Nov. 24, 1959 H. J. HOMER ET AL 2,913,813

COMPOSITE METAL PRODUCT

Filed June 22, 1955 2 Sheets-Sheet 1

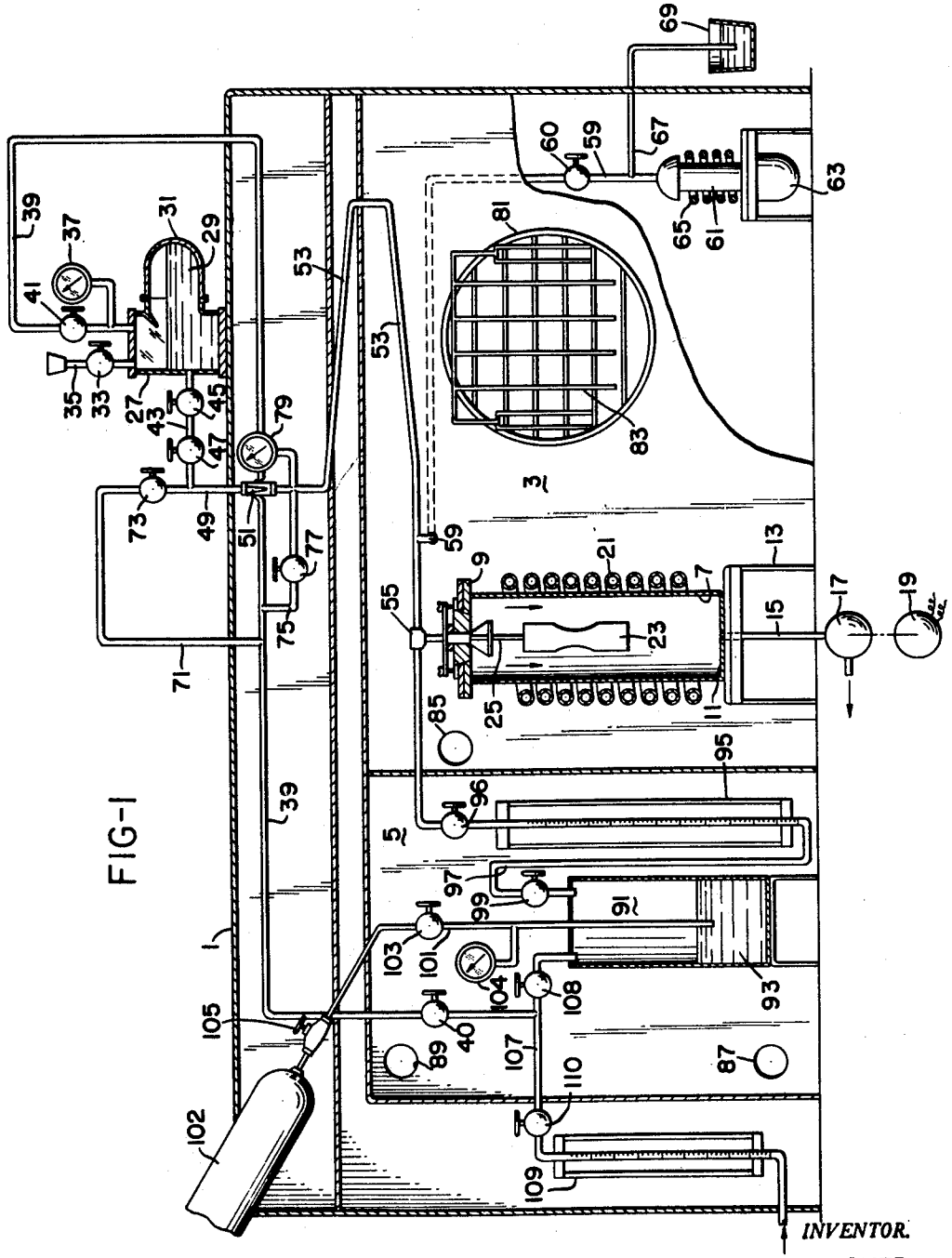


FIG-1

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Filed June 22, 1955 2 Sheets-Sheet 2

