

[54] **REFRACTORY METAL PHOSPHATE AND PHOSPHIDE COATINGS FOR REFRACTORY METAL LEADS AND PROCESS FOR PRODUCING METAL PHOSPHIDES**

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Related U.S. Application Data

[60] Division of Ser. No. 3,937, Jan. 19, 1970, which is a continuation-in-part of Ser. No. 647,106, June 19, 1967, abandoned.

[52] U.S. Cl. **117/201**, 117/106 R, 117/231, 313/345

[51] Int. Cl. **C23c 11/00**, H01j 1/88

[58] Field of Search 117/201, 231, 106 R, 107.2; 313/345

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[57] **ABSTRACT**

Lamps operating at high temperatures, and more particularly incandescent or arc lamps having sealed-in lead-in electrical conductors with improved service characteristics and longer service life are fabricated with a "coating" on the aforesaid leads comprising at least one of the following: a phosphate or phosphide of tungsten, or a phosphate or phosphide of molybdenum.

Illustrative of the results obtained upon service testing 400-W, 120-V quartz-iodine lamps, at operating temperatures of 500°-600° C., using

A. untreated, uncoated, molybdenum electrode assemblies,

B. platinum-clad, molybdenum electrode assemblies (exemplary of the prior-art techniques), and

C. tungsten phosphate-coated molybdenum electrode assemblies,

are as follows:

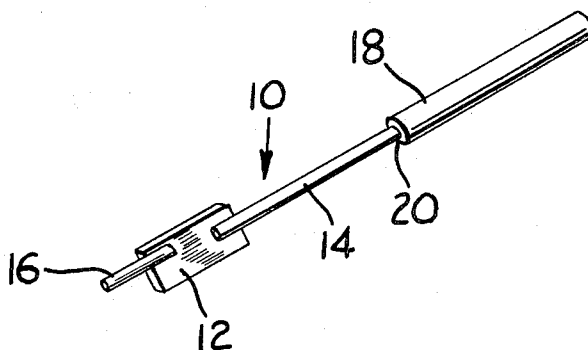
A. failed through oxidation and subsequent disintegration, with accompanying seal and lamp failure at 100 hours' operation,

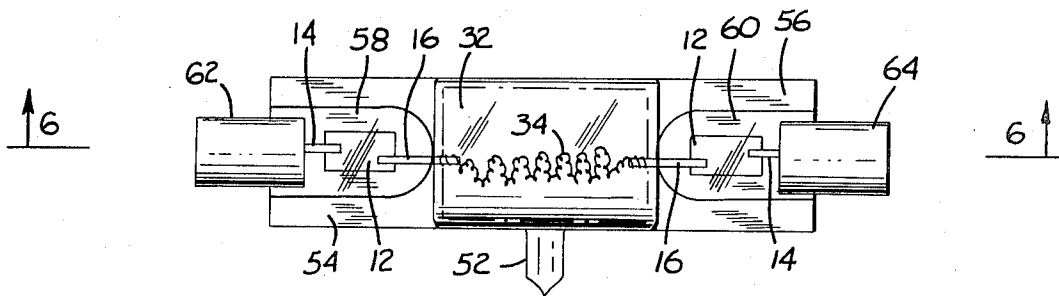
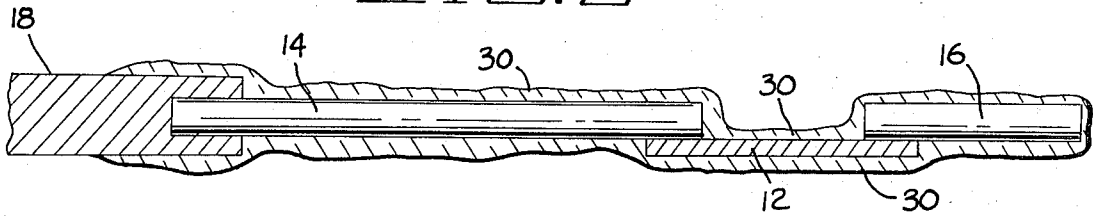
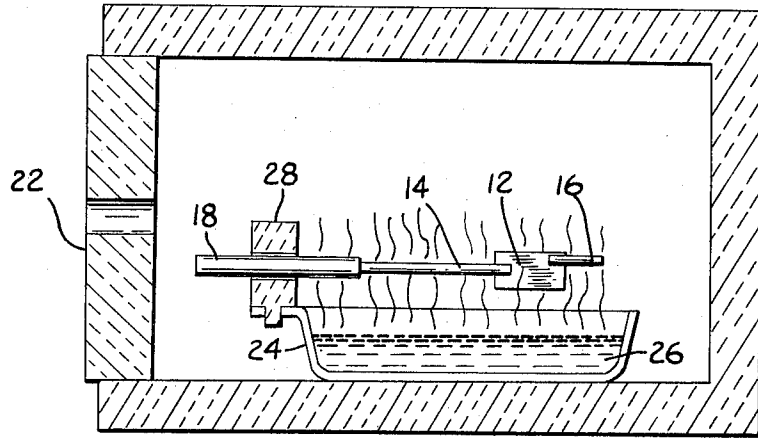
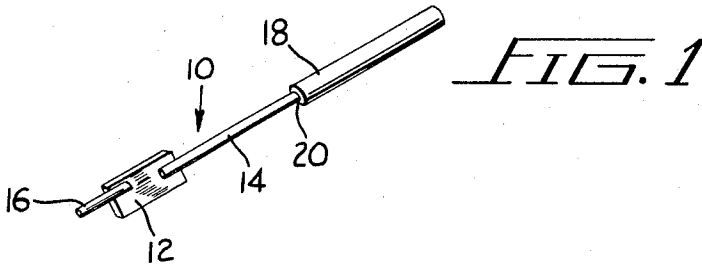
B. failed at approximately 150 hours of life testing,

