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PREOXIDATION OF STAINLESS STEEL

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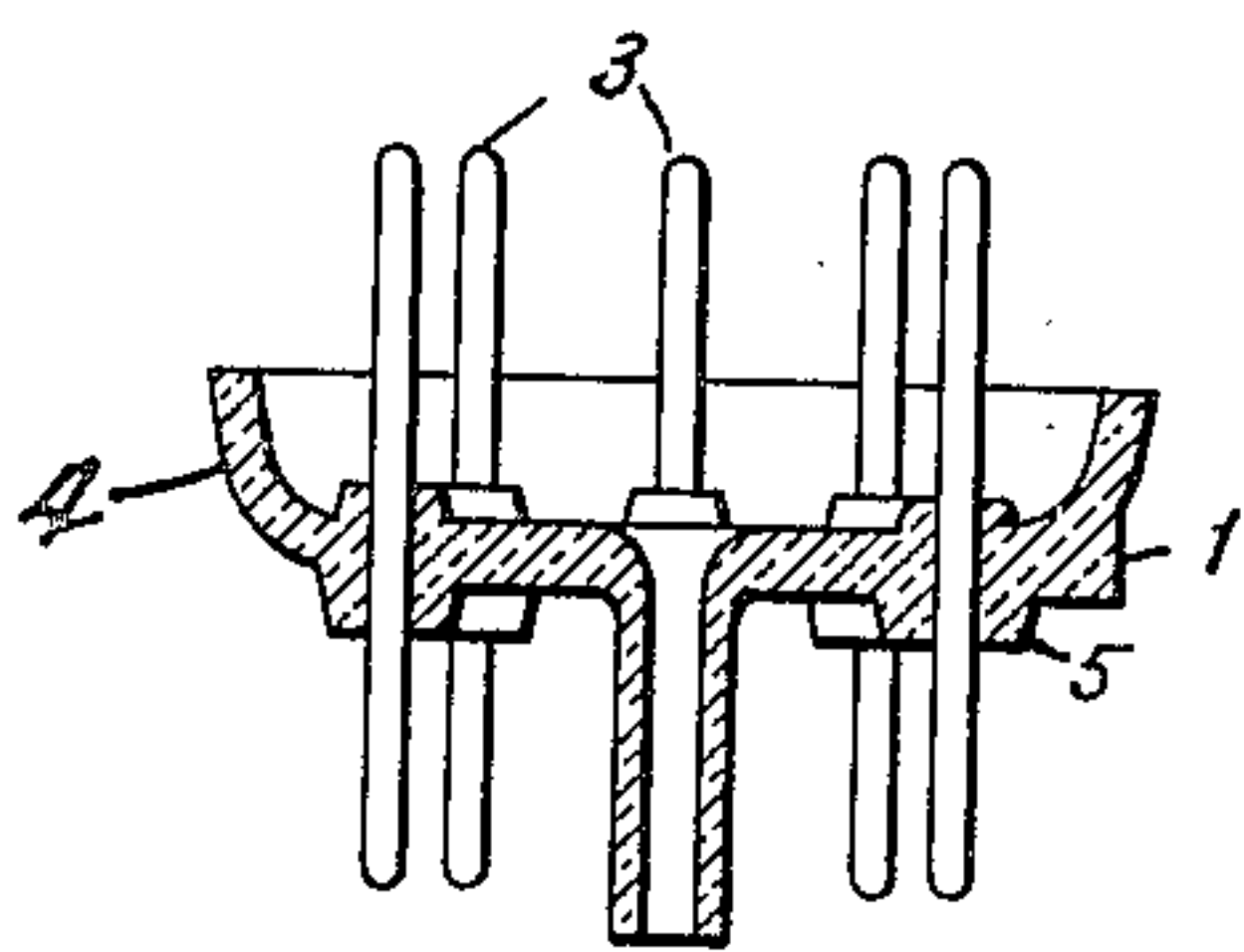


Fig. 2.

