

**March 7, 1967**

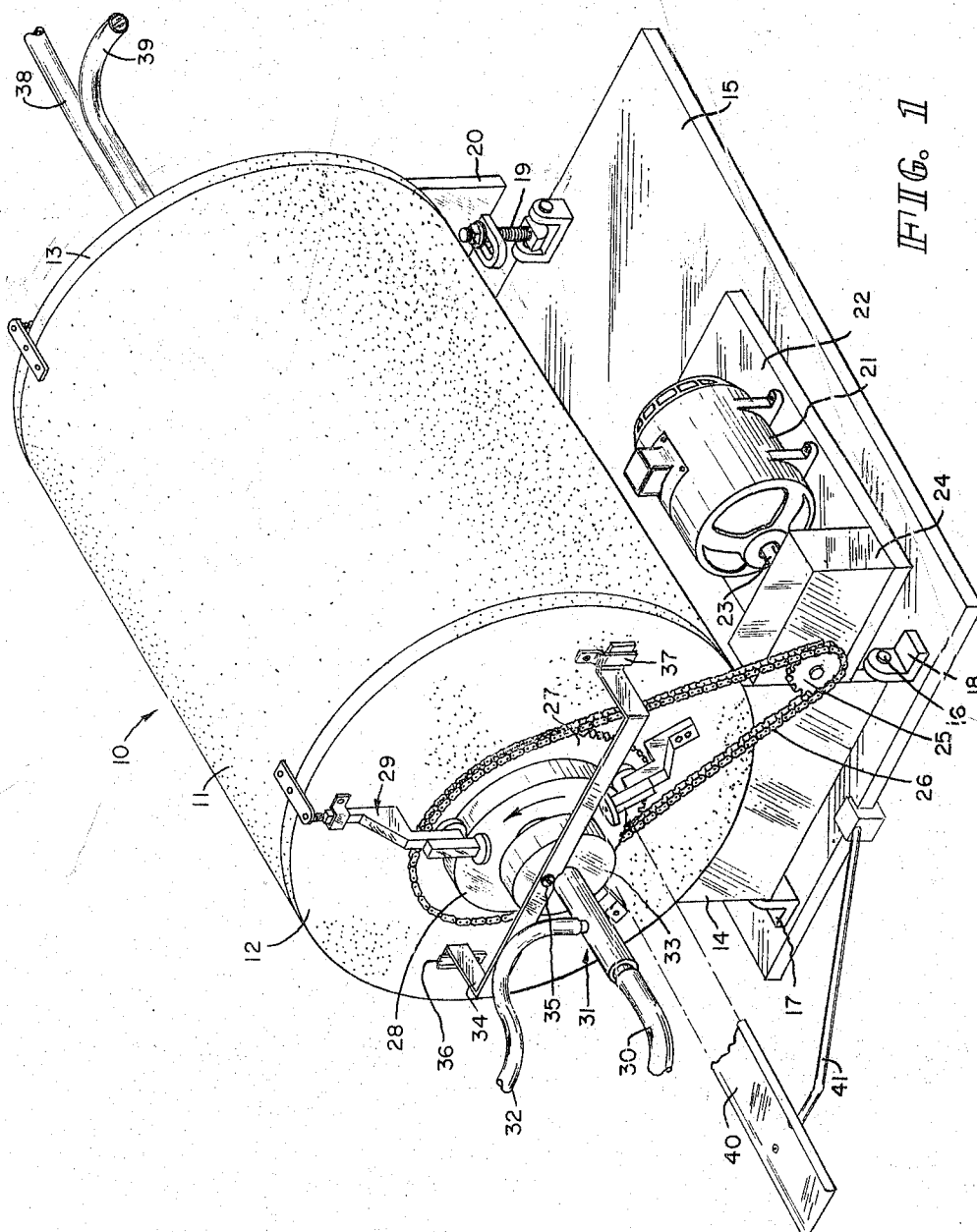
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3,307,515