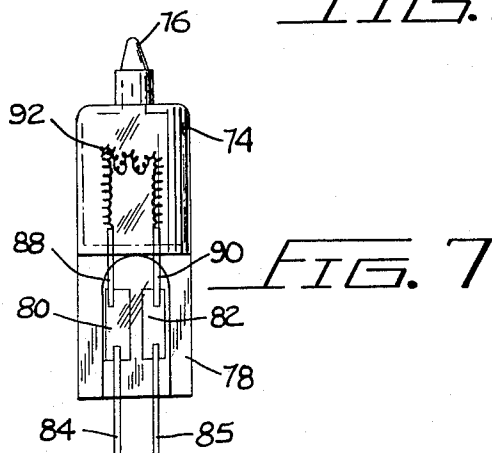
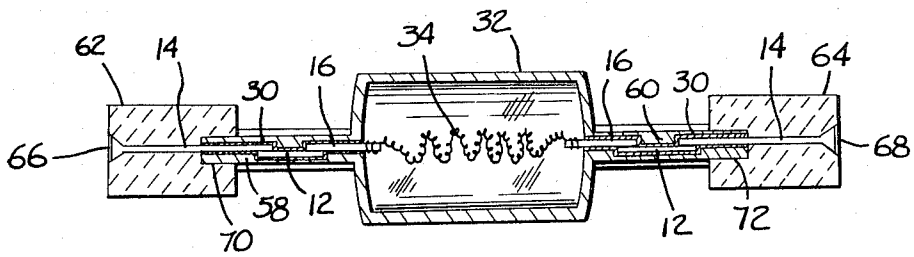
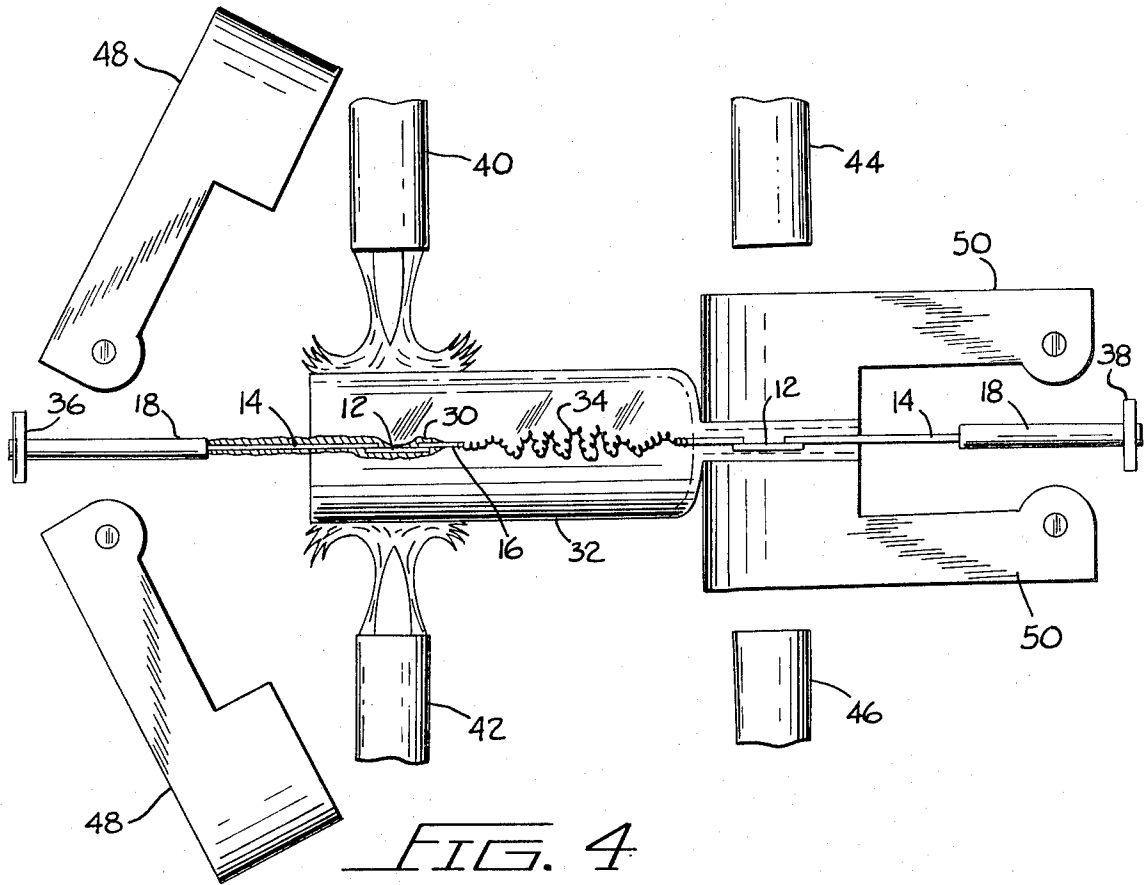
C. was still operating on a life test after 200 hours.