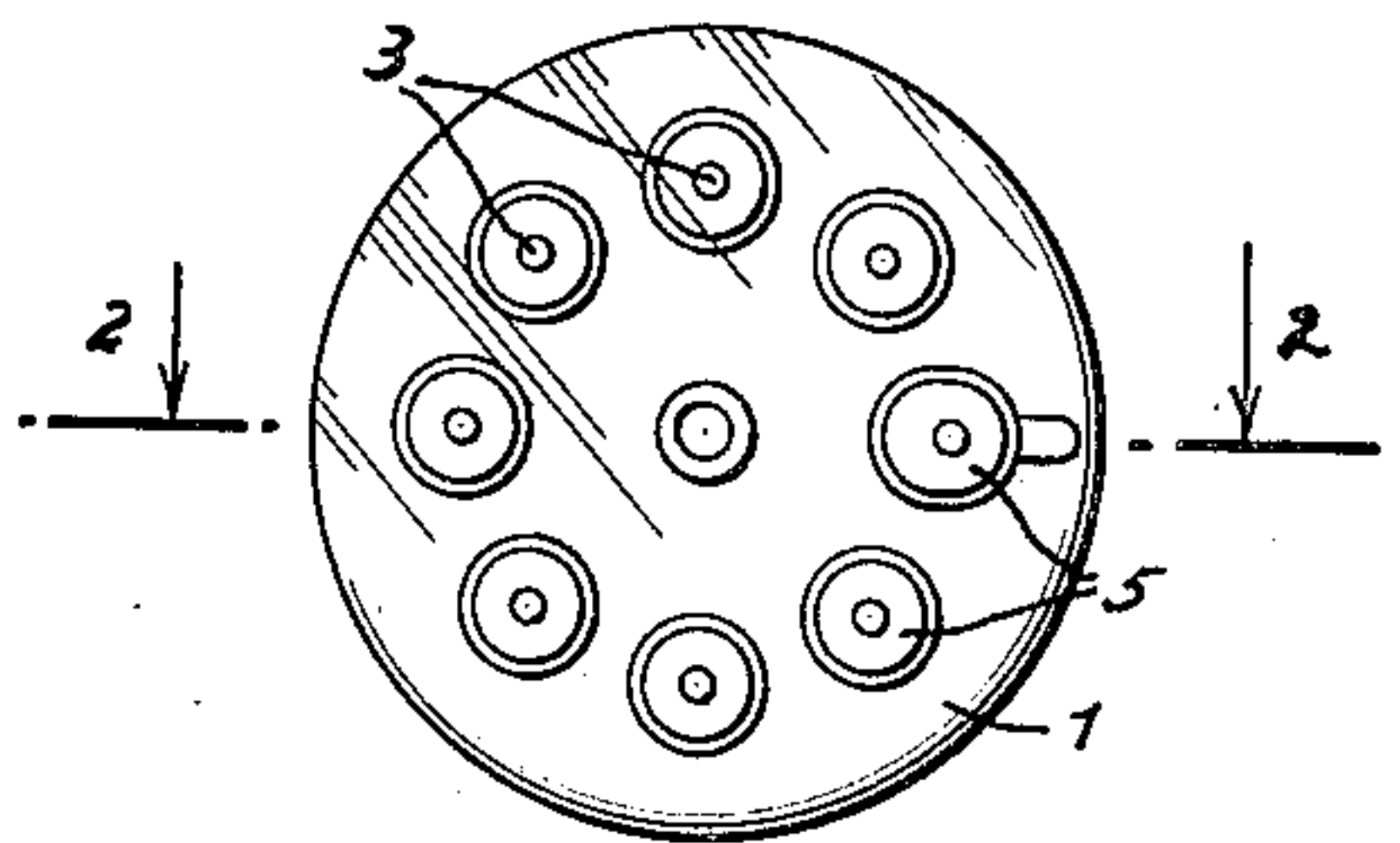


Fig. 1.