FIG-3

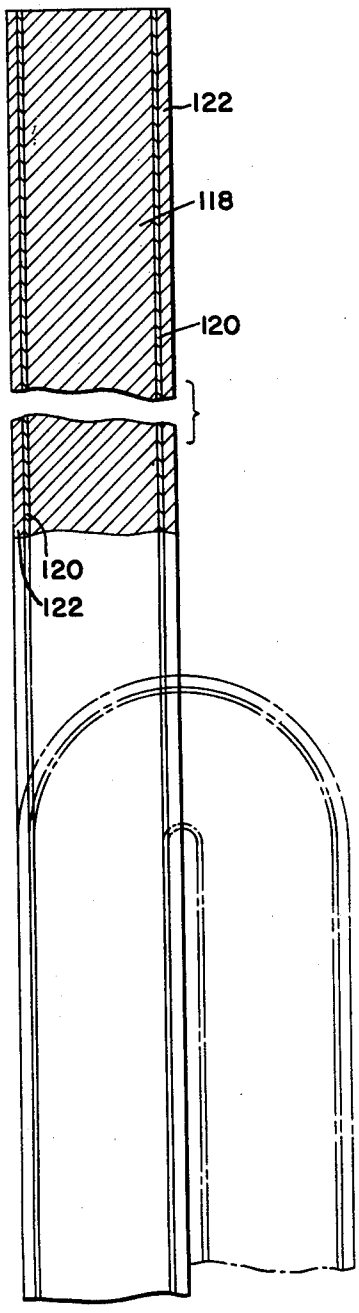
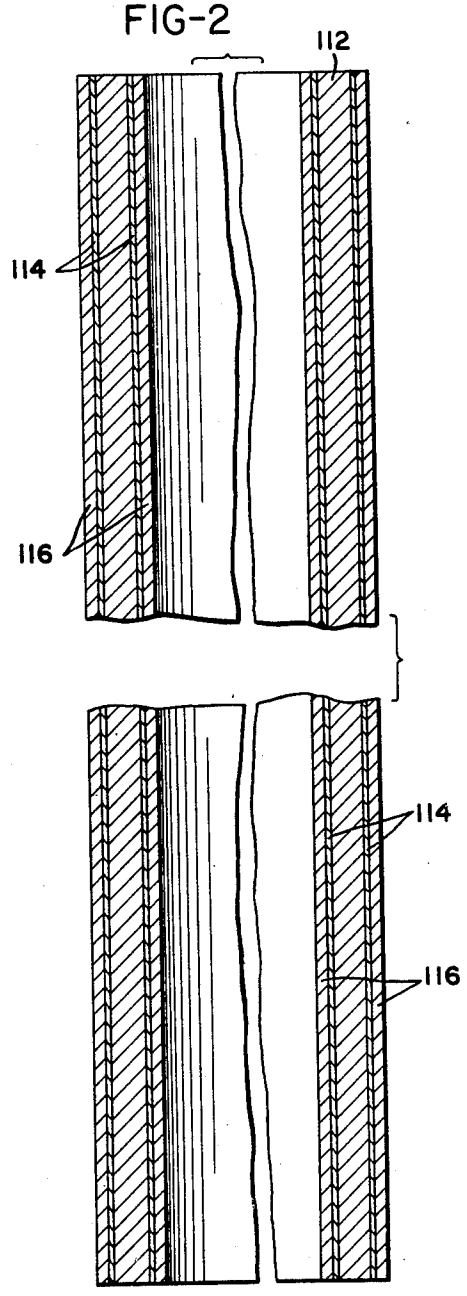



FIG-2




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2,913,813

# COMPOSITE METAL PRODUCT

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Application June 22, 1955, Serial No. 517,208

4 Claims. (Cl. 29—194)

This invention relates to the protection and the bonding of metals and is particularly applicable to metals which form surface oxides readily when the metal is exposed to the air; oxides thus formed tend to prevent the adherence of protective metal coatings which coatings in many applications would be useful in conjunction with such an oxide-forming metal.

The invention particularly contemplates the joining of metals of dissimilar characteristics without affecting desirable physical properties of the metals joined. Thus bodies of aluminum metal or aluminum containing alloys which bodies are utilized in many applications because of their lightness in weight may be joined to a protective coating of nickel in such an amount of the latter as to secure the corrosion and pit resistant characteristics of the nickel while substantially retaining the desirable light weight characteristics of the aluminum.

