

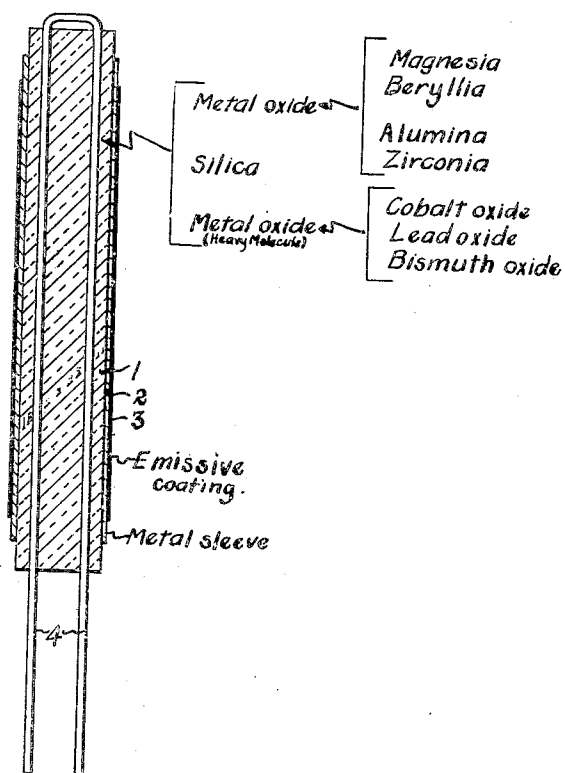
Aug. 13, 1935.

H. L. CROWLEY

2,011,173

CERAMIC PRODUCT

Filed Feb. 8, 1933



INVENTOR
Henry L. Crowley
BY *Darby Dent*
ATTORNEYS.

UNITED STATES PATENT OFFICE

2,011,173

CERAMIC PRODUCT

Henry L. Crowley, West Orange, N. J., assignor to
Henry L. Crowley & Co., Inc., West Orange,
N. J., a corporation of New Jersey

Application February 8, 1933, Serial No. 655,783

2 Claims. (Cl. 250—27.5)

This invention relates to improvements in ceramic insulators, particularly of the type and construction employed in electron discharge devices, such as audions.

5 An important object of this invention is to provide insulating supports and spacers for electron discharge devices comprising metal oxides treated so that the resulting product is exceedingly stable under the temperature and pressure conditions of operation to which such insulators and spacers are subjected in use.

10 A further object of this invention is to provide an exceedingly stable insulator or spacer having a high magnesia content.

15 A still further object of this invention is to provide a ceramic insulator which is exceedingly rugged, inexpensive to manufacture and dependable and stable in use.

20 A further and resultant object of this invention is to provide ceramic insulators for use in vacuum tubes which are relatively noiseless when used in electron discharge devices, and particularly audions as employed in radio circuits.

25 These and many other objects, as will appear from the following disclosure, are secured by means of this invention.

This invention resides substantially in the ingredients, steps, series of steps, and the product, all as will be described in complete detail below.

30 The single figure is a vertical cross sectional view through a cathode structure employing the insulator of this invention having legends applied thereto to indicate the ingredients of the insulator.

35 While the invention of this disclosure has a wider field of use than in connection with electron discharge devices its advantages when so used will be described in detail since such use will be illustrative of the characteristics and advantages of the invention.

40 As will be apparent from the following description, the improved characteristics of the insulator of this invention will readily find many uses under conditions comparable with those encountered in electron discharge devices. As is well known, the electrodes of audions operate under relatively high temperature conditions within a vacuum.

45 A common type of audion now used commercially is known as the indirectly heated type in which the cathode structure comprises a small rod of insulating material having bores there-through which the legs of a hairpin filament are threaded to provide a heater. This insulator is tightly surrounded or nested with a metal tube, usually of nickel, on the surface of which a coat-

ing of electron emissive material is applied. When the filament is heated the heat is conducted through the thin walls of the insulator to the nickel sleeve thereby raising its temperature so that the coating will emit electrons in the desired quantity. Such a filament is most commonly made of tungsten.

5 Such an indirectly heated cathode is illustrated in the single figure in the drawing. It comprises an insulator body 1 having a pair of longitudinal bores therethrough in which the legs of a hairpin filament or heater 4 lie. Surrounding the insulator body is a thin metal sleeve 2, the surface of which is coated with an electron emissive coating as indicated at 3.

10 In the most desirable form the spacing insulator, through which the filament legs are threaded, is made of compressed or extruded mixture of metal oxides and then heat treated to form a strong, self-sustaining body. The metal oxide most commonly used for such insulators is magnesia. At this point, while the cathode insulator will be referred to in detail, it will be understood that this discussion and this invention may be employed in connection with other insulating parts used in such devices and, in fact, the insulator of this invention will find many and wide uses.

