LEAD INDUSTRIES ASSOCIATION, INC.

292 MADISON AVENUE

NEW YORK, N. Y. 10017

TELEPHONE — AREA CODE 212

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May 27, 1964

SUBJECT: Reprint on Lead Anodes

To Members of the Lead Industries Association, Inc:

We have obtained copies of the attached reprint on lead alloy anodes for cathodic protection, for distribution to members of the chemical construction and others concerned with protecting structures against corrosion.

In addition, this reprint will be offered in the "Lead Library" listing in LEAD magazine, which is sent to about 8,000 design engineers and almost 3,000 chemical engineers.

Members may obtain 25 copies of this reprint free of charge, and larger quantities at our cost of 25 cents per copy.

Very truly yours,

Robert Travis

Robert Travis

RT:bd
Attachment

Look Ahead with Lead

Lead Alloy Anodes

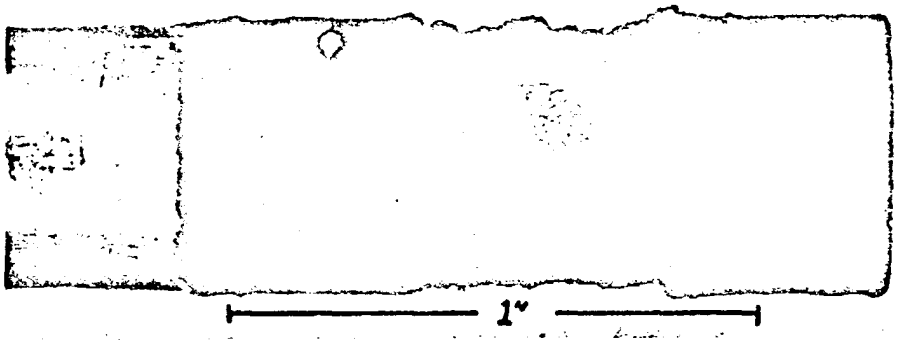

Figure 3—Lead alloy anode one percent silver 0.6 percent antimony showing deterioration 126.1 pounds per ampere year after it was machine grooved exposing bare lead and electrolyzed in 1000 ohm cm at 10 amperes per square foot (amp/sq ft). Lead dioxide coating re-formed but was loosely adherent, putty, and brittle. Note the white lead salts in small damaged areas, the coating may re-form adequately but not as protective as the original film.

for cathodic protection in various electrolytes*

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Lead Alloy Anodes for cathodic protection in various electrolytes*

SUMMARY

Contains data describing use of lead-silver anodes in cathodic protection systems operating in sea, fresh, and brackish waters. Lead samples were operated in various electrolytes to determine deterioration rates. Variables investigated include current density, specific resistance of the electrolytes, alloy composition, mechanical damage to protective coatings, and galvanic couples with other materials. In low specific resistance electrolytes, which were similar to sea water composition, favorable anode performance was noted. High resistance electrolytes, especially at 1000 ohm-cm, caused severe anode deterioration. Galvanic couple tests indicated that exposed titanium mounting devices appear suitable for use with lead alloy anodes.

Lead alloy anodes using external direct current sources for cathodic protection of ship hulls provide certain advantages over galvanic anode protective systems. Mainly, they avoid the gross determination of anodes inherent in operation of galvanic systems. Replacement of corroded anodes usually involves dry docking the ship.

Most of the U. S. Navy's vessels operate in sea water, but many times they are docked in harbors or rivers containing both fresh and brackish water. The influences of these conditions, therefore, urge development of most accurate materials and design for optimum operation in all situations.

For example, a ship moving from sea water into brackish or fresh water encounters changes in specific resistance of the electrolyte, and anodes in any system must be sufficiently corrosion resistant under all conditions.

The importance of cathodically protecting high speed surface and submarine vessels has long been recognized by the Navy.[1] Recent development in controllers and regulated power supplies have increased popularity of impressed current systems. Also, impressed current systems can provide high capacity, long life, uniform geometry which can be designed for minimum drag and noise generation, and lighter weight. However, galvanic systems have certain advantages. These include requiring no external power sources, current control devices, or maintenance except for periodic anode replacement.