The practice of this invention includes the steps of providing a metallic interlayer or tie ply between the metals to be joined, the interlayer consisting preferably of a single metal such as lead. The lead is adhered to the body of the oxide-forming metal by deposition of the lead from a gaseous heat decomposable metal bearing compound at a temperature or temperatures at which the oxide-forming metal is unaffected in physical characteristics; the temperature however is preferably such that the lead deposit is somewhat plastic. A corrosion-resistant metal is then applied to the lead preferably also by deposition from a gaseous heat decomposable metal bearing compound.

The deposition of the lead interlayer is effected in a non-oxidizing atmosphere and the interlayer as it deposits is itself oxide-free. Lead however has an affinity for oxygen and tends to inter-diffuse with the oxide layer of the oxide-coated metal base and to combine with the oxide layer to form a bond of high physical properties. The lead is itself, particularly when at a temperature approaching the plastic condition, receptive to deposits of other corrosion resistant metals such as nickel and chromium.

In specific application the invention provides for the production of cladded metal products containing a major portion of aluminum having a non-deoxidized face. Such aluminum bodies, when they are formed or are being formed into airplane wings for example, are subjected to cleaning operations as by sand blasting. Pitting of the bodies is a frequent occurrence and may be avoided by protecting the bodies in the first instance with the cladding metals of this invention. While such generally will not eliminate all necessity for the cleaning operation it will minimize the extent thereof and due to the thinness of the cladding metals to secure the protection the weight of such airplane wings for example will not be materially increased.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:



Figure 1 schematically illustrates apparatus useful in the practice of the invention;

Figure 2 is a sectional view of a cylinder metallized in accordance with the practice of the invention; and

Figure 3 is a sectional view of a relatively long flat piece of aluminum metallized in accordance with the principles of this invention.

Referring to the drawings there is indicated at 1 in Figure 1 a hood having therein a heated compartment 3 normally maintained at a temperature of about 275°–350° F. A second compartment 5 adjacent the first is maintained at a temperature of about 75°–100° F.

Compartment 3 contains a plating chamber 7 which is preferably of Pyrex glass; chamber 7 is provided with a removable sealing closure member 9 at its upper end and a sealing closure member 11 at its lower end. These closures most suitably are of metal and are pressed or threaded onto the Pyrex glass. The chamber 7 is supported at its lower end by a suitable mounting 13 to permit of passage of an outlet conduit 15 from the chamber; conduit 15 is connected to a vacuum pump 17 and motor 19 for assisting withdrawal of gases from the chamber 7. The pump 17 exhausts to the atmosphere.

An induction heating coil 21 surrounds the plating chamber and an aluminum object 23 to be metallized is positioned to be heated when coil 21 is energized. The object 23 is suitably suspended by a strap 25 of heat insulating material from closure 9.

Mounted on the upper outer side of the hood 1 is a steel container 27 which retains a supply 29 of tetraethyl lead. Sight glass 31 provides for viewing the supply. Valve 33 provides for charging the container through conduit 35 and for sealing the supply from the atmosphere.

The container 27 is provided with a pressure gauge 37 and a conduit 39 having valves 40 and 41. Conduit 39 is connected to a source of nitrogen gas which gas as indicated passes into the hood from the leftward end from a supply (not shown) through compartment 5; valve 41 controls the flow of the nitrogen to container 27.

Container 27 is provided also with a conduit 43 having a shut-off valve 45 and a flow control valve 47 for metering the flow of liquid tetraethyl lead to conduit 49. Conduit 49 is itself provided with a restricted opening or jet 51 and liquid tetraethyl lead passes the jet in small drops into a conduit 53 connecting with conduit 49. Most suitably the conduit 49 and the jet forming structure are transparent and of Pyrex glass to permit of viewing the liquid drops.

The conduit 53 is within compartment 3 for a greater part of the conduit traverse and is hence subject to the heat within the compartment, which heat is maintained at such a level that the flowing tetraethyl lead vaporizes.

The lower end of conduit 53 is provided with a T-connector 55 one arm of which communicates with the plating chamber 7 through a pipe 57 which extends through closure 9. The other arm of the T-connector communicates with chamber 5 and such will be described in detail hereinafter.

Conduit 53 is angled downwardly in hood 1 to permit any liquid tetraethyl lead present to flow; the numeral 59 indicates a pipe connected to conduit 53 and pipe 59 with valve 60 open is effective to permit liquid to flow to trap 61 which trap consists of a steel container and is provided with a sight glass 63; a coil 65 for passage of water about trap container 61 provides for maintaining the material passing through pipe 59 in a liquid state. Most suitably the trap is vented through line 67 to a liquid receiver at 69 for absorption of gases which may pass the trap.

