April 24, 1962 R. G. BOURDEAU 3,031,338

METAL DEPOSITION PROCESS AND APPARATUS

Filed April 3, 1959

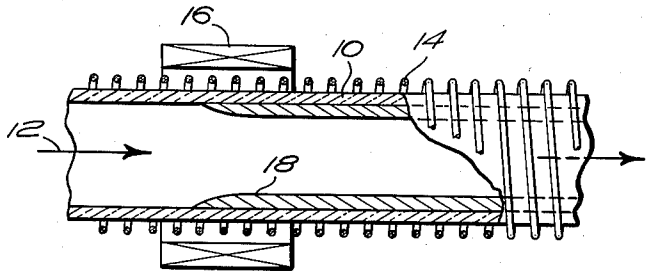


FIG. 1

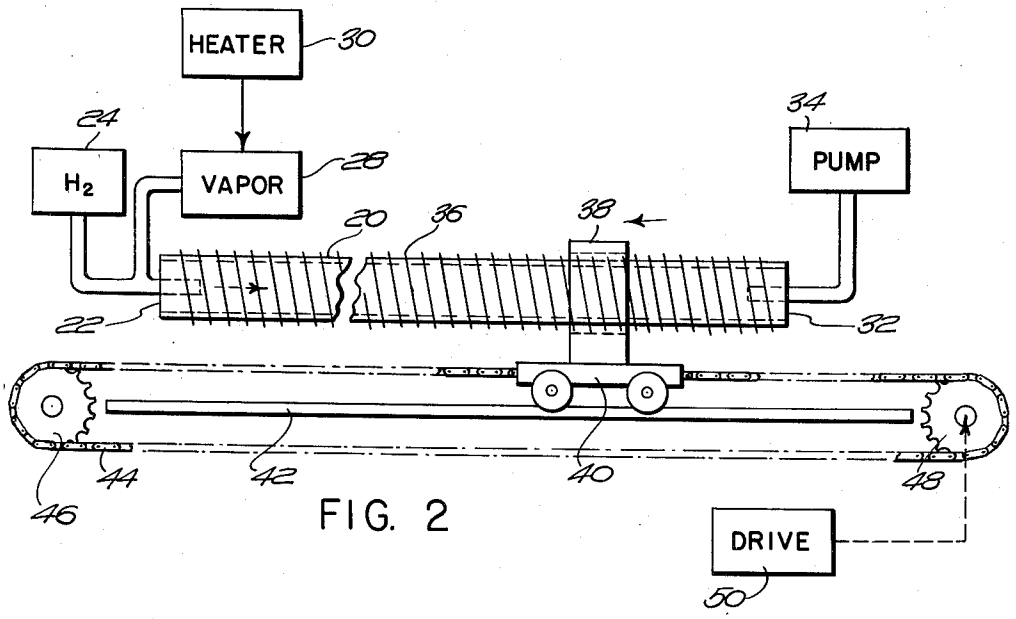


FIG. 2

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United States Patent Office 3,031,338 Patented Apr. 24, 1962

3,031,338

METAL DEPOSITION PROCESS AND APPARATUS

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Filed Apr. 3, 1959, Ser. No. 803,874
5 Claims. (Cl. 117—97)

The present invention relates to metal deposition and, more particularly, to coating the inner surfaces of long tubes with particular metals. It is often desired to coat the inner surface of a long tube with a particular metal in order to impart predetermined physical, chemical and mechanical characteristics. Thus, for example, it may be desired to coat a steel or glass tube internally with a refractory metal. It has been proposed to coat such a tube internally by directing a vaporized compound of the metal through the tube and decomposing or reducing the vaporized compound at elevated temperature in order to deposit the metal. However, in the past, such processes have resulted in the deposition of impure metal in forming the coating and in poor adhesion between the coating and the tube substrate apparently because of the deposit of a low quality powdery form of the metal on the tube substrate as the temperature rises prior to the deposit of the high quality pure metal at the desired elevated temperature. This difficulty is especially important in the case of tubes that are extremely long in relation to their diameters.

