

PATENT SPECIFICATION

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(54) ALUMINIUM MARINE ANODE WITH CORE ACTIVATOR

(71) We, SABINS INDUSTRIES, INC., a corporation organised and existing under the laws of the State of California, 2735 East Spring Street, Long Beach, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to aluminium marine anodes with core activators.

In its broadest aspect, the invention provides a sacrificial anode, for use in marine environments, comprising:

- a mass of marine aluminium alloy having a surface potential measured with respect to a silver-silver chloride half cell more negative than -1,000 millivolts configured as an anode;
- a structurally rigid core of material selected such that the potential difference between its surface potential (measured with respect to a silver-silver chloride half cell) and that of said marine aluminium alloy is at least 200 millivolts greater than the corresponding potential difference between iron and said alloy, embedded in said mass of marine aluminium alloy and extending therefrom to constitute means for mounting said anode to a ship's hull;

the ratio of exposed surface of said alloy to exposed surface of said core material being no greater than 15:1.

There will now be described a novel assemblage, preferably embodied as an anode assembly, and a system which utilizes the anode assembly (or its equivalent) to prevent the formation of an inhibitive coating on the surface of the anode. Although the invention is applicable generally to metallic structures exposed to corrosive electrolytic environments, it will be described herein with particular reference to ferrous—e.g., iron or steel, hulled ships in sea water.

In general, the preferred anode assembly comprises a mass of sacrificial marine aluminum alloy metal, in both physical and electrical contact with a suitable activator material. As use herein, the term "anode" is applied to the sacrificial portion of the assembly; i.e., the mass of marine alloy itself, not including the activator or other structural components of the anode assembly. In most embodiments, the activator material is selected with regard to both its electrical and physical properties. Ideally, the activator is sufficiently rigid and strong to be worked into the forms required for an element of the structural mounting of the anode to the ship's hull. Moreover, it has been determined that for use with steel hulls, the surface potential of the activator should be no more negative than -400 millivolts with respect to a silver-silver chloride half cell.

It has become conventional practice in the cathodic protection art, particularly as applied to the protection of steel hulls, to measure surface potentials of materials with respect to a silver-silver chloride half cell standard. On this basis, the surface potential of zinc of high purity is measured at approximately -1,030 millivolts and the surface of the steel is approximately -630 millivolts. The potential difference between zinc and steel or iron is thus only approximately 400 millivolts which is known to be inadequate to avoid the inhibitive process inherent with even high purity zinc. Experience has shown that maintaining a potential difference of 750 millivolts or higher between the zinc and another metal forming a couple with zinc provides sufficient electrical potential to cause the surrounding zinc surfaces to continue to go into solution. By maintaining the solution process active, new atoms of zinc metal are constantly exposed to the electrolyte. There results a certain attritional loss of the anode material, but this loss is relatively minor due to the greater attritional loss to the other metal in the couple.

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Similarly, the surface potential of certain special aluminum alloys falls within the range of -1,000 millivolts and -1,300 millivolts with respect to a silver-silver chloride half-cell. Such alloys are classified as marine alloys when they also exhibit the chemical and physical properties desired for use in marine environments. These alloys offer a potential difference with respect to a steel or iron hull comparable to that available with high purity zinc, and experience an inhibiting process similar to that of zinc. The use of an activating couple is thus useful with the marine aluminum alloys to maintain the sacrificial solution process active. It has been found, however, that the yield, (which may be defined as the number of ampere hours of cathodic protection available in each pound of anode material consumed) of these aluminum alloys is substantially greater than is high purity zinc. The following table lists pertinent information concerning several marine aluminum alloys available from the Kaiser Aluminum Company, Oakland, California, United States of America.