The experiments described in this article primarily are concerned with the electrochemical behavior of lead alloy anodes in various electrolytes. Advantages of lead alloys include: ductility, low melting for ease in casting, and relatively high electrical conductivity. Resistance to deterioration, however, largely depended on the formation of adherent, brown-black protective coatings of lead dioxide (PbO_2) which exhibited good electrical conductivity.

In lead acid storage batteries, this coating contributes to longer life by minimizing positive grid corrosion in the sulfuric acid electrolyte. Lead alloy anodes also are used in chromium plating.

Specifically, the experiments consisted of determining deterioration rates of lead alloy anodes involving current density, specific resistance of electrolytes, alloy composition, mechanical damage to protective coatings, and galvanic couples with other materials.

Test Apparatus and Procedure

Electrolytic test cells were 10-gallon, glass walled aquaria arranged in batteries of four. Each cell contained 40 liters of diluted synthetic sea salt electrolyte with concentrations corresponding to specific resistances of 16.3, 50, 1000, and 5000 ohm-cm. Temperature was maintained at 45 C, slightly above ambient, for ease of control. Corrosion rates are slightly accelerated with this increased temperature but not to the point of severity.

The 16.3 ohm-cm electrolyte provided a composition similar to that found in average sea water containing 19 parts per thousand chlorinity.

Lead alloy anode rod specimens (0.50 inch in diameter, four inches long) were masked with a synthetic resin pressure sensitive tape and gaskets to expose 1.93 square inch areas. Specimens were either extruded, molded, or cast. Cathodes consisted of mild steel strips formed into nine-inch diameter rings. The anodes were

* Excerpt of a paper titled "Electrochemical Behavior of Lead Alloy Anodes in Various Electrolytes" presented at 18th Annual Conference National Association of Corrosion Engineers, March 17-21, 1962, Kansas City, Mo.

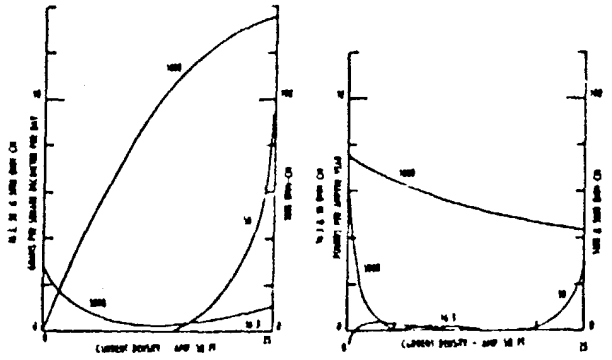

Figure 1—Deterioration rates of lead alloy anodes (one percent silver, six percent antimony) as a function of anode current density measured in amperes per square foot (amp/sq ft). Graph at left shows deterioration rates in grams per square decimeter per day. At right the rates are recorded in pounds per ampere year.

positioned concentrically within the rings.

The anodes were electrolyzed at current densities from ¼ to 25 amperes per square foot (amp sq ft). Electrolyses were interrupted periodically and the anodes rinsed, dried, cooled in a desiccator and weighed. Figures 1 and 2 show the results in terms of deterioration rates.

Results and Analysis

The results of the tests are divided into several sections as follows:

- Electrochemical behavior of lead containing one percent silver and six percent antimony.
- Effect of damage to PbO$_2$ protective coatings.
- Platinum microelectrode in lead anode in high resistivity water.
- Galvanic couples of PbO$_2$ coated surfaces with other materials.
- Various other lead alloy anode compositions.

Lead Alloy Anodes (one percent silver, six percent antimony)

Deterioration rates of lead-silver-antimony anodes are presented in Table 1 and as a function of current density in Figure 1. Anodes exposed for 31 days at ¼ amp sq ft are shown in Figure 2. Differences in behavior in the low 16.3 and 50 ohm-cm and the high specific resistance electrolytes were immediately evident. Anode weight changes in the low resistance solution, were small while severe deterioration and weight loss occurred in the high resistance solutions.

In the 16.3 ohm-cm electrolyte, consistently favorable performance was obtained at current densities between ¼ and 25 amp sq ft. Rapid anodic polarization to the PbO$_2$ forming range, adherent thin oxide films, and low deterioration rates were typical in this electrolyte.

