

Feb. 26, 1952

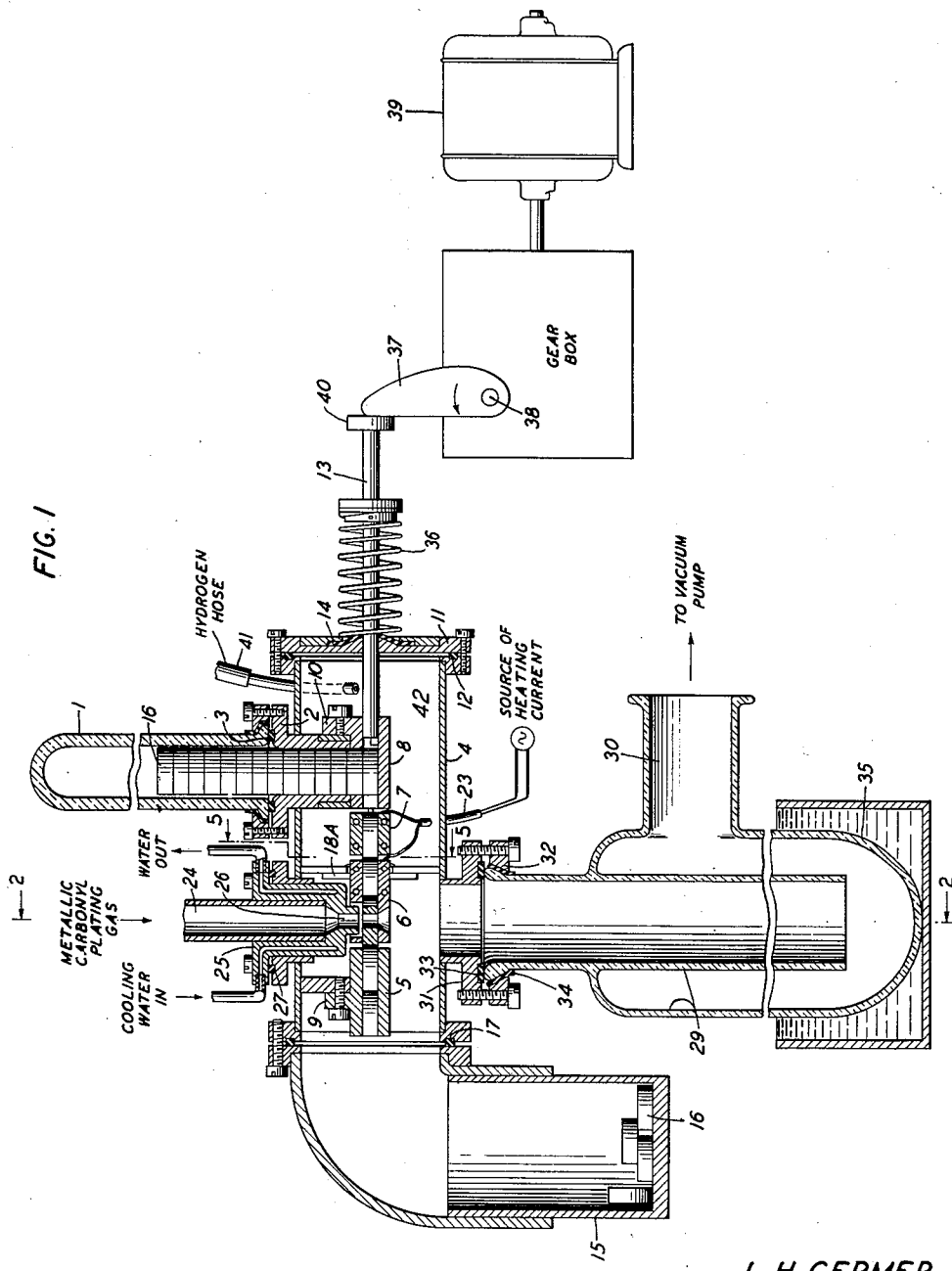
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2,587,036