Processes for forming metal phosphides from metal phosphates and process for coating leads with refractory metal phosphates and phosphides are also disclosed.

6 Claims, 7 Drawing Figures







REFRACTORY METAL PHOSPHATE AND PHOSPHIDE COATINGS FOR REFRACTORY METAL LEADS AND PROCESS FOR PRODUCING METAL PHOSPHIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of Ser. No. 3,937, filed Jan. 19, 1970, which is a continuation-in-part of our application Ser. No. 647,106, filed June 19, 1967, now abandoned, which is assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

This invention relates broadly to electrical devices, e.g., lamps, operating at high temperatures; and especially to such lamps comprising a sealed bulb or envelope made of a high temperature-resisting vitreous substance and which contain an electric energy translation means. The scope of the invention includes both method and article features. The invention further relates to a process for manufacturing metal phosphides specifically, tungsten, molybdenum and gallium phosphides.

The invention is especially concerned with incandescent or arc lamps having sealed-in leads or lead-ins, i.e., electrical conductors made of highly refractory metal that are capable of withstanding the fusion temperature of the aforesaid vitreous substance, and which are sealed in a highly refractory insulating material, e.g., fused quartz or other fused silica compositions containing about 95-96 percent, or more, of silica. Still more particularly the invention is concerned with the lead-in wire and seal construction of such lamps or other electrical devices.

Certain incandescent and high-pressure arc lamps operate with very hot envelopes since they have very high wattage ratings per unit of volume. There has long been a problem in connection with the leads that pass through the seals of such high-temperature lamps. So-called "quartz-iodine" lamps, which are exemplary of improved electrical devices of the instant invention, typically have molybdenum leads (lead-ins) comprised of a molybdenum foil having fixedly attached thereto a molybdenum wire (or rod) passing through a pressed quartz seal. In making such lamps the quartz tube is pressed and sealed to the molybdenum foil and wire at temperatures that may reach as high as 1,500° C. In lamp-manufacturing practice, the molybdenum foil and wire are at least partially exposed to air, resulting in formation of molybdenum oxide which, in turn, causes or tends to cause cracking of the quartz and deterioration of the seal. During operation, the temperature reached by the leads as they exit from the seals may be as high as 500° C. or even higher in some cases. Thus it is seen that the leads are exposed to high temperatures not only during manufacture of the lamp but also to a relatively high temperature during service use.

In an attempt to solve the problem and to obviate or minimize the above-described difficulties, platinum rod or platinum-clad molybdenum rods have been used and are still being used in the construction of leads for lamps operating at high temperatures and/or wherein high temperatures are encountered during lamp manufacture. However, the high cost of platinum and the difference in its coefficient of linear thermal expansion as compared with molybdenum (the said co-efficient for

platinum being approximately twice that of molybdenum) have been drawbacks to the more extensive use of platinum or platinum-clad molybdenum rods in the fabrication of leads. Furthermore, the properties of platinum are such that it has certain inherent disadvantages in such applications; for one reason because its use results in higher operating temperatures due to its higher electrical resistivity, and for another reason because of its relatively poorer heat-conduction as compared with, for example, molybdenum.

Although pressed quartz seals with sealed-in molybdenum leads for high-temperature lamps can be and are being made, such seals are troublesome to manufacture in that it is difficult to maintain oxygen-free conditions during manufacture and it is difficult to prevent formation of oxides during sealing. Another difficulty arises in obtaining a seal that is bubble-free in the area of the molybdenum foil and rod. The gas bubbles, presumably air, are a potential source of leaks and/or oxidation (more particularly, oxidation of the molybdenum lead) that eventually lead to a failure of the seal.

Furthermore, the leads operate at such a high temperature during service use of a high-temperature lamp that, unless effectively protected against oxidation, they oxidize slowly. Since molybdenum oxides do not form a protective layer on the leads, the seal deteriorates and eventually fails with the result that the lamp is destroyed.

The phosphides of W, Mo and Ga in particular and refractory metal and/or semi-conductor phosphides in general are usually prepared by one of the following two methods:

1. The metal powder and phosphors are mixed in various proportions, and heated in evacuated and sealed tubes. Heating times are generally varied between 1 hour to 1 month with temperatures between from 550° C. to 1,100° C. The best results are usually obtained with a uniform temperature rise from room temperature up to about 800° C. for about 2 days, then cooling to room temperature over a period of about an additional day.

2. Hydrogen phosphine, PH_3 , generally obtained from white phosphorus and potassium hydroxide solution, is dried and passed together with dry, oxygen-free hydrogen, over the desired metal powder which is heated in an electric furnace. Temperatures are maintained between 700°-900° C. for about 2-10 hours to thereby obtain the metal phosphide.

Disadvantages of The Old Methods

All of the preparations reported in the literature have at least some of the following disadvantages.

1. Because of the high vapor pressure of phosphorus at elevated temperature, explosions of the silica tubes are liable to take place at high temperatures.

2. The time required for preparation is commercially impractical since up to two days time is generally required.

3. PH_3 , one of the raw materials in one of the processes, is difficult and hazardous to use on larger-than-laboratory scale.

