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A POLY-NITRO-SUBSTITUTED AROMATIC
POLYCARBOXYLIC ACID
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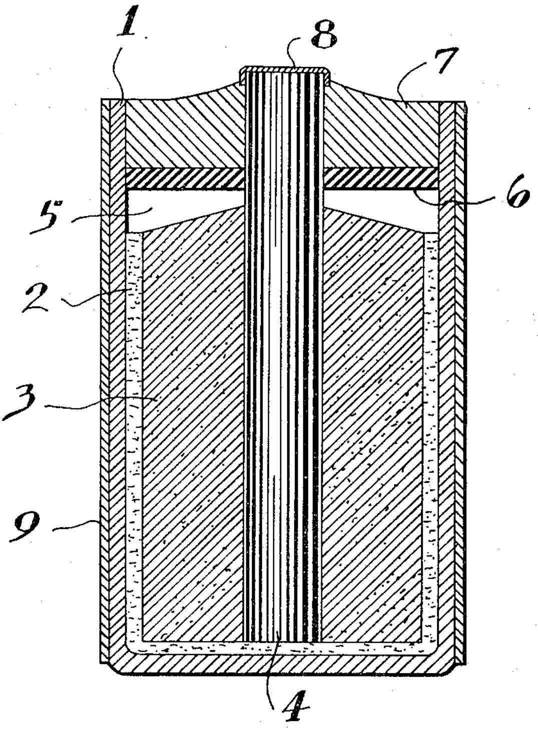

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DRY CELL HAVING AN ELECTROLYTE CONTAINING A POLY-NITRO-SUBSTITUTED AROMATIC POLYCARBOXYLIC ACID

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This invention relates to systems in which magnesium is associated with a corrosion inhibitor, and more particularly, provides novel systems in which magnesium is associated with a salt of a nitro-substituted aromatic carboxylic acid, and novel methods of protecting magnesium from corrosive attack comprising associating magnesium with such salts.

Magnesium is a reactive metal, to the extent, indeed, that it is pyrophoric under some conditions. Some of the uses for magnesium are such that passivating the surface or alloying the metal to reduce its activity interferes with its utility for the intended purposes. For example, this is the case where magnesium is used as the anode metal in a primary cell.

In primary voltaic cells using magnesium metal as the anode, the magnesium anode is electrolytically connected to a cathode section comprising a cathode depolarizer, through an aqueous electrolyte. Cathode depolarizers are oxidizing agents, and may attack a reactive metal like magnesium. When the depolarizer is a compound substantially insoluble in the electrolyte, such as manganese dioxide, the concentration reaching the magnesium anode by way of solution in the electrolyte is usually insufficient to be troublesome. To utilize a soluble depolarizer, a reserve cell construction can be employed, in which one cell system component, usually the fluid electrolyte, is omitted until just prior to use.

The aqueous electrolyte in a primary cell is normally a solution of an ionizable salt such as a halide or oxyhalide. The solution contains relatively high concentrations of such salts and is maintained in contact with the anode metal throughout the shelf and usage life of primary cells of the dry cell type. Such solutions are corrosive to anodes made of a reactive metal like magnesium, and it is necessary to have a corrosion inhibitor present in the cell to obtain an appreciable shelf life for a dry cell.

It is an object of this invention to provide a novel method of inhibiting the corrosion of magnesium.

A particular object of the present invention is to provide a novel method for inhibiting the corrosion of magnesium in voltaic cells.

These and other objects will become evident from a consideration of the following specification and claims.

In accordance with this invention, there is now provided a novel method of inhibiting corrosion of magnesium metal comprising associating a water-soluble salt of a nitro substituted aromatic carboxylic acid with magnesium metal subject to exposure to an aqueous corrosive environment.

The invention further provides novel dry cells, comprising a magnesium metal anode, an aqueous electrolyte and a cathode depolarizer, wherein the said anode is associated with a corrosion-inhibiting amount of a water-soluble salt of a nitro-substituted aromatic carboxylic acid. In this connection, reference may be made to the drawing, in which the figure illustrates a dry cell as provided by this inventiion.

The discovery that the stated salts inhibit corrosion of magnesium metal is unexpected. The association of water-soluble oxidizers like these salts with magnesium metal in an aqueous environment could be expected to

produce, rather than inhibit corrosion. Thus for example, for utilization of such soluble salts in a primary cell, so far as we are aware the system expected to be useful would be a reserve cell, and not a dry cell.

