

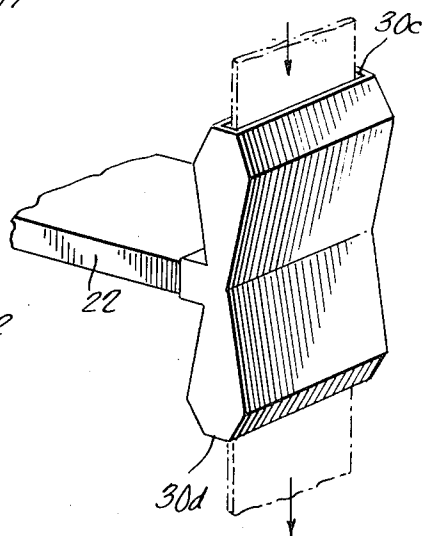
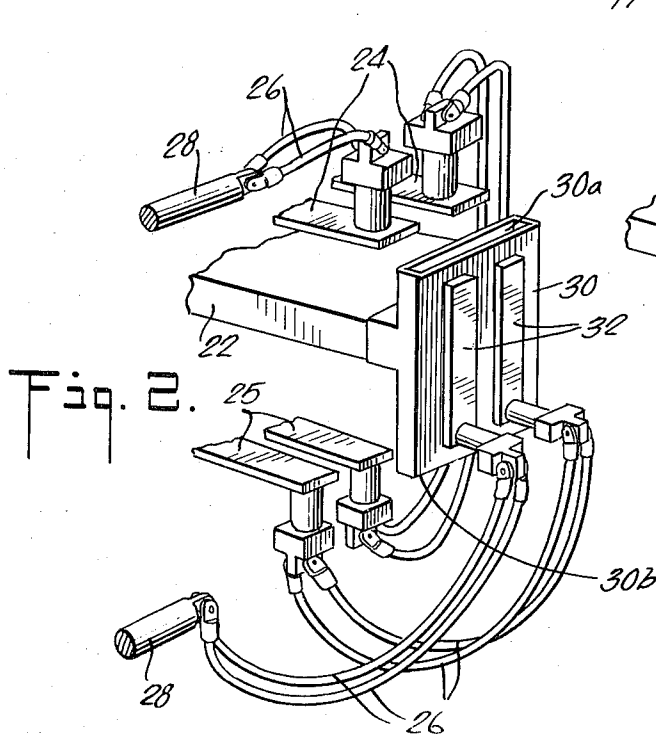
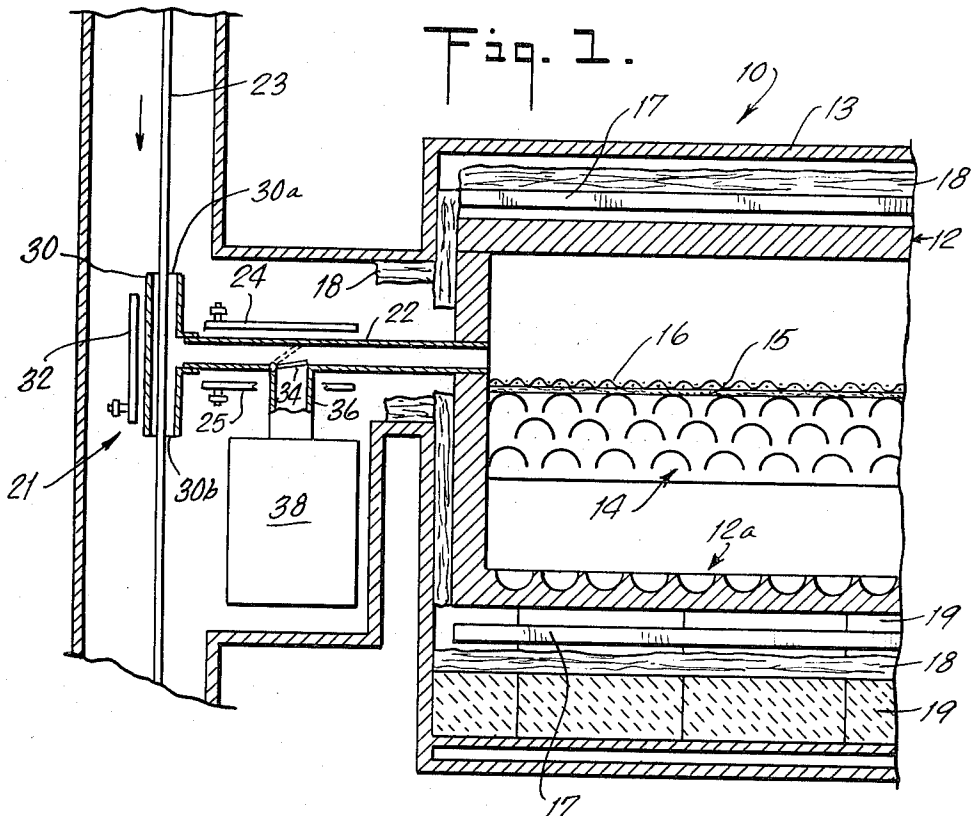
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APPARATUS AND METHOD FOR CONTINUOUSLY CONDENSING
METAL VAPOR UPON A SUBSTRATE
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APPARATUS AND METHOD FOR CONTINUOUSLY CONDENSING METAL VAPOR UPON A SUBSTRATE

