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PROCESS FOR PROVIDING PROTECTIVE METAL COATINGS

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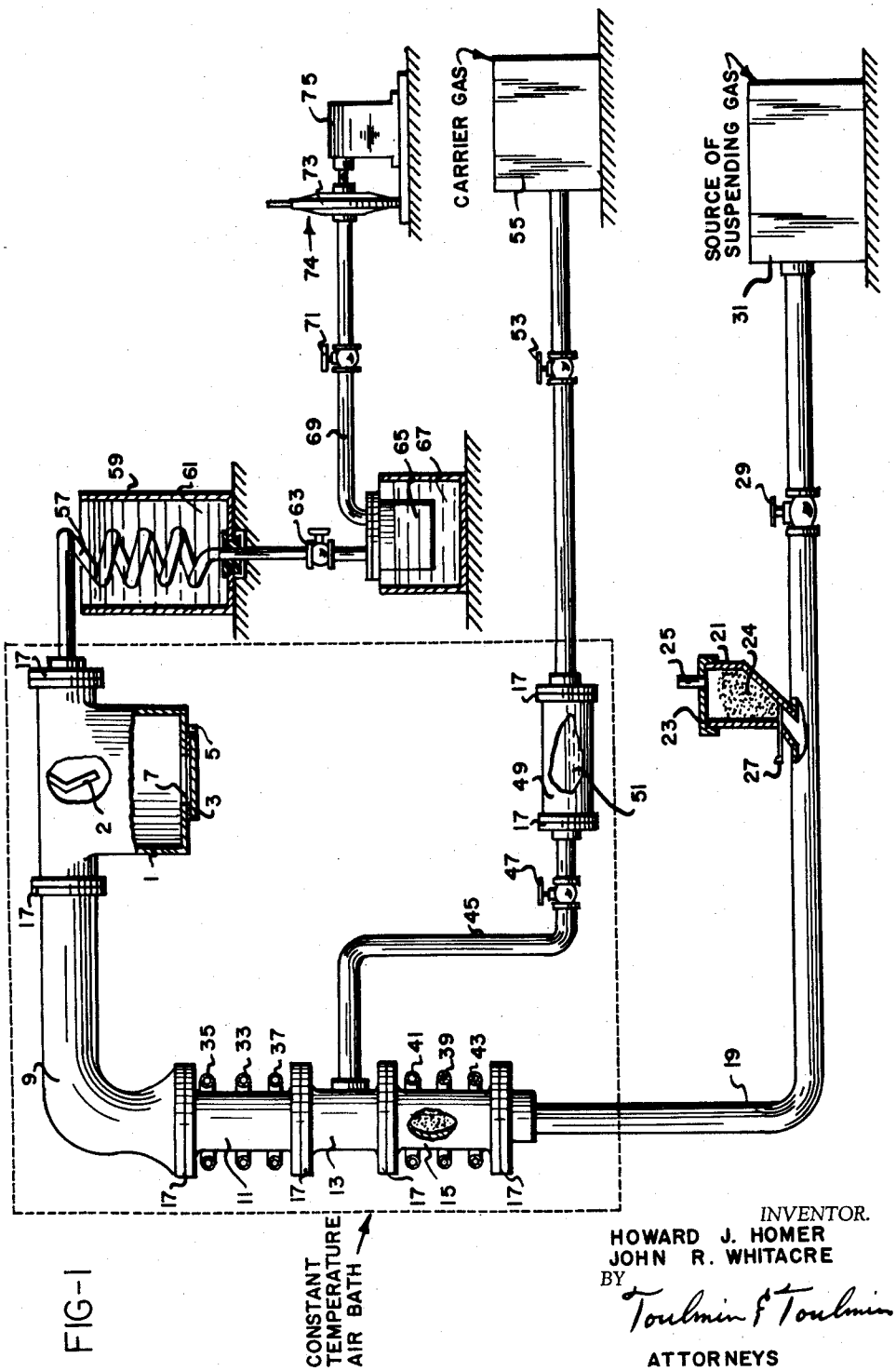


FIG-1

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PROCESS FOR PROVIDING PROTECTIVE METAL COATINGS

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3 Claims. (Cl. 117—50)

This application is a division of Howard J. Homer and John R. Whitacre Application Serial No. 513,014, now Patent No. 2,839,423, filed June 3, 1955, and assigned to the same assignee as the present invention.

This invention relates to the production of protective coatings on metals, particularly the metals of the alkaline-earth group; further the invention relates to the protection of such metals when they are in finely divided form and most subject to attack by the atmosphere, for example.

The transportation of the alkaline-earth metals in bulk has been hindered by the necessity for protecting the metals during transit and storage. It is a primary object of this invention to describe a novel method for the protection of the alkali-earth metals, particularly calcium.