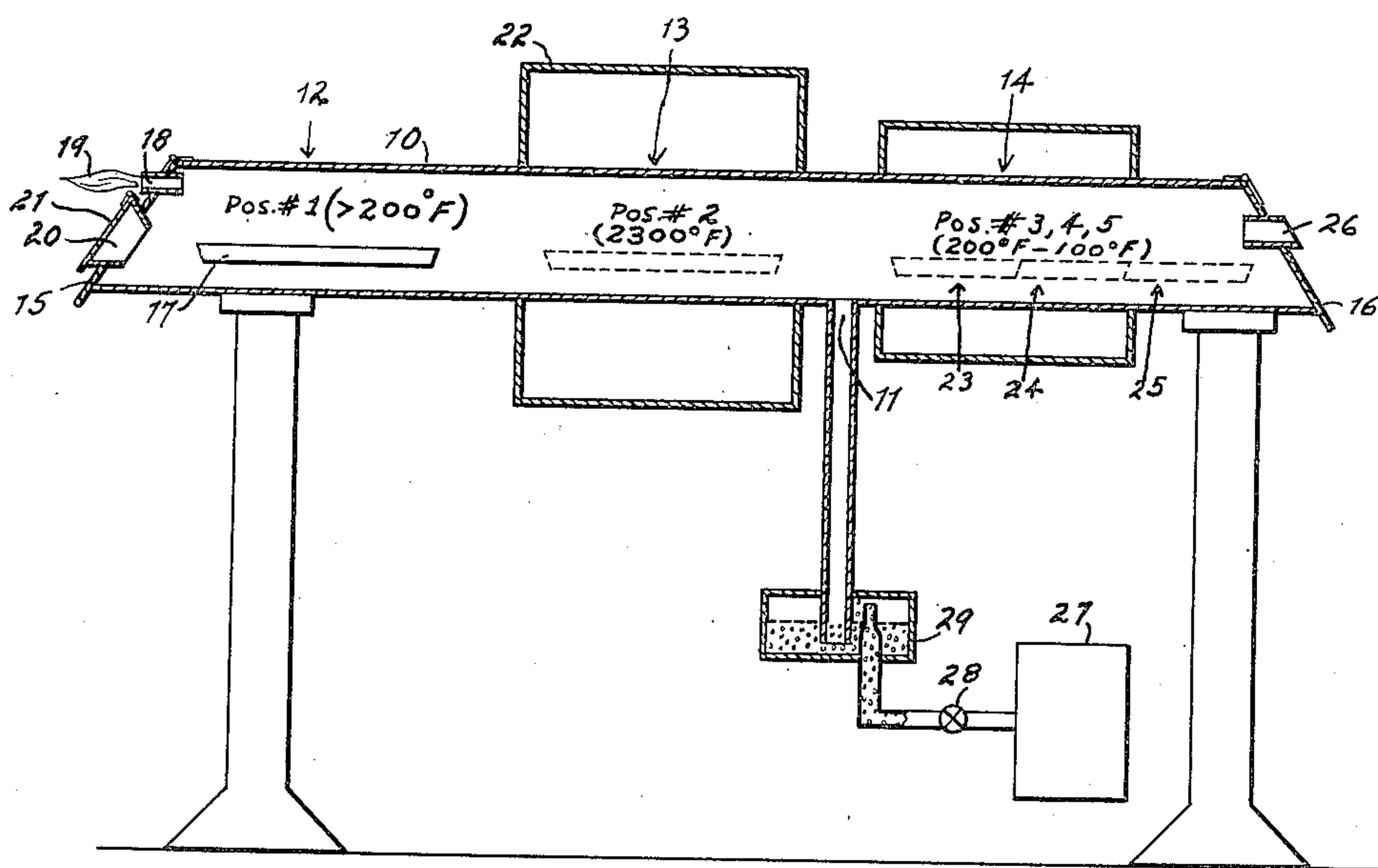


Fig. 3.