VAPOR DEPOSITION APPARATUS INCLUDING TUMBLER

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3 Sheets-Sheet 1



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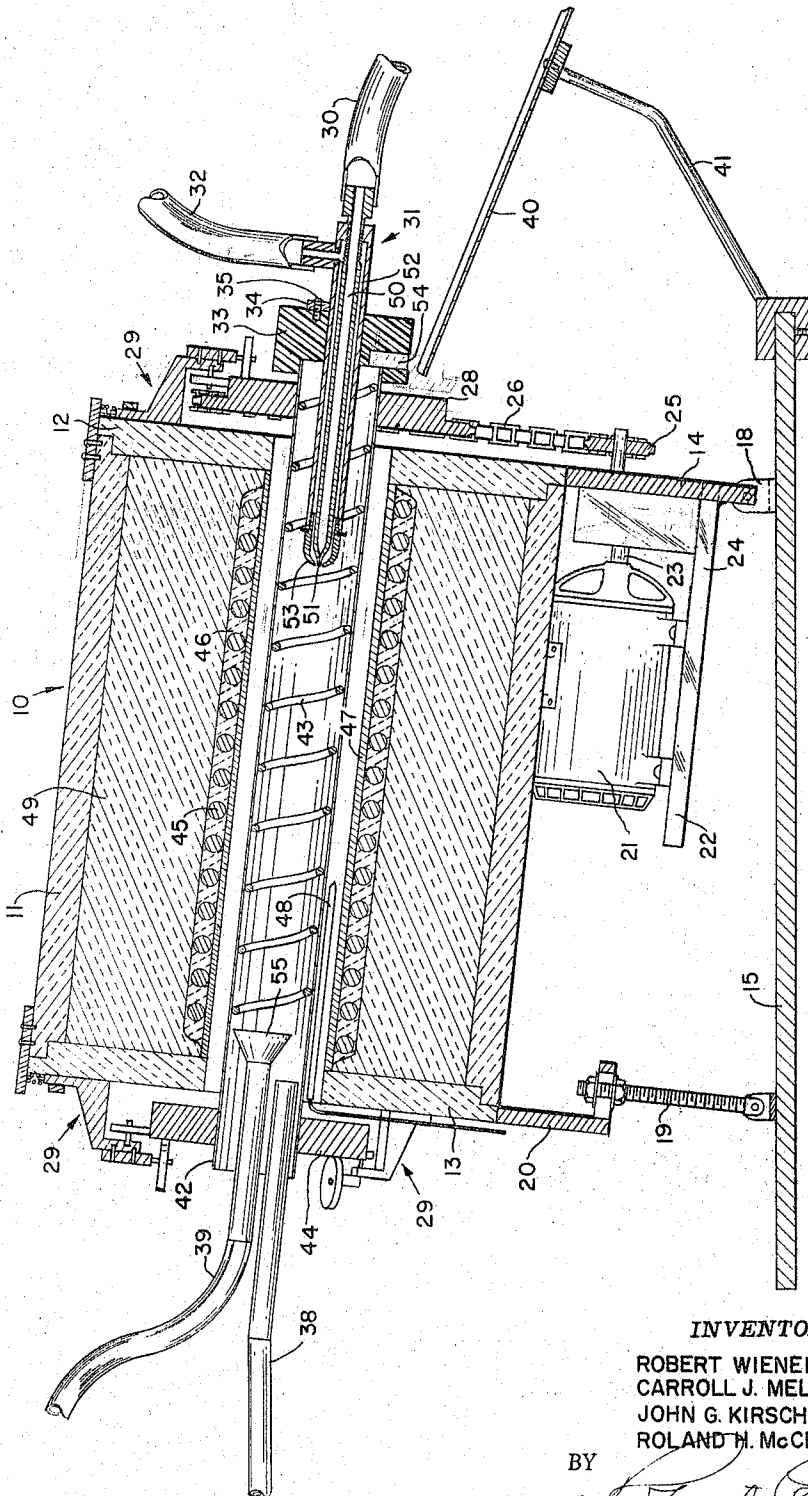
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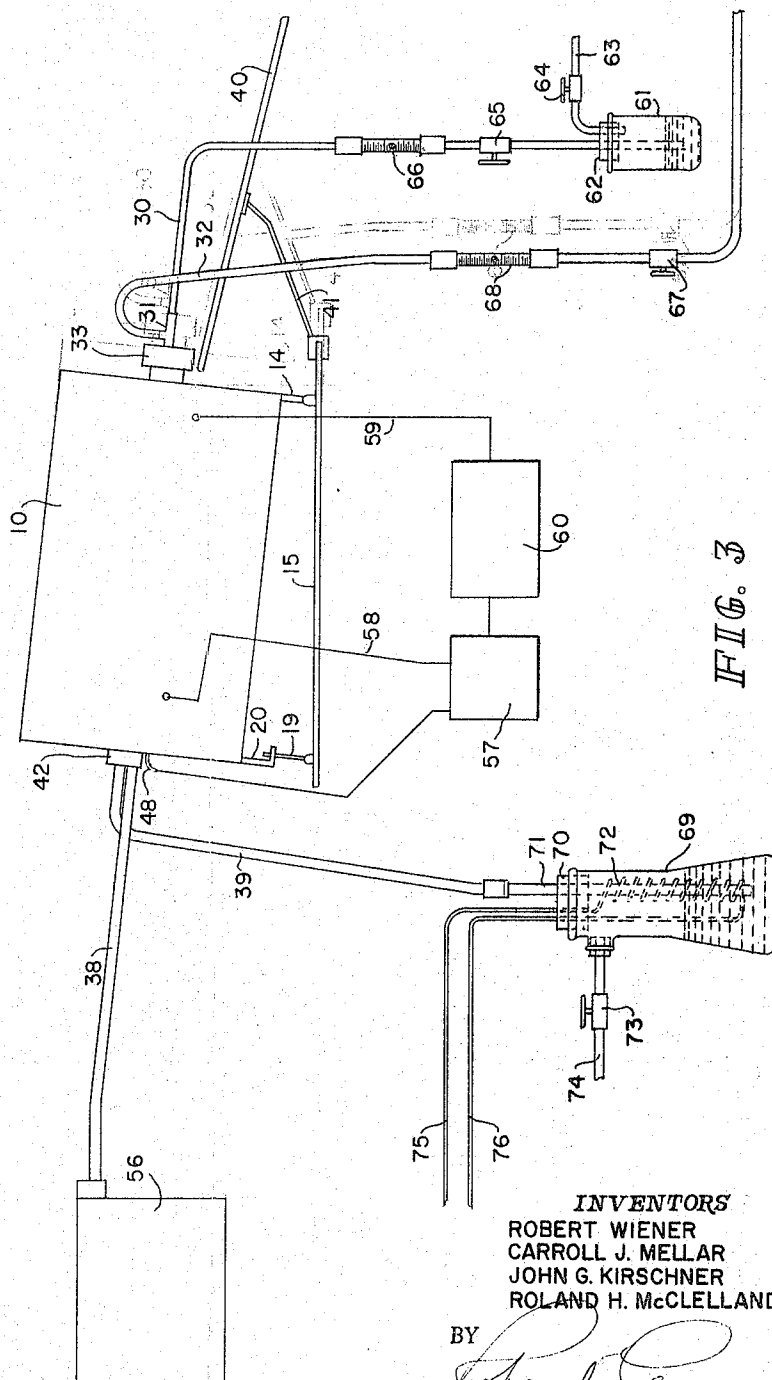


