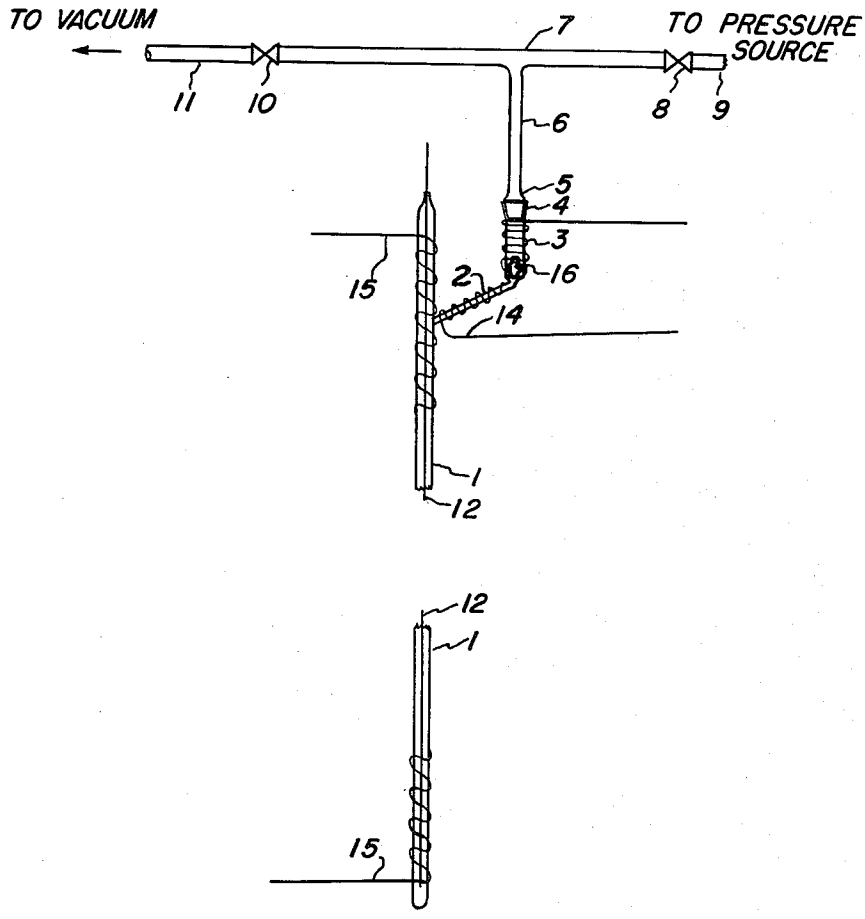
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MANUFACTURE OF ELECTRODE CAPSULES

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MANUFACTURE OF ELECTRODE CAPSULES

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This invention relates to the manufacture of electrodes. More specifically the invention relates to the manufacture and preparation of glass capsule electrodes having a charge within the capsule of an alkali metal. It has been shown by Eding and Glassbrook, in application Serial No. 279,662, filed Mar. 31, 1952, now Patent No. 2,665,412, dated Jan. 5, 1954, that non-ferrous alloys can be analyzed by inserting a reference metal specimen within a body of the alloy to the analyzed. The reference metal specimen is enclosed in a capsule of vitreous material permeable to ions thereof, and the alloy composion is determined by measuring the electrical potential developed between the reference metal and the alloy. For example, alloys of lead and alkali metals can be analyzed by this procedure, employing, for example, pure sodium metal as the reference metal enclosed within a capsule of heat resistant boro-silicate glass.

Adaptation of the above method to commercial equipment has presented certain ancillary problems. In particular, it has been found quite difficult to insert a reference alkali metal specimen in a capsule without having corrosion products formed. Even when a charging operation is carried out in an atmosphere of commercially available inert gas, contaminating products of the alkali metals are formed because of its reactive material and the presence of trace amounts of oxygen or moisture in the inert gas. These contaminants, principally oxides or hydroxides of the alkali metal, shorten the service life of the capsule and also are responsible for inconsistencies in the relationship of the electromotive potential measured and the composition of the alloy. The problem of preparation and charging of such capsule is aggravated by the necessity of extreme length relative to the diameter, and the minor fraction (less than 10 percent) of the capsule volume occupied by the reference metal specimen.

Accordingly, the object of the present invention generally is to provide a new and improved method of charging an alkali metal specimen to glass capsules. More specifically an object of the present invention is to charge a capsule with a high purity alkali metal specimen by a simple and inexpensive technique. An additional object of the present invention is to provide a process suitable for manufacture of the subject capsules on a production basis. A still further object is to provide a method for producing capsules of an extensive length-diameter ratio wherein the metal specimen charge will be virtually free of contaminating compounds even though a commercial grade of "inert" gas is employed during the charging operation. An additional and more specific object is to provide a method for accomplishing such charging wherein any contaminants which are formed inadvertently or unavoidably due to impurities in the "inert" gas are concurrently removed and separated from the alkali metal during the charging.

The process is equally applicable to the several alkali metals such as lithium, potassium and sodium. In most

instances, sodium is the preferred reference metal specimen. Accordingly, the description and examples following includes the use of sodium as an illustrative but not exclusive embodiment.