PROCESS AND APPARATUS FOR SEMICONTINUOUS PLATING

Filed March 12, 1946

2 SHEETS—SHEET 1



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2 SHEETS—SHEET 2

FIG. 2

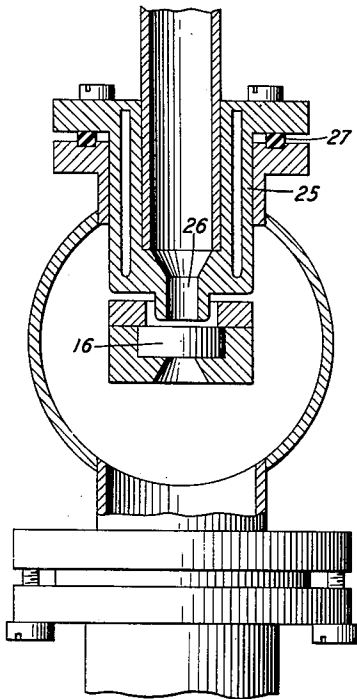


FIG. 3

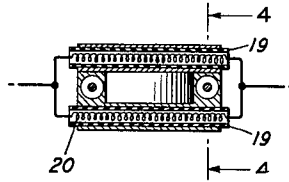


FIG. 5

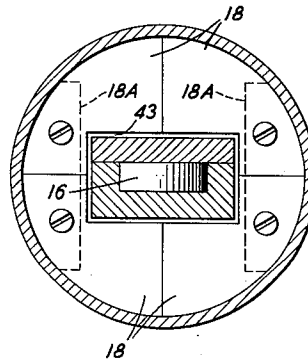
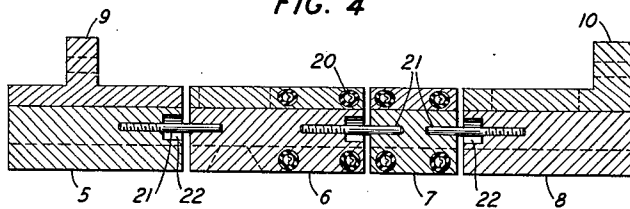


FIG. 4



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PROCESS AND APPARATUS FOR SEMI-CONTINUOUS PLATING

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14 Claims. (Cl. 117—106)

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This invention relates to apparatus and processes for coating metals such as iron, steel, nickel, copper or other metals, and ceramics or vitreous materials, or other materials capable of withstanding sufficiently high temperatures, with those metals, or carbides, or compounds of those metals which can be plated by deposition from metallic carbonyls or mixtures of metallic carbonyls.

More particularly, the invention relates to semi-continuous process machines and processes whereby a considerable number of articles to be plated on a surface or surfaces may be loaded into a suitable reservoir or supply chamber and plated in a more or less continuous operation.

Hitherto the plating of objects or surfaces by decomposition of metallic carbonyls at the surface to be plated while maintaining the surface at an elevated or other suitable temperature has been accomplished by loading individual articles or a few articles into a plating chamber which is then suitably evacuated and supplied with suitable gases coincidentally with production and maintenance of a suitably heated condition of the surface to be plated. Upon completion of the plating the articles were removed by opening the plating chamber and removing them whereupon other articles were inserted and the process repeated. This procedure is wasteful of operator's time, wasteful of power, wasteful of hydrogen, and wasteful of power necessary to re-evacuate the plating chamber upon each operation as well as slow.

An object of the invention is to reduce the usage of plating and other gases, to reduce the power necessary to evacuate the closed vessel in which the plating is formed, to speed up the process, and to provide equipment capable of operating without attention for relatively long periods of time to accomplish the plating of considerable numbers of articles.

In the specific embodiment of apparatus herein disclosed, a supply reservoir in the form of an elongated closed tube may be loaded with a large number of articles, for example, several dozens or more, this reservoir is then attached to the plating chamber by gas-tight means; a closed gas-tight receptacle is provided and also attached to the plating chamber by gas-tight means; the entire apparatus is then evacuated; the articles to be plated are fed one by one through a heating element heated to a desired temperature, then fed into a zone to which the plating gas is supplied to them while they are maintained in a heated condition; and after

being plated upon the desired surface they are ejected into the receptacle. After the entire number is finished the plated articles may be emptied from the receptacle and a new supply placed in the supply reservoir and the operation repeated. It thus becomes necessary to re-evacuate the plating vessel only once for several dozens or perhaps a hundred or more articles to be plated.