The present invention is embodied to particular advantage in a primary dry cell, since the nitro-substituted aromatic carboxylic acid salts can act as cathode depolarizers in cells having magnesium anodes. The potential delivered is significantly higher than that obtained from the corresponding nitro-substituted aromatic hydrocarbons which are essentially insoluble in aqueous electrolyte, while the rate of chemical corrosion of the magnesium anode is significantly less. Thus cells comprising the stated salts as cathode depolarizers have unexpectedly desirable performance properties, even after prolonged storage.

Referring now in more detail to the practice of the present invention, the present methods of achieving corrosion inhibition and systems wherein the corrosion inhibitor is associated with magnesium may be employed with any magnesium metal susceptible to corrosion and subject to exposure to an aqueous corrosive environment. By a magnesium metal is meant both magnesium and its various alloys, which may include other metals such as zinc, aluminum and the like. In such alloys, magnesium will comprise at least about 50% by weight of the total alloy weight, and more usually, above about 90% by weight of the total alloy weight. Thus for example, an alloy composed of 96% magnesium, 3% aluminum and 1% zinc is suitable for use as a magnesium anode. Other compositions, including compositions lower in magnesium content, are particularly adapted for use as materials of construction, for example, in the production of aircraft and the like.

To achieve corrosion inhibition of the magnesium, a water-soluble salt of a nitro-substituted aromatic carboxylic acid will be maintained in access relation to the metal surface exposed to the corrosive aqueous environment. In general, the water-soluble salts of such acids will comprise salts wherein the cation is an alkali metal such as lithium, sodium or potassium. The nitro-substituted aromatic carboxylic acids, salts of which are contemplated hereby, are those with plural nitro and carboxylic substituents wherein the carboxylic functional groups are attached directly to aromatic ring carbon atoms, and the nitro groups also are attached directly to ring carbons. The cyclic structure on which the substituents appear may be benzene ring, a naphthalene fused ring system, a biphenyl joined ring system, or other hydrocarbon aromatic ring system. Thus for example, presently useful salts are alkali metal salts of acids such as dinitrophthalic acid (3,4-, 3,5- or 3,6-), dinitroterephthalic acid (2,3- or 2,5-), dinitroisophthalic acid (each possible isomer), dinitropyromellitic acid, 3,6-dinitronaphthalic acid, tetranitronaphthalenetetracarboxylic acid, dinitrotrimellitic acid, dinitrotrimesic acid, dinitroprehnitic acid, 2,3,6,7-tetranitronaphthalic acid, 4,4′-dinitro-2,2′-biphenylyl dicarboxylic acid, dinitro, trinitro-, and tetranitrophenanthrenedicarboxylic acids and the like.

As will appear hereinafter, in a dry cell embodying the invention, the salts can be maintained in access relation to the magnesium whose corrosion is to be inhibited, by maintaining the magnesium and the salt each in contact with the aqueous electrolyte in the cell. When the magnesium is not maintained in contact with an aqueous solution in which the corrosion inhibitors of this invention can form a solute, the magnesium surface subject to exposure to a corrosive aqueous environment may advantageously be provided with a coating of the salt. To confer substantivity to the metal surface, the salt may be combined with a binder such as a polymeric, film-forming, adherent material. Where barrier protection is desired for the magnesium surface, this may be a water-impermeable film such as a coating of polyvinyl acetate, including or overlying a layer of a nitro-substituted aromatic carboxylic acid salt, which is available at failure points in the film, such as pin holes or cracks, to inhibit corrosion in an aqueous environment. Alternatively, the salts may be included in a water-soluble film, such as a polyvinyl alcohol film. With the latter arrangement, the salt is enabled to dissolve in such moisture as the environment of the magnesium surface contains, making this solution corrosion-inhibitive, instead of corrosive.

Proceeding now to a consideration of the primary cells embodying the present invention, the above-described method of applying the nitroaromatic acid salts to the magnesium surface in a polymeric film may be employed in this connection. In such case, the embodiment employed will be one permitting the electrolyte in the cell to contact the magnesium surface, and thus polymers employed to apply the salts to the surface are desirably water-soluble or water-permeable membranes, such as the coatings produced using polymers such as polyvinyl alcohol, natural polymers such as gum arabic, cellulose derivatives such as a carboxymethyl cellulose, and the like. Another manner of practicing the present invention comprises solution of the nitro-aromatic acid salt in the aqueous electrolyte phase of the cell.