	Alloy Designation	Alloying Metals	Potential with respect Ag/Ag/Cl Half Cell	Yield Ampere Hours/lb
30	KA-95	Hg	1050	1,250
	KA-46	Zn,Sn	1080	1,000
	KA-90	Zn,Sn	1030	1,230
	KA-804	Sn,(Unknown)		

The presence of mercury is regarded as undesirable in marine applications. The marine alloys of aluminum with zinc and tin are thus the preferred materials for use in accordance with this invention. The KA-804 alloy offers no special advantage over high purity zinc and exhibits a similar yield. Alloys similar to KA-90 are regarded as ideal for outside ship bottoms with painted surfaces, largely because higher surface potentials tend to cause stripping of paint from painted surfaces. For deep tanks, drilling rigs and unpainted areas, where paint stripping is not a consideration, alloys similar to KA-46 are generally preferred.

Activator materials suitable for use with the invention, particularly with anodes of marine aluminum alloy or high purity zinc, should have a potential difference between their surface potential and that of the anode at least 200 millivolts greater than the corresponding potential difference between the anode and the structure to be protected. When the structure is of steel, suitable activators are generally those which are no more negative on the aforementioned scale than -400 millivolts. Preferably, the activator should be substantially less negative, more on the order of -300 millivolts or less, to achieve the 750 millivolt potential difference observed to be the magnitude of the operating potential difference required to insure continuous attrition of the aluminum alloy surface. Certain copper-tin alloys (e.g., bronzes) can be utilized, although they exhibit a potential difference with respect to aluminum of only approximately 700 millivolts. Accordingly, the activation provided by their use is "border-line" from the standpoint of this invention.

Nevertheless, even this level of activation is very helpful in inhibiting or delaying the deposition of an inactive surface on the anode. A potential difference of less than 600 millivolts is generally unsatisfactory. From most standpoints, copper is an ideal material, exhibiting approximately -220 millivolts of surface potential, although many other materials could be used were it not for their expense or undesirable physical properties. For example, monel, silver and platinum are all operable, but impractical because of cost.

The presently preferred activator material is copper because of its good mechanical properties and its adequate surface potential. A "red bronze" alloy of copper, containing on a weight basis, about 3 per cent zinc, 6-1/2 percent tin and 1-1/2 percent lead, is presently regarded as an ideal activator material. Monel, while operable, is generally too expensive. Either carbon or lead activators may be employed. Less exposed surface is required for such activators than when copper is used. Moreover, in each instance, these materials tend to drive electrons from the surface of aluminum to an extent which causes unduly rapid activator-induced attrition from the anode surface. By "activator-induced attrition" is meant weight loss of anode metal in excess of the galvanic metal loss attributable to protection of the ship's hull. Sacrificial metal loss due to the galvanic couple of an anode and ship's hull varies considerably, depending upon factors such as ship speed, temperature and salinity of the water, composition of the anode, etc., but in any event is distinguishable from the attrition of anode metal due solely to the activator itself. While some activator-

induced attrition is desirable to maintain the anode sacrificial in its galvanic couple with the ship, the ratio of exposed surface areas of activator to anode metal, respectively, is desirably selected to maintain the annual activator-induced attrition rate (weight loss) of the anode to below about 10 percent, preferably between about 1 percent and 5 percent.

A typical anode is expected to be in service for two years. Initially the activator-induced attrition rate will be lower, usually about 1 to 3 percent. By the end of its service life, the activator-induced attrition rate will normally have increased to as high as about 5 to 10 percent due to the changing surface ratios of anode to activator as attrition proceeds. The activators and anodes can be shaped to counteract this tendency, but normally the increased attrition rate is desirable to balance the inherent increased tendency of the zinc surface to become passive (probably because of concentrating impurities). Hence, the anode configuration shown in the drawings is highly preferred. The ratio of exposed surface areas of activator to anode alloy, respectively, is desirably selected to maintain the attrition rate of the anode to below about 10 percent, preferably between about 1 percent and 5 percent.