Acceptable performance was achieved in the 50 ohm-cm electrolyte, which contained a composition approximately that of some highly brackish waters, between ¼ and 15 amp sq ft. Polarization and PbO$_2$ formation were rapid, deterioration rates were low. However, PbO$_2$ coatings were not as thin or adherent as in the 16 ohm-cm solutions, and in some areas thick nodules of PbO$_2$ formed and erratic behavior was noted. At 25 amp sq ft, for example, loss deterioration occurred during the first week of exposure, followed by severe breakdown of the coating and cracking and deterioration of the anode.

In the 1000 ohm-cm electrolyte, which had a specific resistance similar to some fresh waters although fresh waters vary widely in actual compositions, failure to form PbO$_2$ was noted at most all current densities from ¼ to 25 amp sq ft. Anodes formed white coatings, lead chloride, and were rapidly disintegrated.

In the 5000 ohm-cm electrolyte, high deterioration rates were recorded at low current densities. Above two amp sq ft, deterioration rates were close to those obtained in the low resistivity electrolytes but not as low. PbO$_2$ coatings formed but were bulky, poorly adherent, and often mixed with large amounts of white lead salts.

Deterioration rates of the anodes at 10 amp sq ft in sodium chloride solution were slightly higher than in equivalent diluted synthetic sea water, as shown in Figure 3, indicating beneficial effect of other ions, such as sulfate, present in synthetic sea water.

Damaged Coatings

During normal operation of lead alloy anodes in ship cathodic protection applications, the coating may sustain mechanical damage such as by collision with floating debris. In sea water operation, the film forming properties of the alloy indicate rapid repair and extended anode life. However, in fresh waters where the anodes fail to polarize suitably to develop PbO$_2$ coatings, anode behavior is not predictable.

A silver-antimony-lead alloy anode was electrolyzed in 16.3 ohm-cm synthetic sea water to form a protective PbO$_2$ coating. Continued electrolysis in 1000 ohm-cm electrolyte for 12 days at 10 amp sq ft produced no anodic damage. A 1/16-inch wide groove was machined in the coating exposing bare metal, and electrolysis was continued in the 1000 ohm-cm solution for seven days. A PbO$_2$ coating was re-formed although not as tightly adherent as the original, and a relatively low rate of anode deterioration was recorded.

The groove was re-machined 1/2-inch wide to expose bare lead and electrolysis was continued. The PbO$_2$ coating which re-formed was loosely adherent, puffy and brittle, and covered an underlying layer of white salts of lead. Severe anode deterioration at the rate of 26 pounds per ampere year was recorded. However, with the coating undamaged, anodes could safely be exposed for a time in fresh water.

Platinum Wire Insert

Use of a platinum microelectrode on a lead anode in sea water promotes formation of protective PbO$_2$ coating.[2,3] It is particularly beneficial at high current density.

A test was conducted to determine platinum's influence in high resistivity

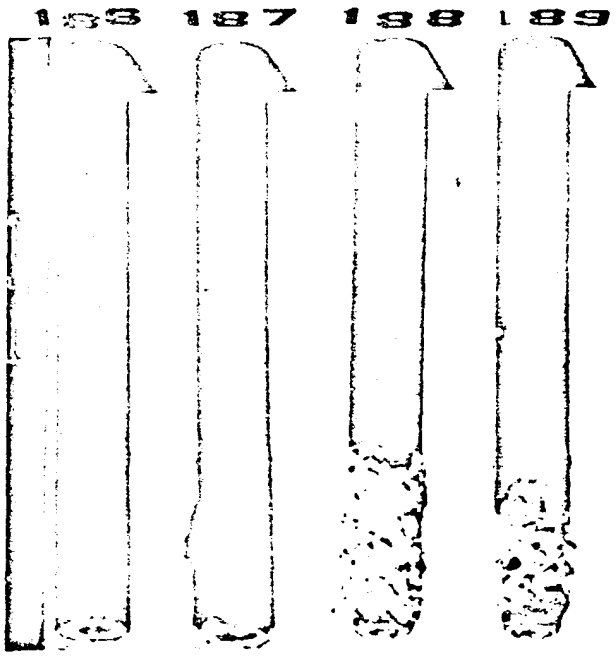

Figure 2—Lead alloy anodes (one per cent silver, six percent antimony) after electrolysis for 31 days at 0.25 amperes per square foot (amp/sq ft) in 16.3, 50, 1000, and 5000 ohm-cm synthetic sea water-base electrolytes. Anode behavior for cathodic protection of ship hulls under various electrolytic conditions are given in Table 1.

rates at low current density. A platinum wire was hammered into a grid and served continuous anode. The anode was electrolyzed at one amp sq ft in 1000 ohm-cm electrolyte. In case cathodically protected ships entering fresh waters would probably operate at low current density as result of high electrolyte resistance and fixed maximum voltage. The anode failed to form PbO$_2$. The lead surface was coated with white lead chloride, and the alloy severely deteriorated.