It is an important object of this invention to describe novel metallic composites which include as the primary metal an alkaline-earth.

It is a primary object of the invention to describe a novel process for the separation of alkaline-earth metal from protective metal coating thereon.

It is a particular object of the invention to describe novel powdered metal products.

The invention particularly contemplates the suspending of particles of an alkaline earth metal or metals in a gaseous atmosphere, heating the suspended particles, and then contacting the heated particles, while they are suspended, with a gaseous heat decomposable metal bearing compound which is decomposable at the temperature of the particles to deposit metal thereon.

The gaseous heat decomposable compound is suitably introduced to the heated particles together with a carrier gas such as carbon dioxide, argon, or neon, which are inert relative to the heated metallic particles. Preferably such a carrier gas is employed to conduct the particles to the metallizing zone where the thermal decomposition of the heat decomposable compound is effected.

The heat decomposable compounds are preferably metallic carbonyls although other compounds which decompose at temperatures below that at which the metal to be plated melts are useful. It is preferred to employ nickel carbonyl as such is readily available and relatively inexpensive; however, chromium hexacarbonyl or iron pentacarbonyl are also useful.

In connection with iron pentacarbonyl it is to be noted that while iron generally is subject to rusting the metal deposited from the gaseous state is pure and does not oxidize in the air over long periods of exposure; further the deposited film like that of nickel and chromium is air-impermeable and hence the alkaline-earth metals are protected by the iron deposit.

Most suitably the heating of the alkaline-earth metal is achieved inductively when the metal is in powder or particle form. However, where the metal is in block form and the metal bearing gas is directed over it the heating may be attained by electrical resistance heating

or conduction or convection. Where particles are employed the particles may also be heated prior to their introduction to the metallizing gas and such heating may be utilized alone or in conjunction with induction heating during metallizing.

The alkaline-earth metals are quite reactive even with air at ordinary temperatures. Calcium, for example, combines slowly with nitrogen at ordinary temperatures and heating materially accelerates the formation of calcium nitride; accordingly it is necessary that reactive gases such as air and nitrogen gas be excluded from the alkaline-earths in the practice of this invention.

The invention will be more fully understood by reference to the following detailed description and accompanying drawing wherein the single figure of the drawing schematically illustrates apparatus useful in the practice of the invention.

Referring now to the drawing there is shown in Figure 1 at 1 a chest having a lower door 3 hinged at 5 and provided on the interior thereof with gasket 7 which extends around the door abutting the walls of the chest adjoining the door to permit sealing of the chest air tight relationship with the atmosphere.

Extending laterally from the chest in an upper portion thereof is a conduit 9 which communicates with an upwardly extending duct 11, which itself communicates with ducts 13, 15. Flanged connections 17 secure the conduit and ducts together as indicated and a lower flange connection secures the piping 19 to the lower duct 15. Most suitably the ducts 11, 13 and 15, and the piping also, if desired, are of an insulating material such as glass to inhibit the heating thereof during the process and to minimize metallic deposits thereon.

The piping 19 is communicable with a hopper 21 having a cover 23 provided with a finger valve 25. Communication between the piping 19 and the hopper 21 is effected by removing slide member 27 from the bottom of the hopper in the direction indicated by the arrow.

The hopper is normally filled with alkaline-earth metal powder, such as calcium metal powder; suitably the particles may have a size in their longest dimension of 10–15 microns. The powder is clean, free of contaminants or combination with any other substance when introduced into the hopper, and the powder is sealed from the atmosphere by a cover 23. When it is desired to remove the cover or to expose the interior to the atmosphere, atmospheric pressure may be established within the hopper by depressing finger valve 25.

Connected to piping 19 through a valve 29 is a source 31 of a carrier gas for the calcium powder. This source in the present instance most suitably contains carbon dioxide as the carrier.

Referring now again to the ducts 11, 13 and 15, the duct 11 is surrounded by an induction coil 33 supplied from a source of high frequency energy (not shown) through leads 35, 37. The duct 15 is similarly surrounded by a high frequency induction coil 39 having its leads 41, 43, connected to a suitable source of alternating current energy (not shown).

The duct 13 is connected through piping 45 and valve 47 to a container 49 which in the present instance is provided with a supply of nickel carbonyl indicated at 51. Flange connectors 17 serve to provide for communication for the container 49 through valve 53 with a source of carrier gas indicated at 55 and which gas in the present instance may be considered to be carbon dioxide.

Referring now again to chest 1 the upper right hand end thereof is connected through a flange connection 17 to a condenser coil 57 which is provided in a tank 59 supported in any suitable manner and containing a refrigerating liquid 61, such as Dry Ice and acetone in combination.