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8 Claims

ABSTRACT OF THE DISCLOSURE

Apparatus and method for continuously condensing metal vapor upon a moving substrate includes generating a continuous quantity of metal vapor, which may be at nonturbulent flow. The metal vapor is directed by a nozzle from the metal vaporizing apparatus toward the substrate at turbulent flow. A chamber in which the substrate continuously moves communicates with the nozzle so as to receive from the nozzle the metal vapor to be deposited upon the substrate. The chamber and the nozzle are maintained at a temperature equal to or in excess of the temperature of the metal vapor to prevent substantial deposition of the vapor upon the walls of the nozzle and the chamber. The substrate is at a temperature substantially less than that of the metal vapor. The flow of metal vapor may be controlled by a valve in the nozzle which divides excess vapor from the flow and directs the excess vapor into a collector box.

BACKGROUND OF THE INVENTION

The present invention relates to metal vapor deposition upon a moving base, particularly zinc vapor coating of a steel substrate.

Vaporized zinc coatings on steel offer many advantages over conventional electroplated zinc coatings and hot dip galvanized coatings. A smooth, non-splattered coating can be produced by vapor deposition while coating thickness can be varied by controlling the zinc evaporation rate and/or the speed of a moving steel substrate. A one-side coating can be easily produced by properly shielding the strip. Composite coatings, e.g. a thin aluminum coating over a thin zinc coating, can be produced by vapor deposition, the steel thus coated having excellent corrosion resistance. Production speed can be considerably faster for vapor deposition than for an electro-plating line or a hot dip galvanizing line because the restrictions of current density and coating roll speed do not apply. There is no inherent limitation on the gage of the steel being coated, unlike galvanizing processes where line speed must be lowered as thickness and width of strip are increased, due to the amount of heat needed to be transferred to the substrate. Furthermore, the cost of vapor deposition is believed to be less than the cost of either electro-plating or hot dip galvanizing.

Metals are generally vaporized in crucibles or chambers simply by heating the metal to a temperature above its vaporization point. The generated vapor is then deposited upon a substrate either within or without the crucible or chamber. However, one frequent problem is that much of the metal vapor adheres to the walls of the deposition chamber rather than to the substrate.

SUMMARY OF THE INVENTION

It is an object of the invention to provide for the vapor condensation of a coating upon a moving substrate without deposition of a substantial portion of the vapor on the walls of the condensing chamber.

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It is another object of the present invention to provide apparatus and method for continuously condensing metal vapor upon a substrate without the inclusion of splatter in the substrate coating.

A further object of the present invention is to provide for the condensing of metal vapor upon a moving substrate to form a coating of uniform thickness.

To these and other ends the present invention contemplates the use of apparatus for continuously generating metal vapor to prevent droplet or particle entrainment in the vapor. The vapor is directed through a nozzle from the metal vaporizing apparatus toward a substrate at turbulent flow: The nozzle is sufficiently wide to direct metal vapor across the entire width of the moving substrate. The turbulent flow in the nozzle distributes the vapor substantially equally across the entire width of the nozzle, although equal distribution is a function of nozzle design. Preferably, the nozzle is maintained at a temperature in excess of the temperature of the metal vapor so that vapor is prevented from being deposited on the interior walls of the nozzle.