A by-pass line 71 is provided between conduit 39 and

jet 51 for the flow of gas through the jet to clean the same; the by-pass is provided with valve 73 for controlling the gas flow.

Conduit 75 having valve 77 extends from conduit 39 through conduit 53 to the pressure gauge 79. Valve 77 permits of supplying a positive pressure of nitrogen to the lead tetraethyl plating material, as it is vaporized, to carry the plating gas to the chamber 7.

Compartment 3 is maintained at the temperature of about 300° F. in the present embodiment by hot air which is blown into the compartment through the duct indicated at 81 in which the electric heaters 83 are incorporated. Thus compartment 3 is a hot air bath in which the vaporizer line 53 and the plating chamber 7 and associated equipment are housed. A hot air outlet is indicated at 85.

Compartment 5 is also suitably maintained at a temperature of about 75° F. by blowing air as required through a conduit 87. Depending upon the conditions of the surrounding atmosphere the air entering the compartment 5 may be heated or cooled as required. The air outlet from compartment 5 is indicated at 89.

Compartment 5 contains a vaporizer 91 which in this embodiment is provided with liquid nickel carbonyl, 93. The numeral 95 indicates a flow meter which is connected to the vaporizer by a conduit 97 having valve 99 which valve is accessible from the exterior of the compartment. Valve 96 controls nickel carbonyl flow to chamber 7. Piping 101 extends into the vaporizer and connects to a source 102 of liquid carbonyl through valves 103, 105; the source 102 is positioned in any suitable manner on or adjacent hood 1 externally of the compartment 5. Pressure gauge 104 indicates the pressure in piping 101.

Nitrogen is supplied to vaporizer 91 through conduit 107 and valve 108; conduit 107 supplies conduit 39. Most suitably the nitrogen supplied to the equipment passes through a flow meter 109 to permit measurement of the volume of carrier gas used.

In the practice of the invention the apparatus, with the air baths at operating temperature, is initially supplied with the tetraethyl lead in sufficient quantity to substantially fill the container 27 and to substantially exclude air from the container. The pump 17 is then operated with all valves closed except valve 77 and most of the air is then withdrawn. Nitrogen is then introduced by opening valves 110 and 40 and the nitrogen is drawn through the system.

Thereafter, with a low pressure of nitrogen prevailing as indicated by gauge 79, the valves 45 and 41 are opened. A nitrogen pressure then exists on the tetraethyl lead and valve 47 is cracked open to permit the liquid to flow slowly.

The induction heater coil is preferably brought to a temperature of at least 600° F. prior to the entry of the flow of the plating gas. Most suitably the object 23 has a temperature of 700° F. to 800° F. when the plating gas enters chamber 7.

As the liquid tetraethyl flows to the orifice 51 drops form and the tetraethyl drips into the vaporizer conduit 53; as the tetraethyl moves it is vaporized by the heat from the air bath and the nitrogen flowing through conduits 39 and 75 pick up the tetraethyl and carry it into contact with the aluminum object 23 in the plating chamber.

The aluminum object is preferably cleaned of any surface grit or grease prior to plating but it need not and suitably is not de-oxidized. The lead tetraethyl striking the hot aluminum surface decomposes depositing lead. The lead at a temperature of 600° F. is plastic and adheres to the aluminum tenaciously coating the same uniformly. At temperatures between 600° F. and 800° F. the lead deposited remains plastic but does not become fluid despite the fact that in the higher ranges of temperature the lead is above its normal melting point; as a theory the lead and the aluminum or the oxide surface of the aluminum combine to form an intermetallic phase having a higher melting point than the lead. No evidence of fluidity appears in the product. However it is to be noted that samples of lead metal when merely placed on a sample during plating under the conditions of the invention, such lead metal melts and runs off. Thus an action takes place when lead is deposited from the gaseous state which is not present when lead is merely placed on the aluminum and heated to the same temperature.

