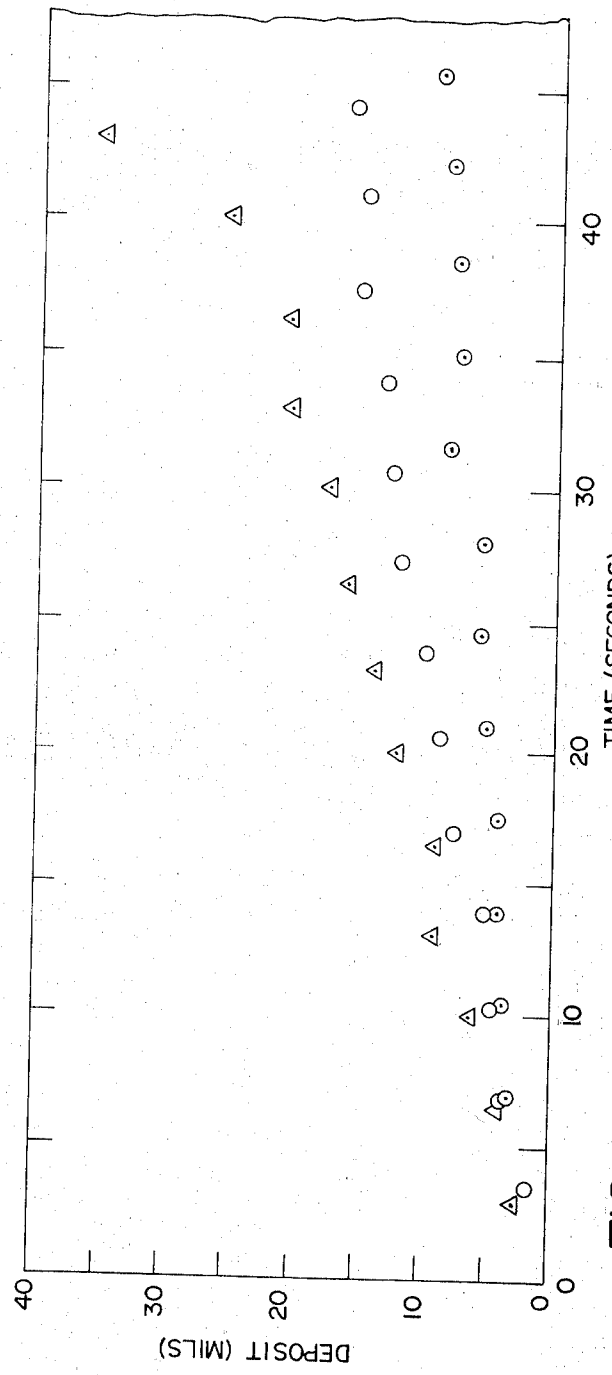


FIG. 2.

