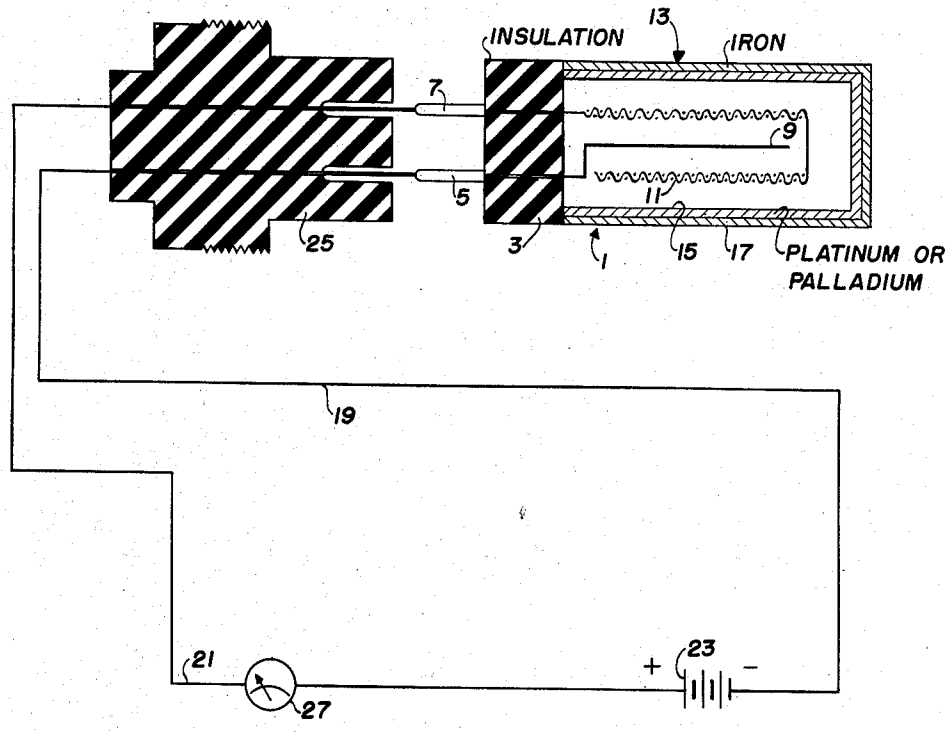
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ELECTRON TUBE APPARATUS FOR DETECTION OF ATOMIC HYDROGEN

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ELECTRON TUBE APPARATUS FOR DETECTION OF ATOMIC HYDROGEN

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This invention relates to new and useful improvements in apparatus for detecting the diffusion of hydrogen into metal, and more particularly to an electrical apparatus which includes an electron discharge tube which is normally non-conductive and which is rendered conductive upon permeation by a predetermined amount of hydrogen.

One object of this invention is to provide an improved electron discharge tube of high sensitivity for detecting the diffusion of hydrogen into metal.

Another object of this invention is to provide an improved electrical apparatus for detecting the diffusion of hydrogen into metal, which includes an improved electron discharge tube which is normally non-conductive and which is rendered conductive when penetrated by a selected amount of hydrogen.

A feature of this invention is the provision of an improved electron discharge tube having a pair of cold electrodes enclosed in a metal shell of a material permeable to hydrogen.

Another feature of this invention is the provision of an improved apparatus for detection of the diffusion of hydrogen through metal which includes an electron discharge tube having a pair of cold electrodes enclosed by an evacuated shell of a corrodible metal permeable to hydrogen, and an electric circuit impressing a predetermined potential across the electrodes and including a signal device arranged for operation by the circuit upon flow of current between the electrodes in response to the permeation of the tube by a predetermined amount of hydrogen.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

In the accompanying drawings, to be taken as part of the specification, there is clearly and fully illustrated a preferred embodiment of this invention, in which drawings the figure shown is a longitudinal, sectional view of an improved electron discharge tube for detection of hydrogen through metal, and a schematic wiring diagram of the signal circuit in which the tube is connected.