Objects of the present invention are: to provide processes and devices for coating the inner surface of a long tube by moving in one direction inside the tube a vapor, comprising a metal compound selected from the class consisting of carbonyls, organometallics, halides, combinations thereof and mixtures thereof, and moving in the opposite direction outside the tube a heating unit that generates a moving heat zone of restricted length within the tube, the rate of movement of the heating unit being such as to deposit metal from a preselected portion of the vapor; and to provide processes and devices of the foregoing type wherein a stationary heat zone of extended length fully encompasses the tube in order to prevent condensation of the vapor in regions not subject to the moving heat zone.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the apparatus possessing the construction, combination of elements and arrangements of parts, which are exemplified in the following detailed disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIG. 1 is an exaggerated, fragmentary view of materials undergoing a process of the present invention; and

FIG. 2 is a schematic diagram of an apparatus for effecting a specific process of the present invention.

Generally, the process illustrated in FIG. 1 comprises coating the inner surface of a long tube **10** by flowing in one direction within the tube a vapor **12** of a metal bearing material, maintaining the vapor at a given temperature and freely in contact with the tube substantially throughout its length as by means of a heating unit **14** of extended length, and moving in the opposite direction outside the tube a heating unit **16** that generates a moving heat zone of restricted length within the tube. The arrangement is such that the temperature gradient in

the vapor at the front of the moving heat zone is sufficiently steep to ensure that initially metal deposition occurs at a desirably high temperature. Thus, any low quality metal deposited at the rear of the moving heat zone does not interfere with the bond between the coating already formed and the tube substrate. This process is particularly adapted for use where the length of the tube is at least 100 times its diameter. The tube, for example, is composed of a metal, such as stainless steel or monel metal, or a fused inorganic material, such as glass or ceramic. Deposition may take place by decomposition of the vapor at the elevated temperature or by reduction at the elevated temperature in the presence of a reducing gas such as hydrogen.

The metal bearing vapor has a first component selected from the class consisting of the transition elements, the rare earth elements, the actinide elements and combinations thereof, and a second component selected from th carbonyls, organics, halides and combinations thereof. Examples of the foregoing are ferric carbonyl, molybdenum carbonyl, nickel carbonyl, chromium chloride, tungsten chloride, molybdenum chloride, bis-cyclopentadienyl metals such as bis-cyclopentadienyls of iron, manganese, cobalt, nickel, rhodium and vanadium, bis-cyclopentadienyl metal halides such as bis-cyclopentadienyl chlorides, bromides and iodides of titanium, zirconium, hafnium, vanadium and tantalum, cyclopentadienyl carbonyls such as cyclopentadienyl manganese tricarbonyl, bis-cyclopentadienyl metal carbonyls wherein the metal is molybdenum, tungsten or iron, dibenzene metals such as dibenzene compounds of chromium, molybdenum and vanadium and dibenzene metal halides such as dimesitylene di-iodide.

As indicated above, the flow rate of vapor **12** and the speed of heat zone **16** are adjusted to produce a coating **18** on the inner surface of tube **10** of predeterminedly desired thickness. The heating zone ranges in temperature from 300° to 1000° C., the carbonyls and the organometallic compounds decomposing or undergoing oxidation reduction within the range of from 250° to 650° C. and the halides decomposing or undergoing oxidation-reduction within the range of from 650° to 1050° C. Instead of a moving heat zone, a succession of stationary heat zones may be employed. The pressure of the metal containing vapors preferably ranges from .5 to 25 mm. of Hg and, when hydrogen is employed as a reduction gas, the total pressure of the vapor ranges from 5 to 50 mm. of Hg. Preferably, the reducing gas is present in excess for the purpose of ensuring that complete reduction occurs. The vapor may be produced by heating the metal containing compounds in solid form.

An apparatus for plating the inner surface of a tube **20** in accordance with the present invention is shown in FIG. 2. At one end of the tube **20**, a reducing gas and a metal containing vapor of the aforementioned type are introduced through a suitable seal **22** from supplies **24** and **26**, respectively. The supply within container **26** is in the form of a powder, the vapor pressure of which is determined by a heater **28** that is kept at constant temperature by a control **30**. At the other end of tube **20**, exhaustion occurs through a seal **32** by a pump **34**. Surrounding tube **20** throughout its length is a heating coil **36** that maintains the vapor from supply **26** in the gaseous phase and prevents any condensation on the inner surface of tube **20** by maintaining a uniformly elevated temperature. Surrounding tube **20** is a heating unit **38**, which is carried by a dolly **40**. Dolly **40** is adapted for reciprocal motion upon suitable rails **42**. The motion of dolly **40** is controlled by a chain **44** and a pair of sprockets **46** and **48**, which are driven by an adjustable drive **50**. It is apparent that the rate of flow of gas from supply **26** may be determined by the tem-

perature of heater 28 and the action of pump 34 and that the rate of movement of heater 38 is determined by adjustable drive 50.