FIG. 3

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VAPOR DEPOSITION APPARATUS INCLUDING  
TUMBLER

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3 Claims. (Cl. 118—5)

This invention relates to the means for coating electrical resistor substrates and has specific pertinence to the deposition of a metal oxide film on ceramic substrates by means of a high temperature vapor-phase reaction.

In the manufacture of electrical resistors of the film type, there are many design and processing criteria to be considered. Some of the fundamental objectives therein may be broadly stated as follows. First, it is desirable to avoid individual handling of the resistor substrates. Since most film resistors are relatively small, individual handling makes the manufacture thereof both tedious and expensive. Secondly, the electrical characteristics of the finished resistors must be consistent. This, of course, require uniformity in the film thickness and the area of coverage. Thirdly, the film should possess reliability and stability in regard to electrical, mechanical, thermal, and chemical properties. For example, some resistive films have been found to be markedly unstable such that the resistance varies excessively with age, and with exposure to high ambient temperatures, humidity, etc. Finally, for small substrates, success of the film deposition process should not depend upon the heat capacity of the substrate.

Examples of desired mechanical properties would include suitable film hardness, satisfactory adhesion of the film to the substrate, and the ability to provide film thicknesses of practical resistive value having a temperature coefficient within acceptably low values. The temperature coefficient of a resistive film denotes the resistive value change per degree of temperature change as heat is applied to the film. Said coefficient is deemed positive or negative, respectively, according to whether it varies directly or inversely with temperature.

Film type resistors are generally comprised of a substrate material having disposed thereon a deposit of carbon, metal, or a metallic oxide. The substrate material is typically glass, ceramic, or similar composition. One coating method well known in the art comprises the evaporation of a suitable metal by heating under a high vacuum, and allowing the vapors to condense on the substrate. In the apparatus of the present invention, a metal oxide film is deposited on a small ceramic substrate by means of a high temperature vapor-phase reaction. It has hereby become possible to attain high production rates while applying a uniform resistive film on small substrates having low heat capacity. Hence, the method disclosed herein is not dependent upon substrate heat capacity. It has further become possible to attain excellent control of the parameters affecting mechanical and electrical properties of the deposited metal oxide film.

In the illustrated embodiment of the present invention, a tin chloride solution is atomized within a heated chamber in the presence of a plurality of tumbling substrates. The high temperature vapor-phase reaction produces tin oxide for deposition on the heated substrates. An undesirable result of the same reaction, however, is the evolu-

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tion of a vapor containing an appreciable quantity of hydrochloric acid. Hence, the selection of an appropriate material for the reaction chamber elements required careful consideration herein.

It has been found that ceramic materials tend to react with active hydrochloric acid vapor upon prolonged exposure at elevated temperatures. A typical end result of this reaction is the devitrification of quartz. Although most ferrous metals would be considered unlikely choices for an acidic environment of this nature, stainless steel was chosen as the reaction chamber material. This metal, although not resistive to hydrochloric acid corrosion, has rendered very satisfactory performance in the embodiment of the present invention. Because the tin oxide produced from the reaction process tends to coat the reaction chamber members as well as the tumbling substrates, a protective coating is formed on the members in a manner which prevents corrosive action. Since the coefficient of thermal expansion and contraction of stainless steel is significantly higher than that of tin oxide, the tin oxide layer is caused to flake off during kiln shutdown periods, thus providing a self-cleaning action.

Broadly stated, the apparatus of the present invention comprises a stationary cylindrical kiln with a rotating stainless steel tube inserted through the heat zone of the kiln, the stainless steel tube serving as the actual reaction chamber for the deposition process. The resistor substrates are guided through the kiln by means of a helix of stainless steel rod press-fitted along the inside diameter of the reaction tube. The duration of time that each substrate is exposed to the reaction zone is determined by the pitch of the helix and the rotational speed of the reaction tube. To further assist the substrates in traversing the kiln, the entire assembly is inclined so as to employ partial gravity feed assistance.

It is an object of the present invention, therefore, to provide an apparatus for the continuous-process deposition of a resistive film on small resistor substrates in a manner which affords high production rates.

A further object of the present invention is to provide an apparatus employing a substantially closed system for uniformly coating small resistor substrates with metal oxide by means of a high temperature vapor-phase reaction, and wherein the substrate heat capacity is not a critical factor.

Another object of the present invention is to provide a coating apparatus in which the substrates tumble continuously through a rotating reaction chamber while being exposed to a controlled metal halide vapor which produces a metal oxide film.

Another object of the present invention is to provide an apparatus wherein a metal oxide film may be deposited upon a large quantity of ceramic substrates simultaneously, and wherein the resulting film has desirable electrical and mechanical properties.

Still another object of the present invention is to provide a coating apparatus wherein individual handling of the substrates is avoided, but wherein excellent control is maintained over those parameters which affect the mechanical and electrical properties of the deposited film.

Yet another object of the present invention is to provide a coating apparatus wherein the reaction atmosphere is so controlled that the deposition process is not critically dependent upon the heat capacity of the substrate. Prior art difficulties in filming substrates of low heat capacity are thereby overcome.

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Still another object of the present invention is to provide a continuous-process deposition system wherein the reaction atmosphere is maintained constant while the reaction products are continually replaced and exhausted, with external atmospheric contamination being minimized.