15 Under the temperature conditions encountered in the operation of tubes, and under the vacuum conditions which exist within the glass envelope, such magnesia insulators have been found to have a number of serious defects. Because of the fact that pure metal oxides, such as magnesia, alumina, beryllia zirconia, and the like which are used in cathode insulators have a much lower vaporization point than their melting point there is a tendency for the metal oxide to reduce down to a pure metal, which action is accelerated by the high temperature encountered and the fact that the insulator is under a vacuum. This reducing action appears to be accelerated by the presence of the hot tungsten of the filament which has a great affinity for oxygen and tends to act as a reducing agent, thereby reducing the oxide to a pure metal, such as magnesium, aluminum, beryllium, zirconium, and the like, depending upon the particular oxide forming a basis of the insulator. This action is more noticeable the greater the percentage of the metal oxide in the insulator. The freed metal, such as magnesium, is at a temperature at which it exists in the form of a vapor and such vapor is highly charged electrically due to the field in which it is created.

The metal vapor therefore leaves the cathode structure at high velocities and collects on the cool inner surface of the glass vessel which encloses the electrodes. The result is a magnesium mirror deposit on the inside wall of the vessel.

The formation of such a magnesium mirror in electron discharge devices is undesirable because it upsets the electrical characteristics thereof. For example, in audions which have a lead passing through the wall of the vessel at the top, the mirror thus formed is in contact with this lead and thereby changes the capacity of the tube. This deposit likewise forms on the other electrodes of the audion where exposed, thereby changing their electrical characteristics, and particularly their capacity, thereby causing leakage and hence interfering with the characteristics and efficiency of the audion. Furthermore, these deposits tend to become a source of noise in the output of the audion, interfering with its correct operation.

The reduction of the metal oxide of the insulator under these conditions not only causes the presence of magnesium within the device, as described above, but likewise causes the presence of oxygen. Some of this oxygen combines with the hot tungsten filament, while the remainder of it collects within the glass vessel, partially reducing its vacuum, and tending to oxidize the metal parts. Some of the metal of the hot tungsten filament likewise passes slowly through the insulator under the influence of the electric field present and deposits on the inner wall of the nickel cathode sleeve. The tungsten is deposited as a black deposit of colloidal tungsten on the inner wall of the sleeve which is relatively colder than the hot filament.

As a result of all of these actions the insulating spacers employed to hold the electrodes in spaced relation are covered with a metallic coating which causes leakage and noise and the freed oxygen collects within the vessel. All of these undesired actions and reactions are the result of the fact that the vaporization point of the metal oxide or oxides of the insulators is below the melting point. In accordance with this invention these tendencies are overcome by the introduction of a material into the insulator composed of heavier molecules, thereby raising the vaporization point of the finished insulator. Suitable materials for this purpose are cobalt oxide, lead oxide, bismuth oxide and the like. The molecule of these oxides is relatively heavy molecule, which is apparently the necessary characteristic to increase the vaporization point of insulators including other metal oxides, such as those of magnesium, aluminum, beryllium, zirconium and the like.

In accordance with this invention a suitable insulator would consist of 60% magnesia, 38% silica, and 2% cobalt oxide. The percentages of the various ingredients may be varied within relatively wide limits, particularly the percentages of the magnesia and the silica. With regard to the cobalt oxide, 1% or 2% thereof is most satisfactory, but it has been found that satisfactory results may be secured with percentages of cobalt oxide, or its equivalent, up to approximately 7%. If the percentage of magnesia is increased the percentage of silica is proportionately decreased.

It should be noted that, in accordance with this invention, useful products may be made from a mixture of magnesia and silica without the use of cobalt oxide. Mixtures of magnesia

and silica having a magnesia content of between the limits of 35% and 90% form upon treatment in accordance with this invention useful insulating bodies. Extruded powdered mixtures of magnesia and silica when fired, produce magnesium silicates which are actually different compounds from either of the ingredients employed. Mixtures of various percentages between the limits above mentioned, produce eutectic points forming definite magnesium silicate compounds.

The percentage of magnesia employed cannot be carried too low because while the resulting product has a high vaporization point, it has a melting point which is too low for many uses, for example, the melting point would be too low for use as an insulator in an audion where the operating temperatures would be liable to cause softening and even melting of the insulator. It is for this reason the percentage of magnesia should not approach the neighborhood of 35%.