In the specific embodiment disclosed the articles to be plated are in the form of toroidal rings and the object is to plate the internal surface of the toroids to a maximum extent with little or no plating upon other surfaces. In order to accomplish this a carbonyl gas to be decomposed at the surface to be plated is supplied through the opening in each toroid in succession after it has been raised to a suitably high temperature.

A feature of the invention consists of an arrangement whereby access of carbonyl gases to the elements to be plated is substantially prevented until they have been elevated to the desired plating temperature; experience has shown that for the particular article and the particular plating to be applied there is a preferred temperature or range of temperatures at which the plating is most successfully accomplished. To allow access of carbonyl gas to the object when it is heated partially may result in inferior plating, a non-adherent plating, or decomposition of the carbonyl gas, which may result in undesired materials being precipitated in the plating vessel in the form of powder, carbon or other undesired materials.

The apparatus comprising an exemplary form of equipment embodying the features of the invention is illustrated in the appended drawings in which:

Fig. 1 is a cross-section through the essential elements of the plating apparatus with a driving motor for periodically advancing a new article to be plated being shown diagrammatically;

Fig. 2 is a partial section through the apparatus on the line 2—2 of Fig. 1;

Fig. 3 is a cross-section through the combined guide way and heating elements for the piece parts to be heated;

Fig. 4 is a section through the entire heating element structure taken near one side thereof and on the line 4—4 of Fig. 3; and

Fig. 5 is a cross-section on the line 5—5 of Fig. 1 showing the baffle arrangement between the main plating chamber and the supplemental space on the side of the apparatus toward the

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end from which the articles to be plated are supplied.

The elements of the apparatus include a long tube 1 closed at one end for containing a supply of toroidal rings to be plated. The tube 1 may conveniently consist in whole or part of glass or other transparent material so that the approximate number of articles stored therein may be observed. The tube 1 is screwed down to a flange 2 by machine screws, as shown, and a seal 3 which may consist of a rubber or other suitable gasket renders the structure gas-tight. Suspended within the main casing 4 is a combined guide way and heating element structure consisting of four blocks 5, 6, 7, 8 which are fastened together by pins to form a structure supportable at its two ends before being placed in the main casing. Upturned ears 9 and 10 serve to attach the combined guide way and heating element structure within the main casing. The right-hand end of the plating chamber is closed by a cylindrical disc or head 11 attached by screws and also provided with a suitable seal 12 which may consist of a rubber or other suitable gasket.

Actuating push rod 13 extends through the plate 11 and the opening around the push rod is rendered gas-tight by means of a seal 14 which is conventionally illustrated. In practice, the seal 14 may consist of two or more seals or other more complicated structure for keeping the opening around the push rod air-tight. In operation, pressure outside the vessel is always greater than the inside hence the seal 14 is arranged to prevent the ingress of gas. On the left-hand end of the plating vessel a receptacle 15 constructed of any suitable size, shape and material, is provided to retain the plated objects 16 and allow them to cool. The receptacle 15 has a right angled elbow at the upper end and is likewise fastened to the main vessel 4 by means of machine screws or bolts and is provided with a suitable seal 17 which may consist of a rubber or other suitable gasket. It will be seen that upon dismantling the plate 11 and the receptacle 15 the heating element structure 5, 6 and 7 may be loosened and removed from the casing 4 for convenient replacement after the baffle 18 which consists of four quarter segment shaped plates 18, is removed. The baffle consists of four separate plates 18 to facilitate removal or replacement of the baffle as well as removal of the structure 5, 6, 7, 8 from the chamber 4. These plates 18 are supported and held in place by screws which enter openings in two flanges 18a which are integral with or brazed or otherwise suitably attached to casing 4. By reference to Figs. 3, 4 and 5, as well as Fig. 1, the manner of constructing the heating elements and guide way structure may be observed. This structure consists of four metal blocks having aligned passage ways through their central sections so that a continuous passage through all of them provides a guide way for the toroidal discs which are to be plated. The blocks 5 and 8 are not provided with heating elements and blocks 6 and 7 are provided with heating elements. These heating elements are in the form of insulated resistance windings extending through opening 19 and the blocks 6 and 7. Insulated heating windings 20 may be of any convenient number, form and construction necessary to bring the objects to be plated to a sufficiently or suitably high temperature. In plating copper toroids, plating is or may be started at a higher temperature than that at

