March 1, 1955 P. J. CLOUGH ET AL 2,703,334

COATING

Original Filed June 30, 1950 2 Sheets-Sheet 1

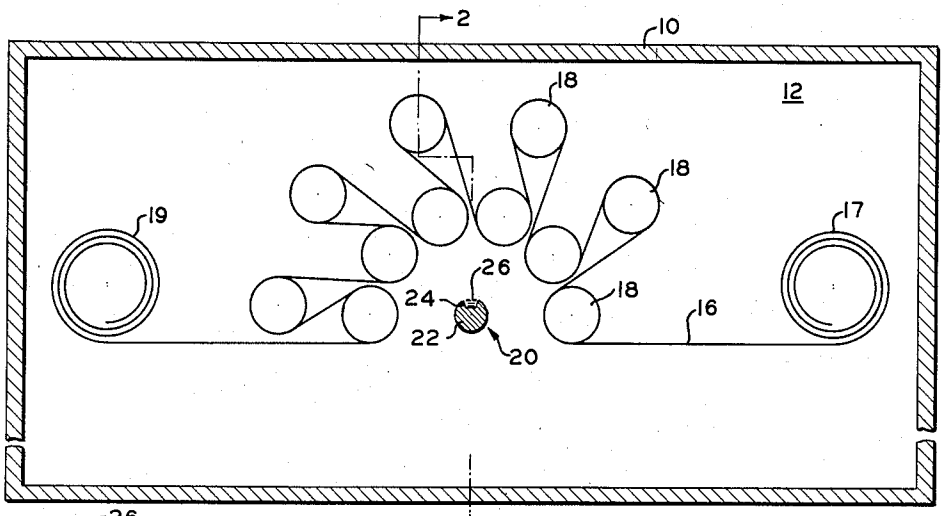


FIG. 1

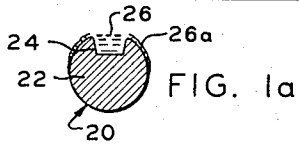


FIG. 1a

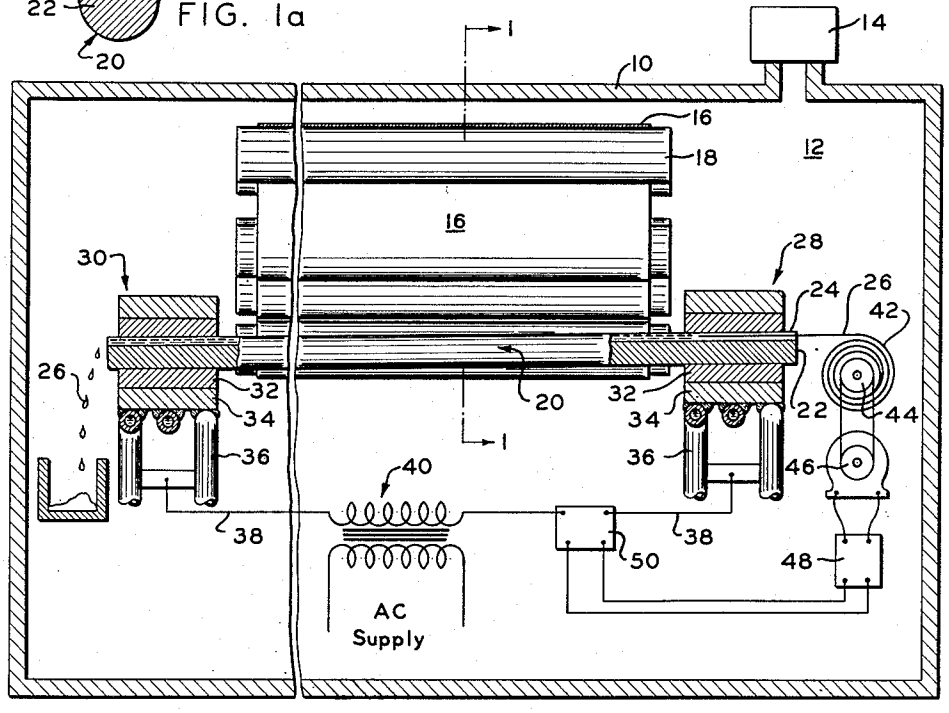


FIG. 2

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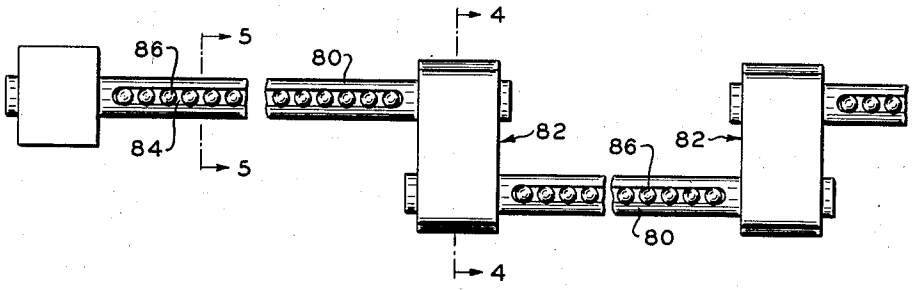


FIG. 3

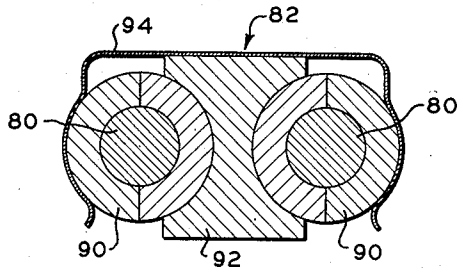


FIG. 4

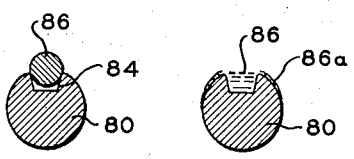


FIG. 5 FIG. 5a

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COATING

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Original application June 30, 1950, Serial No. 171,432. Divided and this application July 14, 1950, Serial No. 173,922

8 Claims. (Cl. 13—22)

This invention relates to coating and more particularly to vacuum deposition coating wherein aluminum is evaporated in a vacuum and condensed on a substrate. This invention is particularly directed to sources of aluminum vapors and methods of manufacturing such sources. This application is a division of the copending application of Clough et al., Serial No. 171,432, filed June 30, 1950, now Patent No. 2,665,227, granted January 5, 1954.

It is a principal object of the present invention to provide a new and improved source for heating aluminum in a vacuum to generate aluminum vapors to be used in vacuum deposition coating.

Another object of the present invention is to provide an improved source of the above type which is cheap, easy to manufacture, and which has a long life even though used with aluminum at temperatures in excess of about 1300° C.

Still another object of the invention is to provide such a source which can be readily heated to operating temperatures by its own internal resistance and which can be brought to its operating temperature in an extremely short period of time.