A condensing chamber through which the substrate continuously moves communicates with the nozzle to receive the metal vapor therefrom for deposition upon the substrate. Preferably, the chamber is maintained at a temperature sufficiently great (typically equal to or in excess of the temperature of the metal vapor) to prevent substantial deposition of the vapor upon the interior walls of the chamber. Deposition of vapor on the interior walls of the chamber is further negated by ensuring that the substrate is at a temperature substantially less than the temperature of the metal vapor. To prevent vapor from being dissipated into the external environment, the condensing chamber substantially encloses a portion of the moving substrate. The chamber may be relatively box-shaped so that the substrate enters through one end and exits through an opposing end of the chamber. The entrance and exit ends of the chamber may flare toward the substrate to prevent vapor leakage from the chamber.

A valve may be provided in the nozzle for controlling the flow of metal vapor by dividing out excess vapor from the flow. The excess vapor divided out of the flow by the valve may be received in a collector box secured to the nozzle.

By use of the method and apparatus of the present invention, zinc metal vapor can be deposited on a continuously moving substrate, such as copper-coated steel strip, to form a coating thereon. A heated deposition chamber which surrounds the strip prevents escape of any significant amount of metal vapor and ensures the deposition of substantially all of the vapor on the strip. As the condensing chamber and metal vaporizing chamber are separate instrumentalities, splatter in the coating on the substrate will be substantially eliminated.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view, partly in block diagram form, of representative apparatus in accordance with the present invention.

FIG. 2 is a perspective view of a condensing chamber and heating means in accordance with the invention.

FIG. 3 is a perspective view of a modified form of condensing chamber.

DETAILED DESCRIPTION

Referring to FIG. 1 of the drawings, there is shown metal vaporizing apparatus 10 which is maintained under vacuum and which includes a crucible 12 in which molten metal is disposed to be vaporized. The crucible 12 is enclosed by an outer shell 13 fabricated of low carbon steel, for example. A baffle structure 14, a filter 15 (typi-

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cally felt) and a screen 16 are included which together serve to remove liquid droplets from the generated vapor. Molten metal is added to the crucible by any suitable means, e.g., by means of an inlet pipe (not shown). The crucible is typically fabricated of a heat-conductive material which is non-reactive with the molten metal and which is also not "wetted" by the molten metal. Thus in the case of zinc metal which is to be vaporized, the crucible 12 may be made of graphite.

Disposed between the outer shell 13 and the crucible 12 are a plurality of heating elements 17 which provide heat for vaporizing the molten metal. The heating elements 17 may be of any suitable type, such as furnace heater tubes enclosing burning gas, resistance heating graphite rods or the like. The heating elements 17 may be disposed at both the top and bottom of the crucible so that sufficient heat is provided to vaporize the molten metal.

The bottom portion 12a of the crucible is grooved or scalloped as shown to provide for good heat transfer to the molten metal within the crucible as well as to permit the vaporization of the molten metal while minimizing liquid inclusions in the vapor. Insulation designated 18 may be included within the outer shell 13 to provide for proper retention of heat within the crucible. Refractory bricks 19 may also be included below the crucible 12.

The apparatus just described is representative and may take any suitable form, as long as metal vapor is generated suitable for application to a nozzle 22. The specific apparatus just described, including the scalloped crucible bottom 12a, the baffle structure 14, the filter 15 and screen 16 is the subject of copending application Ser. No. 49,370, filed June 24, 1970, for "Apparatus and Method for Vaporizing Molten Metal," in the names of John M. Roblin, Frank J. Cole and James G. Bourne, and assigned to the assignee of the present application. The flow of vapor in the crucible 12 may be non-turbulent, in which case liquid droplets may tend to settle out of the metal vapor.

The metal vaporizing apparatus 10 is maintained under a vacuum at an absolute pressure less than about 100 microns. Vapor produced at an absolute pressure of about 25 to 50 torr within the crucible 12 exits therefrom into vapor condensing apparatus 21, which includes the nozzle 22. The nozzle 22 is fabricated from Type 430 stainless steel, e.g., and directs the metal vapor at a temperature of about 1180° to 1300° F. (a median temperature of about 1250°) toward the substrate (moving strip 23). The nozzle is elongated and extends across the entire width of the moving substrate so as to direct metal vapor completely across the substrate. Because of the width of the nozzle 22, it is preferred that the flow of metal vapor therein be turbulent. Turbulent flow in the nozzle 22, achieved by appropriate selection of the nozzle cross-sectional area (decreasing the area increases the tendency toward turbulent flow), results in uniform distribution of the metal vapor across the width of the nozzle as well as provides a constant velocity of the metal vapor in all areas of the nozzle. The velocity of the metal vapor in the nozzle 22 may be about 100 to 500 ft. per second and the mass velocity may be about 0.1 lb. per min. per sq. in. to 1.0 lb. per min. per sq. in. Turbulent flow in the nozzle 22 and non-turbulent flow in the crucible 12 (if non-turbulent flow in the crucible is desired) are achieved by appropriate selection of respective volumes.