Anode potentials were below the lead dioxide and chlorine formation ranges. *In the sea water tests previously reported,*[4] applied potentials and anode current densities were considerably higher than in the above test. This facilitated lead dioxide and chlorine production.

Galvanic Couples

The cathodic nature of protective PbO$_2$ films formed on lead anodes and the potentials that could result from galvanic coupling with other metals led to the following investigation. Test specimens of lead alloy (five antimony) were anodized for about 20 days at 10 amp sq ft in 16.3 ohm-cm synthetic sea water to form tight PbO$_2$ coatings. This was followed by alternate periods of galvanic coupling at the anode to various materials and anodizing the couple at 10 amp sq ft both in 16.3 ohm-cm synthetic sea water. Specimens were periodically rinsed dried, and weighed. The following tests were among those conducted:

Open Circuit Lead Dioxide, Anode 243

Periods of open circuit condition resulted in no visible damage to the PbO$_2$ coating, and relatively little shift in electrode potentials. Small weight losses were recorded in contrast to slight weight gains noted on similar anodes that were anodized continually.

Lead Dioxide Coating and Lead, Anode 244

Lead and PbO$_2$ coupling could occur when PbO$_2$ coatings were mechanically damaged. In the galvanic periods, two equal areas of lead and PbO$_2$ were exposed on the same specimen by removing some of the masking tape. Discharge of the PbO$_2$ and oxidation of the lead occurred as anticipated, with white lead chloride forming in both areas. The lead chloride on the base metal was not adherent and most washed off during rinsing. Anodizing to regenerate the PbO$_2$ resulted in significant weight loss, indicating metal loss in the overall process.

Lead Dioxide Coating and Titanium, Anode 245

Current rectifying properties of titanium and tantalum metal introduced the possibility of using the metals as connectors or mounting devices with lead anodes for cathodic protection. A PbO$_2$ coated anode was coupled to a panel of titanium. The couple was alternately anodized and allowed to seek open-circuit PbO$_2$-Ti coupled. No change in appearance of the PbO$_2$ coating was noted and anode weight loss was slightly less than in open-circuit uncoupled periods. The high electrolytic resistance of the anodized titanium dioxide film prevented current flow in the galvanic sequence and depolarization of the PbO$_2$ coating.

Lead Dioxide Coating and Steel, Anode 246

The possibility of accidental grounding of lead anodes to steel hulls when a cathodic protection system is not energized led to the following investigation. During galvanic sequences a PbO$_2$ coated anode was coupled to a steel panel. The PbO$_2$ surface was reduced to white lead chloride and exposed grey base metal in some areas. A loss in anode weight was recorded. In anodizing sequences, the coating became progressively thicker. Coatings exhibited blistering and longitudinal cracking and contained areas of white lead chloride. As a result of the thicker coating and poor conductivity of unconverted lead chloride, coating resistance rose markedly as indicated by a greatly

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increased anode potential, and the anode soon was rendered ineffective.

Lead Dioxide Coating and Steel via Selenium Rectifier, Anode 247

In galvanic sequences, an anode was coupled to a single plate selenium rectifier resistant to reverse current (about 1.7 x $10^{[illegible]}$ ohms). This sharply limited current flow between the PbO_2 coated anode, and the steel panel and restricted reduction of the coating to small, scattered white spots of lead chloride. A progressive loss of weight was recorded, but no increase in anode resistance was observed.