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## UNITED STATES PATENT OFFICE

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## PREOXIDATION OF STAINLESS STEEL

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1 Claim. (Cl. 148—6.35)

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This invention relates to stainless steel alloys, such for example as those used in metal-to-glass seals and more particularly to a process of pre-oxidation of the surface of stainless steel parts prior to the step of sealing the glass to the metal surface.

Certain chromium nickel-iron alloys adapt themselves particularly well for matching their thermal expansion coefficient to that of a number of glasses over a wide temperature range, whereby internal stresses in a composite body made by sealing the alloy surface to a properly matched glass are reduced to a minimum. In order to obtain a uniform, vacuumtight and mechanically strong bond between the metal surface and the glass to which the metal body is to be sealed, it is necessary to provide a uniform layer of metal oxide on the surface of the metal body, which oxide is soluble in the glass and which adheres very strongly to the metal itself. While an oxide layer of this character can be obtained on the surface of chromium bearing alloy parts by exposing them at elevated temperature to an atmosphere of wet hydrogen, great difficulty has, however, been experienced in obtaining a uniform, thin chromium oxide coating. This results from the fact that variations in the thickness and in the composition of the surface oxide may easily occur if the processing is not properly controlled.

In order to obtain the proper kind of surface oxide, it is necessary that the external surface of the alloy be covered with a self-protective chromium oxide layer of sufficient density and thickness. This dense protective layer prevents the penetration of oxygen below and into the lower levels of the alloy body during the sealing-in process. Should a considerable amount of oxygen penetrate during the sealing-in, the result would be the formation of a ferrous oxide, which is flaky in character and is the cause of air leaks.

In the mass production of electron discharge tubes, it is essential that all metal-to-glass seals be perfectly vacuumtight when subjected to standard high speed sealing methods. As an example, in the production of glass stems or headers for electron discharge devices, through which lead-in conductors of chromium-nickel-iron alloys are to be sealed, the lead-in conductors must have a well defined kind of oxide on their surface. It is important that this surface layer must not contain the ferrous oxide, which flakes off the metal surface and results in air leaks because of the separation between the metal surface and the oxide layer in the finished seal. In view of the fact that the lead-in conductors

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are frequently used as contact prongs to be introduced directly into the tube socket, it is necessary that the oxide formed during the pre-oxidation can be easily removed from the external parts of the lead-in conductors, so as to insure a good metallic electrical conductive contact engagement between the lead-in conductors of the tube and the socket contacts. Furthermore, the surface oxide must be removed from the parts of the lead-in conductors inside the discharge tube, to which are to be welded the tube electrodes, as the mechanical and electrical properties of the connection between the tube elements and lead-in conductors depend to a large extent on the absence of oxide on the surfaces to be welded together.

I have found that the uniformity of the desired oxide layer, in particular of lead-in conductor pins made of a chromium-nickel-iron alloy can be obtained with maximum speed by following a heat treatment of the pins which consists of a number of steps which form the subject matter of my present invention.

It is, therefore, an object of the invention to provide a method of pre-treating the surface of chromium-nickel-steel bodies to be sealed to glass in a vacuum-tight manner, so as to insure a uniform and stable oxide layer of the kind desired for this purpose.

It is another object of the invention to provide a reliable method of pre-oxidizing chromium-nickel-steel parts in a controlled atmosphere, whereby a thin, uniform chromium oxide layer, tightly adherent to the alloy surface is produced in the shortest possible period of time.

It is still a further object of the invention to provide a method of pre-oxidizing chromium-nickel-steel parts to be sealed to glass, in which the formation of a flaky iron oxide is completely eliminated.

A feature of the invention relates to the flushing of the air adherent to the surface of alloy parts to be pre-oxidized at high temperature in a wet hydrogen atmosphere, by exposing the parts to a stream of hydrogen at low temperature prior to their exposure to the controlled atmosphere at high temperature.