A dry cell as provided by the invention will have a construction comprising means including an aqueous electrolyte to provide ionic while excluding electronic contact between the anode metal and the cathode depolarizer. The magnesium surface participating in the electrochemical reaction will be wetted by this electrolyte during the life of the cell. Accordingly, the aromatic acid salts employed as corrosion inhibitors in accordance with this invention may be introduced into the cell as a solute in the electrolyte.

The electrolyte solvent component may be simply water, including tap or distilled water, where provision is otherwise made for the presence of salt-forming ions in the electrolyte. Thus, the stated nitro aromatic acid salts may act as the ions providing the electrolytically conductive solute. Usually it will be advantageous to introduce a soluble ionizable salt into the electrolyte aqueous medium providing for immediate ionic conductance in operation of the cell. The cation of the stated ionizable salt may be an alkali metal such as lithium, sodium or potassium, an alkaline earth metal such as magnesium, zinc, strontium, cadmium or barium, or a non-metallic cation such as ammonium. The anion of the salt may be a halide such as chloride, bromide and the like, an oxyhalide such as perchlorate, and so forth. Thus for example, illustrative of useful salts are magnesium bromide, magnesium perchlorate, and so forth.

The electrolyte contacting the anode metal may be saturated with the nitro aromatic acid salt, or contain a lesser concentration, provided this is a corrosion-inhibiting amount. The electrolyte may also include additional, inorganic corrosion inhibitors, exemplary of which are barium chromate, mixtures of barium chromate with lithium chromate, and the like. When the salts of the present invention are employed in conjunction with other corrosion inhibitors such as the stated chromates, the amount necessary to achieve corrosion inhibition may be less. In any case, a corrosion-inhibiting amount, sufficient to produce an appreciable prolongation of the life of the cell, will be included.

In the dry cells contemplated by this invention, the cathode depolarizer will normally comprise a particulate material, and separation between the anodic metal and the cathode section of the cell is preferably provided by a separator structure. This separator structure must permit connection between the anode and cathode section by the fluid electrolyte, and accordingly the separator is a porous material which may be permeated by the electrolyte, such as a porous bibulous material. Bibulous separators which may be permeated by the electrolyte may comprise porous cellulosic materials including absorbent papers such as kraft paper, woven materials such as cotton fabrics, gel-like materials such as a starch gel, and so forth, alone or in combination. Useful starch gels are prepared by combining starch or a mixture of starch and a cereal flour such as wheat flour with the fluid electrolyte, following which gelatinization may be produced by the action of the electrolyte, by heating, and so forth. Other porous organic materials such as films of a plastic like porous polyethylene or inorganic porous products such as ceramics or glass can be used.

Referring to the cathode section, this will comprise a cathode current collector, a cathode depolarizer, and a cathodic material comprising a particulate conductive carbon. The cathode current collector will be a coherent inert structure possessing electrical conductivity, and is desirably an inert conductive material such as conductive carbon. For example, it may be a graphite rod or bar. In the bulk of the cathode depolarizer mass contacting the stated current collector, the cathode depolarizer is associated with an electronically conductive, inert particulate material distributed through the mass. The stated conductive particulate material will normally be a conductive carbon of the kind known as a battery black. Generally this is a carbon black produced by pyrolysis of an unsaturated carbon compound, such as an acetylene black. The ratio of conductive carbon to cathode depolarizer may vary, for example, between 90:10 and 10:90 (by weight), but is generally about 1:2.

The cathode depolarizer in the cells of this invention may be an insoluble inorganic oxide, such as manganese dioxide, copper oxide, silver oxide, nickel oxide, and so forth.

In a further embodiment of this invention, the depolarizer may consist essentially of a soluble salt of a nitro-substituted aromatic carboxylic acid. Sealed cells with the stated depolarizer composition, consisting essentially of these soluble nitro compounds having corrosion-inhibiting properties, have especially prolonged storage stability. Salt provided with the cathode mix in excess of the solubility of the salt in the electrolyte provides a reservoir for maintaining saturation of the electrolyte with corrosion inhibitor throughout the life of the cell. The cells also have an advantageously high and essentially flat operating voltage.

In still another embodiment of the present invention, the cell depolarizer may comprise an organic oxidant which is an insoluble cathode depolarizer. The insoluble, nitro-substituted aromatic compounds like m-dinitrobenzene, 1,4,5,8 - tetranitronaphthalene, 2,5-dinitropyrrole, 3-nitrocinnoline and dinitrocinnoline are exemplary of these organic depolarizers. Other types of organic water-insoluble depolarizers, including nitroso compounds such as 4-nitrosophenol, 1-nitroso-2-naphthol, 1,4-dinitrosonaphthalene and m-nitronitrosobenzene, quinones such as benzoquinone and anthraquinone, and the like, may also be used.