The mode of operation of the anode may be explained as follows, although the specific mechanism involved is of consequence only as an assistance in calculating the amount of surface area of anode required to suitably protect a particular structure in a particular environment. Assuming an array of KA-90 marine aluminum anodes with copper activator structures cast in place with exposed surfaces, the copper is in intimate physical and electrical contact with both the KA-90 alloy and the sea water environment. The potential difference between the KA-90 alloy and the copper surfaces is approximately 810 millivolts, which tends to drive electrons from the surface of the alloy to the surface of the copper. Ultimately, the two surfaces would tend to equalize in potential, except that the surface potential of the copper activator becomes so negative with respect to its normal surface potential that electrons are emitted to the sea water. As a consequence, a continuous flow of electrons from the alloy surface to the copper is maintained. In this fashion, new metal atoms from the alloy are continuously exposed, maintaining the active surface potential of the KA-90 alloy at approximately -1,030 millivolts. Concurrently, electrons are migrating to the ship's hull, providing additional loading

on the anodes. But for the copper activator surfaces, the surface potential of the hull adjacent the anode would ultimately approximate that of the KA-90 alloy, thereby inhibiting the activity of the anode surface rather than activating it.

Generally, when copper is used as the activator surface, each standard KA-90 alloy anode (containing approximately 19 pounds of KA-90 alloy) used in sea water in a galvanic direct couple to a steel or iron hull will protect approximately 500 square feet of wetted surface and will deliver a minimum of approximately 23,000 ampere hours of protective current per year (approximately 5 milliamps per square foot). Under these conditions, each anode will sacrifice, through attrition from its surface, an average of about 0.06 lbs of alloy metal annually. A typical standard anode has a surface area of approximately 1-3/4 square feet, so that under the aforescribed conditions, the ratio of anode surface to hull surface is approximately 1 to 300.

Generally, when copper is used as the activator surface, each standard 68 lb zinc anode used in sea water in a galvanic direct couple to a steel or iron hull will protect approximately 500 square feet of wetted surface and will deliver a minimum of approximately 13,000 ampere hours of protective current per year (approximately 3 milliamps per square foot). Under these conditions, each anode will sacrifice, through attrition (attributable to its galvanic couple with the hull), from its surface, an average of about 26 lbs of zinc metal annually. The standard anode surface is approximately 2.5 square feet, so that under the aforescribed conditions, the ratio of anode to hull surface is approximately 1 to 200. Typical activator-induced attrition of zinc metal under these conditions should be about 1-1/2 pounds the first year and about 3 pounds the second year.

A special mounting assembly is provided in accordance with the invention whereby anodes may conveniently be exchanged without welding. Thus, anodes may be replaced by divers without dry docking the ship if desired. The mounting is structured so as to maintain positive physical and electrical coupling between the aluminum alloy anode material through a continuous mass of metal structure, including the activator core material, to the ship's hull. Ideally, the anodes are formed as cylindrical bars cast around cylindrical cores and are of standardized lengths to facilitate interchangeability. It has been found that attrition of such anodes in use tends to proceed primarily from the ends toward the middle.

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Brief Description of the Drawings

In the drawings which illustrate what is presently regarded as the best mode for carrying out the invention;

Figure 1 is a plan view, partially in section, of a preferred form of the invention, wherein marine aluminum alloy is cast with a copper core in place within the anode;

Figure 2 is a view in section along the section line 2—2 of Figure 1 viewed in the direction of the arrows;

Figure 3 is an end view of the anode of Figure 1;

Figure 4 is a top plan view of a mounting assembly of the invention;

Figure 5 is an exploded side elevation view of the mounting of Figure 4; and

Figure 6 is an end view of the mounting of Figures 4 and 5.

Description of the Illustrated Embodiment

The anode illustrated by Figures 1 through 3 comprises a mass 11 of marine aluminum alloy metal, preferably KA-90 alloy cast around a copper rod core 12, embedded in the mass of alloy as best seen from Figure 2. End portions 13 of the core 12 extend as mounting lugs, each of which is provided with a hole 15 adapted to register with appropriate pins or bolts of mountings (Figures 4—6) fastened to the hull of a ship or other structure (not shown) it is desired to cathodically protect. The exposed surfaces of the lugs 13 provide an initial activating surface which normally suffices, without more, to retain the aluminum alloy anode mass 11 sacrificial. As attrition of the alloy 11 proceeds, the surface area of the lugs is inevitably supplemented by the exposure of increasing portions of the activator core 12.