Still another object of the invention is to provide improved processes for manufacturing such sources.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components, and the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

Fig. 1 is a diagrammatic, schematic, partially sectional view of one embodiment of the invention;

Fig. 1A is a fragmentary, enlarged view of a portion of Fig. 1;

Fig. 2 is a diagramamtic, schematic, partially sectional view taken along the line 2—2 of Fig. 1;

Fig. 3 is a diagrammatic, fragmentary, schematic, partially sectional view of still another embodiment of the invention;

Fig. 4 is a diagrammatic, fragmentary, schematic, partially sectional view taken along line 4—4 of Fig. 3;

Fig. 5 is a diagrammatic, fragmentary, schematic, partially sectional view taken along line 5—5 of Fig. 3; and

Fig. 5A is a diagrammatic, fragmentary, schematic view similar to Fig. 5 but showing a different condition of use thereof.

In one preferred embodiment of the invention there is provided a vacuum chamber in which the substrate to be coated may be moved past a source of aluminum vapors. The present invention is directed particularly to improvements in such aluminum-vapor sources. In one preferred aluminum-vapor source there is provided an elongated rod which is positioned transversely of the path of the substrate during the coating. This rod is preferably one which has at least a surface stratum which is wettable by molten aluminum, the rod preferably being formed of carbon and having a carbide surface stratum which is wettable by molten aluminum. Of the carbides,

the carbides of the group IV*a* and group V*a* metals as hereinafter enumerated are preferred.

For holding the aluminum in contact with the rod, there is preferably provided a groove along the top of the rod, the apparatus being arranged so as to maintain this groove substantially completely filled with aluminum during the coating operation.