4. The products generally contain mixtures of mono-di and sub-phosphides and therefore require further purification.

OBJECTS AND SUMMARY OF THE INVENTION

It is a primary object of the present invention to pro-

vide "high-temperature" electrical devices (i.e., electrical devices which normally operate at high temperatures) including electric incandescent or arc lamps that are provided with leads (inlet and outlet leads), e.g., leads of molybdenum, tungsten, and alloys thereof with each other or with other refractory metals, having thereon an effective and inexpensive protective "coating" (hereafter more fully described and defined) that is easy to apply and/or form in situ.

Another object of the invention is to fabricate such devices wherein the leads are provided with a coating that will strengthen the bond between the refractory metal lead and the refractory vitreous substance, e.g., fused quartz or silica glass of high silica content.

Still another object of the invention is to provide high-temperature electrical devices that have a longer service life as a result of having sealed-in leads wherein the seal is more resistant to deterioration than conventional seals employed for this purpose.

A specific object of the invention is to provide a practical, improved method for making tungsten phosphide, molybdenum phosphide and gallium phosphide.

Another object is to provide a commercially feasible process for making metal phosphides, particularly refractory metal phosphides and semiconductor phosphides from oxides.

Another object of the process is to provide the metal phosphides by a method which by-passes direct reaction of phosphorus and metal under conditions involving long reaction periods, high pressures, sealed tubes and/or high temperatures.

Other objects of the invention will be apparent to those skilled in the art from the following more detailed description and from the appended claims.

The objects of the invention are attained by providing the refractory, electrically conducting, metallic leads of electrical devices operating at high temperatures, especially electrical incandescent lamps having molybdenum and/or tungsten leads and connections in wire, rod, foil or other form, with a particular inorganic compound of phosphorus and either tungsten or molybdenum (i.e., tungsten or molybdenum phosphides); or an inorganic compound of phosphorus, oxygen and either tungsten or molybdenum (i.e., either tungsten or molybdenum phosphates); or mixtures of the aforesaid inorganic compounds in any proportions.

The present invention is based on our discovery that coatings of molybdenum or tungsten phosphate glasses, as well as molybdenum or tungsten phosphides adhere firmly to surfaces of refractory metals such as molybdenum and tungsten, e.g., in wire, foil or other form, and protect them from oxidation in air up to temperatures of approximately 800° C. over long periods of time and up to approximately 1,200° C. for periods of minutes. In addition, such coatings dissolve the oxides of molybdenum and tungsten, thus serving as a flux to create clean, wettable metal surfaces for bonding; and, at the same time, they are completely wettable by the silica and silicates of which the lamp envelopes are formed, thereby facilitating the formation of sound press seals.

We have found that refractory metal and semiconductor metal phosphides can be produced in essentially pure form by a process comprising forming a solution of the desired metal cation, either in elemental metal form or as the metal oxide, and orthophosphoric acid, H_3PO_4 , heating the resulting solution to form the metal

phosphate and to remove the water present and followed by the reduction of the metal phosphate by heating in a hydrogen atmosphere under controlled temperature conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel features that are characteristic of the invention are set forth in the appended claims. The invention will best be understood from the following more detailed description especially when considered in connection with the accompanying drawing wherein

FIGS. 1 through 6 illustrate somewhat schematically the fabrication of an incandescent lamp wherein the electrically conducting leads have been sealed in position using the above-described coating material thereby to obtain one form of the improved lamp of the invention; and

FIG. 7 is a view of a different form of such a lamp.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The general method of fabricating the lamps with which this invention is concerned, e.g., incandescent lamps having a generally tubular shape and having within the envelope thereof an incandescible filament of a coiled electrical conductor such as tungsten or an alloy thereof, can be carried out in accordance with known means of making such lamps in substantially all aspects with the exception of the coating of the electrode assembly including the leads. Thus, when it is necessary to seal a longitudinally supported, extending tungsten filament through both ends of a light-transmitting glass envelope and fill the envelope with an inert gas to retard the vaporization of the tungsten during subsequent illumination, one means in common use is essentially as follows: First the support filament is press-sealed through one end of the envelope while the other end is temporarily plugged and while an inert gas is flowing into the envelope through a centrally appended exhaust tube. While continuing the flow of inert gas through the exhaust tube, the plug is removed, the other end of the envelope is press-sealed and the exhaust tube then tipped off, thus sealing the lamp from the atmosphere and providing a filling of inert gas. The method provides an inert fill gas within the sealed lamp at a pressure of approximately 1 atmosphere.

Lamps constituting an embodiment of the instant invention also can be fabricated using the technique of the invention disclosed and/or claimed in Gustin U.S. Pat. No. 3,162,499 dated Dec. 22, 1964, and assigned to the same assignee as the present invention, and which by this cross-reference is made a part of the disclosure of the instant application.

Referring now to the drawing, wherein the same numbers have been given to the same elements in the different views, there is shown by way of illustration in FIG. 1 a perspective view of a sub-assembly, specifically an electrode assembly, 10 comprised of a foil of refractory, electrically conducting metal 12, e.g., molybdenum. At one end of the foil is a lead wire or rod 14 made, for example, of molybdenum, which is platinum-brazed to the said foil. A wire or rod 16 made, for instance, of tungsten, is similarly fixedly attached by platinum brazing to the other end of the foil. The larger rod 18 which is rigidly fastened, e.g., by brazing, to the

other end of the lead 14 to form the joint 20 is used for convenience in handling the work, and may be made of any suitable metal, e.g., nickel. It is later cut off from the assembly.