A feature of the invention relates to the temperature-time-schedule to be applied for pre-oxidizing chromium-nickel-steel parts in a controlled atmosphere, for the purpose of obtaining a vacuum-tight metal-to-glass seal on a part of the metal parts, which oxide can be easily removed from the surface of the parts where a good electrical contact is desired.



The invention will now be described in connection with the drawing, in which,

Fig. 1 shows a bottom view of a finished glass header for an electron discharge tube, including chromium nickel alloy pins sealed through the header after pre-oxidation according to the invention.

Fig. 2 is a sectional view of Fig. 1, along line 2-2.

Fig. 3 is a schematic sketch of a furnace illustrating my new method of oxidation.

Referring now to Figs. 1 and 2, the contact pins 3 sealed through beaded or thickened portions 5 of a glass header 1, which may be formed in the shape of a cup, with a skirt portion 4, may be made of an alloy consisting of 38 to 45% nickel; 3 to 15% chromium; up to 2% of a metal which forms a comparatively refractory and stable oxide when formed at high temperatures, such as a metal of the group consisting of aluminum, zirconium and calcium; the rest of the alloy being substantially entirely iron. This alloy matches particularly well the expansion coefficient of a glass consisting of 63%  $\text{SiO}_2$ ; 20%  $\text{PbO}$ ; 0.28%  $\text{Al}_2\text{O}_3$ ; 0.94%  $\text{CaO}$ ; 7.6%  $\text{Na}_2\text{O}$ ; 5.5%  $\text{K}_2\text{O}_3$  and 0.88%  $\text{Mn}_2\text{O}_3$ . A preferred composition of the alloy for making the lead-in conductor is approximately 42% Ni; 5 to 8% Cr; .02 to 2% Al; balance substantially iron. The contact pins 3 have a diameter large enough to make them sufficiently strong and rigid, so their lower parts may be used as contact prongs for insertion into a tube socket, and their upper ends can serve as main supports for discharge electrodes to be joined to the pins by welding.

The part of each pin sealed into the glass header is to be pre-oxidized in the manner about to be described, for the purpose of forming a vacuumtight, mechanically strong metal-to-glass seal. As explained above, the upper and lower ends of the pins should be freed from oxide after the metal-to-glass seal has been made.

In order to obtain pins which have the proper oxide for making the metal-to-glass seal, and from which the oxide can be removed at the upper and lower portions extending above and below the glass header, the pins are loaded in metal trays and passed through a controlled atmosphere at high temperature. The atmosphere consists of hydrogen which is saturated with water vapor at a temperature of 80° to 100° F. In the mass production of stems of this type, it is desirable that the process of pre-oxidizing be carried out at high speed, and high temperatures of the controlled wet hydrogen atmosphere are, therefore, desirable.

It has been found that the desired thin, uniform oxide layer cannot be obtained at temperatures above 1600° F., unless special precautions are taken. At this temperature, the desired oxide will only form after an exposure of several hours. If the temperature of the oxidizing atmosphere is elevated, say to 2300° F., in order to accelerate the formation of the oxide, the surface of the pins will not oxidize uniformly, but a heavy oxide develops in some parts of the surface, and flaky iron oxide is formed in others. This phenomenon results from the fact that the air introduced with the pins into the hot chamber causes irregularly distributed high oxygen concentrations at the surface of the pins, which, at the sudden exposure to the high temperature in the furnace disturb the critical composition of the controlled atmosphere, and causes the formation of undesired flaky iron oxide in spots,

and leads to a varying thickness of chromium oxide over the surface.

According to the invention, this effect is eliminated by flushing the air from the metal parts prior to introducing them into the high temperature chamber. This insures the uniformity of the composition of the controlled atmosphere when the metal parts are introduced.

If the pins are introduced into a stream of hydrogen for about one minute at a temperature of less than 200° F., all the adherent air is flushed out, and the pins obtain their desired uniform thin oxide surface within about 30 minutes' exposure to the wet hydrogen atmosphere, at a temperature of about 2300° F.

