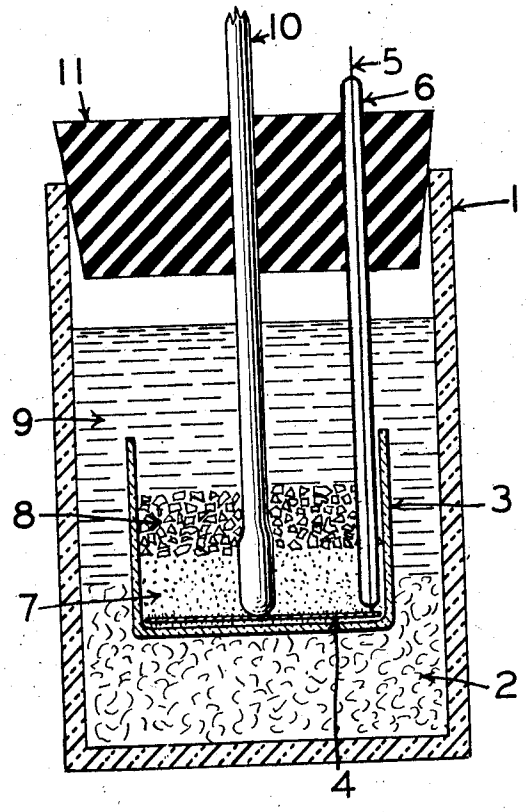
Jan. 11, 1944. S. EWING 2,338,713

HALF-CELLS FOR MAKING POTENTIAL MEASUREMENTS IN SUBSTANCES

Filed Aug. 18, 1939



INVENTOR

Scott Ewing

BY J. F. Mothershead

ATTORNEY.

Patented Jan. 11, 1944 2,338,713

UNITED STATES PATENT OFFICE

2,338,713

HALF-CELL FOR MAKING POTENTIAL MEASUREMENTS IN SUBSTANCES

Scott Ewing, Washington, D. C.

Application August 18, 1939, Serial No. 290,856

3 Claims. (Cl. 204—195)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

The features of novelty herein described and claimed may be manufactured, used and sold or any of the foregoing by or for the Government of the United States, or by or for its citizens without the payment to me of any royalty thereon.

This invention relates to improvements in the design of electrodes or half-cells for making contact between a conducting solution and substances and a metallic circuit which contains potential measuring instruments. The method greatly reduces the polarization at the metal-solution interface and the potential of the electrode is more nearly constant and reproducible than that of the half-cells heretofore used for this purpose.

An object of the invention is to improve the precision of potential measurements in any solution or substance or between structures therein and the reference half-cells. By means of my improved device it will be possible to regulate the flowing stray currents in the soil, solution or other substance more accurately. It will also be possible to adjust the potentials in cathodic protection currents so that protection of buried structures against corrosion will be obtained with a minimum expenditure for electrical energy and a minimum cost of the cathodic protection installation.

An object of my invention is accomplished by using an electrode on the surface of which a deposit of finely divided or spongy metal has been placed, or an electrode which is a combination of a metal with or a solution of a metal in a mercury base having a definite composition, i. e., an amalgam. Furthermore, the arrangement of the half-cell is such that the deposit or coating remains in place on the electrode and is effective in controlling the potential of the electrode.

Other objects, which are also accomplished, will be apparent from the following detailed description and accompanying drawing.

It is believed well known that the potentials of all metals with respect to solutions of their salts are more or less variable and subject to sudden changes without assignable cause. For instance, a copper electrode in a saturated solution of copper-sulfate has been widely used as a reference half-cell in measuring potential differences in the earth, contact between the ground and the copper-sulfate solution being made through a porous material. However, I have noticed certain peculiarities in the behavior of this electrode, such as very high resistance in the porous medium and relatively large variations in potential without assignable cause.

As another example, similar but smaller variations were also observed with cadmium electrodes in a saturated cadmium sulfate solution.

With respect to copper, I have discovered that when a clean copper surface is left for a time in a solution of copper-sulfate exposed to the air, numerous ruby-colored crystals appear on the metal surface. After a time these crystals disappear and a greenish-blue material appears. These products do not form if air is excluded from the solution. The ruby crystals are probably cuprous oxide (Cu_2O), and the greenish-blue deposit is probably a basic salt of copper. Both products are soluble in dilute sulfuric acid. The appearance of these products will be delayed if a very small amount of acid is added to the copper sulfate-solution. The more the amount of acid to the solution, the longer the delay in the appearance of the red crystals. Atmospheric oxygen and the acid probably slowly attack the copper with the formation of copper sulfate. After the sulfuric acid is consumed oxygen then probably combines with the copper to form crystals of cuprous oxide. These crystals appear to have no noticeable effect on the potential of the electrode so long as the electrode is not illuminated. However, when the crystals are illuminated with a 100-watt incandescent lamp placed about one foot from the beaker containing the electrode, the potential of the electrode changes as much as 40 millivolts. The effect of light entirely disappears when 1 milliliter of concentrated sulfuric acid is added to 500 milliliter of copper sulfate solution.