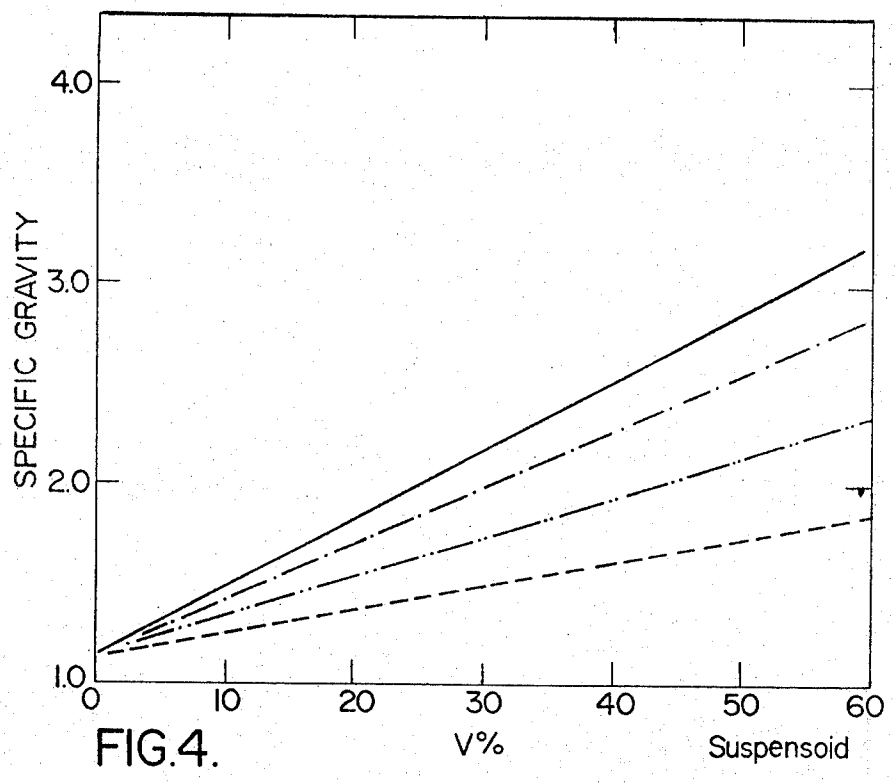

SPECIFIC GRAVITY
4.0
3.0
2.0
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10
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V%
Suspensoid

FIG.4.

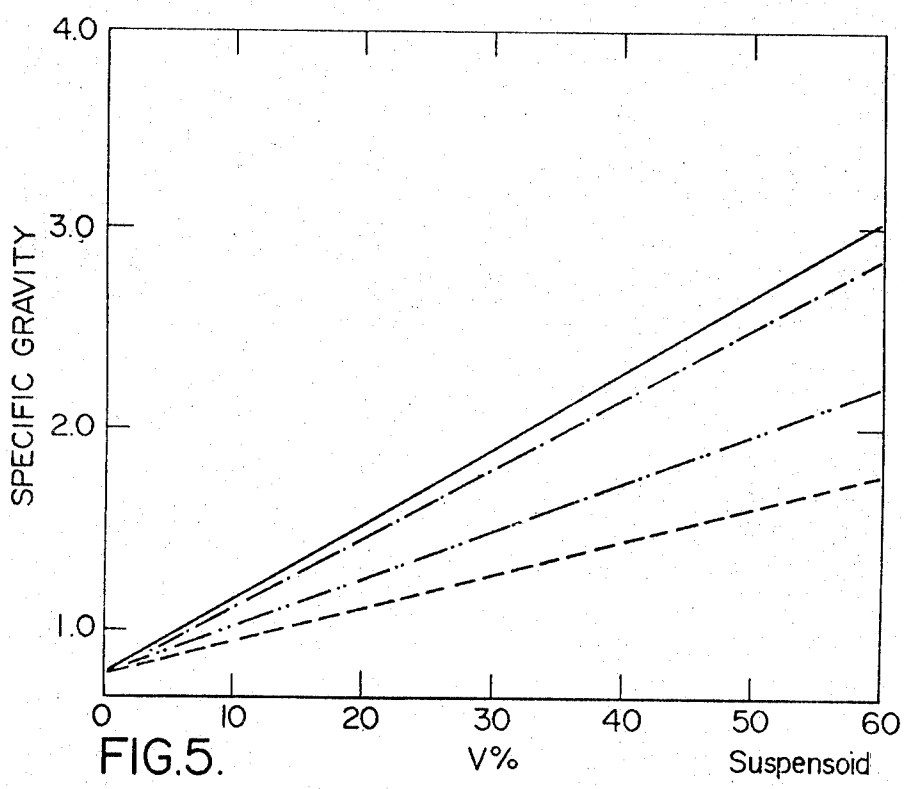

SPECIFIC GRAVITY
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2.0
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V%
Suspensoid

FIG.5.