The form of the cell may vary. For example, the magesium anode may be a sheet or bar, may be formed in a cup to provide the container for the cathode mix, or may be powdered. The cell may have a round, cylindrical shape, or may be flat. It may be an inside-out cell, in which the exterior is the cathode. When the anode and cathode are particulate materials, they may be applied to a permeable bibulous separator in conjunction with binders, improving the adherence thereof to the separator, such as polyvinyl alcohol, carboxymethyl cellulose, and so forth.

The cells contemplated by this invention are sealed, to adapt them for storage prior to use. The sealed cells comprise the total electrochemical system, including magnesium metal anode, cathode depolarizer, aqueous electrolyte and a corosion-inhibiting amount of a soluble nitro-substituted aromatic carboxylic acid salt. These cells remain serviceable after storage for months or years, and are immediately ready to deliver power, even after such storage, upon connection into an external electrical circuit.

The invention is illustrated but not limited by the following examples.

Example 1

This example illustrates the corrosion-inhibiting effects of the soluble nitro-substituted aromatic carboxylic acid salts.

A series of aqueous solutions are prepared having the following compositions (g./ml.=grams per milliliter).

	G./ml.
No. 1: $Mg(ClO_4)_2$	0.249
No. 2:	
$Mg(ClO_4)_2$	0.249
$Li_2CrO_4 \cdot 2H_2O$	0.001
$BaCrO_4$, to saturation.	
No. 3:	
$Mg(ClO_4)_2$	0.249
Tetrasodium dinitropyromellitate	0.25
No. 4:	
$Mg(ClO_4)_2$	0.249
Disodium 3,6-dinitrophthalate	0.25
No. 5:	
$Mg(ClO_4)_2$	0.249
$Li_2CrO_4 \cdot 2H_2O$	0.001
$BaCrO_4$, to saturation.	
m-Dinitrobenzene, to saturation.	
No. 6:	
$Mg(ClO_4)_2$	0.249
$Li_2CrO_4 \cdot 2H_2O$	0.001
$BaCrO_4$, to saturation.	
Tetrasodium dinitropyromellitate	0.25

Six beakers are respectively half-filled with 20 ml. each of the above-described six aqueous solutions. In each beaker there are immersed two cans of a magnesium alloy of a type formulated for use in dry cells, identified as ASTM alloy AZ–10, which is 0.1% Al, 0.05% Zn, 0.01% Ca, balance magnesium. The assemblies are then held under a nitrogen atmosphere at room temperature and examined periodically.

At the end of 12 days, the magnesium cans in solution No. 1, comprising magnesium perchlorate electrolyte without any added inhibitor, are completely converted to magnesium hydroxide precipitate. The metal structure is entirely destroyed.

After a 30 day time lapse, the cans immersed in solution No. 2, containing standard chromate inhibitor additives, are slightly pitted on the surface. The bulk of the metal is in good condition.

After the same time interval, the cans immersed in solutions No. 3 and 4 are in equally as good condition as those protected with the chromate inhibitors. The nitro-substituted aromatic carboxylic acid soluble salts have protected the metal from attack by the electrolyte.

In solution No. 5, in which dinitrobenzene has been dissolved in the electrolyte together with the chromate inhibitors, after the month's interval the condition of the cans is comparable to that of those in the inhibited electrolytes.

However, the cans immersed in solution No. 6 for a month, with the electrolyte having chromate inhibitors and the nitro aromatic acid salt both dissolved in it, show no evidence of corrosion at all. The cans are substantially as bright and free of surface attack as before exposure to the electrolyte solution.

When a can has been maintained for 60 days in solution No. 5, containing m-dinitrobenzene and chromate inhibitors, the pitting has proceeded so far that the can has split open. The same is true of a can held 60 days in solution No. 2, containing chromates. But a can in solution No. 6, containing the dinitropyromellitate salt and chromate inhibitors, held under the same conditions for 60 days, is still intact and shows only very slight pitting.

Example 2

This example illustrates cathode depolarizing properties of the nitro aromatic acid soluble salts.