In practice, the pre-oxidizing is carried out in a furnace illustrated in Fig. 3. A tube 10 is supplied with a flow of wet hydrogen at a point 11. The tube is divided into three temperature zones. An entrance zone or chamber 12 of tube 10 is kept at about 150° F.; the main oxidizing zone 13 is kept at about 2300° F.; and cooling zone 14 is kept at a temperature between about 200° and 100° F. The ends of the tube are provided with hinged doors indicated as 15 and 16 in Fig. 3. When the oxidizing process is started, door 15 is opened, and the hydrogen flow is increased to about three times its normal flow. A metal tray 17 containing the pins is introduced into entrance chamber 12 into position 1, and door 15 is closed again. Door 15 has two openings, a small opening 18 through which hydrogen passes out continuously. The escaping hydrogen is ignited, and forms the flame 19, whose length indicates the hydrogen pressure. A second larger opening 20 is provided in door 15 and high rate of hydrogen flow is kept up for about one minute to insure a speedy removal of the air adherent to the pins in the tray 17 by the hydrogen stream. Opening 20 can be opened and closed by a hinged shutter 21, and is kept fully open during the flushing period. After this period of time, tray 17 can be safely introduced into heating chamber 13 at the high temperature, where it remains for about 30 minutes in position 2. The chamber 13 is heated to the desired temperature by any suitable electric or gas heater 22. The flow of hydrogen is reduced during this period and opening 20 of door 15 is closed, leaving only the small opening 18 for the hydrogen to escape.

After this heating for 30 minutes, the tray 17 is successively pushed into positions 3, 4 and 5 in cooling chamber 14. Preferably the cooling chamber 14 is made long enough to permit further graduated cooling zones 23, 24, 25, before the tray is removed through door 16 on the exit end of the furnace. An opening 26 is provided in door 16, as usual, to permit a continuous flow of hydrogen through this end of the furnace. If desired, a special cooling unit such as a water jacket 30 may surround the zone 14, and if found necessary a similar water jacket may be provided around the zone 12.

The process may then be carried on continuously. When the first tray 17 is moved from position 2 to position 3, another tray is placed into position 1, the hydrogen flow is increased for one minute, and the new tray is moved into position 2. After thirty minutes, the new tray is moved into position 3, and the first one into position 4, and a third tray is introduced into position 1. When the next tray is introduced into position 1, the first tray is pushed to position #5 and is ready for removal to air. In this



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way, a full tray of pre-oxidized pins may be taken from the furnace every 30 minutes.

The advantage of the new method of pre-oxidizing consists of the speed obtainable, and in the uniformity of the desired oxide layer. It will be noticed that the temperature in the oxidizing chamber 13 is about 400° F. below the melting point of iron. While it is possible to increase the oxidizing temperature slightly further in order to obtain a still higher speed of oxidation, this should be avoided, as at higher temperatures there is an inclination to develop a very loose heavy chromium oxide which is undesirable from a sealing standpoint. Also exaggerated grain growth results, which is detrimental to the physical and vacuum sealing properties of the alloy. It should also be noted that the hydrogen tank 27 is provided with a flow regulator valve 28 and is bubbled through a water pan 29 so that it is saturated with water vapor when it enters the furnace.

What I claim is:

The method of pre-oxidizing the surface of chrome-nickel steel parts as a preliminary step prior to sealing them into glass, characterized in that the parts are exposed for about one minute to a high velocity stream of wet hydrogen at a temperature below 200° F. for the purpose of flushing away entrained air at the surface of

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the steel parts, and then in a wet hydrogen atmosphere at a temperature about 400° F. below the melting point of iron for about 30 minutes, and then are cooled for approximately 30 minutes in a hydrogen atmosphere at a temperature of less than 100° F. the hydrogen atmosphere having been previously saturated with water vapor at a temperature between 80° F. and 100° F.

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