METHOD OF FORMING FOUNDRY MOULDS

This invention relates to a method of forming foundry moulds.

In the metal founding industry there are a number of critical operations which contribute to the success or failure of a given casting. Each of these play their role in ensuring that the final product meets the combined demands of soundness, dimensional accuracy and surface finish. Improvements and/or modifications of any of the operations will have a bearing on the quality of the finished product.

In the investment casting foundry particular stress is placed on all three of the criteria listed above, and painstaking care is exercised in the production of the pattern, forming of the mould and the melting and pouring of the metal.

It is an object of the present invention to provide a method of forming foundry moulds by electrophoretically depositing refractory particles from a suspension.

Basically the electrophoretic disposition of refractory particles from liquid on to a deposition electrode consists of inducing migration of the particles from the liquid by the application of a suitable electrical potential. It has been proposed to use either an alternating or a direct electrical potential, although an alternating electrical potential is of limited utility. The chief disadvantages with an alternating electrical potential are that the particles migrate under the influence of a non-uniform electrical field, and that the direction of migration is dependant on the relative dielectric strengths of the liquid and the particles.

Electrophoresis using a direct electrical potential is more readily controlled than that using an alternating electrical potential, and the migration of the particles is accomplished through the establishment of an electrically charged layer on each particle. It has now been found that since the charge is carried by particulate solids, rather than ions, as in electroplating, the apparent efficient use of electrical current is relatively high when compared with electroplating. Ionic contamination is in fact to be avoided for optimum performance.

Whilst the literature abounds with various descriptions of electrophoretic processes and techniques, duplication of the experimental conditions rarely resulted in the duplication of the claimed results as for instance was noted by P. Morlidge in his work "Electrophoretic Deposition of Iron," University of Nottingham, England, Dept. of Metallurgy, BSc project 1964. This may be attributable to trace substances inhibiting mobility.

Tests using reported processes for electrophoretically depositing refractory particles from a suspension to form a refractory mould have shown that for a given electrical potential the rate of deposition on a unit area of a support member in a particular period of time is frequently undesirably low, and furthermore these rates have been shown to vary from one test to another.

It is an object of the present invention to provide a method of forming foundry moulds by electrophoretically depositing refractory particles from a suspension, wherein for a given electrical potential the rate of deposition on a unit area of a mould former in a particular period of time is rather more predictable, and wherein

the rates are relatively more predictable, than with known methods of electrophoretically depositing refractory particles from a colloid.

According to the present invention there is provided a method of forming foundry moulds, comprising treating particles of a refractory material which are substantially free from ionic contamination to expose fresh, uncontaminated surfaces of the particles and render the particles electrophoretically mobile when in suspension, dipping a mould former with an electrically conductive surface in a suspension of the treated particles containing a metal sol binder selected from the group colloidal silica, colloidal alumina, colloidal zirconia, colloidal hafnia, colloidal thoria and colloidal titania, and which is substantially free from ionic contamination, applying a direct electrical potential between the mould former electrically conductive surface and the suspension to electrophoretically deposit refractory particles from the suspension as a coating on to the electrically conductive surface, removing the mould former with the coating thereon from the suspension, applying further refractory particles to the coating to form a foundry mould therefrom, and then separating the foundry mould from the mould former.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings in which:

FIG. 1 is a graph showing the electrophoretic deposition of synthetic mullite in a suspension of isopropanol.

FIG. 2 is a graph showing the electrophoretic deposition of synthetic mullite from a suspension in isopropanol containing ethyl cellulose as a binder, and

FIGS. 3 to 5 graphically illustrate the specific gravity of the suspension as a function of solids content by volume.