However, even cold water is satisfactory as the refrigerant in the present instance. The coil 57 is connected through valve 63 to a trap 65 housed in a suitable refrigerant 67 and from the upper end of which there extends piping 69 having a valve 71 through which the piping 69 communicates with a vacuum pump 73 and a motor 75.

Referring now to the process of invention with valves 71, 63 open and valves 47, 53, 29 closed, and with the door 3 closed the motor 75 and pump 73 are first actuated to clear the system of all air. To facilitate this member 27 which closes the bottom of hopper 21 is open slightly and as air is evacuated from the system it is also drawn from the hopper 21. During this time energy may be supplied to the induction coils 33, 39.

With the system evacuated to a low pressure, for example, 0.1 of a millimeter of mercury, valve 29 is opened to permit carbon dioxide gas to flow freely through the system and to assist in the evacuation of any gases remaining therein. At this time the closure member 27 of hopper 21 is so arranged that no powder will be drawn into the system. When the system has been evacuated the closure member 27 is withdrawn slightly to permit calcium powder to flow down into the conduit 19 and to be gathered in by the flowing stream of carbon dioxide which carries the partciles upwardly into the duct 15, which is essentially a pre-heating chamber.

Induction coil 39 heats the calcium particles flowing therethrough and the temperature of the particles may be raised to approximately 350°–450° F. thereby. Valve 53 and valve 47 are this time opened and carrier gas flows through the container 49 over the liquid nickel carbonyl, entrains some of the same and carries it into the duct 13 where it mixes with the carbon dioxide gas bearing the calcium powder. Some slight amount of decomposition of the nickel carbonyl may take place at this time, but the on-rushing carbon dioxide carries the paritcles into the duct 11 before very much of such action has occurred.

The carbonyl flows with the carbon dioxide into the duct 11 where the induction coil 33 which surrounds the duct 11 is effective to heat the calcium particles therein to a temperature of approximately 550° F.

The carbonyl gas contacting the calcium particles with which it is now intimately mixed, decomposes and deposits nickel metal on the same. Since the walls of the duct 11 are assumed to be of glass substantially no deposition will occur thereon, and such deposition as may occur will generally be insignificant with respect to the surface area of the wall and the cross sectional area of the channel through the duct.

The length of duct may vary with relation to the pressure of the carbon dioxide gas urging the calcium particles upwardly; in fact, the relationship is such as to retain the particles within the duct defining the plating chamber for a sufficient length of time to effect the desired extent of nickel deposit. Generally the nickel deposit is required to be extremely minute, merely sufficient to provide an integral coating over each calcium particle.

The carbon dioxide gas together with the gases of decomposition of the carbonyl, the undecomposed carbonyl and the carbonyl dioxide carrier gas flow to the conduit 9. The pressure is such that the particles are impelled against a baffle 2 supported from the wall of the chest 1 and the particles drop downwardly to the bottom of the chamber as shown at 6, from whence they are later removable. The flowing gases, the only condensible one of which is undecomposed nickel carbonyl, then pass through the coil 57 and the carbonyl is liquified and flows downwardly to the bottom of the trap 65, the carbon monoxide and carbon dioxide passing out through the piping 69 to the exhaust 74 of pump 73. The effect of the expansion of the gases on the velocity is most signicant and in some instances where contact with the baffle would be undesirable the expansion alone is sufficient to occasion the particles to settle.

It is to be noted that in the practice of the invention the calcium powder flows into the piping 19 under its own weight, substantially all air having been removed from the hopper 21 in the evacuation of the apparatus. Therefore there is little opportunity for contamination of the plated particles.

Further in the preferred mode of operation the particles are suspended by a suspending gas against the force of gravity and accordingly due to the fineness of the particles, the particle motion is itself relatively slow depending upon the volume of flow by the suspending gas as well as the duct sizes.

It is further to be noted that the chest 1 is somewhat larger than the conduit 9 and as the gases bearing the coated particles flow into the chest 1 towards the baffle 2, the volume of flow of the gases reduces slightly due to the expansion. This latter factor may be used to control the impingement of the particles on the baffle 2.

To facilitate the opening of the system after complete exhaustion therefrom valves 29 and 47 having been closed after the end of the plating operation, the valve 63 is likewise closed and valve 25 depressed to permit entry of the air into the piping 19 and the ducts and also chest 1. Thereafter opening of the chest door 3 is simplified since atmospheric pressure has been restored to the system.