Generally the process is carried out as follows. The glass capsule for receiving the sodium specimen is prepared in the usual manner up to the point of being readied for receiving the sodium charge. Thus, the capsule has the operative end sealed forming a closed end for receiving the sodium specimen, and a lead wire is inserted in the approximate position wherein it will ultimately be in contact with the sodium specimen and in addition is sealed at the opposite end of the extended tube capsule. A branch connection to the capsule is provided generally positioned adjacent the end opposite to that receiving the sodium specimen for final usage. This branch consists of three portions, viz.; a restricted portion that is a channel of quite small dimensions, a cup or funnel portion, and a connection portion preferably of the ground glass type for coupling to conventional conduits for applying either vacuum or positive inert gas pressure. The capsule being ready for charging, a solid specimen of sodium metal is placed in the above mentioned cup portion of the branch and the capsule and branch is then connected to a permanent conduit connection. Vacuum is applied and concurrently the apparatus and more specifically the cup and the sodium charge therein is heated to a moderate temperature, above the melting point of the sodium metal. During the above described melting and evacuating operations, it has been found that inevitably some contamination of the sodium metal occurs and in fact some contamination is virtually unavoidable even with respect to the sodium which has been charged to the cup prior to the melting operation. The further contamination occurring during the evacuation is attributed to the fact that it is considered virtually impossible without quite elaborate precautions to maintain a perfectly dry and inert gas atmosphere within the capsule at all times. Accordingly, at this point in the process the sodium is in a liquid state and is contaminated by accompanying impurities which are largely sodium oxide or hydroxide. The evacuation step is then terminated and a positive pressure of inert gas is applied through the above described branch and to the surface of the liquid sodium. It has been discovered that the impurities present tend to move to the boundaries of the sodium metal charge even to the extent of "floating" on the surface of the sodium. This is probably a function of the surface tension of the liquid metal as the absolute density of the impurities will be greater than that of the sodium. Further, as the sodium flows out of the cup container the impurities tend to deposit on and adhere to the walls of the cup. Accordingly, application of pressure to the surface of the sodium causes a flow of quite pure and refined liquid sodium metal to pass through the restricting portion of the branch and into the body of the capsule proper. This flow is continued until substantially all the sodium is within the body and at such time the restricted portion of the branch is fused. The cup and connecting joint portion of the branch are severed, leaving the restricted portion of the branch forming part of the capsule wall. An advantageous feature of the process described is that by appropriate adjustment of the size of the cup portion and the quantity of sodium charged assurance is provided that the impurities present or formed will not accompany the sodium as it flows into the capsule proper. This result is provided largely owing to the adhesion effect upon the walls of the cup rather than because of the restricted size portion of the branch of the capsule.

The further details of the method and its preferred embodiments will be more readily understood from the examples and description hereafter given and from the accompanying figure, the figure being a representation of the capsule with the branch attached thereto and a charge of solid sodium in said branch, plus appropriate means for applying vacuum and for heating the apparatus. Turning to the figure, the above described portions of the apparatus are shown. A capsule **1** is an extended tube of Pyrex brand of boro-silicate glass which in the usual instances is approximately 5 feet long and about one-half an inch in outside diameter. A branch near the upper end of the capsule **1** includes a slanting capillary portion **2**, a cup portion **3**, and a female segment **4** of a standard ground glass joint. Attaching at this point is the male segment **5** of the ground glass joint which is affixed to a tube **6** connected to a manifold **7**, which in turn is terminated by valves **8** and **10** which permit connecting the interior of the capsule through the branch line to either a vacuum source through line **11** or to a source of inert gas through another line **9**. Before attaching the capsule and its branch to the permanent assembly for supplying pressure or vacuum as described a lead wire **12** is inserted in the capsule and is sealed at the wall terminating the upper end. A charge **16** of relatively pure solid sodium is introduced in the cup prior to the juncture of the male and female ground glass joints. Separate heating elements **14**, **15** are provided for the branch including the cup **3** and for the capsule proper **1**, respectively. The heating elements (connected to power sources, not shown) are of such capacity that the capsule and the branch can easily be heated up to a temperature above approximately 100° C. in a few minutes.

As a working example of the method of the filling of a capsule, a capsule having the dimensions of one-half inch by five feet and a capillary extension tube of approximately three inches length, with a cup **3** having a volume of about two cubic inches was prepared. To the cup **3** was charged 10 grams of pure sodium and then the ground glass male member **5** was connected to the female member **4** and a tight joint achieved. The vacuum was then applied to the system and a vacuum of 10^{-5} mm. of mercury was provided. Concurrently, during the evacuation process a flow of current was started through the heating elements **14**, **15**. The temperature of the apparatus rapidly rose, to a temperature of about 100° in the space of about three minutes. At this point the sodium charge **16** was melted and this liquid pool was surmounted by a glazed layer of sodium impurities. The evacuation source was then disconnected by valve **10** and positive nitrogen pressure was applied to the upper surface of the sodium, forcing liquid sodium down through the capillary portion of the branch **2** and into capsule **1**. Substantially all of the previously referred to impure compounds of sodium adhered to the walls of cup **3**, and the metal reaching the inside of the capsule was bright and silvery. This liquid charge rapidly descended to the bottom of the capsule and formed a liquid pool at that point. The pressure of the inert gas after the sodium charge was introduced was approximately one atmosphere. The restricted portion to the branch was then fused with a flame and the opening thus sealed and the branch separated at this point. The charging and separation process was carried out in approximately five minutes. The sodium specimen so charged retained its bright metallic luster during an extensive period of service and did not deteriorate in a measurable degree until the capsule itself failed from mechanical and thermal shock, after an exposure period at a temperature of about 450° C. for approximately one month.