Example

In a specific example of the foregoing process effected by the above described apparatus, tube 20 was 20 inches in length, had an external diameter of 7 mm. and an internal diameter of 5.0 mm. At one end of the tube, the vapor of molybdenum carbonyl, heated to approximately 90° C., and hydrogen, at approximately five times the pressure of the molybdenum carbonyl was introduced. The entire tube was heated to a temperature of approximately 90° C. At the other end of the tube exhaustion occurred in order to cause a flow rate of 20 mols per hour. The molar ratio of the vapor was 10% molybdenum carbonyl to 90% of hydrogen. The moving heat zone, at a temperature of approximately 450° C., was moved at a speed of approximately six inches per hour. The thickness of the high quality deposit produced on the surface of the tube was approximately .050 mm.

Since certain changes may be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A process for coating the inside of an elongated tube section, said process comprising the steps of directing a mixture of a heat decomposable gaseous metal compound and an auxiliary gas through said tube from one end thereof to the other, heating the entire interior of said tube section in order to maintain said mixture in the gaseous phase at a predetermined temperature, said mixture being in contact with substantially all of the inner surface of said tube section, and moving a heat zone in the direction along said tube from said other end thereof to said one end thereof, said heat zone generating a temperature above the temperature at which said decomposable metal compound decomposes.

2. A process for coating the inside of an elongated tube section, said process comprising the steps of directing a mixture of a heat decomposable gaseous metal compound and an auxiliary gas through said tube section from one end thereof to the other, heating the entire interior of said tube in order to maintain said mixture in the gaseous phase at a predetermined temperature, said mixture being in contact with substantially all of the inner surface of said tube section, and moving a heat zone in the direction along said tube from said other end thereof to said one end thereof, said heat zone generating a temperature above the temperature at which said decomposable metal compound decomposes, said mixture being produced by contacting said auxiliary gas with said decomposable metal compound and introducing the resulting mixture into said one end of said tube section, and exhausting said other end of said tube section in order to maintain the pressure of the decomposable metal gaseous compound at between .5 to 25 mm. Hg.

3. A process for coating the inside of an elongated tube, said process comprising the steps of directing a mixture of molybdenum carbonyl vapor and hydrogen through said tube from one end thereof to the other, heating the tube throughout its entire length in order to maintain said mixture in the gaseous phase at a first temperature, said mixture being in contact with substantially all the inner surface of said tube, and moving a heat zone at a second temperature in the direction along said tube from said other end thereof to said one end thereof, said first temperature being below the temperature at which deposition of metal from said heat decomposable metal compound occurs, said second temperature ranging from 650 to 1050° C. in order to deposit said molybdenum on the inner surface of said tube.

4. A process for coating the inside of an elongated tube, said process comprising the steps of directing a mixture of molybdenum carbonyl vapor and hydrogen through said tube from one end thereof to the other, heating said tube to a first temperature throughout substantially its entire length in order to maintain said mixture in the gaseous phase at a predetermined temperature, said mixture being in contact with substantially all the inner surface of said tube, and moving a heat zone at a second temperature in the direction along said tube from said other end thereof to said one end thereof, said heat zone having a temperature ranging from 650 to 1050° C. in order to deposit said molybdenum on the inner surface of said tube, said molybdenum carbonyl being initially at a temperature of 90° C., said hydrogen being at approximately five times a pressure of said molybdenum carbonyl, said temperature throughout said tube being approximately 90° C., the molar ratio of said vapor being 10% molybdenum and 90% hydrogen, the total pressure within said tube of said mixture ranging from .5 to 25 mm. Hg.

5. An apparatus for depositing a metallic coating on the inner surface of an elongated tube, said apparatus comprising a first means for introducing gaseous decomposable metal compound to one end of said tube and for exhausting the other end of said tube, second means extending throughout the length of said tube for generating an extended heat zone in order to maintain said vapor at a predetermined first temperature while flowing within said tube, third means extending within a restricted section of said length for generating a restricted heat zone within said tube at a predetermined second temperature said second temperature being above said first temperature, and fourth means for driving said third means in the direction along said tube from said other end to said one end at predetermined speed, said second means enveloping said tube throughout its length, said third means enveloping said tube within a restricted section.

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