This invention consists of an improved electron discharge tube and signal circuit associated therewith for detection of the diffusion of hydrogen through metal. The electron discharge tube consists of a pair of cold discharge electrodes (i.e., non-thermionic electrodes) enclosed in an evacuated metal shell of a corrodible metal less noble than hydrogen and permeable to hydrogen. Preferably, the shell is of a metal highly permeable to hydrogen and having a thin coating of a corrodible metal less noble than hydrogen thereon. The tube is connected in an electrical circuit and a potential is impressed across the electrodes corresponding to the breakdown voltage required to ionize hydrogen at a selected pressure in the tube. When the tube is exposed to certain acid or other corrosive conditions productive of atomic hydrogen, the hydrogen diffuses into the tube. When the hydrogen pressure reaches a predetermined

level, the hydrogen is ionized to permit the flow of current between the electrodes and to energize a suitable signal device in the electric circuit. By proper selection of the tube dimensions and shape, the device can be made to respond to the diffusion of either small traces or large amounts of hydrogen through the corrodible metal. For example, a tube having a high surface-area/volume ratio (such as a flat tube) should be used where sensitivity to very small amounts is desired. A tube having a low surface-area/volume ratio (such as a sphere) should be used where sensitivity to large amounts of diffused hydrogen is desired. It is also possible to vary the sensitivity of the device by variation of the potential across the discharge electrodes, since the breakdown voltage for discharge between cold electrodes varies in a known and predictable manner for different pressures of pure hydrogen in the tube.

This apparatus in its preferred form is illustrated more fully in the drawing. The apparatus comprises electron discharge tube 1 having insulated base 3 and electrical connector prongs 5 and 7. A pair of cold (non-thermionic) electrodes 9 and 11 are supported on base 3 and connected to prongs 5 and 7, respectively. The tube is provided with a hollow shell 13 which is sealed to base 3 and evacuated to a very high vacuum (viz. 10^{-2} to 10^{-6} mm.). Shell 13 is composed of an inner supporting layer 15, about 0.025 inch thick, of a material highly permeable to hydrogen, such as platinum or palladium, and has an outer layer or coating 17 of iron which is sufficiently thin, about 0.0005 inch thick, to permit diffusion of hydrogen therethrough in a short time. In order that hydrogen will be liberated when the metal corrodes, the corrodible metal must be less noble than hydrogen, and is preferably the metal used in fabricating the equipment exposed to the corrosive environment. Since most equipment is of iron or ferrous alloys, these metals generally will be used. However, others may be used in certain cases. Prongs 5 and 7 are connected by electrical leads 19 and 21, respectively, to a power source 23, preferably a D.C. power source such as a battery or rectifier. Electrical leads 19 and 21 may extend through a pressure-tight fitting 25 if the apparatus is to be used in a high-pressure system. Electrical lead 21 has a suitable indicator 27 connected therein to signal the flow of current. Indicator 27 is shown as an ammeter, but may be any suitable signalling device, such as a sensitive relay for operating a signal bell, light, buzzer, or the like.

In the operation of this apparatus, the voltage applied to electrodes 9 and 11 is not sufficient to cause an arc discharge in the highly evacuated space within tube 1. However, as hydrogen diffuses into the evacuated interior of tube 1, the occurrence of a predetermined hydrogen pressure will result in ionization and flow of current, in the form of a glow discharge, between electrodes 9 and 11. The breakdown voltage for discharge between cold electrodes has been determined for hydrogen at very low pressures and is found to follow a smooth, approximately parabolic curve when plotted on semi-logarithmic paper. Thus, at a hydrogen pressure of about 0.04 mm. Hg the breakdown voltage for discharge between cold electrodes is about 400 v., at a pressure of 0.06 mm. Hg the breakdown voltage is about 200 v., and at 0.5 mm. Hg is at a minimum of about 60 v. Thus, tube 1 is impressed with a selected voltage and is exposed to corrosive conditions which are conducive to the formation of atomic hydrogen at the outer metal surface by the corrosion reaction, with attendant diffusion of the produced hydrogen into the corroding metal. At a predetermined hydrogen pressure the hydrogen will ionize and permit conduction in the form of a glow discharge between electrodes 9 and 11. The flow of current between the electrodes is indi-

cated on meter 27 or other signalling device which may be used.

In one application, this device can be used as an aid in the prevention of hydrogen embrittlement of sucker rods in wells. Hydrogen embrittlement of metals is caused by diffusion of atomic hydrogen into the metal. This diffusion of hydrogen into the metal requires conditions beyond those at which simple corrosion occurs. However, the atomic hydrogen is formed in such instances by corrosion at the metal surface and its formation can be prevented by use of suitable corrosion inhibitors, thus preventing the occurrence of hydrogen embrittlement. This, of course, requires the maintenance of adequate inhibitor concentrations in the corrosive environment. This apparatus can be used to assure the maintenance of such concentrations. It also can be used to detect the presence or absence of conditions at which diffusion of hydrogen into metal will occur, even though corrosion is taking place. In this application, the tube 1, with dimensions and shape chosen to provide sensitivity to trace amounts of diffused hydrogen, is attached to the sucker rod and lowered into the well. A voltage is impressed across the electrodes of the tube of a magnitude such as to cause conduction in the tube when trace amounts of hydrogen have diffused therein. When corrosion starts, small amounts of atomic hydrogen are formed and enter the tube, where they combine to form molecular hydrogen which, upon reaching the preselected pressure ionizes and causes a current to flow. The current flow triggers the alarm, or other indicating means 27 at the surface, whereupon the engineer retrieves the sucker rod and the tube from the well, adds more corrosion inhibitor to the well, attaches a new tube to the rod, returns the rod to the well, and resumes operation. The discharge tube can be made susceptible to regeneration by providing an outlet and valve means whereby the required high vacuum is regained by degassing. In this manner, the formation of atomic hydrogen and attendant hydrogen embrittlement of rods are prevented. The construction of the tube, utilizing a platinum or palladium shell coated with a very thin layer of iron, makes the tube respond quickly to the diffusion of atomic hydrogen through the corroding metal and thus to the corrosive media which are productive of atomic hydrogen. Thus when the tube is placed in a liquid containing water or acidic materials, the iron surface of the tube is corroded and atomic hydrogen is formed and diffuses directly into the evacuated interior of the tube to provide a rapid indication of corrosion.

This device is also useful in monitoring processes where diffusion of atomic hydrogen into a corroding metal must be maintained at or below a given level. It is especially useful in processes wherein metals are plated or cleaned, and in cathodic protection installations where hydrogen is normally formed.

While we have described fully and completely a preferred specific embodiment of this invention it should be understood that within the scope of the appended claims this invention may be practiced otherwise than as specifically described.

What is claimed is:

1. An electron discharge tube consisting of a pair of cold electrodes and electrical connectors therefor, supported on an insulated base and enclosed by a shell evacuated to a high vacuum, in which said shell comprises a hollow, closed-end tube of a material highly permeable to hydrogen and having a thin external coating of a corrodible metal, less noble than hydrogen, thereon.

2. An electron discharge tube according to claim 1 in which said shell is of a metal of the class consisting of platinum and palladium.

3. An electron discharge tube according to claim 1 in which said corrodible metal is of the class consisting of iron and ferrous alloys.

4. A cold cathode discharge tube consisting of a pair of cold electrodes and electrical connectors therefor, supported on an insulated base and enclosed by a shell evacuated to a high vacuum, in which said shell comprises a hollow, closed-end tube of a material highly permeable to hydrogen and having a thin external coating of iron thereon.

5. An electron discharge tube according to claim 4 in which said shell is of a metal of the class consisting of platinum and palladium.

6. A method of detecting conditions productive of hydrogen in a corrosive liquid which comprises contacting with said corrosive liquid an electron discharge tube consisting of a pair of cold electrodes and electrical connectors therefor, an insulated base supporting said electrodes and connectors, and a metal shell permeable to hydrogen, supported on said base, enclosing said electrodes, and being evacuated to a high vacuum, the external surface of said shell being of a corrodible metal less noble than hydrogen and operable to react with said corrosive liquid to generate hydrogen for diffusion into said tube, impressing an electrical potential across said electrodes corresponding to the ionization potential for a predetermined pressure of hydrogen in said tube, and electrically indicating the flow of current between said electrodes resulting from the ionization of hydrogen at said predetermined pressure.

7. A method in accordance with claim 6 in which said tube shell is of a metal of the class consisting of platinum and palladium and the external corrodible surface of said shell is in the form of a thin external plating of a metal of the group consisting of iron and ferrous alloys.

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