The ingredients magnesia and silica in the desired proportions, either with or without cobalt oxide or its equivalent, are prepared in finely divided powder form and are thoroughly mixed in any suitable manner. They are then heat treated to burn out the impurities and to agglomerate the impurities so that they may be separated out by sifting or the like. This purification is along the lines employed in the disclosure in Patent No. 1,885,234, issued November 1, 1932 to Robert M. Crowley and myself. The ingredients may be heat treated to burn out the impurities before mixing, if desired.

The purified mixture is then extruded under sufficient pressure to form a self-sustaining body which is strong enough to be handled during the final processing. If desired, a suitable binder may be mixed therewith, such as gum acacia which will later burn out during the firing of the extruded product so as to leave no impurities therein.

The extruded bodies are then heat treated by a firing to a temperature of from 1300° to 1900° C., a suitable temperature being 1500° C. At these temperatures, if a binder is employed, it is entirely burned out so as to leave no undesirable impurity in the finished product. The firing of the extruded bodies is preferably carried out in a strongly oxidizing atmosphere such as air or oxygen atmosphere and may be followed with a second firing step in a neutral or reducing atmosphere, but this second firing is not necessary. The result of this treatment is a product which does not have the characteristics of either magnesia or silica but has its own characteristics, of which stability and substantial freedom from disintegration, are important. The compounds thus produced are magnesium silicates of considerable stability under high temperature when in use.

Where these insulators are not immediately put in use, it is sometimes desirable to re-fire them just before they are put into use in order to remove absorbed vapors, moisture and the like. This second firing is best carried out at a temperature of from the order of 1200° C. for ten minutes to 1050° C. for thirty minutes. This second firing operation is best carried out in a reducing atmosphere, such as hydrogen. When a reducing atmosphere is employed, higher temperatures than those given should be avoided. The insulators when allowed to stand after the first firing, tend to break down into suboxides and the re-firing under the above conditions re-

turns the insulator to its original state and removes the absorbed impurities. If this second firing operation is carried out in a reducing atmosphere of hydrogen, there is a further tendency to clean the surface of the insulator by removing any grease or other impurities deposited thereon. Of course, if the insulator is immediately put into use after the first firing operation, the second firing operation is usually not necessary.

An insulator thus prepared has a much higher vaporization point and one which is closer to the melting point of the insulator than in the case where the oxide, such as magnesia oxide, or aluminum oxide, is prepared in a relatively pure form and without substantial combinations as above; further the addition of an oxide, such as cobalt oxide of a heavier molecule, is a further improvement. The result is that in the operation of an audion employing such an insulator the magnesia is not reduced to the pure metal and the magnesium deposit on the walls and electrodes of the tube does not occur. Thus the electrical characteristics of the audion are not interfered with in operation, free oxygen does not collect within the glass vessel, and an important source of noise in the output of the audion is eliminated. Furthermore the tendency for the metal of the filament to migrate through the insulator and deposit on the cathode sleeve is materially reduced.

The percentages of metal oxide employed may range from 40% to as high as 90% within the scope of this invention, the silica content of course being correspondingly decreased. It should also be noted that other heavy molecule oxides can be employed besides cobalt oxide, lead oxide, or bismuth oxide, such for example, as tantalum oxide, tungsten oxide, thorium oxide and the like. Tantalum oxide, tungsten oxide

and thorium oxide are not as suitable as cobalt oxide, lead oxide and bismuth oxide because these materials have a tendency to emit electrons which gives rise to a so-called back emission which is undesirable. Hence, a heavy molecule oxide which does not, itself, emit electrons is preferable. Of course, as pointed out above, other metal oxides may be used in place of magnesia, such for example, alumina, beryllia, zirconia, and the like.

The ingredients of the insulator are preferably employed in as pure a form as possible and particularly are they free of alkali.

From the above description it will be apparent that this invention resides in certain ingredients, combinations and percentages thereof, steps and series of steps, all of which may be varied by those skilled in the art without departure from the scope of this invention. I do not therefore desire to be strictly limited to the disclosure as given for purposes of illustration but rather to the scope of the appended claims.

This application is a continuation in part of my co-pending application Serial No. 603,609 for an invention in "Cathode structure", filed April 6, 1932.

What I seek to secure by United States Letters Patent is:

1. A cathode insulator comprising an extruded and baked body of insulating material containing approximately 60% magnesia, approximately 38% silica, and approximately 2% cobalt oxide.

2. A cathode insulator as described comprising a self sustaining body of one of the metal oxides of the group magnesia, alumina, beryllia and zirconia; 10 to 65 per cent of silica; and a small percentage of one of the heavy molecule metal oxides of the group cobalt oxide, lead oxide and bismuth oxide.

HENRY L. CROWLEY.