In some of the tests carried out which contributed to the present invention, refractory particles substantially free from ionic contamination and suspended in a variety of liquids were comminuted by being milled for periods varying from hours up to 7 days in an attempt to expose uncontaminated surfaces of the particles and render them electrophoretically mobile. Portions were taken from each of the freshly milled suspensions and each portion was tested in an electrophoretic cell. In each instance the freshly milled powder, whether suspended in a polar or non-polar liquid, migrated to an electrode when a suitable electrical potential was applied. In general, prolonging the milling time resulted in a lower electrical potential being required to induce electrophoretic mobility and at the same time gave a drier and denser deposit, or alternatively, for a given potential a heavier deposit. It was also found that, in general oxide ceramic powders migrated to the positive electrode in a neutral fluid, but changed their polarity upon acidulation.

In other tests carried out which contributed to the present invention dry, refractory powders substantially free from ionic contamination were vacuum heat treated, that is, dry, refractory powders at a pressure of 10^{-2}, to $5\text{–}10^{-3}$ m/m mercury at a temperature of 400° to 450°C for periods of 24 to 28 hours, after which the powders were cooled whilst still under vacuum. The refractory particles of these powders were found to have been provided with fresh, uncontaminated surfaces and exhibited electrophoretic mobility when in which was substantially free from ionic contamination.

Thus the present invention provides two methods by which the refractory particles may be treated to expose fresh contaminated surfaces on the particles and render the particles electrophoretically mobile.

Tests were then carried out to evaluate the rate of deposition of the powder as a function of the applied electrical potential. From these tests it was concluded that the timing of the power whilst electrodes were immersed in a suspension was an impractical method of determining the rate of deposition of the power. The reasons for this are thought to be:

i. during the application of the electrical potential, electrophoresis, as well as electro-osmosis occurs, i.e. the suspending vehicle migrates in the opposite direction to that of the powder, resulting in a drier, denser deposit.

ii. upon removal of the electrical potential, electro-osmosis ceases and the migrated vehicle tends to return to restore the overall balance of the distribution of the suspension. The returning vehicle transports the particles suspended in it, and so the thickness of the electrophoretic deposit varies with variations of the elapsed time between the removal of the electrical potential and that of the support member, being coated, from the suspension.

Thus it was found that unduly prolonged dwell of the mould former in the suspension after the removal of the electrical power resulted in a thinning of the electrophoretically deposited particles due to "dilution," and washing off of the deposit.

It was further noted from the tests that relatively thick deposits could be deposited in a matter of seconds and this is graphically illustrated in FIG. 1 which shows the deposition of synthetic mullite in a suspension of isopropanol. The values ⊙ were obtained when 75 volts per centimeter of distance between the depositing and charging electrodes was used. The values ⊙ were obtained when 750 volts per centimeter of distance between the depositing and charging electrodes was used. A closer scrutiny of this Figure will also show the following:

a. increasing voltage results in increasing thickness of deposit as well as an increased rate of deposition.

b. the relation between applied potential and deposition rate is not linear.

Although not evident from the illustrations presented other observations indicated the following:

i. prolonging milling time generally increases deposition rate and maximum deposit thickness — or for a given deposit thickness and/or deposition rate, lowers the voltage requirement;

ii. denser slurries, i.e., those with higher solids content deposited a given thickness in a shorter time;

iii. deposits from "thin" slurries though formed more slowly, were drier and firmer;

iv. the relation between the rate of deposition and slurry density was not linear;

v. deposits from heavy slurries tended to be wetter and displayed a tendency to "sag."

vi. deposits found under higher potential gradient tended to be drier and less prone to sag.

Coatings produced on support members during the above tests were found to be prone to dust off, and various remedies were tested to prevent this. One remedy tried was to impregnate the dry coating to strengthen it, but this did not prove to be successful. Another remedy tried was to incorporate various binders such as, for example, thosed in U.S. Pat. No. 3,575,838, in the suspension but all of them had a pronounced inhibiting effect on the electrophoretic mobility of the particles as well as severely limiting the maximum thickness obtainable of electrophoretic deposit on the support member as shown in FIG. **2,** the binder in this instance was a cellulosic compound (ethyl cellulose), in a suspension containing synthetic mullite. The values ⊙ were obtained when 200 volts per centimeter of distance between the depositing and charging electrodes were used. The values ⊙ were obtained when 345 volts per centimetre of distance between the depositing and charging electrode were used. The values ▲ were obtained when 740 volts per centimeter of distance between the depositing and charging electrodes were used.