In the utilization of the apparatus described above, the vacuum chamber, after insertion of the substrate and aluminum supply, is evacuated to a low pressure on the order of a micron of mercury and then the rod is heated to a high temperature on the order of 1300° to 1500° C. by passing an electric current therethrough. Aluminum is then fed to the rod (if the rod was not initially filled with aluminum) so that aluminum may be evaporated from the rod. The aluminum carried by the groove in the rod, in a preferred embodiment of the invention, wets the whole outer surface of the rod and thus completely surrounds the rod so that aluminum is evaporated from all surfaces of the rod, thereby giving a line vapor source having a high vapor concentration.

In the various embodiments described above, the distribution of the aluminum along the groove in the rod is primarily achieved by the wetting action of the aluminum over the surface of the rod, however it also may be aided by gravity. In this case the rod may run downwardly from the aluminum supply (either solid or liquid) so that a flowing stream of aluminum is maintained in the groove at all times.

Referring now to Figs. 1, 1A, and 2, wherein like numbers refer to like elements in these and the other figures, there is shown a modification of one preferred embodiment of the invention wherein a grooved rod is employed as a source of the aluminum vapors, and aluminum in wire form is fed to a cool end of the grooved rod. In these figures, **10** represents a vacuum-tight housing defining therewithin a vacuum coating chamber **12** which is arranged to be evacuated by a vacuum pumping system schematically indicated at **14**. Within this chamber the substrate **16** to be coated is guided from a supply **17** thereof past a plurality of water-cooled guiding rolls **18** to a take-up spool **19**. During the process of the passage from supply **17** to take-up spool **19**, the substrate **16** passes in a series of convolutions near a source **20** of aluminum vapors. The guiding rolls **18** are preferably driven and are so arranged that they do not "see" the vapor source **20**. Thus the guiding rolls are not coated by the vapors from the source and are not exposed to direct heat radiation from the source. The source **20** preferably comprises a carbon rod **22** having a groove **24** in the upper surface thereof, this groove being preferably maintained full of molten aluminum **26**. One end of the carbon rod **22** is preferably supported by a first rod holder **28** while the other end thereof is supported by a second rod holder **30**. These rod holders preferably comprise an inner collar element **32** preferably formed of segmental pieces of carbon supported inside an outer copper clamp **34**. The rod holders are preferably arranged so that there is a poor electrical contact with the carbon rod and the various elements of the holders so as to generate some heat in the holders. In the preferred embodiment shown, these holders are cooled by cooling coils **36** which are in contact with the lower part of outer clamps **34**, these cooling coils conveniently serving as one of the means to which electric current leads **38** are attached. Leads **38** are connected to a suitable source **40** of electrical energy, this source **40** being indicated as a transformer.

The aluminum **26** is preferably supplied from a wire coil **42** thereof, this wire coil being schematically indicated as being mounted upon a spindle **44** driven by a motor **46**. This motor is controlled by a control means **48** which may, for example, be a rheostat. This control means **48** is in turn preferably controlled by a current-measuring device **50** which is arranged to measure the amount of current flowing through the leads **38**, thus measuring the amount of current flowing through the rod **22** and the aluminum carried thereby.

In the operation of the device shown in Figs. 1, 1A, and 2, the roll **17** of the substrate **16** is positioned with-

in the vacuum chamber 12 and the substrate is guided around the various rolls 18 and connected to the take-up spool 19. A spool of aluminum wire 42 is positioned on the spindle 44 and one end of the wire is guided into groove 24 adjacent that end of the rod 22 which is supported by the rod holder 28. Cooling water (at about 40° F. or lower) is then circulated through rolls 18 by suitable piping (not shown) so as to chill rolls 18. The vacuum chamber 12 is then evacuated to a low pressure, on the order of one micron of mercury, by means of vacuum pumping means 14. When the requisite low pressure is achieved the substrate is advanced, preferably by driving the take-up spool 19 and the various guiding rolls 18. Current supply 40 is then energized so that a current flows through the rod 22. Since the resistance of the rod 22 is relatively high, the current-measuring device 50 will indicate a need for aluminum. This indication is transmitted to the controlling means 48, thus energizing the motor 46 and causing aluminum wire to be fed from the spool 42 along the slot 24. In a preferred method of practicing the invention that end of the rod to which the aluminum wire is fed is maintained at a temperature somewhat above the melting point of aluminum (i. e. about 700°–800° C.). However, this temperature is not sufficiently high to cause immediate melting of the aluminum wire due to the high heat conductivity thereof. This temperature is readily controlled by the amount of heat generated in the rod holder 28, due to its internal resistance, and the amount of cooling achieved by cooling coil 36 associated therewith. As the wire is advanced along groove 24 it finally reaches a point, preferably at about the left side of the holder 28, where the wire melts and the aluminum flows along the groove 24. The aluminum moves along the groove 24 by the wetting action of the aluminum on the wettable surface of the rod. As the aluminum wets the rod 22 a portion of the aluminum climbs out of the groove 24 and wets the circumference of rod 24 as indicated at 26*a* in Fig. 1A. After enough aluminum wire has been fed to the groove so that the groove is substantially completely filled with aluminum, the current flowing through the rod and the aluminum carried thereby will increase to a point where the current-measuring device 50 indicates that no further feed of aluminum is necessary in which case the controlling means 48 will prevent further feed of aluminum by stopping the motor 46.