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which it is continued. This may be accomplished by the apparatus shown by bringing the objects to be plated to a suitable high temperature in the block 7, maintaining them substantially at this temperature in the right-hand end of the block 6 (as seen in Fig. 4), and allowing them to cool down somewhat in the left-hand end of the block 6, in which position (plating point) the plating occurs. It is desired to maintain the blocks 5 and 8 relatively less hot than the blocks 6 and 7, and also to permit the blocks 6 and 7 to be at somewhat different temperatures. In order to accomplish this, the main bodies of the blocks are positioned slightly apart so that they do not touch one another but are separated by a distance of the order of one or two millimeters. The blocks are held together by pins 21 which are tightly fitted into one block and which may be threaded into the other in the fashion of a machine screw. In order to reduce heat conduction through the pins one adjacent surface of each pair of blocks is hollowed out to form a cylindrical cavity through which the pin extends. The length of this cavity 22 in the longitudinal direction is several times as great as the distance between the faces of the blocks so as to furnish a relatively long path for the conduction of heat from one block to another. Inasmuch as the entire apparatus contains gas at a relatively low pressure the block 8 may be maintained relatively cool; the block 7 for a specific purpose at 700° C.; block 6 at about 650° C., and the block 5 at a lower temperature depending upon the amount of heat transmitted thereto by the successive plated toroids moved into it. In general, the temperature of the block 5 may fluctuate by increasing each time a new heated toroid is pushed into it and becoming cooler as the toroid cools down. This enables the toroids to be relatively cool when they are deposited in the receptacle 15, which is desirable.

Insulated electric conductors for supplying heating currents to the windings 20 may be extended through the casing 4 by any suitable gas-tight sealing structure. Arrangements of this kind are well known in the art and it is deemed unnecessary that the details thereof be illustrated or described. The portions of the wires inside the casing 4 may be longer than illustrated and provided with terminals for detachable attachment to the windings 20 or the portions of the conductors 23 contained within the casing 4 may be sufficiently long so that upon removal of the guide way and heating structure it may be brought entirely out of the casing without separating the terminals which may then be conveniently separated and reattached to substitute elements as desired. Plating gas in the form of a metallic carbonyl may be applied in regulated amount and at a regulated temperature through an inlet passage 24. In practice, a suitable vessel or container of metallic carbonyl maintained at a low temperature may be attached at a remote point on the inlet pipe 24 by means of an air-tight attaching structure. The pipe may contain valves for regulating the ingress of metallic carbonyl gas and of other gases with it, if other gases are used and the container of metallic carbonyl may be surrounded with a suitable water jacket or vessel for regulating its vaporization. These elements have been invented and described by another and form a part of the present invention only to the extent that they are necessary or means equivalent to them is necessary for sup-

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plying metallic carbonyl or a mixture of metallic carbonyls at a suitable rate.

The plating head or inlet end of pipe 24 consists of a fairly massive casting or machined structure 25 terminating in a nozzle 26. This structure may conveniently be kept cool, in order to prevent the deposition of plating thereon, by means of a water jacket through which a continuous flow of cooling fluid is maintained by any suitable means. Even with the provision of a water jacket a certain amount of plating may occur around the mouth of the nozzle 26 and for this reason the structure 25 is made removable. In operation, it may be screwed down to a flange, which is a part of the main casing, and maintained gas-tight by means of a suitable seal 27 which may consist of a rubber or other suitable gasket. Likewise, some plating of the guide way and heating structure, more particularly of the block 6, may occur and this is one of the reasons why the heating structure is made conveniently removable so that replacements of substitute elements may be made from time to time. The metallic carbonyl plating gas issues from the nozzle 26 and passes through the central opening of the particular toroidal ring 16 which, at the moment, is in position for plating. Most of the deposition of metal occurs on the interior cylindrical surface of the annular ring. Plating gas passes through the ring and into the main body of the plating chamber to which is connected a carbonyl trap 29 and an outlet passage 30, all combined in a structure as shown and fastened in a gas-tight manner to a flange 31 by means of screws, a clamping ring 32 and suitable seals 33 and 34, which may consist of rubber or other suitable gaskets. The outlet passage 30 is connected to a powerful vacuum pump or vacuum pump system. The lower end of the structure 29 may be somewhat elongated to form an extension 35, the purpose of which is to condense or trap gaseous undecomposed metallic carbonyl in order to prevent it from being wasted by passing out through the evacuation apparatus. To more effectively accomplish this, the extension 35 may be and should be kept sufficiently cool to condense undecomposed gaseous metallic carbonyl. One way of doing this is to pack the extension 35 in iced brine or surround it by liquid air, or keep it sufficiently cold by any other desired means. The condensed carbonyl may be removed by detaching and emptying the structure 29 when the container is refilled.

