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## CORROSION INHIBITORS

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This invention relates to the inhibition of corrosion of zinc and it more particularly refers to the inhibition of corrosion of zinc in alkaline environment and to the prevention of the formation of excessive amounts of gas in alkaline galvanic cells.

Zinc has been the most common anode material for galvanic cells for many years. In the past few years galvanic cells which utilize an alkaline electrolyte have gained prominence for many applications. It has been found that there is a certain amount of corrosion of the zinc anode in these cells which is not productive of useful electric power. Very often this corrosion occurs when the cell is in storage, and this, of course, tends to reduce the effective life of the cell when it is finally put in service.

A solution has been proposed for this problem which is based upon the saturation or near saturation of the electrolyte with products of zinc corrosion thus putting the system in equilibrium with respect to zinc corrosion. This has been accomplished by adding zinc oxide or zincate ions to the electrolyte. It has also been found that the amalgamation of the zinc anode very often aids in the inhibition of non-productive corrosion by electrolyte. These proposals have worked well; however, it is desirable to have alternate materials which are effective by themselves to inhibit zinc corrosion.

It is a primary object of this invention to provide materials which inhibit the corrosion of zinc in alkaline environment.

It is another primary object to prevent the formation of large volumes of gas within a zinc cell and thus preserve the structural integrity of the cell.

It is a more particular object to inhibit the non-productive corrosion of zinc anodes in alkaline galvanic cells.

It is another object to improve the characteristics of alkaline galvanic cells having zinc anodes.

This invention is based upon the discovery that there are certain organic compounds which prevent the corrosion of zinc in alkaline environment without relying on the establishment of equilibrium conditions between zinc, alkali, and zinc corrosion products.

In accord with this invention and the above stated objects, the inhibition of the corrosion of zinc is accomplished by the presence of an inhibiting amount of N,N-diethylcarbanilide. This compound is characterized by the fact that it is: substantially passive to the electrochemical reaction between zinc and an alkaline environment, chemically inert to both zinc and the alkaline environment, and resistant to oxidation.

It has been found that this compound inhibits the corrosion of zinc in both the solid form and in the powdered form. This inhibitor does not interfere with the normal operation of the zinc as an electrode and yet is effective to inhibit non-productive corrosion of the zinc, and to reduce gassing associated therewith.

The term "corrosion," refers to non-productive corrosion of the zinc anode which does not produce a usable galvanic current, unless otherwise indicated.

The above described corrosion inhibitor is effective when used with both amalgamated zinc and non-amalgamated zinc. The corrosion of amalgamated zinc, which is normally less subject to corrosion than non-amalgamated zinc, is inhibited to a greater degree by the



presence of the herein described inhibitor. The corrosion inhibiting character of N,N-diethylcarbanilide has been found to be substantially stable and does not diminish appreciably with the passage of time under normal storage and operating conditions.

The inhibitor compound can be incorporated in the cell in several ways. For example, the selected inhibitor can be added directly to the electrolyte prior to gelling the electrolyte. Alternatively the inhibitor can be dissolved in a suitable solvent, e.g., acetone, and the powdered zinc anode material then soaked in the solution. The solvent is then evaporated and the treated zinc incorporated in the cell. As another method the inhibitor solution can be sprayed into the anode material. For use in galvanic cells it is preferred to add the corrosion inhibitor to the anode material. In any event a homogeneous distribution of the inhibitor is desirable to provide uniform protection.

The compound described is employed in an inhibiting amount, that is, an amount which is sufficient to inhibit or substantially prevent the occurrence of non-productive corrosion and the formation of gas. In general, amounts of about 0.01 to about 1.0 weight percent based on the weight of anode material to be protected, i.e., on the weight of zinc, provide satisfactory corrosion inhibition. The actual amount of inhibitor necessary to provide adequate inhibition in any particular situation can easily be determined by methods well known in the art.

In order to test the simple corrosion inhibition effects of this compound in alkaline environment with respect to zinc, a mixture of 0.1 to 0.5 weight percent of the compound in a 30 percent aqueous solution of potassium hydroxide was made. A strip of zinc having a surface area of 6.15 square centimeters which weighed about 2 grams was immersed in each mixture. Table I below is a compilation of data taken from these tests showing the weight loss of each strip, given in milligrams, after a specific immersion time, given in days. These tests were run at 21° C. and 45° C. and the results at both temperatures are reported.