The anode metal mass 11 may be formed in various shapes, but preferably takes the anode shape shown. This shape has been found advantageous for core-activated anodes generally, whether of the zinc type or the marine aluminum alloy type. As shown, each anode has somewhat enlarged end portions 16 extending a few (in the illustrated instance, about 3) inches in length, and generally about 2-1/2 to about 3 inches at their widest transverse dimensions (Figure 3).

The remaining length of the anode mass 11, usually about 20 inches to about two feet (in the illustrated instance, 22-1/2 inches), is of circular cross-section. The enlarged ends 16 accommodate the flattened extensions 13 of the core 12. As illustrated, the core 12 is a copper rod about 5/8 inch in diameter, and the annular alloy anode 11, has an outer diameter of

about 2-5/16 inches. This construction provides an initial exposed surface ratio of anode to core of about 8:1. As attrition proceeds under use conditions, this ratio increases until it ultimately approaches 1:1. In practice, the initial ratio of exposed surfaces may be selected within the range of about 5:1 to about 15:1, although the most useful initial ratio when copper cores are utilized appears to fall within about 7:1 to about 10:1.

Anodes of the type illustrated may be standardized to be readily replaced on standardized mountings. A representative standard fresh anode of this type would include approximately 250 square inches exposed anode surface, 19 lbs of KA-90 marine aluminum alloy metal, approximately 22-1/2 square inches of exposed activator surface, and approximately 4-1/2 lbs of copper core material.

The copper cores 12 provide all of the activator surface required by the anode and cathodic protection systems of this invention. It is to be understood that other materials such as lead or carbon might be substituted for the copper cores illustrated, although steps would then need to be taken to reduce the exposed surface area of these materials as well as to provide for rigidity and suitable structural properties of the overall assembly. It is particularly desirable that the copper cores be mounted in such a manner that there is electrical continuity by direct coupling between the mounting lugs 13 and the steel hull.

As used herein and in the claims, the term "direct coupling" refers to physical contact between two metallic surfaces sufficient to provide electrical conduction across a substantial surface area of the two materials, as opposed to through a wire or cable conductor interconnecting the two materials. Such coupling may be through intermediate metallic surfaces, such as those inherent in a mounting assembly.

A highly preferred mounting assembly is illustrated by Figures 4, 5 and 6, from which it may be seen that a steel foundation base 18, in the form of a bracket with opposed sides 19 and a slotted top 20, is adapted for welding directly to a ship's hull. A tee bolt 24, preferably of forged steel, is received between the sides 19 of the base 18 and extends up through the slotted top 20 and through the hole 15 in the anode mounting lug 13. The lug 13 rests atop a pad 25, which may be a brass or bronze washer, silver soldered or oven brazed to the base 18. A specially configured top washer 27, preferably of brass or bronze, slips over the threaded end of the tee bolt, and a nut 28 presses the assembly together to assure direct physical coupling between the lug 15,

the pad 25, the base 18 and the hull (not shown). The nut 28 is covered with a plastic cap 30. To exchange anodes, it is merely necessary to remove the cap 30 and nut 28, slip off the top washer 27 and lift the anode from the mountings. No welding or other elaborate dry dock procedures are required.

Even the high purity Military Specification zinc anodes preferred by the art will at some point during their first several months in sea water develop a surface coating which actually inhibits or lowers the surface potential of the zinc to lower in the galvanic series than the surrounding ship surfaces. At that time, the zinc no longer serves or functions as an anode to the ship but becomes cathodic with respect to the ship, thereby causing the ship to function as an anode in the region around the zinc anode. Inspection of zinc anodes during annual docking of ships has revealed a measured surface potential as low as -300 or -400 millivolts with respect to a silver-silver chloride half cell compared to the normal potential of -1,030 millivolts. A similar phenomenon occurs when marine aluminum alloy anodes are used in place of zinc anodes. Use of the activating cores taught by this invention in the cathodic protection system provides sufficient voltage differential between the alloy and the bus bars to destroy the resistive or inhibiting coatings normally developed by the anode in use.