Preferably the conditions, that is, the pressure of the plating gas, the pressure and velocity of the suspending gas, and the temperature, are so related that only a very thin deposit of nickel is attained on the calcium powder. With such a thin deposit of the protecting nickel metal the composite may be utilized without removal of the nickel when a shipment is at a desired locale. However, the nickel may be readily removed by heating the mass of particles slightly above the melting point of the calcium, that is, to about 850°–900° C., to cause the calcium to become molten and to rupture the nickel coating. The nickel which at this temperature remains solid then drops to the base of the container while the lighter calcium separates in an upper liquid layer. Such separation may suitably be effected in a covered graphite crucible without contamination of the calcium metal.

Barium and strontium both exhibit materially lower specific gravities than the protective metals such as iron, chromium and nickel, and accordingly separation is achieved readily.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

We claim:

1. In a process for providing a protective metal coating on an alkaline-earth metal selected from the group consisting of strontium and barium, the steps of providing a source of a metal bearing heat decomposable gas, the metal constituent of which is a protector for the alkaline-earth metal, establishing a source of the alkaline-earth metal in powder form, reducing the pressure within a metallizing system by evacuating air therefrom, flowing an inert gas through the system to substantially free the closed system of nitrogen and oxygen and to provide a pressure of the inert gas within the system, introducing into the system and the flow of inert gas from the established source the alkaline-earth metal powder which is to be coated, flowing the inert gas sufficiently to support the alkaline-earth metal powder and to intimately mix and move the powder with the inert gas flow, heating the alkaline-earth metal powder as the powder is moved upwardly in the stream of the inert gas, heating the alkaline-earth metal powder in the flow of inert gas to the decomposition temperature of the metal bearing gas, introducing the metal bearing gas into the heated flowing inert gas and powder to effect contact of the metal bearing gas with the heated powder to occasion thermal decomposition of the metal bearing gas and deposition of

metal on the alkaline-earth powder, separating the metal coated alkaline-earth powder from the inert gas and undecomposed metal bearing gas, and thereafter removing the coated alkaline-earth metal powder from the system.

2. In a process for providing a protective metal coating on an alkaline-earth metal selected from the group consisting of strontium and barium, the steps of providing a source of a metal bearing heat decomposable gas, the metal constituent of which is a protector for the alkaline-earth metal, establishing a source of the alkaline-earth metal in powder form, reducing the pressure within a metallizing system to substantially 0.1 millimeter of mercury by evacuating air therefrom, flowing an inert gas through the system to substantially free the closed system of nitrogen and oxygen and to provide a pressure of the inert gas within the system, communicating the established closed source of the alkaline-earth metal in powder form with the system to cause air to be withdrawn from the established source through the system, introducing into the system and the flow of inert gas from the established source the alkaline-earth metal powder which is to be coated, flowing the inert gas sufficiently to support the alkaline-earth metal powder and to intimately mix and move the powder with the inert gas flow, heating the alkaline-earth metal powder as the powder is moved upwardly in the stream of the inert gas, heating the alkaline-earth metal powder in the flow of the inert gas to the decomposition temperature of the metal bearing gas, introducing the metal bearing gas into the heated flowing inert gas and powder to effect contact of the metal bearing gas with the heated powder to occasion thermal decomposition of the metal bearing gas and deposition of metal on the alkaline-earth powder, separating the metal coated alkaline-earth powder from the inert gas and undecomposed metal bearing gas, and thereafter removing the coated alkaline-earth metal powder from the system.

3. In a process for providing a protective metal coating on an alkaline-earth metal selected from the group consisting of strontium and barium, the steps of providing a source of metal bearing heat decomposable gas, the metal constituent of which is a protector for the alkaline-earth metal, establishing a source of the alkaline-earth metal in powder form, reducing the pressure within a metallizing system to substantially 0.1 millimeter of mercury by evacuating air therefrom, flowing an inert gas through the system to substantially free the closed system of nitrogen and oxygen and to provide a pressure of the inert gas within the system, communicating the established closed source of the alkaline-earth metal in powder form with the system to cause air to be withdrawn from the established source through the system, introducing into the system and the flow of inert gas from the established source the alkaline-earth metal powder which is to be coated, flowing the inert gas sufficiently to support the alkaline-earth metal powder and to intimately mix and move the powder with the inert gas flow, heating the alkaline-earth metal powder as the powder is moved upwardly in the stream of the inert gas, heating the alkaline-earth powder in the flow of the inert gas to the decomposition temperature of the metal bearing gas, introducing the metal bearing gas into the heated flowing inert gas and powder to effect contact of the metal bearing gas with the heated powder to occasion thermal decomposition of the metal bearing gas and deposition of metal on the alkaline-earth powder, expanding the volume of the flow sufficiently to decrease the velocity of the flow to an extent which causes the heavier coated alkaline earth metal in the powder form to separate from the gases of the flow, and thereafter removing the coated alkaline-earth metal powder from the system.

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