The inorganic phosphorus-containing compounds used in making the seals for the leads of the high temperature-operable lamps of this invention are solids at normal temperatures. They can be volatilized and deposited on the work to be coated by so-called "vapor-deposition," which is the preferred technique employed in fabricating the quartz-iodine type and other lamps of this invention.

FIG. 2 is a view, partly in section, illustrating the application of the inorganic coating material to the electrode assembly shown in FIG. 1. For ease in description, in both this figure and in subsequent figures, tungsten phosphate will be taken as exemplary of the phosphorus-containing compound employed. The inorganic phosphate (e.g., tungsten or molybdenum phosphate) may be in the form of a granular solid or in liquid state, e.g., a concentrated syrupy aqueous solution.

Any suitable means for heating the metal phosphate, specifically tungsten phosphate, to its vaporization temperature can be employed. Thus the heating means may take the form of the furnace 22, e.g., an electric furnace, in which is placed the vessel or boat 24 containing tungsten phosphate 26 in molten state, as shown, at operating temperature. The vessel 24 may be constructed of, for example, platinum, fused quartz, high-temperature-resistant silica compositions of high silica content such as Vycor, and the like. Any suitable support is provided, e.g., the support indicated at 28, for holding the assembly 10 in the proper position in the furnace above the molten tungsten phosphate so that the evolved vapors (indicated by the wavy lines) will condense and be substantially uniformly deposited upon the said assembly. The tungsten phosphate is conveniently heated in a non-reducing atmosphere, e.g., air, at a temperature within the range of from about 900° C. to about 1,150° C. in order that the desired thin coating will be deposited most effectively.

FIG. 3 is an enlarged view, partly in section, of a portion of the assembly 10 after it has received the treatment illustrated in FIG. 2 and showing, greatly exaggerated, the solid coating 30 of glassy, phosphorus-containing compound in side section. The composition of this coating may be either a refractory metal phosphate or phosphide, or a mixture of a phosphate and a phosphide in any proportions, more particularly at least one member of the group consisting of tungsten phosphate, tungsten phosphide, molybdenum phosphate and molybdenum phosphide. The phosphides, alone or admixed with the corresponding phosphate, are produced in situ by treating the coated assembly, having thereon the corresponding phosphate coating, in a reducing atmosphere, e.g., an atmosphere of hydrogen (H₂), at a temperature within the range of from about 700° C. to about 1,100° C.

FIG. 4 illustrates the formation of the seal showing, at one end, the seal of the lamp as having been made and, at the other end, preheating of the end of the envelope 32 prior to making the seal.

The lamp sub-assembly shown in FIG. 4 is comprised of two of the electrode assemblies 10 illustrated in FIG. 1 with the leads 16 pointing toward but spaced from each other and with the intervening coiled filamentary wire 34 of refractory metal, specifically tungsten, con-

nected to the facing ends of the said leads; or, the leads 16 may be end legs of the coiled wire 34. Any suitable means, e.g., supports 36 and 38, can be used to support the sub-assembly for the lamp after it has been inserted in the envelope 32 prior to press sealing the ends of the latter.

In the fabrication of lamps wherein the coiled filamentary wire 34 is considerably elongated, for instance several inches or more in length, small spacers of refractory metal, generally tantalum, are positioned about the wire along its length to prevent sagging during the life of the lamp. When the wire 34 is relatively short or when non-sag wire is used, such spacers may be eliminated as has been done in the case of the fabrication of the lamps illustrated in the drawing of this case.

With further reference to FIG. 4, the burners 40, 42, 44 and 46, together with other similar burners (not shown) if and when required, provide means for heating the ends of the tubular envelope 32 in order to soften the fused quartz, high silica glass, or other heat-resistant vitreous substance of which the envelope may be composed, prior to pressure-sealing the said ends. The envelope 32 is clamped within clamps (not shown) of a pressure-sealing machine. When the envelope with the aforementioned sub-assembly therein is in proper position within the two pairs of press sealers 48 and 50 (shown in open position at the left and in the closed position at the right of FIG. 4) flames from the burners (as illustrated with respect to the flames from burners 40 and 42 only) are directed at the open ends of the envelope to soften the glass. When the glass is sufficiently soft, the press sealers are closed and then re-opened in accordance with conventional glass-sealing techniques.

As shown best in FIGS. 5 and 6, when the press seals are made the pressure-sealing machine forms the raised edges 54 and 56, and the depressed sections 58 and 60.

Filling of the envelope with an inert fill gas is effected in known manner, for instance as briefly described hereinbefore or as disclosed in the aforementioned Gustin U.S. Pat. No. 3,162,499. After filling, the exhaust tube is sealed, as is illustrated at 52 in FIG. 5 wherein the exhaust tube is shown as having been tipped off, thus sealing the lamp from the atmosphere and providing a filling of inert gas. Examples of inert fill gases that are suitable for use in the high temperature-operable lamps of the kind with which this invention is concerned are argon, helium, neon, xenon and krypton; also, certain other gases that are inert or non-reactive with the filament or associated metal parts, e.g., nitrogen. Gasified halogens, e.g., iodine, bromine, or mixtures of iodine (or bromine) and nitrogen, also can be used.

