Feb. 17, 1931. S. BOYER 1,793,303

TEMPERATURE RESPONSIVE DEVICE

Filed Nov. 19, 1925

Fig. 1.

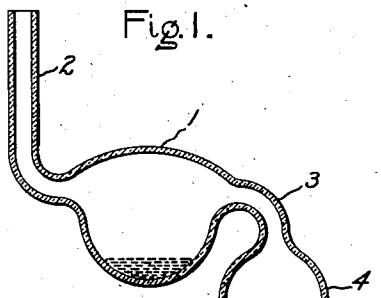


Fig. 2.

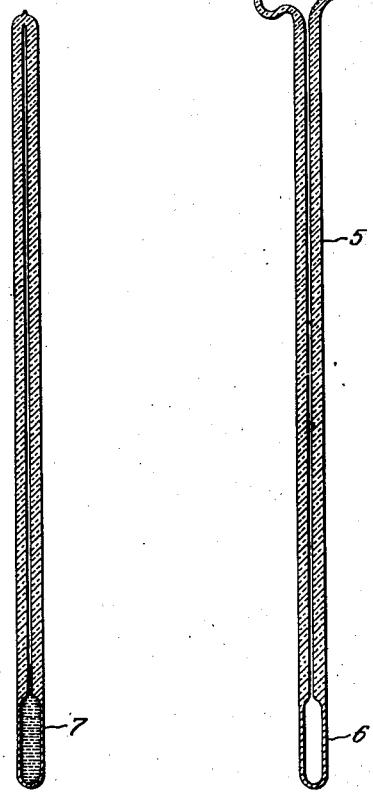
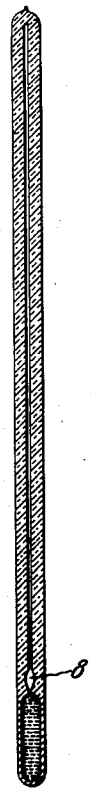


Fig. 3.



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UNITED STATES PATENT OFFICE

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TEMPERATURE-RESPONSIVE DEVICE

Application filed November 19, 1925. Serial No. 70,191.

This present application is a continuation in part of my earlier application, Serial No. 5,362, filed January 28, 1925.

The present invention relates to physical instruments such, for example, as thermometers or electric circuit controlling devices, and which in accordance with my invention contains as the indicating agency a metal or alloy having certain of the properties of gallium at elevated temperatures.

Thermometers comprising a glass tube and containing mercury can be used to measure temperatures up to about 500° C. To measure higher temperatures it is necessary to use less convenient devices, such, for example, as thermo-couples or other devices making use of thermo-electric properties of metals. These devices are less accurate than a thermometer and often are inconvenient for general use. There is an urgent need for a thermometer containing an indicating medium capable of use at higher temperatures than mercury. Such a medium must flow readily over the surface of the container, which ordinarily is a capillary tube of vitreous material, it must be liquid over a useful temperature range and must have a low vapor pressure.

I have discovered that gallium and indium either alone or in combination with other metals, meet the exacting requirements of a thermo-responsive device, and are capable of use in a range of temperatures for which mercury cannot be used. I have provided in accordance with one feature of my invention a thermometer, containing such an indicating medium, which is capable of use at temperatures as high as about 1000° C.

In accordance with another feature of my invention I have provided gallium metal in a new chemical and physical state, that is, free from oxygen and dissolved gas and capable of flowing over vitreous surfaces, such as glass and fused quartz.

Gallium is a silvery metal resembling mercury in general appearance and related to aluminum in chemical properties. Although it may be solidified by crystallization at a temperature between 29° and 30° C., it may be supercooled to temperatures below 0° C. without solidifying. Its boiling point has not as yet been accurately determined but it is estimated to be relatively high—say, about 2000° C.

Indium is a white metal, which in most of its chemical properties resembles gallium, but has a higher fusing point. As room temperature it is softer than lead and is very malleable and ductile. It occurs in its ores associated with gallium and zinc. Indium melts at about 155° C.

It has been found that gallium as heretofore obtainable adhered both to glass and quartz. I have found that this tendency of gallium to adhere to vitreous surfaces is due partly to the formation of a thin film of oxide on the surface of metallic gallium and partly to the effect of gas contained in the metal as heretofore available.

The accompanying drawing shows in Fig. 1 a thermometer in the initial stage of manufacture; Fig. 2 shows a complete instrument; and Fig. 3 shows a thermometer adapted for alloys of gallium or indium.

Gallium may be freed from metal impurities by a process described by Theodore W. Richards and myself in the Journal of the American Chemical Society, vol. 41, page 133 (1919), and the Journal of the American Chemical Society, vol. 43, page 274 (1921). The metal thus obtained contains gas, largely hydrogen, absorbed during the process of electrolysis. It becomes coated with surface oxide even by contact with the atmosphere.

Pure indium like pure gallium may be prepared by the fractional electrolysis of the sulfate solution, as described in the journal of the American Chemical Society, vol. 29, page 485, 1907. The metal deposits in a branched tree form and may be dried and used in an atmosphere of hydrogen.

In accordance with one of the features of my invention, gallium is rendered substantially free from oxide and absorbed gases by the following procedure.

Gallium, which is free from metallic impurities, is treated with hydrochloric or other suitable halogen acid, thereby dissolving the surface film of oxide and forming a protective film of chloride on the metal. Concentrated hydrochloric acid diluted with an

equal volume of water may be used for this purpose. Conveniently the gallium produced by electrolysis is fused in contact with the hydrochloric acid solution, then is resolidified and the excess of acid removed.

The metal is placed in a treatment bulb 1, Fig. 1, which is connected by a conduit 2 to a vacuum pump, and by a conduit 3 to a reservoir 4. This reservoir in turn is connected to the stem 5 and bulb 6 of a thermometer which preferably consists of fused quartz.

After a thorough exhaust during which the quartz container is highly heated to drive off water vapor and gases, the gallium in the bulb 1 is heated, thereby volatilizing the skin of gallium chloride, and possible traces of oxide, these impurities being deposited in the upper part of the bulb 1. The metallic gallium is left in the bulb 1 in a clean, bright condition and is free from oxide. The gallium then is heated to redness to free the metal from hydrogen and other gases, the operation of the vacuum pump being continued to remove the liberated gas. Preferably, the metal is cooled and reheated a number of times and finally it is transferred to the bulb 4 by tilting the apparatus. The conduit 3 is finally sealed off by fusion. A required amount of metal is caused to run into the bore of the stem 5 and to enter the bulb 6. The thermometer then is placed in an oven leaving the bulb 4 projecting and is heated several times to a temperature of about 800° C., or higher, to completely eliminate gas from the metal.

Gas bubbles are caused to enter the chamber 4 by tilting and tapping the thermometer. The stem of the thermometer finally is sealed off from the bulb 4, leaving the completed thermometer as shown in Fig. 2, containing a quantity 7 of gallium suitable for service. Most of the gas eliminated during the last stage of manufacture is contained in the sealed-off bulb. The small amount of gas remaining in the stem of the thermometer does no harm. When subjected to this pre-treatment gallium will move freely in the bore of the thermometer without adhering or tailing out and will give accurate temperature indications over a wide range of temperatures. It is undesirable to have a gas present in the thermometer as customary in thermometers containing mercury.

Alloys of gallium may be used in a scientific instrument as above described, for example, an alloy of gallium and tin, or an alloy of gallium and indium, or an alloy of gallium, tin and indium. The alloy first is prepared by fusing a desired mixture of the metals as well understood. Alloys containing substantial proportions of tin may be purified by the same process, as the tin forms a compound with the acid which is volatile as well as the gallium compound. The alloy thus prepared is treated in the manner described above in connection with gallium alone. As some of these alloys are plastic at room temperature, care must be exercised during the filling process to maintain the temperature high enough to keep the alloy fused.