Further tests were then carried out using aqueous and non-aqueous suspensions of, for example, powdered refractory oxides such as silica, alumina, also refractory silicates such as mullite and zircon. Milled slurries displayed pronounced electrophoretic mobility, those in aqueous vehicle at much lower electrical potentials than slurries having other carrier liquids.

Binders were incorporated into aqueous suspensions in a form of silica sols (other colloids such as U.S. Pat. No. 3,575,838 and others having been found severely thickness limiting). The choice of sol was limited to the types of minimum ionic content (e.g. Nalcoag 1034A supplied by Nalco Chemical Company, Chicago, Ill., U.S.A.)

It was noted from the tests that, unlike the tests with other vehicles, the deposits hardened very rapidly whilst still drying. One reason for this may be that the electro-osmosis effect referred to previously causes a loss of associated water from the colloid and results in its coagulation so that dilution of the deposit by the vehicle once the electrical potential is removed is substantially retarded. This feature is particularly desirable because it facilitates the deposition of successive layers interspersed, if desired, with the deposition of coarser stucco followed by another layer of electrophoretic deposit, without the danger of washing off the underlying layer.

Since there appears to be a certain low quantity of ions present in commercially available silica sols it has often been found advantageous to dilute such a sol with an equal or greater volume of distilled or distilled-de-ionized water prior to its incorporation in the suspension. Whilst this reduced the mechanical strength of the shell somewhat, post-forming impregnation with a sol of full strength may be used to restore mechanical strength.

It was further found during these tests that by progressively increasing the magnitude of the electrical potential the increase in electrical resistance of the deposit as it became thicker could be compensated for, and that by increasing the electrical potential in this manner a substantial thickness of coating could be built upon a support member.

The formers on which the moulds are deposited may be conductive, for example, a former of frozen mercury or a low melting point metal alloy.

In other embodiments of the present invention a shell mould may be electrophoretically deposited on a wax or plastic former, and to accomplish it is necessary to

provide an electrically conductive surface on the wax or plastic former.

It was found that silver can readily be deposited on a sensitized surface of an investment casting pattern of plastic or wax of vegetable, animal or mineral origin, by the reduction of an ammoniacal silver solution with sugar syrups. Difficulties traced to insufficient wetting were overcome by applying the sensitizer dissolved in isopropanol, etc., as well as adding wetting agents to those solutions which tolerate such an additive. However, since the reduction of the silver proceeds through the bulk of the solution, the efficiency of the method is very low, and two or more applications were on occasions required to build up a coating of sufficient thickness, thence conductivity. It was found that the silvering solutions may be mixed in a Y tube and allowed to impinge on the sensitized surface until the thickness of the coating was deemed sufficient.

Wax patterns thus silvered were successfully coated electrophoretically with milled slurries, as described above, suspended in isopropanol, aliphatic nitroparaffins, or alcohol-hydrocarbon mixtures, or silica sols.

Whilst the above process of applying an electrically conductive coating the silver to a wax mould was succesful the process used was considered costly, and so attempts were made to apply a copper coating to a non-conductive mould. The chemical copper plating solutions given below in Table 1 was successfully used to apply an electrically conductive copper coating to a non-conductive mould.

TABLE 1

$CuSO_4$	20 g	35 g
$AgNO_3$	2 g	—
Rochelle Salt	40 g	170 g
K_3H	40 g	—
Na OH	—	50 g
Na_2CO_3	—	30 g
Vesene 7	—	20 ml
Water — o	1 l	1 l
Reduce with	1 vol 5% HCOH	1/5 vol 37% HCOH

The chemical copper plating solutions tabulated above deposited their metal in a bright, continuous film on a previously silvered, or palladium chloride sensitized nonconductive pattern of wax or plastic approximately 20 to 30 minutes. Prolonged immersion caused the film to turn dark and spongy.