The anodes are best embodied as an array arranged in number and location to provide cathodic protection to a steel or iron ship's hull. The number of anodes required in a given array depends on several factors, including the wetted surface area of the hull. This area is typically determined by a rigorous formula related to the type of hull involved. For example, the wetted surface area of a well streamlined hull, such as a C-4 cargo ship, is regarded as the sum of sixty percent of the product of the length and beam dimensions plus a factor of 1.7 times the product of length and depth dimensions (i.e.,

$$L \times D \times 1.7 + L \times B \times 0.6 = \text{wetted surface}).$$

Similar formulas have been worked out for various shapes of hulls. Given the wetted surface area the number and placement of anodes in the array may be determined.

Desirably, each of the anodes is associated with between about 100 and about 1300 square feet of wetted surface area, giving an initial anode-to-hull surface area ratio of between about 1:50 and about 1:750.

WHAT WE CLAIM IS:—

1. A sacrificial anode, for use in marine environments, comprising:

- a mass of marine aluminium alloy having a surface potential measured with respect to a silver-silver chloride half cell more negative than -1,000 millivolts configured as an anode;
- a structurally rigid core of material selected such that the potential difference between its surface potential (measured with respect to a silver-silver chloride half cell) and that of said marine aluminium alloy is at least 200 millivolts greater than the corresponding potential difference between iron and said alloy, embedded in said mass of marine aluminium alloy and extending therefrom to constitute means for mounting said anode to a ship's hull;

the ratio of exposed surface of said alloy to exposed surface of said core material being no greater than 15:1.

2. An anode according to Claim 1 wherein said alloy comprises aluminium, zinc and tin.

3. An anode according to Claim 1 or 2 wherein the core material is copper.

4. An anode according to Claim 3 wherein the marine alloy material is KA-90 marine aluminium alloy.

5. An anode according to any preceding Claim wherein said core is formed as a rod of circular cross-section with flattened ends shaped as mounting lugs extending from opposite ends of said mass of alloy.

6. An anode according to Claim 5 wherein said alloy mass is shaped as an annular ring around the portion of said core having a circular cross-section.

7. An anode according to any preceding Claim wherein the potential difference between said core materials and said alloy is at least 600 millivolts.

8. A system according to any preceding Claim wherein the core material comprises a material having a surface potential less negative than bronze on the galvanic series of potentials measured with respect to a silver-silver chloride half cell.

9. An anode according to any preceding Claim wherein the initial ratio of exposed surface of said alloy to said core is within the range 7:1 to 10:1.

10. An anode in accordance with any preceding Claim and incorporating mounting structure comprising: a metallic base to be physically coupled to a ship's hull and including

- spaced, upstanding sides and a top;
- a tee bolt between said upstanding sides with a threaded shank extending up through said top;

the pad 25, the base 18 and the hull (not shown). The nut 28 is covered with a plastic cap 30. To exchange anodes, it is merely necessary to remove the cap 30 and nut 28, slip off the top washer 27 and lift the anode from the mountings. No welding or other elaborate dry dock procedures are required.

Even the high purity Military Specification zinc anodes preferred by the art will at some point during their first several months in sea water develop a surface coating which actually inhibits or lowers the surface potential of the zinc to lower in the galvanic series than the surrounding ship surfaces. At that time, the zinc no longer serves or functions as an anode to the ship but becomes cathodic with respect to the ship, thereby causing the ship to function as an anode in the region around the zinc anode. Inspection of zinc anodes during annual docking of ships has revealed a measured surface potential as low as -300 or -400 millivolts with respect to a silver-silver chloride half cell compared to the normal potential of -1,030 millivolts. A similar phenomenon occurs when marine aluminum alloy anodes are used in place of zinc anodes. Use of the activating cores taught by this invention in the cathodic protection system provides sufficient voltage differential between the alloy and the bus bars to destroy the resistive or inhibiting coatings normally developed by the anode in use.