I have prepared in this way a thermometer provided with a gallium alloy containing more than 50 per cent tin. In that case the thermometer tube preferably is provided with an expansion chamber, as indicated at 8 in Fig. 3 of the drawing, to permit ready expansion of the plastic metal before its liquefaction at temperatures just above room temperature. Without this expansion chamber the thermometer containing a plastic alloy would be apt to crack the container before the indicating metal can be liquefied. The unliquefied metal will not enter the capillary passage of the thermometer. It will expand, however, into the chamber 8.

A scale for reading temperatures may be marked on a backing strip of opaque quartz (not shown) or may be marked on the stem. Although the tube 3 and the bulb 4 of the thermometer preferably consist of fused or vitreous quartz, hard glass may be used for purposes which do not require the thermometer to withstand temperatures at which the glass will soften. When the stem or fine bore tube 5 consists of glass, then the bulb 1 should consist of quartz, and may be joined to adjoining glass parts during manufacture by the form of seal described in Thomson Patent No. 1,173,688, of February 29, 1916.

Quartz is of particular value as a material for the container of a high temperature thermometer as it has a substantially zero temperature coefficient and hence is adapted to give accurate readings.

The advantages of gallium and its alloys of remaining fluid over a wide range of temperatures may be utilized in other devices having a liquid metal element, such as circuit making and breaking devices, and I mean to include such other applications of gallium within the scope of the appended claims.

I intend by the appended claims to cover indium as an equivalent of gallium, and also to cover devices containing as a movable element an alloy in which more than half of the metal consists of constituents other than gallium, for example, devices containing an alloy of 60 per cent tin, 30 per cent gallium, and 10 per cent indium.

What I claim as new and desire to secure by Letters Patent of the United States is:—

1. A thermo-responsive device comprising a vitreous receptacle containing an indicator comprising gallium which is free from impurities which would affect the adhesion of the metal to solid surfaces.

2. An instrument comprising an evacu-

ated container and a body of metal therein, in which gallium is a constituent and which flows over the interior surface of said container during use of said instrument, said metal being free from impurities which would cause it to adhere to the interior surface of said container.

3. A thermometer comprising a receptacle consisting of a vitreous material capable of being heated to a temperature in excess of 500° C. without softening, and a quantity of metal contained therein comprising gallium as a constituent and being sufficiently free from impurities to permit movement over the interior surface of said receptacle without adhering thereto.

4. A thermometer comprising a container of vitreous material and a thermometric medium therein comprising an alloy of gallium and indium free from impurities affecting adhesion properties of said alloy.

5. A thermometer comprising a container of vitreous material and a thermometric medium therein comprising an alloy of tin, gallium and indium free from impurities affecting adhesion properties of said alloy.

6. A thermometric device comprising an evacuated container of vitreous silica and a temperature responsive medium therein comprising gallium in a state of purity permitting free movement over the interior surface of said container.

7. A thermo-responsive device comprising a receptacle and a body of metal therein containing about 60 parts tin, 30 parts gallium and 10 parts indium, said metal being free from impurities which would cause it to adhere to said receptacle.

8. A thermo-responsive device comprising a container, a filling therein comprising gallium said container having a bulb, a tube of capillary dimensions and an expansion chamber connecting said bulb and tube and positioned to receive said filling when expanding in the solid state.

9. The combination of a sealed container and an indicator therein comprising metallic gallium, said metal being substantially oxygen-free and being capable of flowing over the interior surface of said container without adhering thereto.

10. The combination of a receptacle of vitreous material and a body of gallium alloy contained therein which is substantially oxygen-free and is capable of flowing over vitreous surfaces without adhering thereto.

In witness whereof, I have hereunto set my hand this 17th day of November, 1925.

SYLVESTER BOYER.