Jan. 11, 1966 M. J. PRYOR 3,228,866

PROCESS FOR ACTIVATING ALUMINUM CONTAINING ANODE AND ANODE

Filed June 6, 1963 2 Sheets-Sheet 1

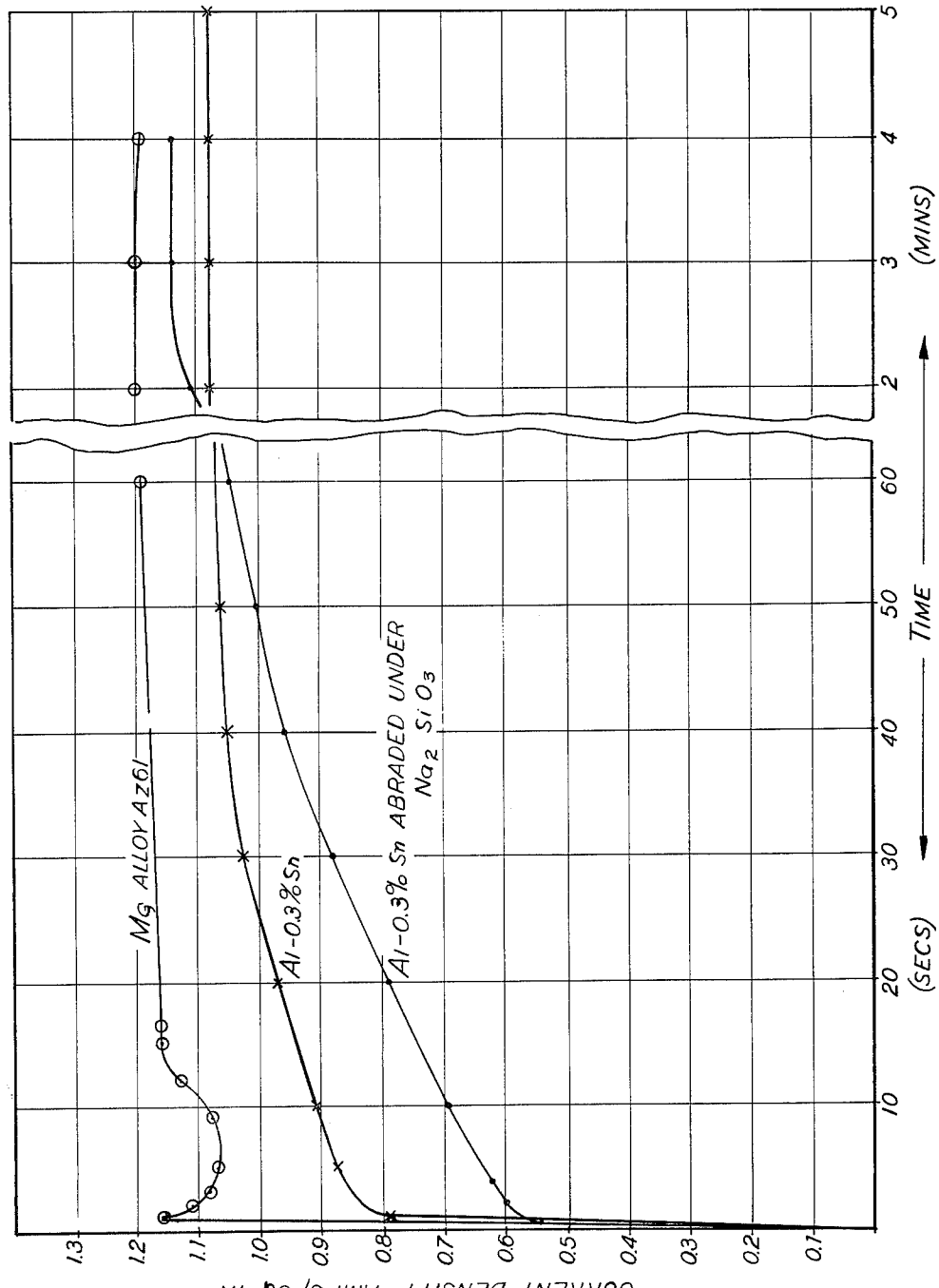


FIG. 1

INVENTOR.
MICHAEL J. PRYOR
BY Robert H. Bachman
ATTORNEY

Jan. 11, 1966 M. J. PRYOR 3,228,866

PROCESS FOR ACTIVATING ALUMINUM CONTAINING ANODE AND ANODE

Filed June 6, 1963 2 Sheets-Sheet 2

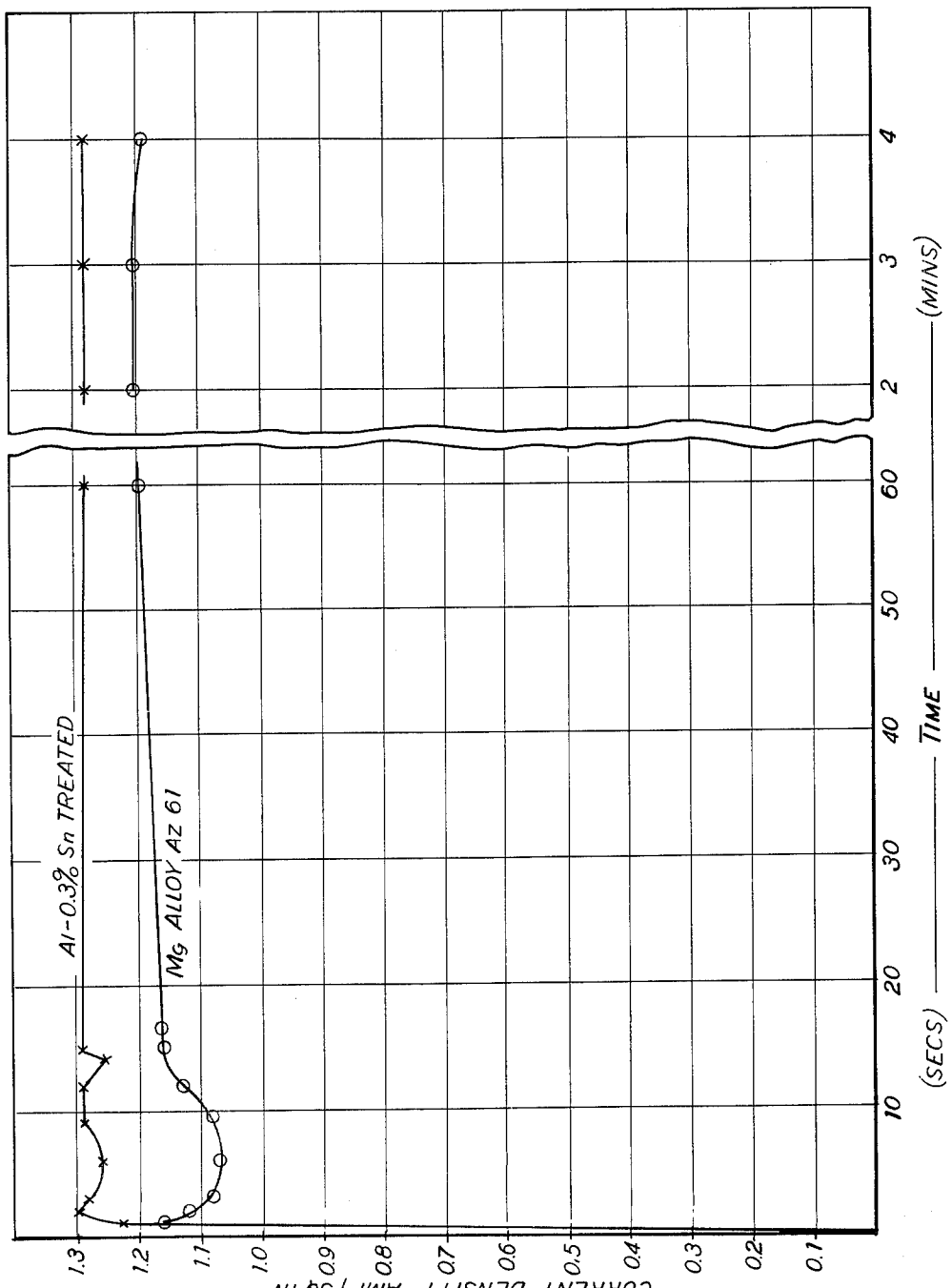


FIG-2

INVENTOR.
MICHAEL J. PRYOR
BY Robert H. Bachman
ATTORNEY

United States Patent Office 3,228,866
Patented Jan. 11, 1966

3,228,866

PROCESS FOR ACTIVATING ALUMINUM CONTAINING ANODE AND ANODE

Michael J. Pryor, Hamden, Conn., assignor to Olin Mathieson Chemical Corporation

Filed June 6, 1963, Ser. No. 286,056
12 Claims. (Cl. 204—197)

The present invention relates to a process for activating aluminum-containing anodes and to the improved aluminum-containing anode thereby obtained.