Still another object of the present invention is to provide a reaction chamber constructed of a material which permits buildup of a protective coating of metal oxide thereupon during the deposition process, but which, due to a differential expansion, creates a self-cleaning action to dislodge the oxide coating during shutdown of the apparatus.

Yet another object of the present invention is to provide a coating solution spray device wherein atomization air is used to prevent boiling of the solution within the device when the later is exposed to reaction chamber heat.

Yet another object of the present invention is to provide an accurate means for controlling the duration of exposure of each substrate to the deposition reaction.

The present invention, in another of its aspects, relates to novel features of the instrumentalities described herein for teaching the principal object of the invention and to the novel principles employed in the instrumentalities whether or not these features and principles may be used in the said object and/or in the said field.

Other objects of the present invention and the nature thereof will become apparent from the following description considered in connection with the accompanying figures of the drawing and wherein like reference characters describe elements of similar function therein, and wherein the scope of the invention is determined rather from the dependent claims:

In the drawings:

FIGURE 1 is a perspective view of the kiln and reaction chamber assembly of the present invention wherein a resistive film is deposited on a suitable substrate.

FIGURE 2 is a longitudinal section view of the kiln and reaction chamber assembly.

FIGURE 3 is a schematic view of the apparatus and components comprising the complete system of this invention.

Generally speaking, the present invention provides the means for efficiently forming a metal oxide film on resistor substrates with resulting electrical properties of high order, regardless of substrate size and heat capacity. By providing a controlled deposition vapor of a metal halide within a high temperature reaction chamber, a metal oxide coating is formed upon the substrates as they are advanced through the reaction chamber at a determined rate. Through maintenance of a closed and controllable reaction atmosphere, consistency of electrical properties in the finished resistor is assured without dependency on the substrate heat capacity.

Referring now to FIGURE 1 of the drawing, the kiln and reaction chamber assembly is seen in perspective view. Kiln assembly 10 is similar in appearance to the conventional cylindrical kilns used extensively for combustion analysis in the field of analytical chemistry. Kiln housing 11 is a hollow cylindrical member composed of suitable insulating material such as transite. Kiln end plates 12 and 13, also of transite material, complete the enclosure of kiln assembly 10. Steel plate 14 supports the drive end of the apparatus in pivotal relationship to base plate 15 through pivot shaft 16 and attaching brackets 17 and 18. Inclined adjustment of kiln assembly 10 is facilitated by adjusting screw 19, which transmits motion through steel supporting bracket 20 on the opposite end of the kiln.

With continued reference to FIGURE 1, rotation of the reaction tube assembly is accomplished by means of a chain drive mechanism. Variable speed motor 21 is mounted on plate 22 which is rigidly attached to, and per-

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pendicular with, kiln support plate 14. Shaft 23 of drive motor 21 engages speed reducer 24, the output of which comprises drive sprocket 25. Rotary motion is transmitted from drive sprocket 25 through chain 26 to a driven sprocket 27. Sprocket 27 is integrally formed in reaction tube support member 28. Axial and radial piloting of reaction tube support member 28 is maintained by means of three equally-spaced roller guide assemblies, shown typically at 29.

Introduction of the substrate coating solution into the reaction chamber is made through hose 30 and spray gun assembly 31. Metered air is supplied through hose 32 and a separate passage of spray gun 31 in such a manner that atomization of the coating solution takes place in the reaction chamber, not within the spray gun. Physical support of spray gun 31 is afforded by means of stationary cap 33, which makes a slip fit with the rotating reaction tube. Cap 33, therefore, functions as a bushing within which the reaction tube may rotate. It is composed of suitable bushing material for low speeds and light loads, herein being polytetrafluoroethylene. Cap 33 is held stationary by means of anti-rotation bracket 34, attaching screw 35, and anti-rotation clamps 36 and 37.

With further reference to FIGURE 1 of the drawings, the uncoated substrates are admitted to the reaction chamber through feed tube 38 located at the anti-drive end of the apparatus. Adjacent to feed tube 38 is stainless steel exhaust tube 39 which carries away the surplus products of the vapor-phase reaction. As the substrates advance through the reaction chamber and become coated with metal oxide, they are ultimately guided through a bottom discharge hole in cap 33. Thereupon, the coated substrates drop onto cooling tray 40, said tray being supported by bracket 41.