As is apparent from the foregoing description, the specific proportions of the capsule and the branch line components can of course be varied to a large degree. Generally, the capsule is always a quite elongated tube, because of the necessity and subsequent usage of having the specimen located within a body of alloy at an appreciable distance from the surface, coupled with the necessity of the junction point or transmission point of the lead wire **12** through the capsule wall at a point outside the zone of the high temperature of the melted non-ferrous alloy. The branch line segment which is restricted may as in the foregoing example be a capillary tubing or it can be in effect simply an orifice. However, if an orifice is employed the task of closing this portion of the branch is somewhat more cumbersome and it lends itself to easy sealing with less facility than a capillary portion of the branch.

As already indicated the exact size of the restricted portion of the branch section is not critical providing it is not so large that the sodium specimen flows readily through the opening before there is an opportunity for the always present impurities to rise to the surface and thus have an opportunity to be retained or entrapped by the walls of the cup section of the branch. Accordingly, for all practical purposes the size of the restricted section is maintained not less than approximately one thirty-second of an inch in diameter and not over about three thirty-seconds of one inch. It is found that this size range results in charging under slight inert gas pressure, but is also sufficiently small that even after the sodium is liquefied that it will not flow through without some pressure applied thereto.

The particular size of the cup section of the branch of the capsule is also not critical, providing that adequate peripheral area is provided to allow adhesion of substantially all the impurities present. As a convenient rule for apportioning the design of this portion of the apparatus it is found that the peripheral area of the cup below the surface line of a normal charge of melted sodium should be equivalent in magnitude to the cross sectional area of the cup. This assures, generally, that as the sodium is forced or pushed into the capillary or restricted portion of the branch that the impurities having moved to the boundaries of the melted charge will cling to the side wall and there will be ample opportunity for retention without forcing into the capsule proper. This above described limitation is very easily met, inasmuch as it will be customary to make the cup appreciably larger in volume than the volume of the melted sodium because the initial charge, being solid, will occupy appreciably more vertical distance than the liquefied material.

Having described the invention in some detail and illustrated its best embodiments, what is desired to claim is:

I claim:

1. A glass capsule assembly for receiving an alkali metal specimen including an elongated, glass, closed end capsule, a branch generally adjacent one of the closed ends, said branch including a portion having a relatively small internal diameter in contrast to other portions of the branch, a cup portion for receiving a solid alkali metal specimen, and connecting means for attachment to an external conduit, the small diameter portion joining the capsule and the cup portion, the capsule containing an electrical conduit, the conduit passing through and being sealed in the capsule wall at a point adjacent the branch, and extending within the capsule to a point near the opposite end for making electrical contact with an alkali metal specimen after charging.

2. The method of charging an elongated, glass walled electrode capsule with a purified alkali metal specimen, said capsule being provided with an electrical lead wire passing through the wall thereof for contact with the alkali metal specimen, and with a branch conduit of restricted cross section surmounted by a cup portion, comprising inserting in said cup portion a solid alkali metal specimen having surface oxide impurities, applying a vacuum to the cup portion to evacuate the capsule and conduit and melting said alkali metal by the application of heat, then discontinuing the vacuum and applying a positive pressure of inert gas to the melted alkali metal,

and forcing the alkali metal through said conduit while retaining the surface oxide impurities on the walls of said cup portion, and then sealing said conduit.

3. The method of charging and manufacturing an elongated glass walled electrode capsule having a purified sodium specimen occupying a portion of the space within and at one end of said capsule and in electrical contact with an electrical conductor communicating with the exterior of the capsule, comprising providing an elongated glass walled capsule with an electrical conductor passing through the wall thereof, and further providing a branch on said capsule, said branch having a restricted portion of from 1/32 to 3/32 inch in diameter, a cup portion, and a joint means for connecting to conduits, inserting a solid sodium metal specimen in the cup portion, said specimen having oxide surface impurities, connecting the joint

means to a conduit for applying successively vacuum and pressure under inert gas, then applying vacuum to the capsule through said branch and concurrently heating the cup and the sodium metal therein and melting the sodium metal, then discontinuing the vacuum and applying inert gas pressure to the surface of the sodium and forcing the sodium through the restricted portion and into the capsule, while retaining the oxide impurities on the walls of the cup portion, then sealing the branch at the restricted portion and severing at that point.

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