Referring again to FIGS. 5 and 6, these figures show a lamp, which has been fabricated as hereinbefore described with reference to FIGS. 1 through 4, provided at its end with tubular, end-cap connectors 62 and 64 through which leads 14 pass to terminals 66 and 68 for connection with a source of electrical energy.

The end-cap connectors 62 and 64 can be formed of any of a wide variety of electrically insulating materials that can be molded, have adequate mechanical strength in molded form, and which are capable of withstanding temperatures above 500° C. for prolonged periods of time without deterioration. Hence, mainly

because of these temperature-resisting requirements, inorganic insulators are normally employed. Examples of such insulating materials are the various ceramic, electrically insulating substances such as thoria, magnesia, zirconia, beryllia, alumina, silica and titania, combinations of the foregoing in varying proportions; and ceramic materials in which heat-resisting oxides such as the foregoing predominate and which otherwise meet the physical and electrically insulating requirements in the electrical devices with which this invention is concerned.

Referring particularly to FIG. 6, which is a sectional view taken along the line indicated at 6—6 in FIG. 5, it will be noted that the connectors 62 and 64 are slotted to form the slots 70 and 72 into which the ends of the depressed sections 58 and 60 of the lamp are, respectively, fitted. The fit is made so that the leads 14 pass through the central opening in each of the aforesaid connectors to the terminals 66 and 68. The connectors are fixedly sealed in position by any suitable means. For example, the insulated connectors 62 and 64 can be connected to the depressed sections 58 and 60 of the pressed seal using a liquid porcelain cement, more particularly Sauereisen liquid porcelain cement, as the bonding agent. The Sauereisen cement is applied to the surface of either the insulated member or the pressed seal member at the area of bonding, and the members are fitted together. Bonding is completed by force-drying the assembly at a temperature of about 150° F. for a period of up to 24 hours, followed by baking at a temperature up to about 300° C. or higher to obtain thorough drying and hardening of the cement.

FIG. 7 is illustrative of another type of high-temperature lamp that can be made with leads sealed in position in accordance with the present invention. It is comprised of a bulb or envelope 74 having a sealed exhaust tube 76 at one end and a press-sealed opposite end that forms the seal 78. This seal is made in essentially the same manner hereinbefore described with reference to the sealing of one of the ends of the lamp illustrated in FIGS. 4, 5 and 6. The materials of construction of the electrode assembly and the prior coating of the said assembly with a tungsten or molybdenum phosphate or phosphide are the same as have been broadly and specifically described hereinbefore with reference to the other figures of the drawing.

For example, the electrode assembly shown in FIG. 7 includes the molybdenum foils 80 and 82. At the lower end of the seal and extending through said seal to an end-cap connector (not shown) are the molybdenum leads 84 and 86, which are platinum brazed to the aforesaid foils. Platinum brazed to the other ends of the individual foils are the tungsten wires or rods 88 and 90. Each end of the helically coiled filamentary wire 92 positioned within the envelope 74 is fixedly attached to the wires 88 and 90; or the latter may be end legs of coiled wire 92 having a diameter and stiffness such as will provide support for the said coiled wire, especially after the seal 78 has been made.

The invention is, of course, not limited to coating of the parts to be coated by vapor deposition of the phosphorus-containing compound, since other methods can be employed. Thus, a tungsten phosphate with an atom ratio of tungsten to phosphorus of, for example, 1 to 8 can first be prepared by dissolving 1 mole of tungsten trioxide (WO_3) in 8 moles of orthophosphoric acid

(H_3PO_4). There is formed a glass which, upon cooling, is broken up and dissolved in water, using 50 g. of tungsten phosphate per 100 ml. of water. The solution is concentrated by evaporation to a syrupy consistency. A tungsten, molybdenum or other refractory metal wire or the like to be coated is passed through the solution, heated successively for 15 minutes first at 400° C. and then at 1,000° C. The wire is then used for leads in incandescent lamps of the kind with which this invention is concerned. Tungsten phosphate glasses can similarly be made containing other ratios of tungsten to phosphorus, for example, W:P atom ratios of from 1:5.9 to 1:9. Optimum results are usually obtained when the W:P atom ratio is within the range of from 1:7 to 1:8, and still more particularly a W:P atom ratio of 1:7.6.

Instead of tungsten phosphate, one can apply molybdenum phosphate as a coating in the manner described in the preceding paragraph using, for example, molybdenum phosphate glasses wherein the atom ratios of Mo:P are within the range of from 1:5 to 1:10. Wires, foils and the like also can be coated by vapor deposition with molybdenum phosphate by passing the refractory metal to be coated over the hot, molten molybdenum phosphate glass at 1,000° C. In this way a thin coating is applied to the metal. Thin coatings are preferred in order to provide a coating having optimum adhesion and flexibility, and from a cost standpoint.

Furthermore, it is not necessary that the phosphorus-containing compounds, specifically tungsten phosphate and molybdenum phosphate, be separately prepared prior to application to the refractory material to be coated. For example, such phosphates can be prepared directly on the metal, i.e., in situ, by exposing the respective metal, viz., tungsten or molybdenum, to the vapors of P_2O_5 generated when orthophosphoric acid and/or metaphosphoric acid is heated to temperatures within the range of from about 700° C. to about 1,000° C.