The longitudinal section view of FIGURE 2 illustrates the interior construction of the kiln and reaction chamber assembly. Reaction tube 42, composed of stainless steel, is approximately twelve inches in length with a nominal inside diameter of one inch. These tube dimensions have been found to be appropriate for coating miniature substrates of the nominal size of 0.060 inch diameter by 0.400 inch long. A helix 43 of stainless steel rod is press-fitted along the inside diameter of reaction tube 42. Axial and radial piloting of the anti-drive end of reaction tube 42 is afforded by support member 44 in cooperation with roller guide assemblies 29. Support members 44 and 28 are each affixed to the outside diameter of reaction tube 42 in a manner which prevents relative motion therebetween.

Referring again to FIGURE 2, the high chamber temperature necessary for vaporization of the coating solution is attained by means of a resistance heating element. A coil of nichrome wire 45 traverses the length of the reaction chamber in proximity to reaction tube 42, and is embedded in high temperature cement 46. The coil winding is separated from reaction tube 42 by a cylinder 47 of refractory material, herein composed of mullite. In the air space between cylinder 47 and reaction tube 42 there is disposed a plurality of thermocouple probes, shown typically at 48, which serve as part of an automatic feedback system for setting and maintaining the desired temperature for the reaction process. The cylindrical volume between cement 46 and kiln housing 11 is filled with a suitable insulating medium 49, herein being composed of expanded mica-vermiculite.

To supply the fluid necessary for the high temperature vapor-phase reaction, spray gun 31 is inserted through cap 33 so as to substantially penetrate one end of reaction tube 42. Since the tin chloride coating solution employed herein is corrosive, spray gun 31 is constructed of titanium metal. Because spray gun 31 projects into the hot section of kiln 10, there is a tendency for the incoming coating fluid to boil inside the spray gun. By a special construction of spray gun 31, however, boiling is eliminated. With reference to FIGURE 2 of the draw-

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ings, it is observed that the coating fluid enters spray gun 31 by way of hose 30, and is thereafter conducted through fluid nozzle 50 to be discharged, while still in a liquid state, through nozzle tip 51. It is further observed that air enters by way of hose 32 and is conducted through passage 52, which surrounds, and is separated from, fluid nozzle 50. By this method, the incoming air, prior to causing atomization of the coating solution, serves to insulate from excessive heat that part of the gun which conducts the fluid, thereby avoiding boiling. Outside orifice member 53 is radially adjustable with respect to nozzle tip 51 to provide concentricity and a correct spray pattern.

As hereinbefore stated, atomization of the coating solution takes place within reaction tube 42, not within spray gun 31. The heat prevailing throughout the reaction atmosphere thereupon vaporizes the freshly atomized fluid. This vapor then condenses and reacts upon the surface of the substrates which have entered the reaction chamber through feed tube 38 with the urging of a vibratory parts feeder. As helix 43 tumbles and guides the substrates through reaction tube 42, the vapor reaction deposits a homogeneous coating on the substrate surface in the form of a metal oxide resistive film. The coated substrates are then caused to drop out of the reaction region of tube 42 through exit hole 54 provided in cap 33. Air cooling of the resistors then takes place on cooling tray 40.

Because the deposition process of this invention involves a high temperature vapor-phase reaction, it is mandatory that the reaction section of tube 42 closely approximate an isolated atmosphere of the reacting vapor, thereby resembling a closed system. It is also necessary that the surplus reaction products be properly exhausted. Hence, the system is referred to as "closed" not because it is completely blocked physically from external effects, but rather because the reaction chemicals are continually replaced and exhausted with minimum external atmospheric contamination. To maximize the isolation of the reaction atmosphere, the ends of reaction tube 42 are blocked off as much as possible from external effects. At the substrate entrance of tube 42, this occlusion is performed by flared section 55 at the pickup entrance of exhaust tube 39. There remains room however, for the entering substrates to pass between flared section 55 and the rotating tube 42. The substrate discharge end of tube 42 is covered by cap 33 and spray gun 31, with exit hole 54 as the sole opening.