Other Lead Alloy Compositions

Silver

Deterioration rates of lead alloy anodes containing 2, 4, and 10 percent silver at 1 and 10 amp/sq ft in the low resistivity electrolytes, particularly 16.3 ohm-cm, generally were low because adherent PbO_2 coatings formed rapidly. In the 1000 ohm-cm electrolyte at 10 amp/sq ft, formation of PbO_2 was slow, coatings were bulky and mixed with white lead chloride and deterioration rates were high. However, deterioration rates reduced as the PbO_2 developed. At one amp/sq ft, the anodes failed to produce PbO_2 and deterioration was severe. In the 5000 ohm-cm electrolyte, a mixture of PbO_2 and white lead chloride formed and deterioration rates were high, although not as high as in the 1000 ohm-cm solution. Average anode potentials showed the failure of all anodes to polarize effectively in the 1000 ohm-cm electrolyte at low current density (Table 1).

Increasing the silver content improves the tendency to form PbO_2 *at 10 amp/sq ft in the high resistivity* electrolytes. However, over-all performance in these electrolytes was considered poor. At low current density (one amp/sq ft) and in the low resistivity solutions, no marked change in performance resulted from increased silver content beyond the one to two percent range. Figure 4 shows results of the various tests. *Figure 5 shows progress of deterioration* in several instances.

Mercury, Tin

Deterioration rates of lead-silver alloys containing tin or mercury also are included in Table 2. Performance of these anodes in 16.3 ohm-cm electrolyte was favorable, but no extra advantage was attributable to the additions. Severe deterioration observed in the high resistivity electrolytes, particularly at 1000 ohm-cm, was also present with these alloys.

Coating Weights

In the 16.3 and 50 ohm-cm electrolytes, coating weight is appreciable in comparison with total weight change. However, deterioration rates in these solutions are relatively low. In the 1000 and 5000 ohm-cm electrolytes, coating weight usually constitutes a small part of the over-all weight loss.

Other Anode Studies

Other studies made in connection with developing suitable anodes for cathodic protection include determining the electrochemical behavior of graphite and silicon-iron,[8] and the influences of molybdenum and chromium additions to silicon-iron compositions.[9]

Laboratory experiments with platinum microelectrodes indicate the influence of platinum on polarization and formation of PbO_2 on lead anodes in chloride solutions.[10] In chloride environments, pure lead anodes fail to maintain satisfactory, adherent PbO_2 films and suffer severe deterioration.[3] However, silver-lead alloy anodes appear to overcome this difficulty. Lead alloy anodes containing one percent silver and six percent antimony were reported to show favorable performance in sea water, diluted sea water, and saline mud.[11] Also, tests on a Canadian destroyer in recent years have shown successful service of lead anodes containing two percent silver.[12]

High percentage of silver in lead alloy anodes tested in sea water at 100 amp/sq ft at the Boston Naval Shipyard, showed beneficial effects, attributed to the high silver content.[13] More information on service experiences with lead alloy anodes was summarized in a report by NACE Technical Committee T-2B-7.[14]

TABLE 1—Deterioration rates of lead alloy anodes (one percent silver, six percent antimony) in synthetic sea water base electrolytes.

Negative values denote gain in anode weight. Deterioration rates are based on weights of anodes with coatings present. Linear rates exclude initial test periods. Grams per square decimeter per day are represented as gdd.