The films thus formed were sometimes found to blister, and one reason for these blisters may be due to the difference in size of ionic and atomic copper. Etching of the wax with bromine water- and sodium hydroxide in succession produced a bond between the metal and the substrate which substantially reduced the occurence of blisters. The etching treatment was subsequently modified to that of immersing the wax pattern in a 5%. w/w solution of sodium chloride which was electrolyzed using graphite electrodes.

Wax patterns thus copper plated were subsequently coated with an electrophoretically deposited shell of a refractory powder suspended in a silica sol. To minimize gassing, invariably the lowest electrical potential capable of electrophoretically forming a deposit was employed for the first (critical) layer. Alternate stucco coatings were deposited in a conventional manner, e.g., from a fluidized bed, raining or sprinkling by hand. After stuccoing a subsequent electrophoretic layer could be applied provided the electrical potential applied is increased to compensate for the increased electrical resistance of the coating. This process can be repeated with alternate electrophoretic and stucco layers. A shell sufficiently strong to hold molten metal was built up on the mould with, for example, 10 to 20 minutes.

The mould thus coated was allowed to dry. When dry, the wax from a wax pattern was removed by flash dewaxing, i.e., placing the mould in a furnace held at 250° to 550°C. In this manner, cracking of the shell due to the thermal expansion of the wax was prevented because the outer layer of wax mould melts and in this state diffuses through the refractory shell before the bulk of the wax is thermally expanded.

Flash dewaxing was followed by burning the remainder of the wax off the refractory shell, after which the shell was allowed to cool. A number of shells manufactured in this manner were used for casting.

By and large the shells were found to be sufficiently strong to contain the molten metal, they were found also to have fine, smooth surfaces, and the film of metal oxide adhering to the shell moulding surface was thin, easily detached, and if necessary, readily removed by dissolving it in acid or ammonia. In some instances blisters were noted which, for some castings, may be detrimental to the casting quality.

The blisters may be due to the difference in the respective sizes the copper or silver and their respective oxides, commonly known as Pilling-Bedworth ratio, giving rise to compressive forces.

Other forms of electrically conductive coating may be provided on the pattern. For example, colloidal graphites of certain grades in isopropanol were found to provide a film of satisfactory electrical conductivity, or alternately aqueous graphite suspensions that require post-application heat treatment produced layers of satisfactory electrical conductivity on plastic patterns materials of higher melting than that necessary for the heat treatment, e.g., Electrodag (reg TM of Acheson Colloids, Brantford, Ontario, Canada). These films were not stripped off by immersion in the slurry. Conductive patterns produced by either of the above methods can be coated with layers of refractory from various slurries and by a number of different methods. Those suspended in silica sols set rapidly permitting, for example, the application of a coarser stucco by conventional methods after repeated application of the electrophoretic layer, without the necessity of drying between applications. This feature of the process is thought to be very desirable, since it greatly accelerates the production of shell moulds as well as permits mechanization, since by the suitable adjustment of applied potential, coating of appreciable thickness would be formed.

When dry, the moulds were de-waxed in a flash dewaxing furnace and subsequently burned-off to remove residual wax soaked up by the refractory shell.

Castings were produced by pouring metal in cold moulds as well as pre-heated moulds. Defects were sometimes noted from both, however. These were attributed to two distinct sources.

a. During burn-off the conductive metallic layer oxidized; the bulk of the oxide (Pilling-Bedworth ratio) is greater than that of the parent metal, hence compressive stresses develop causing blistering. (an acidic dissolution — though another operation

— may be employed to remove this source of defect).

b. the second — and less readily correctable — source of blisters was attributed to the lower permeability of the shell. In an electrophoretic deposit the particles are in intimate contact and porosity is confined to regions of misfit. By comparison the particles in a drag-out coat are surrounded by the liquid vehicle, which initially form 45–55 v/o of the slurry.