TABLE I

| Inhibitor | 21° C. | | 45° C. | |
|---|---|---|---|---|
| | Wt. loss (mg.) | Time (days) | Wt. loss (mg.) | Time (days) |
| None | 322 | 341 | 397 | 321 |
| Do | 689 | 754 | 533 | 677 |
| N,N-diethyl carbanilide | 8-25 | 224-245 | 21-43 | 167-181 |

These data dramatically show the effect of the compound of this invention on zinc corrosion in alkali environment. Table II below shows the improved corrosion resistance afforded by this compound in alkaline solution where the zinc has been amalgamated previous to immersion with 2.1 weight percent mercury. The data herein shown were taken at 45° C. and are reported as weight loss in milligrams after a specific immersion time given in days.

TABLE II

| Inhibitor | 45° C. | |
|---|---|---|
| | Wt. loss (mg.) | Time (days) |
| None[1] | 83 | 341 |
| Do.[1] | 224 | 719 |
| N,N-diethylcarbanilide | 10-14 | 196-217 |

[1] Other than mercury.

A comparison of the data presented in this table with that presented in Table I shows that the amalgamation of zinc is effective to inhibit the corrosion of zinc. It also shows that the inclusion of N,N-diethylcarbanilide as disclosed herein reduces the amount of corrosion over and above the reduction effected by the amalgamation of the zinc. Thus, it is seen that N,N-diethylcarbanilide acts as a corrosion inhibitor for zinc in alkaline environment and actually improves the performance of certain conventional corrosion inhibitors.

To further illustrate the advantageous characteristics of N,N-diethylcarbanilide, standard D-size alkaline-manganese dioxide cells were prepared. Powdered zinc, which was amalgamated to the extent of about 4 percent by weight was immersed for about 24 hours in a solution containing one percent N,N-diethylcarbanilide based on the weight of amalgamated zinc. The solvent was then thoroughly evaporated in a vacuum oven at between 40° C. and 60° C. The thus-treated zinc was then incorporated in standard alkaline-manganese dioxide cells employing potassium hydroxide as the electrolyte.

Table III shows the voltage characteristics of cells containing the treated anodes. Both open circuit potentials and those on a one-ampere load (by the interrupter technique) were observed. Substantially no effect on cell performance was noted.

These cells were then discharged at 0.5 to 1.0 ampere continuous drain to approximately 50 percent of their capacity. Open and closed circuit voltages of the used cells were then recorded. The range of voltages of the treated cells was approximately the same as the ranges observed in control cells, thus again indicating little or no effect of the additives on cell performance. This particular test is believed to be a very severe one in that about 90 percent of control cells, so discharged, showed excessive gassing and, in many cases, actual rupture of the cell containers occurred. After 50 percent discharge, a series of treated and control cells were connected to mercury manometers to measure gas pressure build-up over a period of 1 to 6 months at ambient room temperature. As Table III shows, the gassing was substantially reduced in the cells containing the inhibitor compound of this invention. Thus no rupture of sealed cells would be expected with the use of this compound. This compound is also expected to be beneficial with respect to corrosion and gassing under considerably less stringent conditions, e.g., during storage of fresh cells.

TABLE III

| Additive | Voltage of Fresh Cells | | Voltage of 50 percent Discharged Cells | | Gassing of 50% Discharged Cells |
|---|---|---|---|---|---|
| | Open Circuit | Closed Circuit (1.0 amp.) | Open Circuit | Closed Circuit (1.0 amp.) | |
| None | 1.48–1.53 | 1.37–1.46 | 1.24–1.28 | 0.94–1.12 | Excessive in majority of cells: cell rupture observed in several cases even after 1 month and particularly after 6 months at ambient room temperature. |
| N,N-diethylcarbanilide | 1.46–1.51 | 1.36–1.40 | 1.29–1.31 | 1.06–1.10 | Substantial reduction of gassing even after 6 months at ambient room temperature. |

What is claimed is:

1. A method of inhibiting corrosion of zinc exposed to an alkaline environment which comprises effecting said exposure in the presence of a corrosion inhibitor comprising N,N-diethylcarbanilide.

2. The method of claim 1 wherein said alkaline environment comprises .01 to 1.0 weight percent, based on the weight of said zinc, of said N,N-diethylcarbanilide.

3. The method of claim 1 wherein said alkaline environment is an aqueous solution of potassium hydroxide.

4. The method of claim 1 wherein said zinc is amalgamated.

5. A galvanic cell comprising a zinc anode, a cathode depolarizer, and alkaline electrolyte and N,N-diethylcarbanilide in an inhibiting amount.

6. The galvanic cell described in claim 5 wherein the corrosion inhibiting amount is from about 0.01 to about 1.0 weight percent based on the weight of the zinc anode.

7. The galvanic cell described in claim 6 wherein said electrolyte is an aqueous solution of potassium hydroxide and said cathode depolarizer is manganese dioxide.

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