It was found that these variations in potential could be eliminated by the use of metal in finely divided form for the electrode. Such electrodes were produced by placing copper discs, plated with spongy copper, in the bottom of tall beakers and covering the electrode with copper sulfate solution and powdered copper sulfate crystals. Uniform current density over the electrode surface in the plating bath was obtained by placing a disc inside a glass cylinder of slightly greater diameter than the electrode. Contact with the disc was made by means of a thin strip of copper extending from the edge of the disc, and sealed inside a glass tube with sealing wax. The cylinder containing the electrode, approximately 5 centimeters in diameter, was placed in a 250 milliliter high-form beaker, a saturated solution of copper sulfate was poured into the beaker, and powdered sulfate was then carefully placed in the beaker, covering the electrode in the cylinder to a depth of about 2 centimeters. Two half-cells, prepared in this manner, showed potential dif-

ferences no greater than 0.05 millivolts over a period of 20 days. With this arrangement the spongy copper cannot fall off the disc, the solution in contact with the electrode is saturated, and the electrode is rather well protected from oxygen since convection currents are prevented by the layer of powdered copper sulfate. In the laboratory experiments electrolytic contact with the half-cell was obtained by means of an inverted U-tube filled with saturated copper sulfate solution.

Highly reproducible electrodes were also produced with other metals, such as spongy cadmium, prepared in a similar manner. Amalgam electrodes consisting, for example, of 12½% cadmium and a base of 87½% mercury by weight were also found to be highly reproducible. These types of electrodes were found to be only very slightly polarized by the passage of an electric current as compared with ordinary metallic electrodes.

Although the examples given above are limited to three types of electrodes, it is to be understood that my invention is not to be limited to these particular metals and amalgam but may be extended to all electrodes of other metals where the metal is in finely divided form or where it is a mercury alloy or amalgam of definite composition.

A practical embodiment having the characteristics of my invention and by which the same may be practiced is illustrated in the drawing. By reference to that cross sectional view of the half-cell, it will be seen that it comprises a cylindrical crucible, pot or container 1, of porous material such as porcelain. The sides of the container are preferably made impermeable by painting them with warm paraffin or protecting the same with more durable material. The bottom of the container, however, should remain porous or permeable for the reasons given hereinafter. Within the container 1, a layer 2 of insulating material, such as glass wool, is provided as an insulating support for a glass or similar inert insulating vessel 3 placed concentrically in the porous pot 1. The vessel 3, however, may be suspended or otherwise supported within the container. For the purposes given hereinafter, a metallic electrode 4, preferably, but not necessarily, disc or plate-like, is positioned horizontally in the bottom of the vessel 3. This electrode continues into or is connected to a terminal 5 which should be insulated, such as by passing it through a glass tube 6. The electrode 4 is then covered with a layer 7 of powdered crystals of a salt of the metal of which the electrode is composed and may be surmounted with a layer 8 of coarse crystals thereof. The container 1 is then sufficiently filled with a saturated solution 9 of the salt of the metal (7 and 8) to submerge the vessel 3 and its contents. A depth approximately that of half the diameter of the vessel has been found satisfactory. A thermometer 10 is extended into the solution 9 with its bulb sufficiently imbedded in the layers 7 and 8 of the salt as to bring it in close proximity with the electrode 4. A suitable stopper 11, such as rubber, or other convenient cover, is provided for the container 1. This cover or stopper 11 is provided with holes for the support and projection of the thermometer 10 and terminal 5.

The device shown in the drawing is particularly adaptable for use in measuring potentials in the soil, the electrode contact in this case being made through the porous pot. Other arrangements may be more suitable for other purposes but in such arrangements the electrode is preferably positioned in a manner to prevent the finely divided metal from falling off of the base metal and in a manner to keep the same in contact with the electrode; the electrode is preferably positioned in a manner whereby its potential is controlled by a surface which is covered with the finely divided metal and is shielded by a layer or coating of powdered salt; and the unshielded portions of the electrode are preferably arranged so that such surfaces have a negligible effect on the potential of the electrode.

While the type of half-cell described is especially designed for making potential measurements in the soil, it is not intended to imply that the use of the invention is to be restricted to the soil. For example, one skilled in the art could readily construct a half-cell, using a spongy copper electrode, for measuring the potential of the anode or cathode in a copper plating bath. The solution in the half-cell could be the same as the solution in the plating bath and all difficulties and uncertainties resulting from liquid junction potentials, which are inherent sources of error in other reference half-cells, would be eliminated. At the same time a highly reproducible half-cell would be obtained, which is not the case with an ordinary copper electrode. The potential of spongy copper or copper in finely divided form is the same as the potential of large crystals of extremely pure, unstrained copper.

I have conducted experiments with electrodes of the type described and found that any reasonable amount of impurities which may be present in the original chemicals, or may be accidentally introduced into the half-cell, will have a negligible effect on the potential of the half-cell.