The test equipment used in obtaining the data described below comprises a polymethacrylate tube having an 0.5 inch diameter bore, acting as the cathode mix container. At the open bottom of the tube, the depolarizer carbon mix rests on a cation exchange membrane. The polymethacrylate tube is placed in a container partially filled with electrolyte. A counter electrode consisting of a carbon rod about ½ inch in diameter is immersed to a depth of about 2 inches in the electrolyte in the outside container. The electrolyte employed is poured into the tube containing the deloparizer mix, in an amount just sufficient to provide a liquid phase above the top of the mix visible to the eye. A graphite pressure disc is placed over the cathode mix, which is surmounted by a graphite rod (working electrode) carrying a 550 gram weight. Connections to a standard calomel electrode are made through access ports in the side of the cell, to points just above the cathode mix, just below the top of the cathode mix, and at the bottom of the cathode mix. This provides measurements of potential where the drain rate is higher than the imposed load, at the bottom of the assembly, and where it is low, at the top. Measurements are made at room temperature (about 70° F.). The cathode is driven by lead/acid storage batteries connected in series, which are in series with a milliammeter and a variable resistance. The working, counter and calomel electrodes are connected into the circuit, and a voltmeter is also included in the circuit, between the calomel electrode and the working electrode.

In the tests described below, the charge is a mixture of 0.5 gram (g.) of the nitro compound and 0.25 g. of Shawinigan acetylene black (50% compression), and the electrolyte is an aqueous solution of 168 grams of ammonium bromide per liter. The current drain is 0.025 ampere.

With tetrasodium dinitropyromellitate as depolarizer, the initial operating voltage is 0.0 volt (against normal hydrogen electrode) and over a period of better than 5 hours, measured at the top of the depolarizer mix, this has declined less than 0.2 volt. At the bottom of the cathode mix, after better than 2 hours, the potential is still above −0.2 volt. At all levels in the depolarizer mix, during the first two hours of operation, this sodium salt is superior to m-dinitrobenzene, which contains the same number of reducible nitro groups, but lacks the carboxylate salt groups.

With the disodium salt of 3,6-dinitrophthalic acid, the initial operating voltage is 0.08 volt, and after 2 hours the potential at the top of the mix is still over 0 volt, and at the bottom it is −0.14 volt.

Example 3

This example describes a dry cell embodying the present invention, as illustrated in the figure.

The figure is a diagrammatic illustration of a vertical section of a dry cell prepared in accordance with the invention, in which **1** is a cup of magnesium, **2** is a separator made of porous material such as kraft paper lining the interior of the cup, and **3** is a cathode mix prepared by combining acetylene carbon black particles and a depolarizer. For example, this may be a 50:50 by weight mixture of tetrasodium dinitropyromellitate and acetylene black. The paper separator and the cathode mix are permeated by a liquid electrolyte which is for example an aqueous solution of 168 grams per liter magnesium perchlorate, and 1 gram per liter lithium chromate, saturated with tetrasodium dinitropyromellitate and with barium chromate. Centrally located in the cell and prevented from contacting the exterior can **1** by the separator **2** is a carbon rod **4** which is the cathode current collector. An air space **5** above the top of the cathode mix intervenes between it and an insulating washer **6** and cover **7** over the top of the cell.

A cap **8** provides an electrical connection to the cathode current collector **4** and a jacket **9** covering the exterior of the can **1** insulates it from contact on the sides while leaving the bottom free for making electrical contact.

Connection of the cell system, by a cathode lead attached to cap **8** and anode lead contacting the bottom of the can **1**, is made to the remainder of a completed electrical circuit (not shown) in which the current generated is passed through a resistance. The operating voltage is 1.3 volts.

While the invention has been described with particular reference to various specific preferred embodiments thereof, it is to be appreciated that modifications and variations can be made without departing from the scope of the invention, which is limited only as defined in the appended claims.

What is claimed is:

1. A dry cell including a magnesium anode, a cathode depolarizing mix and an aqueous electrolyte, said electrolyte having dissolved in it a corrosion-inhibiting amount of a water-soluble alkali metal salt of a poly-nitro-substituted aromatic polycarboxylic acid consisting of a hydrocarbon aromatic ring structure wherein the nitro and the carboxylic substituents are attached directly to the ring carbon atoms of said aromatic ring structure.

2. The cell of claim **1** wherein said salt is an alkali metal salt of a dinitrobenzene polycarboxylic acid.

3. The cell of claim **1** wherein said salt is disodium 3,6-dinitrophthalate.

4. The cell of claim **1** wherein said salt is tetrasodium dinitropyromellitate.

5. The cell of claim **1** wherein said cell is sealed.

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