The feeding means feeding the objects 16 to be plated consists primarily of a push rod 13 which is spring pressed to the right and may be pushed inward manually at specified intervals to place another specimen to be plated directly in front of the nozzle 26. However, the push rod 13 may be operated inwardly at intervals against the tension of the spring 36 by a cam or arm 37 or any other suitable means which the cam or arm 37 is intended to typify. Specifically, the cam 37 may be mounted on a shaft 38 which is rotated counter-clockwise as viewed in Fig. 1 at a low speed. However, a reducing gearing of conventional type is mounted in a gear box and driven by any suitable means such as the motor 39. It will be seen that the cam 37 during about 95 per cent of the time will be out of contact with the head 40 of the push rod 13 but at relatively long intervals will push the rod to the left exactly sufficient to move another specimen 16 under the plating nozzle 26 and eject the one whose plating has just been finished into the

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passage in the block 5. If means is desired so that the time of motion of the rod 13 to the left is much shorter in proportion to the time between motions, suitable mechanism for accomplishing this may consist of well-known Geneva gears or other devices. It is essential that the rod 13 should not be pushed too violently as this may cause the toroids to pass beyond the proper plating position.

It is desired to prevent access of plating gas to the toroidal rings until they have become well and properly heated. In the practice of processes of this type it has frequently been customary to introduce a large proportion of hydrogen gas into the plating chamber along with the metallic carbonyl. For the purpose of influencing the nature of the deposited plating from several to around 1000 molecules of H_2 may be introduced per molecule of metallic carbonyl. Hydrogen gas may be introduced in the present case with another attendant advantage in that its ingress through a hose 41 is regulated to maintain a slight excess pressure in the right-hand end of the plating chamber 42. A constant flow of hydrogen gas to the left as seen in Fig. 1 then occurs around the edges of the heating and guide way structure through the crack 43 (see Fig. 5). Practically no gaseous metallic carbonyl then enters the right-hand end of the plating chamber and consequently no plating occurs until the elements to be plated are heated up to a proper temperature because this could, in many cases, result in an inferior adherence of the plating to the body to be plated or it could result in other difficulties as above described. The hydrogen gas may be allowed to enter through a hose which may be attached to a nipple on the casing 4. In practice, the hydrogen may be purified before being introduced into the plating chamber and this may be accomplished by filtering it through palladium in a well-known manner. The amount of gas introduced and the velocity of its ingress may be regulated by means of a needle valve or other suitable valve or means.

Under some circumstances the hydrogen used may comprise what is known as wet hydrogen, that is, hydrogen containing a certain amount of water vapor, for example, about 5 molar per cent of water vapor. For this purpose the hydrogen may be allowed to bubble through a water containing chamber and, if necessary, two sources of hydrogen may be utilized, one of which is passed through the water bottle or the chamber, and the other of which is not, both being regulated by means of needle valves so that the desired proportion of water may be introduced.

The apparatus disclosed may be used to plate toroidal objects on their interior surfaces with any one of numerous metals such as molybdenum, tungsten, chromium, iron, nickel and any others from which metals may be deposited by decomposition of the metallic carbonyl or with alloys of these or other metals or their carbides or other compounds. The use of the apparatus is not restricted in this respect. As examples of toroidal or cylindrical objects to be plated may be mentioned rocket nozzles, steel wire drawing dies or copper rings.