The improvement attained by the incandescent lamps of this invention over lamps which are otherwise the same with the exception that the conductor leads are not coated in accordance with the present invention is exemplified by the following comparative results:

Quartz-iodine lamps (400 watt, 120 volt) were constructed in accordance with the general procedure hereinbefore described, using (A) untreated, uncoated, molybdenum electrode assemblies; (B) platinum-clad molybdenum electrode assemblies; and (C) tungsten phosphate-coated molybdenum electrode assemblies. The temperature of the electrode assemblies during operation ranged from 500° to 600° C. On life testing, the uncoated assemblies (A) failed through oxidation and subsequent disintegration, with accompanying seal and lamp failure, at 100 hours' operation. The platinum-clad electrode assemblies (B) failed at approximately 150 hours of life. The tungsten phosphate-coated electrode assemblies were still on the life test after 200 hours of operation.

It will be understood by those skilled in the art that the present invention is not limited to the fabrication of the specific lamps described herein and in the accompanying drawing, or to those lamps, modified in accordance with this invention, that are described in Gustin Pat. No. 3,162,499 to which cross-reference previously has been made. For example, lamps embodying the in-

stant invention can be made by the general procedure otherwise described in such prior-art patents as, for example, U.S. Pat. Nos. 2,667,595; 2,883,571; 3,211,511; 3,211,950, 3,259,778; and 3,170,081.

The coating materials employed in making the improved lamps of the instant invention as a result of the improved seals that are obtained also may be used in making various other seals between a ceramic or ceramic-like material (including high-melting glass and glass-like) materials on the one hand and metals, especially refractory metals such as tungsten, molybdenum and alloys of tungsten and of molybdenum, on the other hand. Such seals may be made and form an essential and critical part of various electrical and other devices used in commercial industry, and in aviation, aerospace and other applications. Thus, the phosphorus-containing materials used in practicing this invention may be employed in making seals, for coatings and in other uses where the parts to be sealed, coated or otherwise modified are exposed to temperatures as high as about 1,500° C. for a brief period of time during sealing, coating or the like, and which are subjected to operating temperatures of the order of 500° C. or somewhat above for a longer period of time.

The terms "coating," "coatings," "coating material" and "coated" as used hereinbefore and/or in the appended claims with reference to at least one substance of the group (A) consisting of tungsten phosphate, tungsten phosphide, molybdenum phosphate and molybdenum phosphide are used both generically and specifically herein. When the aforementioned terms are used specifically the common or dictionary definitions of these words, or as they are ordinarily understood by those skilled in the surface-covering, surface-protective and related arts, is intended.

When employed generically the aforementioned terms include within their meanings not only the common or dictionary definitions of these words, or as they are ordinarily understood by those skilled in the surface-covering, surface-protective and related arts, but they also include the uniform or non-uniform, regular or irregular stratum or strata, or other arrangement, of any solid material that results (e.g., due to heat, pressure, both heat and pressure, or other effect agents or means), separately or concurrently, from one or more or all of the following:

- a. decomposition or degradation of the chosen member(s) of the aforesaid group A;
- b. interaction between different decomposition or degradation products resulting from (a);
- c. reaction between individual members of the aforesaid group A when two or more such members are initially present;
- d. reaction of the chosen member(s) of the aforesaid group A with, and/or diffusion into, the material or materials (e.g., refractory metals, ceramics, glasses including fused quartz, and the like) to be protectively covered or bonded, joined or sealed together; and
- e. reaction of the products resulting from (a), (b) and/or (c) with, and/or diffusion into, the material or materials to be protectively covered or bonded, joined or sealed together.

The aforementioned terms (including their derivatives and grammatical variations) are used and have been defined generically herein because the applicants are presently unable to state with certainty the exact

physical and/or chemical reactions that take place in the course of the formation of (a) the ultimate surface material developed on a substrate or (b) the ultimate sealing component in a bond between two adjacent materials, e.g., between molybdenum or tungsten and fused quartz. In view of the high temperatures involved in manufacturing lamps of the kind with which this invention is concerned, for instance when sealing in the lead-in conductors within the sealed end or ends of a light-transmitting envelope of fused quartz or the like, it is entirely possible and in some cases probable that one or more of the actions set forth in (a) through (e), supra, in the preceding paragraph occur when a tungsten or molybdenum phosphate or phosphide, or a plurality thereof, comprises or constitutes the starting material employed in effecting the desired seal or in protectively surfacing a refractory metal or other substrate.

As previously mentioned the metal phosphides are prepared by a process wherein a solution or orthophosphoric acid and an appropriate metal source is formed and is thereafter heated under controlled conditions to form the corresponding metal phosphate and the phosphate is further reduced to the phosphide by reduction under a hydrogen atmosphere under controlled temperature conditions.

Although, in general, all refractory metal phosphides and semiconductor metal phosphides can be prepared by the process of this invention, tungsten and molybdenum phosphides and gallium phosphides are the preferred products. The source of these metals can be the elemental metals or their respective oxides. Orthophosphoric acid has the formula H_3PO_4 , and in pure form is a solid that melts at about 39° C to form a syrupy liquid. In most instances, pure H_3PO_4 will not be used and acids containing from about 85% to about 98% by weight are preferred. Lower concentrations tend to contain excessive water that has to be removed, therefore, are not generally preferred. Higher concentration, that is, above 98% H_3PO_4 , can be used; however, viscosity problems can result, therefore, are not used with standard equipment.