Casting under reduced pressure may be required to overcome this difficulty.

The graphite conductive layer could only be successfully utilized with suspensions of the lowest conductivity. If aqueous with a siliceous binder a doubly de-ionized silica sol of the type Nalcoag 1034 A (supplied by Nalco Chemical Company, Chicago, Ill., U.S.A.) was found to be necessary. The optimum combination was offered by milling this liquid with 25–40% by volume of alumina powder (C7IFG supplied by Aluminum Company of Canada Limited).

In conventional investment casting particles suspensions of relatively high solids content, e.g., 50% by volume and above, are employed. To minimise the effect of "drag-out" when deposits are formed electrophoretically, suspensions of lower solids content, in the neighborhood of 30–35% by volume were found to possess the optimum properties.

A convenient method of determining the solids content of various suspensions is illustrated in FIG. **3, 4** and **5.** In FIGS. **3** to **5** the specific gravities of various suspensions is plotted against the percentage volume of solids content, and in each figure is —zircon, —·—·—is alumina, —··—··—is mullite, and — — —is silica. In FIG. **3** the liquid vehicle is Nalcoag 1050 (supplied by Nalco Chemical Company, Chicago, Ill. U.S.A.). In FIG. **5** the liquid vehicle was isopropanol.

The present invention may be used to cast shells by electrophoretic deposition on a matchplate. The dimensional accuracy and fine surface finish obtainable with investment casting could by using the present invention, be extented to large parts, use of a permanent metal matchplate on which the refractory particles are electrophoretically deposited would result in a substantial cost reduction.

Metal sol binders which may be used are colloidal silica, colloidal alumina, colloidal zirconia, colloidal hafnia, colloidal thoria and colloidal titania.

I claim:

1. A method of forming foundry moulds, comprising treating particles of a refractory material which are substantially free from ionic contamination to expose fresh, uncontaminated surfaces of the particles and render the particles electrophoretically mobile when in suspension, dipping a mould former with an electrically conductive surface in a suspension of the treated particles containing a metal sol binder selected from the group colloidal silica, colloidal alumina, colloidal zirconia, colloidal hafnia, colloidal thoria and colloidal titania, and which is substantially free from ionic contamination, applying a direct electrical potential between the mould former electrically conductive surface and the suspension to electrophoretically deposit refractory particles from the suspension as a coating on to the electrically conductive surface, removing the mould former with the coating thereon from the suspension, applying further refractory particles to the coating to form a foundry mould therefrom, and then separating the foundry mould from the mould former.

2. A method according to claim **1,** wherein the particles are in a suspension which is substantially free from ionic contamination, prior to being treated, and then the particles are treated by being comminuted in suspension to expose fresh, uncontaminated surfaces of the particles to render the particles electrophoretically mobile prior to the addition of the metal sol binder.

3. A method according to claim **2,** wherein the particles are comminuted in suspension in a liquid selected from the group distilled, de-ionized, and distilled and deionized water.

4. A method according to claim **1,** wherein the further refractory particles are applied as a relatively coarser stucco coatings between electrophoretically applied coatings.

5. A method according to claim **1,** wherein the refractory material is selected from the group refractory oxides and refractory silicates.

6. A method according to claim **1,** wherein the support member is a pattern of a material selected from the group wax or a plastic provided with an electrically conductive outer coating, and the electrophoretically deposited refractory particles thereon are an investment casting shell, and the pattern together with the electrically conductive coating are removed from the investment casting shell by melting a major portion of the pattern material by placement in a furnace at 250° to 550°C, or leaching, and then burning off the residue.

* * * * *