Specific operating conditions for the lead deposition are:

| Sample No. | Compartment 3, T., ° F. | Sample, T., ° F. | T.E.L. Flow, Drops/min. | Carrier Gas, c.f.m. | Time of Run, Min. |
|---|---|---|---|---|---|
| 1 | 250 | 600–800 | 120 | 0.25 | 10 |
| 2 | 285 | 800 | 3 ( ( | 0.21 | 4 |
| 3 | 300 | 77 ! | 120 | 0.25 | 10 |
| 4 | 300 | 800 | 120 | 0.05 | 5 |
| 5 | 310 | 775 | 180 | 0.05 | 10 |
| 6 | 300 | 775 | 100 | 0.05 | 5 |

The amount of the deposit in the above examples was least at 600° F. for the aluminum object and greatest at the higher temperatures and drip rates of the tetraethyl. The coatings were however uniform and it is to be noted that in many instances a very thin coating is to be desired—that is less than one mil—since the adhesion of the subsequently applied nickel depends upon the character of the deposited lead rather than the quantity. However a thickness of about one mil of lead provides a cushion layer which is desirable where the object plated is to be subject to shock.

Upon completion of the lead deposition valves 41, 45 and 47 are closed, valve 73 is opened and nitrogen is passed through the apparatus to clear the same of all tetraethyl. At the same time the temperature of the aluminum object is suitably reduced to about 350° F. by limiting the energy input to the induction coil 21. If desired the temperature of the object may be maintained constant at 600–800° F. during the nickel plating.

Valves 40, 77 and 73 are then closed and valves 96, 99 and 108 are opened to pass nitrogen across the nickel carbonyl in vaporizer 91 to sweep the carbonyl to chamber 7. The combined pressure of the nickel carbonyl and nitrogen may suitably be much greater than that with the tetraethyl and if desired may approach atmospheric. This permits faster deposition of nickel and in general a nickel plating time of about two to three minutes to deposit one mil thickness of nickel is satisfactory.

The waste products of decomposition of the nickel carbonyl like the waste products of the decomposition of the lead tetraethyl are drawn off by the vacuum pump operation. The film of nickel covers the lead and is bright silvery. It may upon removal from the equipment be highly polished and it serves to protect the aluminum against corrosion and pitting. Further the adhesion of the nickel to the lead is excellent.

Argon gas has been substituted for the nitrogen and has provided good results. Hydrogen, while it is useful, tends to be highly heat conductive apparently and at high temperatures of the object above 750° F. intra-gaseous decomposition tends to occur rendering the deposit somewhat non-uniform.

Chromium hexacarbonyl may suitably be employed as a substitute for the nickel carbonyl but is more expensive. Other carbonyl compounds as well as the metal hydrides are useful to supply the outer coat but we have found nickel and chromium to be most satisfactory from an economic standpoint.

Referring now to Figure 2 the tubular aluminum member 112 is shown to have on its inner and outer surfaces, a zone coated overall with a lead deposit 114; a heavier layer of nickel on the lead is indicated at 116.

Referring now to Figure 3 a flat piece of aluminum **118** is coated with lead at **120** and nickel at **122**. Such a piece ¼" thick overall and 6" long may be bent double upon itself without disrupting the bond.

Also a ⅝" O.D. aluminum tube about 6" long, as in Figure 2, when bent double upon itself resisted fracture and peeling of the layers.

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. A composite metallic body comprising a portion containing aluminum having an oxide face sufficient to interfere with the bonding of other metals to the aluminum, a zone comprising a metallic lead portion having opposed faces one of which is in intimate contact with said face, the other face of the lead being oxide free, and nickel bonded to the lead at the other face.

2. A composite metallic body comprising a portion containing aluminum having an oxide face sufficient to interfere with the bonding of other metals to the aluminum, a zone comprising a metallic lead portion having opposed faces one of which is in intimate contact with said face, the other face of the lead being oxide free, and chromium bonded to the lead at the other face.

3. A cladded product comprising aluminum having an oxidic surface, a layer of nickel metal, and interposed between the oxidic surface and the nickel in bonded engagement with each, a layer of lead, the lead layer being of lesser thickness than each of the nickel and aluminum layers and having one face thereof oxide-free and bonded to the nickel.



4. A cladded product comprising aluminum having an oxidic surface, a layer of chromium metal, and interposed between the oxidic surface and the chromium in bonded engagement with each, a layer of lead, the lead layer being of a lesser thickness than each of the chromium and aluminum layers and having one face thereof oxide-free and bonded to the chromium.

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