The anodes are best embodied as an array arranged in number and location to provide cathodic protection to a steel or iron ship's hull. The number of anodes required in a given array depends on several factors, including the wetted surface area of the hull. This area is typically determined by a rigorous formula related to the type of hull involved. For example, the wetted surface area of a well streamlined hull, such as a C-4 cargo ship, is regarded as the sum of sixty percent of the product of the length and beam dimensions plus a factor of 1.7 times the product of length and depth dimensions (i.e.,

$$L \times D \times 1.7 + L \times B \times 0.6 = \text{wetted surface}).$$

Similar formulas have been worked out for various shapes of hulls. Given the wetted surface area the number and placement of anodes in the array may be determined.

Desirably, each of the anodes is associated with between about 100 and about 1300 square feet of wetted surface area, giving an initial anode-to-hull surface area ratio of between about 1:50 and about 1:750.

WHAT WE CLAIM IS:—

1. A sacrificial anode, for use in marine environments, comprising:
 - a mass of marine aluminium alloy having a surface potential measured with respect to a silver-silver chloride half cell more negative than -1,000 millivolts configured as an anode;
 - a structurally rigid core of material selected such that the potential difference between its surface potential (measured with respect to a silver-silver chloride half cell) and that of said marine aluminium alloy is at least 200 millivolts greater than the corresponding potential difference between iron and said alloy, embedded in said mass of marine aluminium alloy and extending therefrom to constitute means for mounting said anode to a ship's hull;
 - the ratio of exposed surface of said alloy to exposed surface of said core material being no greater than 15:1.
2. An anode according to Claim 1 wherein said alloy comprises aluminium, zinc and tin.
3. An anode according to Claim 1 or 2 wherein the core material is copper.
4. An anode according to Claim 3 wherein the marine alloy material is KA-90 marine aluminium alloy.
5. An anode according to any preceding Claim wherein said core is formed as a rod of circular cross-section with flattened ends shaped as mounting lugs extending from opposite ends of said mass of alloy.
6. An anode according to Claim 5 wherein said alloy mass is shaped as an annular ring around the portion of said core having a circular cross-section.
7. An anode according to any preceding Claim wherein the potential difference between said core materials and said alloy is at least 600 millivolts.
8. A system according to any preceding Claim wherein the core material comprises a material having a surface potential less negative than bronze on the galvanic series of potentials measured with respect to a silver-silver chloride half cell.
9. An anode according to any preceding Claim wherein the initial ratio of exposed surface of said alloy to said core is within the range 7:1 to 10:1.
10. An anode in accordance with any preceding Claim and incorporating mounting structure comprising: a metallic base to be physically coupled to a ship's hull and including
 - spaced, upstanding sides and a top;
 - a tee bolt between said upstanding sides with a threaded shank extending up through said top;



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- 5 a non-ferrous metallic mounting pad physically coupled to said top and surrounding said threaded shank, constituting means for direct coupling to a mounting lug of the anode;
- 10 top washer means cooperatively adapted with said mounting pad to clamp said mounting lug therebetween; and a nut for said threaded shank constituting means for pressing said top washer down towards said mounting pad and pressing said tee bolt into firm engagement with said top.
- 15 11. An anode substantially as described herein with reference to, and as illustrated in, the accompanying drawings.
- 20 12. A cathodic protection system for ferrous ship hulls exposed to sea-water, the system comprising an array of individual anodes each in accordance with any preceding Claim and each mounted in direct coupling with said hull so as to come into direct contact with sea-water; each

said anode including a structurally rigid core of material selected such that the potential difference between its surface potential (measured with respect to a silver-silver chloride half cell) and that of said marine aluminium alloy is at least 200 millivolts greater than the corresponding potential difference between the hull and said alloy. 25 30

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