Sample No.	Form	Electrolyte Specific Resistance at 18C ohm-cm	Test Duration days	Test Duration amp-hrs	Current Density Amp Sq Ft	Average Applied Potential volts	Deterioration Rates Over-all lb amp-yr	Over-all gdd	Linear lb amp-yr	Linear gdd
[illegible]	Extruded Rod	16.3	[illegible]	2.40	0.25	[illegible]	0.14	0.01	0.14	[illegible]
157		50	[illegible]	2.40	0.25	1.87	0.51	[illegible]	0.41	[illegible]
158		1000	[illegible]	2.40	0.25	0.71	65.6	2.19	65.6	2.19
[illegible]		5000	[illegible]	2.40	0.25	2.77	62.7	2.10	[illegible]	2.10
177	Extruded Rod	16.3	48.4	15.6	1.0	2.10	0.06	0.01	0.04	0.01
178		50	48.4	15.6	1.0	2.12	0.01	[illegible]	0.06	[illegible]
179		5000	[illegible]	10.2	1.0	1.36	72.8	9.74	72.8	9.74
180		5000	48.4	15.6	1.0	2.75	3.72	0.22	3.17	0.29
159	Extruded Rod	16.3	[illegible]	77.8	2.0	2.34	0.06	0.02	0.02	[illegible]
160		50	[illegible]	77.8	2.0	2.65	0.34	0.06	0.10	[illegible]
161		1000	16.6	10.7	2.0	3.35	78.8	20.5	78.8	20.5
162		5000	36.4	21.4	2.0	10.2	21.4	3.73	21.4	[illegible]
136	Rolled Strip	16.3	2.06	200	4.0	2.93	0.19	0.28	0.23	0.31
137		50	2.06	200	4.0	1.84	0.04	0.04	0.06	0.06
138		1000	5.76	18.5	4.0	16.7	32.2	60.8	31.8	22.7
139		5000	2.06	200	10.0	49.4	0.22	0.30	0.02	0.03
168	Extruded Rod	16.3	11.7	162	15.0	5.31	0.01	0.02	0.00	0.00
169		50	46.5	166	15.0	3.96	0.01	0.02	0.00	0.01
170		1000	1.84	6.0	15.0	21.4	62.6	1.56	62.6	1.56
171		5000	18.5	166	15.0	76.2	0.01	0.20	0.04	0.08
164	Molded Rod	16.3	12.8	103	25.0	3.00	0.00	0.01	0.01	0.01
165		50	12.8	103	25.0	3.52	2.81	9.35	0.01	0.11
166		1000	1.06	13.9	25.0	30.7	40.8	1.36	40.8	1.36
167		5000	12.8	103	25.0	124	0.30	0.06	0.04	0.10

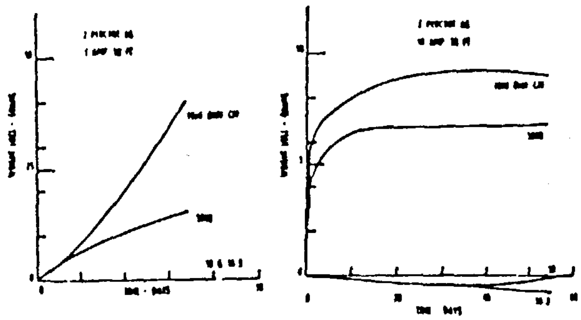

Figure 4—Progress of deterioration of lead alloy anodes (two percent silver) at current densities of 1 and 10 amperes per square foot (amp/sq ft). Low deterioration is indicated in the low resistance electrolytes. Progressive deterioration resulted in the high resistance electrolyte at one amp/sq ft. At 10 amp/sq ft in the high resistance electrolytes, high initial deterioration is indicated followed by formation of protective lead dioxide films.

TABLE 2—Deterioration rates of various lead alloy anodes in sea water electrolytes.

Negative values indicate gain in anode weight. Deterioration rates are based on weights of anodes with coatings present. Sample No. 202 had white and black coatings. Linear rates exclude initial test periods. Linear rates of anodes 255-58 were not established because of insufficient test duration. Grams per square decimeter per day are represented as gdd.

Sample No.	Alloying Elements %	Electrolyte Specific Resistance ohm-cm	Test Duration days	Test Duration amp hrs	Current Density Amp Sq Ft	Average Applied Potential volts	Average Potential versus Saturated Calomel Electrode volts	Deterioration Rates Over-all lb amp-yr	Deterioration Rates Over-all gdd	Deterioration Rates Linear lb amp-yr	Deterioration Rates Linear gdd
[illegible]	2 Ag	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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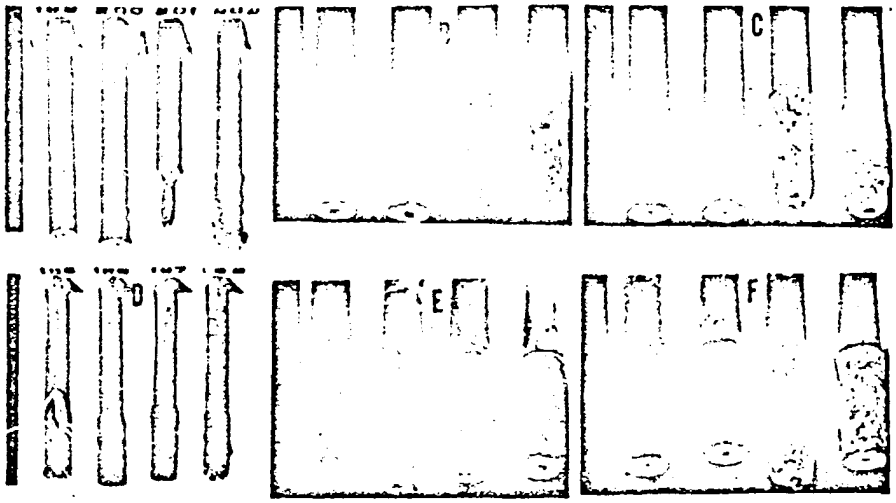