Because of their numerous excellent properties, aluminum-containing anodes have been widely used in a variety of applications, for example, aluminum-containing anodes may be advantageously used (1) in primary electric batteries suitable for use with liquid electrolytes, such as aqueous electrolytes and especially sea water, (2) as sacrificial aluminum-containing anodes in conjunction with a metallic cathode which thereby receives substantial protection against corrosion and (3) in primary cells of the dry type, with the aluminum-containing anode also serving as the container for the cell.

Particularly advantageous are the numerous aluminum base alloys especially formulated to provide good anodic characteristics. Examples of such aluminum-containing alloys may be found in United States patent application Serial No. 251,024, filed January 14, 1963, now Patent No. 3,789,486, which relates to a highly efficient metal anode comprising an aluminum base alloy containing at least 90 percent aluminum and between 0.04 and 0.5 percent tin.

One disadvantage, however, of aluminum-containing anodes which has limited their effectiveness for numerous applications is the relatively long periods of time required for these anodes to achieve full power output. For example, the aluminum-tin alloys disclosed in United States patent application Serial No. 251,024, referred to above, achieve full power output after approximately one minute's operation. This disadvantage is especially significant when aluminum-containing alloys are utilized as the anodes of sea water batteries containing, for example silver chloride cathodes. These batteries are activated by filling with sea water and must achieve full power output in a matter of seconds, especially in view of relatively short life of the battery, often as little as six minutes.

The magnesium alloys conventionally used as anodes in sea water batteries generally achieve full power output after approximately 15 seconds. However, the aluminum-containing anodes have numerous highly desirable advantages over the magnesium anodes and, therefore, it is highly desirable to simply and conveniently overcome the foregoing disadvantage, namely, the relatively slow activation characteristics of aluminum-containing anodes.

The relatively slow activation rate of aluminum-containing anodes is believed to be due to the surface oxide and hydrated oxide corrosion products that form on the anodes during standing in ordinary air. Abrasive removal of the corrosion products is effective in increasing the activation rate; however, the corrosion products quickly reforms when the aluminum surface is allowed to remain in air, even, for example, after 24 hours in a desiccator.

It is therefore, an object of the present invention to provide a process for activating aluminum-containing anodes and to provide an improved anode.

It is a further object of the present invention to provide an improved aluminum-containing anode, and an improved process for obtaining same, said anode being characterized by rapid achievement of full power output.

It is a still further object of the present invention to provide an improved process and an improved anode as

above without impairing the other desirable characteristics of the anode.

Further objects and advantages of the present invention will appear hereinafter.

In accordance with the present invention it has been now found that the foregoing objects and advantages may be readily obtained and a process for activating aluminum-containing anodes or aluminous anodes provided which comprises contacting said anodes, preferably in the substantially film free condition, i.e., having an average oxide film thickness of less than 10 Angstrom units, for at least 5 seconds with a dilute aqueous solution of a fatty acid, or preferably a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of soluble fatty acid per liter or containing at least 0.1 milligram of the metallic component of a soluble metallic soap per liter. The improved, activated anode of the present invention comprises an aluminous anode coated with the foregoing dilute aqueous solution.

In accordance with the process of the present invention it has been surprisingly found that the simple and expeditious process outlined above overcomes the disadvantages in the use of aluminum-containing anodes and achieves full power output in as little as, for example, 15 seconds. Especially surprising and unexpected in accordance with the present invention is that the aluminum-containing anode treated in accordance with the present invention actually attains considerably improved current density and power output.

The process of the present invention is effective in improving the anodic characteristics of any aluminum base alloy. The critical requirement is that the alloy contain a major proportion of aluminum, i.e., greater than 50 percent aluminum, since the aluminum is the factor which retards the rapid attainment of full power output. Exemplificative anodic materials include, but are not limited to, pure aluminum, aluminum base alloys containing varying proportions of alloying ingredients, such as, for example, up to 10 percent zinc to obtain improved galvanic activity, e.g., alloy 7072 and also, for example, aluminum base alloys containing at least 90 percent aluminum and from 0.04 to 0.5 percent tin as discussed in United States patent application Serial No. 251,024. Preferably, the tin is retained in solid solution to the maximum degree, i.e., about 0.1 percent, with the excess tin, or a suitable third ingredient, being provided as taught in co-pending application Serial No. 60,166, filed October 3, 1960, now Patent No. 3,180,728, to improve uniformity of corrosion and to improve anodic efficiency.