In the practical use of the half-cell, the effect of temperature on its potential should be taken into consideration. For example, if two half-cells are used to determine the potential difference between two points, the half-cells should be at the same temperature, or the effect of temperature on the half-cells should be known and appropriate corrections applied. Also the effect of temperature should be determined for each metal and each solution. For example, I have found that the potential of the copper electrode in saturated copper sulfate solution is changed .95 millivolt per degree centigrade over the temperature range of 0 to 50 degrees centigrade; for spongy cadmium in saturated cadmium sulfate solution the change in potential is .62 millivolt per degree and for 12½ per cent cadmium amalgam in saturated cadmium sulfate solution it is .36 millivolt per degree, over the same temperature range. In all these cases the change in potential with temperature over this temperature range is nearly linear.

A potential always exists at the junction of two solutions which differ in composition. Such a potential exists at or near the porous pot of the half-cell and it is not claimed that this source of error has been eliminated in the present construction. In many types of measurement, such as in the measurement of the potential difference between two points, in which two similar half-cells are used with the usual measuring instruments, the two liquid junction potentials balance each other and so do not introduce any error. In measurements where a single half-cell is used it is often possible to contrive means for

avoiding or eliminating the effect of liquid junction potentials. In many of these latter cases, one merely wishes to observe a change in potential. Measurements with various soil samples differing widely in properties, and collected from various localities, show that the error introduced by liquid junction potentials is not likely to ever exceed 5 millivolts. In most practical cases it will not exceed 2 millivolts, with the spongy copper-copper sulfate half-cell, in those cases where the arrangement of equipment is such that the error cannot be avoided entirely. With cadmium or cadmium amalgam electrodes in saturated cadmium sulfate solution the maximum error may, however, be as great as 12 millivolts.

A serious source of error in the half-cells heretofore used has been the polarization produced at the electrode surface by the measuring current which passes through the half-cell. I have made careful and accurate measurements of the polarization on such as smooth copper, finely divided copper, smooth cadmium, finely divided cadmium and 12½ per cent cadmium amalgam electrodes, with a range of current density up to 0.1 milliamperes per square centimeter. These measurements disclosed that the polarization of the finely divided metal is reduced to about one-tenth the value obtained on smooth metal electrodes and was about 1 millivolt at the above current density. While there was a possibility of some polarization on the amalgam electrodes at a current density of 0.1 milliamperes per square centimeter it was so small that it was difficult to measure accurately.

The previously described half-cell has been designed with the object of making its electrical resistance as small as possible, and at the same time retaining its other valuable advantages. In most practical applications the resistance of a half-cell of convenient size will be negligible compared with the resistance of other parts of the measuring circuit. The resistance of any half-cell depends principally upon the resistivity of the solution in it and the size of the cell. One familiar with electrical measurements may readily measure the resistance of any half-cell and apply a correction for its resistance in those cases where such corrections are necessary.

From the foregoing it will be readily understood that my improved half-cell greatly reduces polarization, is more reproducible, remains more reproducible and is more stable than half-cells previously used.

I claim:

1. A half-cell adapted for field use, said half-cell comprising: a closed container having a porous wall portion for contact with a medium to be studied, a liquid electrolyte within said container and extending to a height above said porous wall portion, said electrolyte being essentially a saturated solution of copper sulfate, a cup within and spaced from said container and arranged below the level of said electrolyte, said cup being open at the top, having a substantially flat bottom, and being of impervious, inert, insulating material, a flat copper electrode arranged within said cup to rest on and cover the bottom thereof, the upper surface of said electrode being plated with spongy copper, and a layer of powdered copper sulfate crystals within said cup and covering said plated upper surface of said electrode.

2. A half-cell adapted for field use, said half-cell comprising: a closed container having a porous wall portion for contact with a medium to be studied, a liquid electrolyte within said container and extending to a height above said porous wall portion, said electrolyte being essentially a saturated solution of cadmium sulfate, a cup within and spaced from said container and arranged below the level of said electrolyte, said cup being open at the top, having a substantially flat bottom, and being of impervious, inert, insulating material, a flat cadmium electrode arranged within said cup to rest on and cover the bottom thereof, the upper surface of said electrode being plated with spongy cadmium, and a layer of powdered cadmium sulfate crystals within said cup and covering said plated upper surface of said electrode.

3. A half-cell adapted for field use, said half-cell comprising: a closed container having a porous wall portion for contact with a medium to be studied, a liquid electrolyte within said container and extending to a height above said porous wall portion, said electrolyte being essentially a saturated solution of cadmium sulfate, a cup within and spaced from said container and arranged below the level of said electrolyte, said cup being open at the top, having a substantially flat bottom, and being of impervious, inert, insulating material, an electrode arranged within said cup to rest on and cover the bottom thereof, said electrode being cadmium amalgam, and a layer of powdered cadmium sulfate crystals within said cup and covering said cadmium amalgam electrode.

SCOTT EWING.