Refer to FIGURE 3 for a schematic drawing of the complete system taught by the present invention. Rate of admission of uncoated substrates into supply tube 38 is controlled by vibratory parts feeder 56. As to choice of substrate material, it has been found that either steatite or alumina will provide very satisfactory results. As the substrates enter rotating reaction tube 42, they are advanced at a controlled rate through the reaction atmosphere. The temperature within kiln 10 is automatically regulated in the following manner. Sampling thermocouples, shown typically at 48, are wired into a temperature indicator and controller unit 57. As more or less heat is called for by controller 57, a relay responds to this demand. Thereupon, variable auto-transformer 60 produces the appropriate change in current flow through resistance heating wires 58 and 59. In the embodiment of the invention chosen for illustration herein, excellent control of reaction temperature has been experienced up to 2000° F. Reaction chamber temperature is a critical parameter in the film deposition process.

Equally critical parameters herein are the respective flow rates of coating fluid and atomizing air. With continued reference to FIGURE 3, the coating fluid, herein being a tin chloride solution, is contained in flask 61, and isolated from the atmosphere by stopper 62. Pneumatic pressurization of the tin chloride solution within flask 61 is effected through air hose 63 and air pressure control valve 64. Rate of flow of pressurized tin chloride solu-

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tion through supply hose 30 is controlled and measured by valve 65 and flow indicator 66, respectively. Similarly, the atomization air supplied through hose 32 is controlled and measured by valve 67 and flow indicator 68, respectively.

It has been found that the rate of exhaust of the reaction vapors must also be controlled. The exhausted vapors are directed through tube 39 into the exhaust scrubber system. Within said system is scrubber bottle 69 enclosed by stopper 70. To resist corrosive action, that section of the scrubber system in contact with wet exhaust material is made of titanium, viz, tube section 71 and exhaust cooling coil 72. Valve 73 affords control of exhaust flow rate through the scrubber system, and is located in exhaust scavenging line 74. Hoses 75 and 76 provide cooling water to exhaust cooling coil 72.

Through the apparatus of the present invention, therefore, a large production rate of film resistors can be achieved and maintained. Uniform coating of very small substrates has been efficiently accomplished herein. The versatile control system provided herein assures excellent mechanical and electrical properties in the resistive tin oxide film.

The apparatus of the present invention as hereinbefore described in one of its embodiments, is merely illustrative and not exhaustive in scope. Since many widely different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interposed as illustrative and not in a limiting sense.

What is claimed is:

1. In an apparatus for vapor-phase deposition of a resistive film on a plurality of electrical resistor substrates, an inclined hollow cylindrical kiln having a resistance heating coil traversing the inside diameter thereof, a rotatable reaction chamber concentrically disposed adjacent the inside diameter of said resistance heating coil, said reaction chamber comprising a metal tube having a helix of wire fixedly disposed along its inside diameter, spray means substantially penetrating one end of said reaction chamber for introducing and atomizing a deposition solution within said chamber said spray means comprising a nozzle having a first tubular passage for introducing said deposition solution and a second tubular passage concentric with and surrounding at least the penetrating portion of said first passage, means for passing atomizing air through said second passage to thereby control heating of said deposition solution prior to discharge and atomization thereof, substrate entrance means adapted to introduce said substrates into said reaction chamber, said reaction chamber being adapted to advance and tumble said substrates at a predetermined rate during deposition, discharge means allowing exit of the coated substrates from said reaction chamber, exhaust control means adapted to remove from said reaction chamber the gaseous products resulting from the vapor-phase reaction, the reaction chamber ends being substantially blocked from external atmospheric contamination, and the coefficient of thermal expansion of said reaction chamber being sufficiently different from that of the deposition material so as to cause dislodgement of accumulated coating deposits when said apparatus is allowed to cool.

2. The apparatus of claim 1 including kiln temperature control means adapted to automatically regulate the reaction temperature, said means comprising a plurality of thermocouples disposed in the annular space between said reaction chamber and said resistance heating coil, said means further comprising a temperature indicator and controller device, a relay, and an auto-transformer adapted to regulate the electrical current flow through said resistance heating coil.

3. The apparatus of claim 1 wherein said reaction chamber is variably rotatable, said chamber and helix

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are fabricated of stainless steel, and the nozzle structure comprises titanium, whereby the structure is especially adapted for the deposition of tin oxide from the thermal decomposition of tin chloride.

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