Furthermore, the principles of the process are not restricted to the plating of the inner surface of toroid-shaped discs but may be applied to plate the interior surfaces of cylindrical bodies which are long compared with their diameter. The apparatus may be varied to plate other than the interior surfaces of bodies. In fact, it is obvi-

ous that by modifying the size and shape of the nozzle or using multiple nozzles several openings in a single body or notches, grooves, or selected surfaces of bodies could be plated. In this respect it is the intention that the generic claims define the invention as broadly as possible.

The operation of the apparatus for the intended purpose may now be briefly outlined. Let it be supposed the objects 16 are toroids of copper and that they are to be plated with molybdenum upon their interior cylindrical surface to a thickness of two to three one-thousandths of an inch. The container 1 is filled with copper toroids and screwed into place, as is the receptacle 15 which has been previously emptied. The surfaces of the toroids may be cleaned by abrasion and further cleaned by washing with absolute alcohol before loading into the containing member 1. A fresh nozzle 25 and a fresh guide way and heating structure 5, 6, 7, 8 are provided, if necessary. The entire apparatus is then inspected and evacuated. Pressures which have been used in the plating chamber are of the general order of $\frac{1}{1000}$ to $\frac{1}{16}$ of a millimeter of mercury but any pressure suitable for a particular case may be used. The evacuation may be measured and checked by means of a manometer. After a desired degree of evacuation has been reached hydrogen flow at the proper rate is started through the inlet tube 41 and heating current is applied to the heating windings 20. After the heating elements have become sufficiently hot, push rod 13 may be operated to introduce the first and then the second toroid to be heated and when they have been heated sufficiently the flow of metallic carbonyl plating gas, which in this instance is molybdenum hexa-carbonyl, $\text{Mo}(\text{Co})_6$, through the inlet 24. The push rod is then actuated to bring one toroid 16 into place in front of the nozzle 26. The motor 39 may then be started and except for checking the apparatus at intervals, if necessary, to ascertain that everything is in order, the apparatus may be left unattended for long periods of time. Until the supply of elements to be plated has become exhausted, except for the two contained in the blocks 6 and 7, the apparatus may be opened up, checked, and reloaded for further operation.

For special purposes or reasons carbon monoxide, nitrogen or other gas may be introduced into the plating chamber either along with the hydrogen or as a substitute therefor or along with the gaseous carbonyl.

What is claimed is:

1. A closed vessel, means for heating objects in said vessel, means for supplying vaporized metallic carbonyls into a portion of said vessel, means for causing objects to pass one after the other through said portion, means for discharging said objects into another and cooler portion thereof, and means for maintaining a high degree of vacuum in said vessel during the operation of each of said aforesaid means.

2. Plating apparatus comprising a gas-tight chamber divided into portions by a baffle leaving a small opening between the portions, means for introducing plating gas into one of the portions, means for introducing supplemental gas into the other portion, and means for removing sufficient gas from said one portion to maintain a high degree of vacuum in the entire chamber.

3. Plating apparatus including a structure forming guide way along which objects to be plated are moved, means for enclosing the entirety of said guide structure in a hermetically

tight vessel, heating means comprising an electrically energized winding surrounding said objects for heating said objects as they move along said guide way, a point at which said objects are located after being moved a certain distance, and means for causing plating gas to impinge upon a surface of said objects to be heated when at said point.

4. Plating apparatus including an air-tight plating vessel, a container for holding a numerically large number of objects to be plated hermetically connected to said vessel, a receptacle for receiving plated objects also hermetically connected to said vessel, a nozzle for supplying plating gas hermetically connected to said vessel, means operable externally of said vessel for moving objects in front of said nozzle individually to be plated and thereafter depositing them in said receptacle, in combination with means for maintaining a sub-atmospheric pressure in said vessel, and means for establishing said objects at temperature in the hundreds of degrees C. at the time of their location adjacent said nozzle.

5. In plating apparatus, means establishing a guide way and path of travel for objects to be plated, a hermetically sealed vessel surrounding said means, means for supplying objects to be plated at one point on said path, means for plating said objects at another point on said path, means other than objects to be plated extending through a wall of said vessel by a hermetically tight seal for controlling from the exterior of said vessel the successive movements of said objects from the supply point to the plating point.