After the solution of orthophosphoric acid and the appropriate metal source is formed, the solution is heated to drive off the water that is present or is formed from the reactions between the metal source and the acid. Heating is continued at elevated temperatures, that is, up to about 900° C to insure all the metal source has been converted to metal phosphate. Generally, about 30 minutes at 900° C is sufficient to insure conversion to the metal phosphate that are solids.

The solid phosphates are thereafter heated at temperatures of between about 700° C to about 1,100° C for at least about 3 hours and under a hydrogen atmosphere thereby reducing the phosphates to phosphides. The materials thus produced are pure phosphides, as determined by X-ray and chemical analysis.

To more fully illustrate the process of this invention wherein metal phosphides are produced the following detailed examples are presented. All parts, proportions and percentages are by weight unless otherwise indicated.

EXAMPLE 1

About 1.8 parts of tungstic acid is mixed with 4.9 parts of phosphoric acid 98%, in a suitable container. The slurry is heated slowly with agitation and with an

accompanying loss of water until the temperature reaches about 520°–550° C. Care is exercised to prevent the solution from boiling over until a temperature of about 400° C has been reached. At this temperature the reaction becomes mild. The temperature is then increased to about 900° C and held for about 30 minutes. This completes the dissolution of oxide and the formation of metal phosphate. The deep blue liquid is poured, while still hot, onto a cold surface where it solidifies. After cooling the glassy tungsten phosphide is crushed. The product is typically an amorphous composition of WO_3 and P_2O_5 .

The crushed tungsten phosphide is heated in a tube furnace to about 700°–900° C while hydrogen at a flow of about 8–10 cu. ft./hr. is passed over it. The reaction stops in about 3 hours, and the furnace is cooled while allowing the hydrogen to continue flowing. After cooling to room temperature, a black powdered product is recovered. The black material is identified by X-ray analysis as pure tungsten phosphide. Actual chemical analysis shows that the product contains about 85.12% W and 14.19% P. The theoretical value of tungsten phosphide is about 85.62% W and 14.37% P.

EXAMPLE 2

A mixture of about 160 parts of molybdenum trioxide with about 730 parts of 98% orthophosphoric acid is prepared. The same procedure as in Example 1 is followed. The chemical analysis of the product shows about 75.1% Mo and 24.2% P compared with theoretical of about 75.59% Mo and 24.40% P. The product is identified by X-ray diffraction as being molybdenum phosphide.

EXAMPLE 3

About 1 part of gallium is dissolved in about 25 parts of 85% orthophosphoric acid. The solution is heated slowly to about 100° C until all reactivity had stopped. During the heating, about 12 parts of H_3PO_4 is added to prevent the formation of a heavy syrup through a loss of H_2O . On continued heating a white precipitate is formed in the solution. After cooling to about 40° C resulting solution is diluted with about 100 parts of water. The white precipitate is removed by filtration and washed with water. After drying, the washed solid is transferred to a silica boat and reduced in a tube furnace with a hydrogen flow as in Example 1. After about 3 hours at 900° C an orange powder remains in the boat. The material is allowed to cool under a flow of hydrogen. The material turned yellow. The color change of the material is reversible at about 50° C.

When the material is heated to about 50° to about 500° C, it is orange and below about 50° C it is yellow. The material is identified by X-ray diffraction as gallium phosphide.

While there has been shown and described what is at present considered the preferred embodiment of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A process for coating a refractory, electrically conducting metallic lead selected from tungsten and molybdenum, and wherein said coating is tungsten phosphide or molybdenum phosphide, said process comprising:

1. heating a phosphate selected from the group consisting of tungsten phosphate and molybdenum phosphate in a non-reducing atmosphere and to a temperature sufficient to melt said phosphate;

2. passing said leads of refractory metal over said molten phosphate;

3. condensing vapors of said phosphate on the surface of said lead, to provide a substantially uniform coating on said surface.

2. A process according to claim 1 wherein said coating is tungsten phosphate.

3. A process according to claim 1 wherein said coating is molybdenum phosphate.

4. A process for coating a refractory, electrically conducting metallic lead selected from tungsten and molybdenum, and wherein said coating is tungsten phosphide or molybdenum phosphide, said process comprising:

a. heating a phosphate selected from the group consisting of tungsten phosphate and molybdenum phosphate in a non-reducing atmosphere and to a temperature sufficient to melt said phosphate;

b. passing said leads of refractory metal over said molten phosphate;

c. condensing vapors of said phosphate on the surface of said lead, to provide a substantially uniform coating on said surface; and

d. heating the resulting lead in a reducing atmosphere at a temperature of from about 700° C to about 1,000° C for at least about 3 hours.

5. A process according to claim 4 wherein said coating is tungsten phosphide.

6. A process according to claim 4 wherein said coating is molybdenum phosphide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,798,058 Dated March 19, 1974

Inventor(s) Vincent Chiola, James S. Smith and Clarence D. Vander-
pool

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

At beginning of patent, please insert -- [73] Assignee:

GTE Sylvania Incorporated, a corporation of
Delaware --.

Signed and sealed this 24th day of September 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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