Figure 5—Progress of deterioration of lead silver anodes in 163, 50, 1000, and 5000 ohm-cm electrolytes. Table 2 shows test conditions and deterioration rates. (Sample numbers correspond to numbers in table.) Increased silver content of the anode improved the tendency to form lead dioxide in 1000 ohm-cm electrolyte at the high current density of 10 amperes per square foot (amp/sq ft.). This was not observed at the lower current density of one amp/sq ft. Samples A, B, and C contained 2, 4, and 10 percent silver, respectively, tested at one amp/sq ft. Samples D, E, and F, also containing the above silver content, were tested at 10 amp/sq ft.

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The authors acknowledge the helpful suggestions of W. L. Miller, Inorganic Chemistry Branch director at the Naval Applied Science Laboratory, under whose supervision this work was performed, and H. S. Preiser, formerly of the Bureau of Ships.

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DISCUSSIONS

Question by M. H. Peterson, U. S. Naval Research Laboratory, Washington 25, D. C.

1. Why was 35 C shown as the total temperature?

2. Have coatings performed in sea water subsequently been tested in high resistivity water?

Reply by S. Tudor and A. Ticker:

1. The temperature of 35 C was used in most of the laboratory tests

because it is slightly above ambient at all times of the year and can be readily controlled with a small heater and thermostat switch. Corrosion rates are slightly accelerated by the slight increase in temperature, but these effects are considered not to be severe.

2. See reply to question by Mr. G. L. Doremus.

Questions by Gordon L. Doremus, P. O. Box 66387, Houston 6, Texas

Was any information obtained by the authors on the performance of the lead-silver-antimony alloy anodes where a PbO$_2$ coating was performed in sea water and then transferred to 1000 ohm-cm water but with high density maintained on the anode by increased driving voltage rather than allowing water resistivity control the resultant density? If not, what would be the opinion of the authors as to the probable performance of an anode so formed and operated?

Reply by S. Tudor and T. Ticker:

A PbO$_2$ coating was performed on a lead-silver-antimony alloy anode in 10 ohm-cm synthetic sea water at 1 amp sq ft., and the anode was then operated in 1000 ohm-cm diluted synthetic sea water at 10 amp sq ft for 114 days. No visible change in the appearance of the coating was noted. A small gain in weight was measured. In other tests of anodes with PbO$_2$ coatings preformed in synthetic sea water and operated in 1000 ohm-cm diluted synthetic sea water at low current density, anode deterioration was noted. At the higher current density, anode polarization and maintenance of PbO$_2$ surfaces are enhanced.

Question by Ernest E. Nelson, Socony Mobil Oil Co., Paulsboro, New Jersey

Was the electrolyte changed often enough so the reaction products did not greatly change the properties of the solution?

Reply by S. Tudor and A. Ticker:

Electrolytes were renewed frequently, depending on the anodic current density. For example, at 25 amp sq ft, the electrolyte was renewed approximately every two days. Periodic observations and determinations of pH and specific resistance were made. It is recognized that in a limited volume system of this type, certain changes in the electrolyte are inherent. It is believed, however, that the electrolytes were generally renewed before great changes in properties of the solutions occurred.

SIDNEY TUDOR is research chemist with the U. S. Naval Applied Science Laboratory, Brooklyn, N. Y. He has done extensive research in cathodic protection, electrolytic detarting, polarography, and electrochemical surface reactions. Presently, he is engaged in research and development in electrochemical energy conversion devices, including fuel cells and batteries. A member of NACE, ACS, and the New York Academy of Sciences, he has a BA from Brooklyn College, an MS from New York University, and postgraduate work at Polytechnic Institute of Brooklyn.

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