6. In plating apparatus, a series of members defining a guide way along which objects to be plated are to be passed, a point at which plating occurs in said guide way, means for elevating the temperature of said objects to a maximum extent as they pass along said guide way before reaching said point, means for supplying gas to clean said objects while so heated to a maximum extent, and means for supplying other gas to plate said objects at said plating point.

7. In plating apparatus a plurality of blocks defining a guide way along which objects to be plated are passed, one of said blocks constituting a heating element for said objects, another of said blocks comprising a container for said objects while they are plated, a third of said blocks comprising a cooling member for said objects after being plated, and means for maintaining said objects under a pressure which is a small fraction of an atmosphere during their entire passage along said guide way.

8. In plating apparatus, a hermetically sealed vessel containing a guide way for objects to be plated, a certain point at said guide way designated as a plating point, an injecting head for injecting plating gas into said vessel onto surfaces of said objects while at said plating point, said vessel consisting in part of a sheet of solid matter constituting a wall which separates the space inside said vessel from the space outside thereof, means for hermetically sealing said head into said wall of said vessel, and jacketed cooling means for cooling said head when in use.

9. Means for plating objects comprising a vessel capable of being hermetically sealed, a partition dividing said vessel into two portions, a guide way extending through said partition from one portion to another, means for supplying objects to be plated on one side of said parti-

tion and moving them through said guide way to a plating point at the other side thereof, means for supplying gas including metallic carbonyl on the side of said partition whereat the plating point is located, means for supplying gas including hydrogen but not including metallic carbonyl at the side of said partition opposite that at which carbonyl gas is supplied whereby to cause a constant flow of gas including hydrogen through the opening in said partition away from the point of supply of gas including hydrogen during the operation of said apparatus.

10. Means for plating the interior surface of objects having a general toroidal conformation comprising a long cylindrical container adapted to be filled with toroidal objects to be plated, means for attaching said container hermetically to a plating vessel, a guide way within said vessel extending from a point adjacent the mouth of said container within said vessel to a plating point, means including said container for supplying successive toroidal objects to be plated, means for moving said objects along said guide way to said plating point, heating means for insuring that said objects are sufficiently heated at the time of arrival at said plating point, and means for passing metallic carbonyl gas through the opening of said toroidal objects while at said plating point in combination with means for maintaining a high degree of vacuum in said vessel during said operation.

11. The method of plating objects each of which has a plurality of portions of surface which comprises enclosing a number of such objects in an enclosed space, establishing and maintaining a greatly reduced gas pressure in said space, injecting a stream of gaseous metallic carbonyl into a portion of said space, controlling the successive advance of said objects one by one to a position relative to the path of said stream such that the stream impinges upon a definite portion of said surface, establishing and maintaining the said portion of said surface of each object incident to such advance as it is moved to a point to be impinged upon by said stream at a temperature to decompose the metallic carbonyl at such portion of surface of each object in turn.

12. Means for plating the interior surface of cylindrical objects comprising plating apparatus including a hermetically tight enclosure, means in said enclosure establishing a path of travel for objects to be plated, means for supplying objects at an initial point on said path, means operable externally of said enclosure for moving

said objects from said initial point along said path, a point along said path, means for plating the internal surface of said objects at said point, and shield means for preventing substantial plating of any other surface of said objects to a substantial extent.

13. A heating element for use in plating apparatus comprising a member having the general shape of a parallelopipedon with an opening therethrough extending from one face to another through which cylindrical members to be plated are to be passed in combination with means for heating each such cylindrical member to be plated while it is located in said opening, another opening extending laterally through said member, means supplying members to be plated one at a time opposite said lateral opening, and a nozzle for supplying plating gas to the inner surface of each of said members while opposite said lateral opening.

14. Apparatus for plating objects which comprises a container for supply of objects to be plated, heating elements for heating said objects, means for supplying plating gas and causing it to impinge upon the surface of said objects to be plated, a receptacle for plated objects, actuating means for progressively moving said objects from a point of supply past the position whereat said plating gas is caused to impinge thereupon and thenceafter plating into a receptacle for said plated objects, and means for maintaining said objects under a high vacuum while in said supply container, while being heated, while being plated and while being cooled.

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