In a preferred embodiment of the invention described above, the rod 22 preferably comprises carbon. Preferred forms of these carbon rods have a diameter of about ¼" and a groove 24 of approximately ⅛" wide by ⅛" deep. A preferred method of pretreating the rods so as to form a surface stratum which is readily wet by molten aluminum comprises the steps of preparing a slurry of zirconia (ZrO_2), coating the rod with this zirconia slurry, drying the thus coated rod for about one hour at 110° C., and then baking the coated rod at less than one micron of mercury of pressure and at a temperature of about 1450° C. for a period of about one-half hour. After baking, the loose scale on the surface of the rod is then removed, most of the zirconia having formed a surface stratum of zirconium carbide on the rod. With a rod of the above type, which is about 4" long between the supports 28 and 30, there is obtained an aluminum evaporation rate greater than about 1 gram per minute when the rod is operated at a temperature of approximately 1400° C. At such a temperature and rate of evaporation of aluminum, the substrate is preferably moved at a speed of about 100–150 linear feet per minute. The above rod, when carrying aluminum, has a voltage drop of about 2.5 volts per linear inch between the rod supports 28 and 30. With this voltage drop the current flowing through the aluminum-carrying rod is about 180 amperes, while the current flowing through the rod without aluminum is approximately 40 amperes. The rod can be brought to its operating temperature very rapidly, the time necessary being only 10–15 seconds when the applied voltage is 2.5 volts per linear inch. When the applied voltage is higher, the rod may be brought to its operating temperature in less than a second. However, in this case it is desirable to reduce the voltage to about 2.5 volts per linear inch when the operating temperature is obtained.

While the invention has been described particularly in its preferred use for the continuous coating of a flexible substrate, it is equally applicable to batch type of coating operations wherein a number of metallic or plastic objects to be coated are mounted within a vacuum coating chamber and are coated by creating an atmosphere of aluminum vapors within the vacuum chamber. In this embodiment of the invention, shown in Figs. 3, 4, 5, and 5A, there are provided a plurality of carbon rods 80, these rods preferably comprising zirconium or other carbide surface strata prepared in a manner similar to that described previously. Each of these rods is supported by rod holders 82, it being preferred that short lengths of rod of about 4–6 inches be employed. These are connected in series to give any desired length requisite for the dimensions of the coating chamber. Each of these rods is preferably provided with a groove 84 at the top thereof, these grooves being of such size as to support a plurality of aluminum pellets 86. As shown more particularly in Fig. 4, each rod 80 is supported at its ends by rod holders 82, these rod holders each comprising a pair of segmental collars 90, a yoke member 92, and a spring clamp 94 for securing the collars 90 around the rod. In the use of the device of the type shown in Figs. 3, 4, 5, and 5A, the objects to be coated are placed in the vacuum coating chamber along with the rods 80 carrying the aluminum to be evaporated. The chamber is then evacuated to the requisite low pressure and current is passed through the various rods 80 by applying a suitable voltage, on the order of 2.5 volts per linear inch, to the rods. This current, as mentioned previously, heats the rod to a high temperature on the order of 1400° C., thereby melting the aluminum pellets 86 and filling the grooves 84 with molten aluminum. In a preferred use of this embodiment of the invention, a portion of this molten aluminum, due to the wetting action thereof on the zirconium carbide surface, spreads out and covers substantially the whole outer surface of the rod 80 as indicated at 86*a* in Fig. 5A. However, where directional control of the vapors is desired, the groove 84 may be only partially filled so that evaporation of all the aluminum is achieved before any substantial wetting of the outer surface of the rod occurs.