The preferred manner of preparing the alloys in the above-identified co-pending patent applications is to heat the aluminum-tin sample at elevated temperatures, e.g., between about 570–640° C., for a sufficient period of time to dissolve the maximum amount of tin and to redistribute excess tin or other alloying additions in a coarse, particulate form which produces maximum uniformity of attack and power efficiency. Generally, the heating period within the preferred temperature range may vary between 15 minutes and 24 hours. After the heating period the sample is cooled rapidly, for example, by immersion in a large volume of water at ambient temperatures. For simplicity, this treatment may be termed "homogenization treatment."

It is preferred in accordance with the process of the present invention that the treatment of the aluminum-containing anode be performed when the anode is in a substantially oxide free state. This is not essential but it has been found that greater improvement is thereby obtained.

The pre-existing, heavier oxide coating can be removed

by conventional means, for example, etching or mechanical abrasion or wire brushing, preferably the mechanical abrasion is performed under the contacting solution so as to avoid the reformation of oxide coatings having a thickness of greater than 10 Angstroms. Similarly, if etching is employed or prior mechanical treatments, it is desirable to avoid subsequent formation of excessive oxide coatings.

The process of the present invention comprises contacting the above anode for at least 5 seconds with a dilute aqueous solution of a metallic soap or of a fatty acid. Longer contact times may be preferred to obtain maximum exposure, for example, on the order of 5 to 60 minutes. Extended contact times may be used, if desired, but excessive contact times are not beneficial. The solution should have a pH of from 4 to 7 and contain at least 0.1 milligram of the metallic component of the soluble metallic soap per liter or of soluble fatty acid per liter. Generally up to 10 milligrams per liter may be employed, preferably around 1.0 milligram per liter. While the metallic soaps are preferred in accordance with the present invention, the fatty acids themselves may be conveniently used. The particular method of contacting the anode with the solution is not critical and any convenient method may be employed, for example, immersion, spraying, brushing, coating, etc.

The term metallic soap is used in its conventional sense to contemplate the salts of heavy metals with oleic, stearic, palmitic, erucic, recinoleic, pelargonic, suberic, azelaic and lauric acids, for example, and more generally the salts of long chain fatty acids with the heavier metals, such as cadmium, copper, lead, tin or zinc. Representative metallic soaps include, but are not limited to, the salts of the foregoing heavy metals with the foregoing acids. Generally, it is preferred to use the long chain fatty acids which contain one or more unsaturated bonds. The preferred metals are those whose hydroxides are very weak bases, i.e., with dissociation constants lower than 10^{-4} at 25° C.

Any fatty acid may be conveniently employed and preferably the long chain fatty acids. A representative list of typical and preferred fatty acids includes, but is not limited to, any of the foregoing fatty acids.

The process of the present invention will be more readily apparent from a consideration of the following illustrative examples.

Example 1

This example represents the typical activation characteristics of the conventional magnesium alloy AZ 61, a magnesium alloy containing about 6 percent aluminum, 1 percent tin, 0.3 percent manganese and the balance magnesium.

The test primary cell was constructed in the conventional manner. The anodes were shaped from sheet material, generally about 0.02 inch thick. The cathodes were shaped from silver chloride sheet about 0.015 inch thick. The cathodes were modified to incorporate insulating spacers which would allow them to be placed in close proximity to the anodes without electrical short circuiting. This was done, in one of the conventional art manners, by using glass beads fastened to one side of the sheet. A multiplicity of holes was drilled in the cathode to increase the reactive surface of the silver chloride. In addition, the silver chloride was partially reduced to silver in a conventional manner by immersion in a photographic film developer.

The electrical contact with the silver chloride cathode was furnished by a 0.001 inch thick 99.9 percent pure silver foil held in pressure contact in the conventional fashion. External electrical connections were made to the anode and cathode, suitably insulated from each other and from the electrolyte. The anode, cathode and spacers were then taped together to complete the cell structure.

Provisions were made for collecting and measuring hydrogen gas evolved during the reaction time, for measuring temperature rise in the electrolyte and for measuring the potential on open or closed circuit, the current on short circuit (negligible resistance) or with any suitable simulated load resistance.

In this example the anodic material was the magnesium alloy AZ 61 with no surface pretreatment. The results are shown in the graph of FIGURE 1 which shows that full current output from the untreated magnesium alloy AZ 61 was obtained after about 15 seconds.

Example 2

Example 1 was repeated using an aluminum-0.3 percent tin alloy as the anodic material. The aluminum used was at least 99.995 percent pure and the alloying addition was pure tin. When analyzed after casting this alloy contained 0.30 percent tin and 0.0028 percent iron and less than 0.001 percent each of silicon and copper.

The ingot was given a homogenization heat treatment of about 620° C. for four hours, quenching in water, cold rolled from 0.025" gage to .01" gage and stretched to 0.1 percent of the proportional limit.