The nozzle 22 is maintained at a temperature in excess of the temperature of the metal vapor so that the vapor will not be deposited on the interior walls of the nozzle. Heating the nozzle 22 also serves to convert a portion of any liquid particles in the flow to vapor. Where the metal vapor is zinc which is at a temperature of about 1250° F., the nozzle should be heated to a temperature of about 1275° to 1500° F. Heaters 24 and 25 are provided along the top and bottom of the nozzle 22, respectively, so as to provide heat therefor for maintaining the

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high temperature therein. As best seen in FIG. 2, the heaters 24 and 25 are, for example, of the electrical resistance type, connected together by series connections using flexible conductors 26 attached to electrical bus bars 28.

After passing through the nozzle 22 the metal vapor is received within a condensing chamber 30 of the vapor condensing apparatus 21 through which the substrate continuously moves. The condensing chamber 30 is fabricated from Type 430 stainless steel, e.g., and is secured to the end of the nozzle 22 at substantially a right angle thereto to receive the metal vapor therefrom for deposition upon the substrate. In condensing chamber 30 the vapor is confined so that that portion of the metal vapor which initially fails to adhere to the substrate will not be permitted to dissipate into an external environment and subsequently condense on a surface other than the substrate. Normally, fast-moving metal vapor will expand when exiting from the end of a nozzle and will follow a so-called "line of sight" movement from a source. The expansion of the metal vapor depends upon the mass velocity of the vapor, the vapor pressure, the residual gas pressure, and the distance between the vapor outlet and the surface on which the vapor condenses. By confining the vapors within a small chamber the only pressure drop will be that caused by the condensing vapor itself. The metal vapor will also displace a substantial portion of the residual gases in the coating area so that condensation occurs substantially in an atmosphere of metal vapor. With a high mass velocity and a short distance between the end of the nozzle 22 and the substrate, there will be little expansion of the metal vapor before it reaches the substrate when the condensing chamber 30 is utilized.

It is a feature of the present invention that the condensing chamber 30 is maintained at a temperature at least as great as or preferably in excess of the temperature of the metal vapor. This prevents substantial deposition of the vapor upon the interior walls of the chamber. Thus, where the metal vapor is zinc which is at a temperature of about 1250° F., the condensing chamber 30 is preferably maintained at a temperature of about 1275° to 1500° F. A heater 32 preferably of the electrical resistance type near the wall of the condensing chamber 30 opposite the input from the nozzle 22 is utilized to maintain the temperature of the chamber at the desired level. The heater 32 is connected in series connection by flexible connectors 26 to the heaters 24 and 25 for the nozzle 22 and to the bus bars 28. As the walls of the chamber 30 are maintained at a temperature at least as great as or in excess of the temperature of the metal vapor, metal vapor which does not initially condense on the substrate will rebound off the hot walls to subsequently condense on one of the sides of the moving substrate. The metal vapor is permitted only to expand into the condensing chamber 30, and adiabatic expansion and cooling of the metal vapor is thus greatly minimized. Elimination of adiabatic cooling of the metal vapor substantially obviates the formation of small droplets which might condense upon the substrate in the form of splatter. It is also preferred that the substrate be maintained at a temperature substantially less than the temperature of both the metal vapor and the condensing chamber 30 so that the substrate presents a ready target on which the metal vapor may condense. It should be apparent that heated metal vapor preferably condenses on cool surfaces so that maintaining the substrate at a lower temperature than the condensing chamber 30 allows the metal vapor to discriminate in favor of condensation on the substrate.

The condensing chamber 30 substantially encloses a portion of the length of the moving substrate to prevent metal vapor from being dissipated into the external environment. Metal vapor entering the condensing chamber 30 from the nozzle 22 may only exit the condensing chamber through narrow apertures 30a and 30b through

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which the substrate enters and leaves the condensing chamber. The size of the apertures 30a and 30b is determined by practical tolerances in assembly and disassembly of the unit. It has been found that only a minimal fraction of the metal vapor escapes from the condensing chamber 30 rather than being deposited upon the moving substrate.

In one form of the condensing chamber 30 (FIG. 2) the chamber is relatively box-shaped so that the substrate enters through the aperture 30a and exits through the opposing aperture 30b. However, in a modification of the apparatus (FIG. 3), the entrance and exit ends of the chamber flare toward the substrate (the ends are constricted). Thus, the chamber will have a smaller aperture 30c through which the substrate enters the chamber and a smaller aperture 30d through which the substrate exits the chamber.

It is contemplated that the method and apparatus of the present invention be utilized in coating steel strip with zinc. It should be understood that metals other than zinc might also be used with the present invention but that zinc coating is common in the steel industry. As zinc vapor does not readily adhere to bare steel strip, it is first necessary to preplate the strip with copper. The steel strip is copper plated, e.g., by cleaning in an alkali cleaner maintained at a temperature of about 165° F.; pickling the strip in a 5% hydrochloric acid solution at ambient temperature; and plating the strip in a sodium cyanide-copper cyanide bath maintained at a temperature of about 130° F. The thickness of the copper plating may vary from 2 to 8 micro-inches although a thickness of 3 micro-inches is probably necessary to assure perfect adhesion of the zinc vapor. Copper plating not only promotes adhesion but increases the strip temperature range for perfect adhesion. "Perfect adhesion" may be defined to mean a lack of peeling of the coating after plastic deformation to incipient failure using the conventional Olsen cup test. Adhesion is due to the formation of an alloy layer at the interface of the substrate and the coating, the thickness of the alloy layer being a function of temperature and time. Although the strip temperature for coating may be in the range of 300° to 700° F. perfect adhesion has been found to occur with "unaged" copper-plated steel strip in a temperature range of 450° to 575° F. If the strip temperature is too low, the vapor-coated strip will not have a bright and shiny appearance. Even if the proper temperature range is maintained, perfect adhesion may still be inhibited by surface contamination ("aging") prior to vapor deposition.

To control the flow of metal vapor and hence the thickness of the coating upon the substrate, a valve 34 is provided in the nozzle 22 across the entire width of the nozzle. The valve 34 is pivotable into the flow of vapor so that it may divide out excess vapor from the flow. Varying the opening of the valve 34 (by means not shown) controls the amount of vapor which may pass through the nozzle. Therefore, there may be a steady vaporization rate in the metal vaporizing apparatus 10 while the thickness of the coating on the substrate may be varied. The metal vapor which is divided out of the flow of the valve 34 passes through a down-spout 36 into a condenser or collector box 38 secured to the nozzle 22. In the collector box 38 the excess vapor is condensed and is available for recirculation to the metal vaporizing apparatus 10.

In the operation of the apparatus of the present invention, zinc metal vapor is generated in the vaporization section 14 of the crucible 12 of the metal vaporizing apparatus 10. The metal vapor is directed at turbulent flow through the nozzle 22 toward a copper-coated steel strip. In the condensing chamber 30, through which the substrate continuously moves substantially enclosed, the metal vapor is received from the nozzle 22 and is deposited upon the substrate. Heaters 24, 25 and 32 maintain the temperature of the nozzle 22 and the condensing

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chamber 30, respectively, at temperatures generally in excess of the temperature of the metal vapor. The substrate is maintained at a temperature substantially less than the temperature of the metal vapor. This allows substantial deposition of the metal vapor on the substrate rather than on the interior walls of the nozzle 22 and the condensing chamber 30. The valve 34 controls the flow of metal vapor through the nozzle 22 by dividing out excess vapor from the flow and directing the excess vapor to the collector box 38.

EXAMPLE

Evaporator data

Zinc delivered	-----lbs.	157
Liquid zinc temperature	-----° F.	1275
Evaporator temperature:		
At grooved bottom 12a	-----° F.	1420
At top of crucible 12	-----° F.	1500
Wall temperature of crucible 12	-----° F.	1380
Evaporation rate	-----lb. per min.	5.03
Vapor flow rate (above graphite felt 15)	-----ft./sec.	10

Coating data

Nozzle 22 temperature	-----° F.	1490
Condensing chamber 30 temperature (minimum)	-----° F.	1350
Strip speed	-----ft. per min.	132
Coating thickness	-----in.	1.03×10^{-3}
Steel strip dimensions	-----	1
		¹ 10 in. x .0225 in x 1350 lb. coil.

Condensation rate	-----lb. per min.	4.79
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Material balance

Zinc delivered	-----lbs.	157
Zinc deposited on strip	-----lbs.	48
Zinc escaped from condensing chamber ¹	-----lb.	<1
Deposition efficiency ¹	-----percent.	>98
Prior efficiency (without condensing chamber 30) ¹	-----percent.	90

¹ The amount of zinc escaping from the condensing chamber 30 is determined by collecting and weighing the zinc deposited in the areas above and below the condensing chamber. Most of the zinc condenses on water-cooled plates (not shown) strategically located for the specific purpose of condensing tramp zinc vapors before they reach the vacuum pumps (not shown) and electrical leads 26 and 28. The efficiency of the condensing section 21 is then calculated by the following formula:

Percent condensing chamber efficiency

$$= \frac{\text{wt. of zinc on steel} \times 100}{\text{wt. of zinc on steel} + \text{wt. of zinc in coating area}}$$

The weight of zinc on the steel can be computed accurately from line speed, coating thickness, and elapsed time data.

Nozzle data

Zinc vapor temperature	-----° F.	1275
Zinc vapor pressure at evaporator	-----mm. Hg.	54
Zinc pressure at nozzle	-----mm. Hg.	49
Mass velocity through nozzle	-----	¹ 0.5
Velocity through nozzle	-----ft. per sec.	330

¹ Lb. per min. per sq. in.

Prior to the installation of the coating chamber 30 (using a nozzle alone) it was not unusual to remove between 5 and 10 pounds of zinc from the coating area. After installation of the chamber, the zinc deposits were so light and dusty that they were difficult to collect for weighing. Typical condensation efficiency prior to use of the chamber was 85 to 90%. After installation the efficiency was between 95 and 99%. It should be noted that the difference between evaporation rate and condensation rate does not reflect condensing chamber performance. The difference noted in the example given is caused mainly by the zinc vapors that leak through the nozzle valve 34 to the condenser 38.

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Accordingly, the method and apparatus of the present invention allows the continuous condensing of metal vapor upon a substrate without the inclusion of splatter in the substrate coating, and allows a coating of constant or controllable thickness to form on the moving substrate regardless of the rate of generation of metal vapor. The invention prevents deposition of a substantial portion of the metal vapor on the interior walls of the directing nozzle and the condensing chamber.

I claim:

1. A method of continuously condensing metal vapor upon a substrate, comprising the steps of:

- (a) generating metal vapor in a vapor generating region;
- (b) directing the metal vapor from the vapor generating region through a nozzle and into a vapor deposition chamber that is separate from the vapor generating region permitting independent control of vapor generation and deposition;
- (c) passing said substrate continuously through the vapor deposition chamber to permit metal to be deposited upon the substrate; and
- (d) dividing out a portion of the generated metal vapor prior to its entry into the deposition chamber while the remaining part of said vapor is being directed toward said substrate and collecting said divided out portion in a collecting receptacle to permit independent variation of deposition without changing evaporation rate.

2. A method according to claim 1, including maintaining the vapor deposition chamber at a temperature sufficiently great so as to prevent substantial deposition of vapor upon the walls of the chamber.

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3. A method according to claim 2, wherein the metal vaporized is zinc.

4. A method according to claim 3, wherein the substrate is copper-coated steel strip.

5. A method according to claim 1, wherein vapor is generated in said vapor generating region at non-turbulent flow.

6. A method according to claim 5, wherein the flow of vapor from said nozzle is turbulent.

7. A method according to claim 1, wherein said portion of the generated metal vapor is divided out from said nozzle.

8. A method according to claim 1, wherein the substrate is closely confined within said vapor deposition chamber.

References Cited

UNITED STATES PATENTS

3,205,086	9/1965	Brick et al.	117—107 X
2,879,739	3/1959	Bugbee et al.	117—107.1 X
3,561,993	2/1971	Geffcken	117—107.1 X
2,923,651	2/1960	Petriello	117—107.1 X

OTHER REFERENCES

L. Holland, Vacuum Deposition of Thin Films, John Wiley & Sons, Inc., 1956, New York, pp. 166—168.

ALFRED L. LEAVITT, Primary Examiner

K. P. GLYNN, Assistant Examiner

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