The arrangement of elements shown in Figs. 3 through 5A thus provides a very cheap source of aluminum vapors which may be used almost indefinitely and which can be very readily loaded and reloaded with aluminum pellets. If desired, the rods 80 may be installed in the coating device with the aluminum in solid form completely or partially filling groove 84, this embodiment of the invention eliminating the necessity of loading the individual grooves with pellets prior to the coating operation. However, since the rods will last for a great number of coating operations, they may be readily refilled as soon as all of the aluminum has been evaporated therefrom.

While one preferred type of rod 22 has been described in connection with the various embodiments of the invention, other forms thereof may be employed. For example, the rod 22 may comprise an extruded cemented titanium carbide sintered with cobalt. Additionally, other materials of the type described in the Godley et al. application, Serial No. 158,494, filed April 27, 1950, now Patent No. 2,665,226, granted January 5, 1954, may be used in forming the rods 22.

In one preferred method of forming a wettable carbide surface on the carbon rod 22, a molten bath of aluminum and a group IV*a* or group V*a* metal, for example zirconium, is maintained in a vacuum. While in this vacuum the rod, whose surface is to be formed into a carbide, is dipped into this molten bath, thereby converting the surface of the rod to the desired zirconium carbide.

Equally other methods of feeding aluminum to the rods may be employed as illustrated in the above Godley et al. application. Similarly, resistance measurements may be made of the coated web as it travels through the coating chamber, these resistance measurements being used to control the rate of speed of the web or the temperature of the rods and the aluminum thereon.

The expression "group IV*a* and group V*a* metals" is intended to include those metals in groups IV*a* and V*a* on the "Periodic Chart of the Atoms," Henry D. Hubbard, 1947 edition, W. M. Welch Manufacturing Company. These metals are titanium, zirconium, hafnium, vanadium, columbium, and tantalum.

Since certain changes may be made in the above product and process 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 drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of forming an elongated carbon wick element which is relatively inert to aluminum at temperatures on the order of 1300° C., the process comprising the steps of forming an elongated groove in said element along the surface thereof, coating said elongated carbon element with an oxide of a metal taken from the class consisting of titanium, zirconium, hafnium, vanadium, columbium, and tantalum, said oxide being reducible by carbon at temperatures on the order of about 1400° C., baking the coated element at a pressure less than one micron Hg abs. and at a temperature of about 1400° C. to convert only a surface stratum of said element to the corresponding metal carbide while retaining the interior of said wick element as elemental carbon with a relatively higher electrical resistance than the surface of said element.

2. The process of forming a wick element which is relatively inert to aluminum at temperatures on the order of 1300° C. which comprises coating an elongated carbon rod with a slurry of an oxide of a metal taken from the class consisting of titanium, zirconium, hafnium, vanadium, columbium, and tantalum, said oxide being reducible by carbon at temperatures on the order of about 1400° C., drying said slurry-coated rod, baking the slurry-coated rod under reduced pressure at a temperature of about 1400° C. to convert only a surface stratum of said rod to the corresponding metal carbide, said pressure being reduced to less than 1 micron Hg abs. during at least some portion of the baking operation to degas the rod, and removing excess of said oxide from the carbide-coated, gas-free rod.

3. A wick element for evaporating aluminum in a vapor deposition device, said wick element being wettable by molten aluminum, being relatively inert to molten aluminum and comprising an elongated rod whose surface layer consists essentially of a carbide of a metal taken from the class consisting of titanium, zirconium, hafnium, vanadium, columbium, and tantalum, the interior of said rod consisting of elemental carbon and having a relatively higher electrical resistance than the surface of the rod, said rod being essentially free of all volatiles having a vapor pressure greater than about 1 micron Hg abs. at a temperature above about 1400° C. in order to provide an essentially gas-free rod, the surface of said rod being essentially free of gas-producing oxides of said carbide-forming metals.

4. The wick element of claim 3 wherein said carbide comprises zirconium carbide.

5. The wick element of claim 3 wherein said carbide comprises titanium carbide.

6. The wick element of claim 3 wherein said carbide comprises tantalum carbide.

7. The wick element of claim 3 wherein said carbide comprises vanadium carbide.

8. The wick element of claim 3 wherein said carbide comprises columbium carbide.

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