The activation characteristics of this alloy are shown in the graph of FIGURE 1. This shows that full current was not achieved until about one minute had elapsed.

Example 3

Example 2 was repeated with the exception that the aluminum-tin alloy was abraded for 30 seconds under a 1.0 M sodium silicate solution followed by quenching in cold distilled water and immediately introducing the pretreated specimen into the silver chloride cell. The abrading procedure comprised abrading under the contacting solution with finely divided (300 mesh) alumina powder contained in a stream of argon at a pressure of 50 p.s.i.

The results are shown in the graph of FIGURE 1. It will be seen that the sodium silicate, far from improving the activation time of the aluminum-tin alloy, roughly doubled the time required to obtain a constant current output in this cell.

Example 4

Example 3 was repeated using a 1.0 M of sodium chromate instead of sodium silicate. Similar disadvantageous results were obtained.

Example 5

Lead linoleate extract was prepared by digesting solid technical grade lead linoleate with xylene, coating the inside of a large beaker thinly and allowing the beaker to stand for 8 days to permit the lead linoleate to dry and filling the beaker with deionized distilled water to extract a certain quantity of the lead linoleate in aqueous solution over a period of 8 days. Generally amounts of lead on the order of 200 milligrams per liter were found in the water after this treatment. The pH of the aqueous extract generally was between 5 and 5.5.

Example 6

Example 3 was repeated with the aluminum-tin alloy abraded as in Example 3 under the lead linoleate extract of Example 5 diluted to produce a concentration of 1.0 milligram of lead per liter. The specimens were removed from the aqueous extract, blown dry with compressed air and stored for 2 days in a desiccator to simulate some of the conditions found during natural storage. The activation characteristics of the aluminum-tin alloy so treated is shown in FIGURE 2 in comparison with that of the magnesium alloy AZ 61 of Example 1.

It will be seen that this activation time of the aluminum-tin composition is reduced to about 15 seconds and is now superior to that of the magnesium alloy AZ 61. Furthermore, surface pretreatment with the lead linoleate extract not only improved the activation time but also improves the current density so that the treated alloy generates a substantially higher constant current output than similar un-

treated aluminum-tin alloys or the magnesium alloy AZ 61 in the untreated condition. After two minutes operation the current output of the lead linoleate treated aluminum-tin sample is still about 7 percent superior to that obtained in a similar magnesium-silver chloride cell.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A process for activating an aluminous anode which comprises contacting said anode for at least 5 seconds with a dilute aqueous solution of a long chain fatty acid, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of soluble fatty acid per liter.

2. A process for activating an aluminous anode which comprises contacting said anode for at least 5 seconds with a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of the metallic component of a soluble metallic soap per liter.

3. A process for activating an aluminum anode of an aluminum base alloy which comprises contacting a substantially oxide free aluminum anode of an aluminum base alloy for at least 5 seconds with a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of the metallic component of a soluble metallic soap per liter.

4. A process for activating an aluminum anode which comprises providing an aluminum anode comprising an aluminum base alloy containing at least 90 percent aluminum and between 0.04 and 0.5 percent tin, contacting said anode for at least 5 seconds with a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of the metallic component of a soluble metallic soap per liter.

5. A process for activating an aluminous anode which comprises contacting said anode for from 5 to 60 minutes with a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing from 0.1 to 10 milligrams of soluble fatty acid per liter.

6. A process according to claim 2 wherein said metallic soap is lead linoleate.

7. An activated anode which comprises an aluminous anode coated with a dilute aqueous solution of a long chain fatty acid, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of soluble fatty acid per liter.

8. An activated anode which comprises an aluminous anode coated with a dilute aqueous solution of a metallic soap, said solution having a pH of from 4 to 7 and containing at least 0.1 milligram of the metallic component of a soluble metallic soap per liter.

9. An anode according to claim 8 wherein said aluminous anode is in the substantially oxide free state.

10. An anode according to claim 8 wherein said aluminous anode comprises an aluminum base alloy containing at least 90 percent aluminum and between 0.04 and 0.5 percent tin.

11. An anode according to claim 8 wherein said coating contains between 0.1 and 10 milligrams of said metallic component of a soluble metallic soap per liter.

12. An anode according to claim 8 wherein said metallic soap is lead linoleate.

No references cited.

WINSTON A. DOUGLAS, *Primary Examiner.*

NEWMAN P. BULLOCH, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,228,866 January 11, 1966

Michael J. Pryor

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 28, for "3,789,486" read -- 3,189,486 --.

Signed and sealed this 6th day of December 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents