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MARINE CORROSION HANDBOOK

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DESCRIPTION OF TERMS

- Circuit: A system of conductors and other electrical components in which current flows.
- Conductivity: Ability to carry current; the reciprocal of resistance.
- Corrosion: The interaction of a material with its environment resulting in deterioration or destruction of the material.
- Current: The flow of electrical charge in a circuit. Units are amperes or amps.
- Current density: Current per unit area (i.e., area through which the current flows).
- Electrode: A component of a circuit, usually metal, which is immersed in the electrolyte.
- Electrolysis: A catch-all term incorrectly used to describe all forms of marine corrosion. It is the reduction and oxidation of an ionic electrolyte caused by an electric current passing through it.
- Galvanic action: The corrosion which occurs when two dissimilar metals are electrically connected and immersed in an electrolyte.
- Galvanic series for seawater: A list of metals and alloys arranged according to their relative corrosion potentials in a seawater medium.
- Ground: Electrical connection to the earth. (Sometimes used to refer to a connection to a common conduction framework, such as an automobile frame or appliance chassis).
- Hull potential: Potential of hull (metals) with respect to a standard reference electrode.
- Hydroxyl: (Hydroxide) ion OH^- .
- Impressed current device: A device, usually electronically controlled, which takes a portion of a boat's power supply and applies it to the hull in such a way that the hull is negative and therefore protected.
- Ion: An atomic or molecular species which has either an excess or deficit of electrons, rendering it charged.
- Load: A circuit component which draws current from a voltage source.
- Ohm: The unit of resistance to flow of electrical charge.
- Noble metals: Those generally less prone to corrosion are said to be more noble than others (also more cathodic).
- Ohm's Law: $V = I R$, $I = \frac{V}{R}$, or $R = \frac{V}{I}$, where V is the voltage, I is the current in amperes (or amps), and R is the resistance in ohms (Ω).
A voltage of one volt placed across a resistance of one ohm will cause a current of one ampere to flow.
- Oxidation: Loss of electrons.
- Oxide: A chemical compound consisting of positive ions (usually metal ions) bonded to negative oxygen ions.
- Polarity: The identification of the positive and negative terminals.
- Potential: (See Voltage).
- Reduction: Gain of electrons.
- Resistance: The opposition to current flow by a circuit component when voltage is applied.
- Shaft brush: A device used to provide good electrical contact with a rotating propeller.

Silver-silver chloride electrode (Ag-AgCl): A commonly used reference electrode for measurement of potentials in an aqueous solution.

Stray current corrosion: Corrosion caused by unintentionally impressing a voltage, either A.C. or D.C., between immersed metal components.

Volt: The unit of electrical potential or voltage (given the symbol V).

Voltage (also Potential): A measure of the driving force for flow of current. Often compared to hydraulic pressure.

SCOPE OF TEXT

This booklet has been prepared to enable laypersons unfamiliar with corrosion engineering principles to understand the basic mechanisms by which various corrosion reactions are formed. Methods of detecting corrosion problems and methods to minimize or eliminate them have been presented. Various tables, graphs, diagrams, and photographs have been included to illustrate the written text.

Every effort has been made to present this complex subject to the reader in a clear, fundamental, and easily understandable style. No attempt is made to dazzle the reader with a cumbersome or difficult vocabulary. However, there may be terms presented that are new or not clear in meaning. The majority of these terms will be explained in the "Description of Terms" section.

The text has been prepared in a way that will allow the reader to understand and follow the methods by which different corrosion processes are created and progress. It is important to understand the basic causes and mechanisms of the corrosion reactions in order to gain:

1. the ability to locate the cause of existing corrosion problems and to effect a proper solution; and
2. the knowledge to construct/fabricate materials that will be exposed to a marine environment and will offer the least corrosion problems possible.

The topics on corrosion discussed in this text are valid for both freshwater and saltwater environments. However, because corrosion problems are more severe in salt water, this text will direct most of its discussion to that type of corrosion.

The purpose of this booklet is to impart the basic concepts of corrosion processes to people who are engaged in activities in a marine environment. Armed with this knowledge, their ability to combat the destructive force of corrosion will be much more cost-effective.

I. BASIC ELECTRICITY

A. Ohm's Law as Concerned With Corrosion

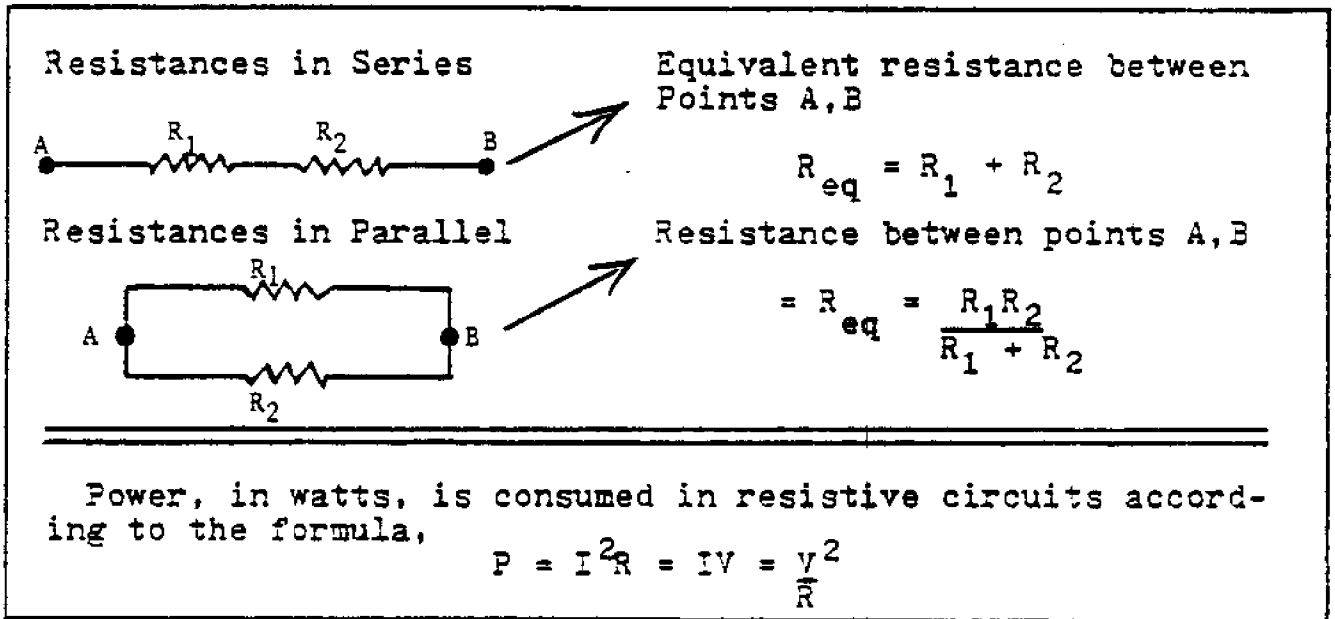
Electrical potential, or voltage, is the driving force necessary for the flow of electricity in an electrical circuit. This flow of electricity resulting from the presence of a voltage difference between two points in a circuit is called current and is proportional to the voltage difference between the two points. Direct current circuits (D.C.) are those in which the current flows in one direction only, depending on the polarity of the voltage source. Alternating current (A.C.) of 60Hz has a polarity reverse every 1/120th of a second. Both D.C. and A.C. circuits can create corrosion problems on board small and large vessels.

In simple circuits, current, resistance, and voltage are related by the relationship $V = IR$ (Ohm's Law), where V is the potential in volts, I is the current in amperes, and R is the resistance in ohms. These units are defined such

that 1 ampere is the current that flows through a 1-ohm resistor which has a potential of 1 volt impressed across it. Voltage dealt with in corrosion work is usually expressed in millivolts (mV), 1,000 mV = 1 volt. Ohm's Law is generally valid for all of a boat's electrical circuits (A.C. or D.C.) which affect corrosion phenomena (5). Resistances are often termed "loads," since they draw power from the energy (or voltage) source. The equivalent resistance of a combination of resistors depends on whether they are in series or in parallel (see Figure 1).

The conventional analogy between a simple electrical circuit and a water system may allow better understanding of the variables used in Ohm's Law. Just as a water tank creates the driving force (pressure) for water circulation, a battery creates the driving force (voltage) for the circulation of electricity.

Figure 1 Equivalent resistance



Pipes distribute water, while wires distribute electricity. Gallons per minute is the general term to denote the flow rate of water, while amperes is the term for the flow rate (current) of electricity. Resistance to water flow, measured in pressure loss, results from pipe friction and energy losses in elbows, valves, etc. Resistance of electricity, measured in ohms, results from energy losses in wires, terminal strips, switches, etc. Electrical equipment forms the load in the circuit, while faucets, heads, etc., act as loads in water systems.

Most small boat electrical systems are Direct Current ranging from 12 to 32 volts. When electrical equipment is installed in a low voltage system, care must be taken not to introduce significant resistance in the circuit (by use of improper wire size or wiring technique). Letting circuit resistance rise in a 12-volt system driving a bilge pump that draws 4 amperes of current causes a change of voltage at the motor which may both damage the motor and induce severe corrosion problems. Small wire diameter and/or long wire length restricts current flow and increases circuit resistance (This will be further discussed in Section J of Chapter III). If circuit resistance becomes significant, the result appears as a voltage drop. Therefore, it is very important, for safety and corrosion reasons, to employ wire sizes adequate to carry the maximum current load, when all equipment is operating, without causing a noticeable voltage drop.

B. Flow Theory: Electron Flow Vs. Current Flow

To fully grasp the various mechanisms by which corrosion is initiated and propagated, it is very important to understand the following simple statements. Current flow within a circuit is from the positive (+) terminal to the negative (-) terminal. However, electron flow within a circuit is from the negative (-) terminal to the positive (+) terminal. The explanations of corrosion phenomena in this text will use only the electron flow convention. Remember, current flow is always opposite to electron flow!

II. BASIC CORROSION THEORY

A. Why Metals Corrode

Metals are formed from compounds found in the earth's crust which are relatively stable (do not react with surroundings). Throughout the various refining processes in which the metal atoms are orientated in a structured pattern, much energy is expended. As a result of the refining, the finished metal contains "free energy" locked up internally (similar to the energy contained in compressed spring). This free energy contained in the metals causes them to be unstable, and they tend to react with their environment and revert back to their more stable (lower energy) form. This reaction is termed corrosion, and frequently the corrosion product is chemically similar to the mineral form which the metal was refined.

All metals are composed of atoms which are electrically neutral; i.e., each atom contains an equal number of positive and negative charges (7). The number of protons and electrons present in a metal determine what type of metal it is. For example, iron has a chemical symbol, Fe, and each iron atom contains 26 protons and 26 electrons, while each atom of copper, Cu, contains 29 protons and 29 electrons. Although all protons and most electrons are bound securely to the center of metal atoms, some of the outermost electrons are only loosely bound. These loosely bound electrons tend to be mutually and freely exchanged between neighboring atoms. This ability of metals to freely exchange or pass along electrons allows them to become conductors of electricity.

If for some reason a metal atom passes one or more electrons along but fails to receive an equal number, it then loses its electrical neutrality and becomes positively charged. Atoms which are not electrically neutral are called metal ions. When most metals are immersed in a solution, which could be fresh or salt water, there is a tendency for the atoms to change into their respective ions and enter into the solution. If iron, Fe, was placed in salt water, then eventually iron ions, Fe^{++} , could be detected in the solution. These iron ions have a positive charge and were formerly iron atoms that gave up two electrons. If copper, Cu, were placed in the solution, then copper ions, Cu^+ , could be detected.

The amount of energy in a metal, and its tendency to release that energy, is called its potential (usually measured in volts). Different metals and alloys contain varying amounts of free energy and therefore have different potentials. If various metals and alloys are arranged relative to their potential, a table can be compiled listing these metals in order of highest to lowest free energy state. When these potential measurements are made in a solution containing ions of the measured metal using a specific reference electrode, the resulting table is called the Electromotive Force Series. If these potential measurements are made in seawater against a specific reference electrode, the table is called the galvanic series for seawater (8). (See Figure 2).

A reference electrode is an instrument used to establish standard potential values that allow uniformity in these measurements. Just as a standard weight of 1 pound may be used as a reference for international weight measurement, a reference electrode is used for potential standardization. There are a variety of reference electrodes such as hydrogen, silver-silver chloride, copper-copper sulfate, and calomel which can be used for potential measurements. Field work is generally carried out with either a silver-silver chloride ($Ag-AgCl$) or copper-copper sulfate ($Cu-CuSO_4$) reference electrode because of their compactness, ease of use, and durability. The values in Figure 2 were established using a calomel reference electrode. The calomel and silver-silver chloride reference electrodes yield potential value readings that are essentially the same. Numerous galvanic series tables have been established for different liquid solutions. In dealing with marine corrosion, it is appropriate to use the galvanic series for seawater to determine metal compatibilities.

B. Basic Galvanic Cell

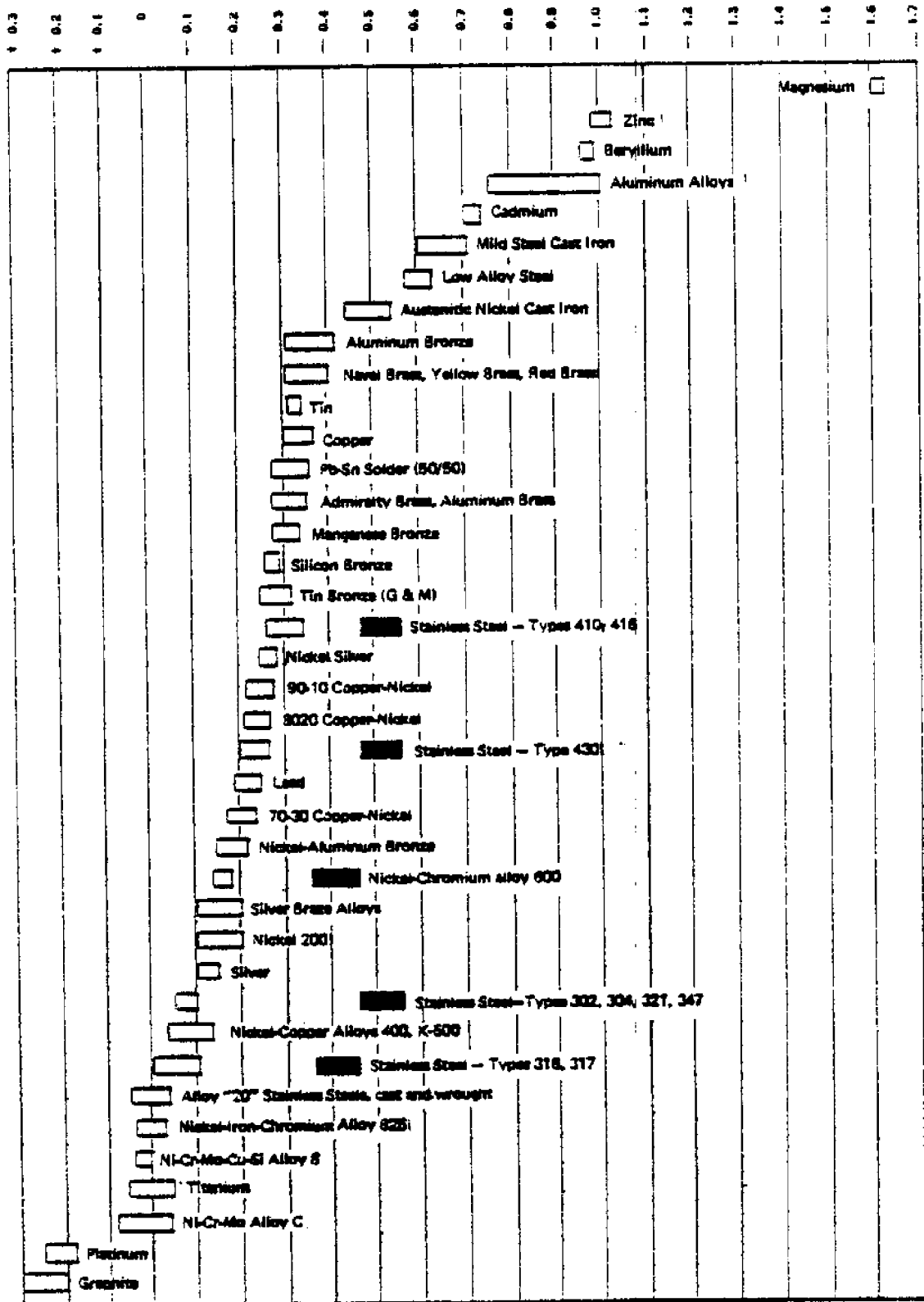
In Figure 2, potentials for various metals are given. These potentials are obtained relative to a calomel reference electrode, which conveniently allows potential differences between various metals to be calculated. For example:

If a strip of copper (Cu) and a strip of zinc (Zn) are immersed in a beaker of salt water (Figure 3), both will react with the solution and become surrounded by a layer of their respective ions. However, because zinc is more reactive (more electrochemically negative) it will be surrounded by more of its ions than the copper strip. Once sufficient ions of each metal have reacted (corroded away) with the solution and formed an electrochemical equilibrium around each strip, the reaction will cease. In this case, the seawater forms

FIGURE 2

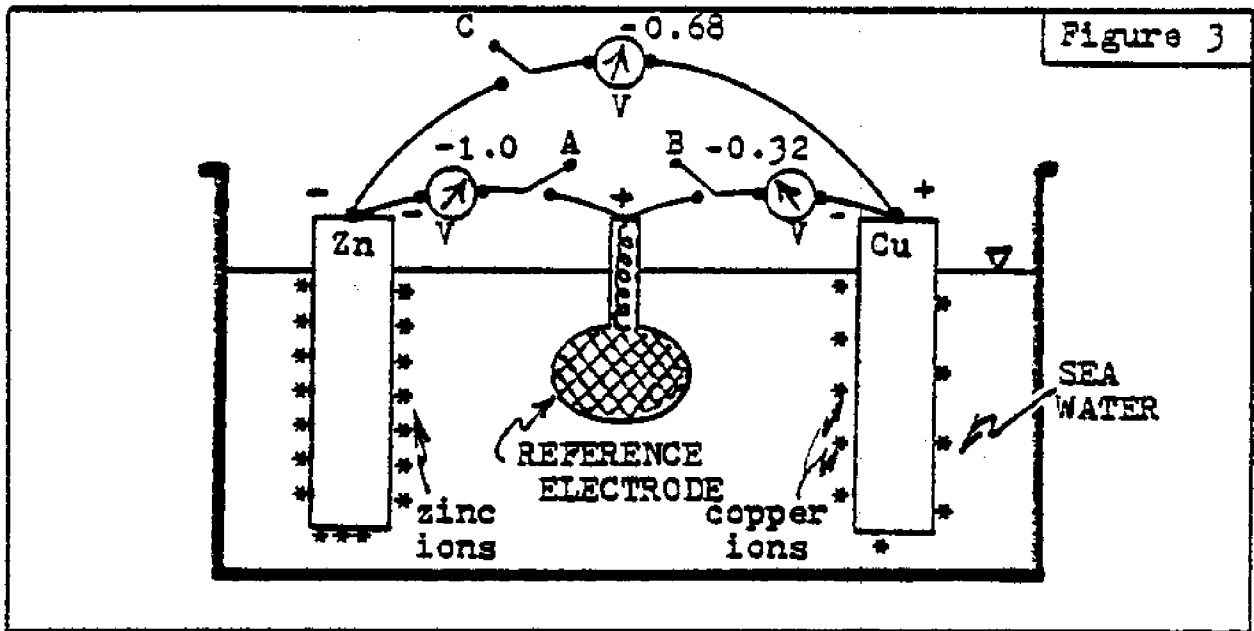
CORROSION - POTENTIALS IN FLOWING SEA WATER
 (8 TO 13 FT./SEC.) TEMP RANGE 50° - 80°F

VOLTS: SATURATED CALOMEL HALF-CELL REFERENCE ELECTRODE



Alloys are listed in the order of the potential they exhibit in flowing sea water. Corrosion alloys indicated by the symbol: ■ in low velocity or poorly aerated water, and as shielded areas, may become active and exhibit a potential near -0.5 volts. Data is from Inco Bulletin A40A, "Guidelines for Selection of Marine Materials".

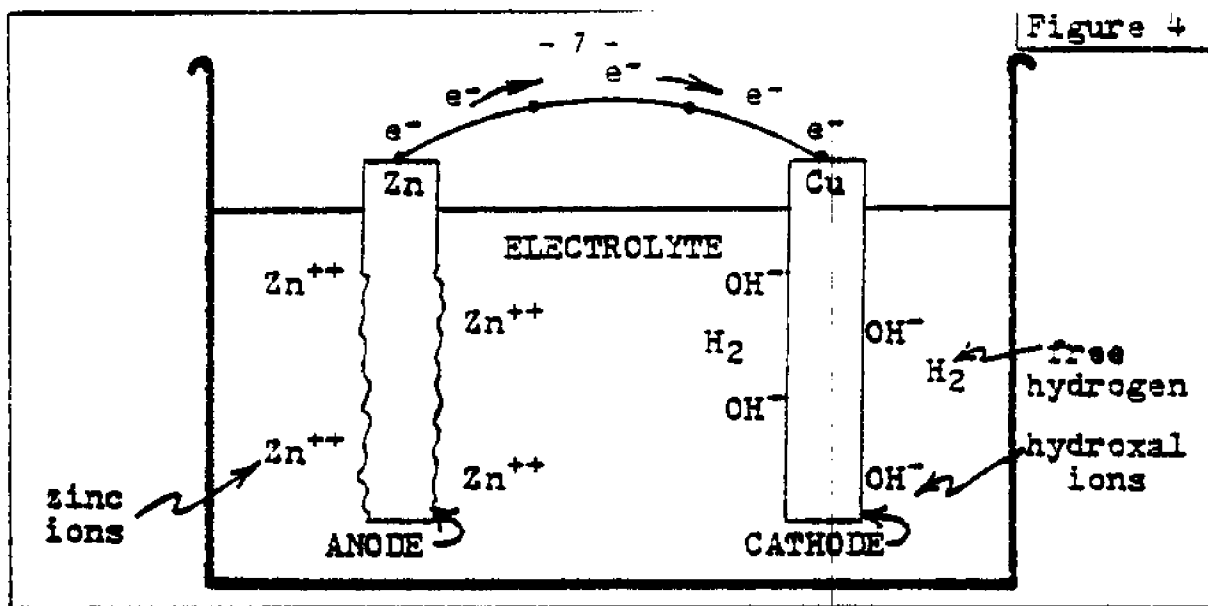
1 The metals are primarily for construction. Anode alloys may be expected to differ.



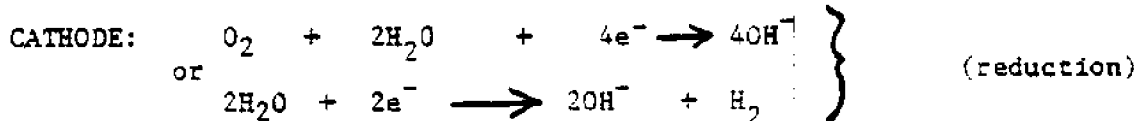
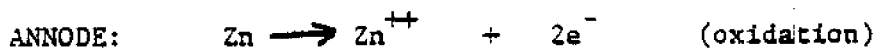
the electrolyte (any liquid that contains ions, electrically charged atoms, or groups of atoms in solution). Pure water, for example, contains positively charged hydrogen ions, H^+ , and negatively charged hydroxyl ions, OH^- , in equal concentrations of about 3 million-million each per drop (4). In Figure 3, if switch "A" is momentarily closed, connecting the zinc to the calomel reference electrode, a potential of approximately -1.0 volts will be read. If switch "B" is momentarily closed, connecting the copper to the reference electrode, a potential of approximately -0.32 volts will be read. Now, if switch "C" is momentarily closed, connecting the zinc to the copper, a potential of approximately -0.68 volts will be read. This reading will be the potential between the two metals and can be calculated directly from the Galvanic Series Chart. From the chart the following potentials are obtained: zinc is -1.0 V and copper is -0.32 V; therefore, the potential between zinc and copper in seawater would be approximately $(-1.0 V) - (-0.32 V) = -0.68 V$. In this manner, potentials between metals can be easily computed for a seawater environment. The exact potential between various metals depends upon variables such as temperature, dissolved oxygen concentration, electrolyte composition, surface of the metals (painted, overgrown, corroded), velocity of electrolyte, distance between metals, and impurities in the metals.

If the zinc and copper strips of Figure 3 are connected by a conductor such as a wire, electrons (e^-) flow from the zinc to the copper, where they are consumed (Figure 4).

The electrons flow in this manner because of the difference in the relative potential of the two metals. For every two electrons released by the zinc, one zinc ion (Zn^{++}) is simultaneously formed, thereby maintaining electrical neutrality of the solution. These positively charged ions are released into the electrolyte in which they are soluble. The zinc is corroded at a rate which is directly proportional to the electron flow.



In a basic galvanic cell such as that in Figure 4, the metal on which oxidation (corrosion) takes place is defined as the ANODE (zinc in Figure 4). The metal on which reduction (electrical breakdown of water molecules, ELECTROLYSIS) takes place is defined as the CATHODE (copper in Figure 4). These reactions are defined as follows (2) (5).



WHERE: H_2O = water molecule H_2 = free hydrogen
 e^{-} = electron Z_n = neutral metal zinc
 OH^{-} = hydroxyl ion Zn^{++} = zinc ion
 O_2 = oxygen molecule

In any galvanic corrosion system, corrosion (oxidation) rates at the anode must be equal to reduction rates at the cathode. In other words, the release of electrons by the anode must equal the consumption of electrons at the cathode. Any phenomena that effects the reaction of the cathode forces a similar effect on the anode and vice versa.

Often when dealing with corrosion the term "noble" is used to denote the least reactive (cathodic) metal in a multimetal system. In a zinc-copper system, the "more noble" metal would be copper, but a copper-nickel combination would have nickel as the "more noble" metal.

Reactions at or near both the anode and cathode surface generally become slightly more involved in real situations. At the anode surface, dissolved anodic ions may combine with other ions present in seawater or dissolved oxygen to form more complex compounds, which may precipitate out of solution

and build up on the anode. At the cathode surface, reduction of hydrogen ions (H^+) can form hydrogen gas (H_2), which can build up a layer of bubbles that can slow down the corrosion process (called cathodic polarization). Also, the generation of hydroxyl ions may combine with various ions and soluble compounds to form various precipitates or localized alkaline conditions.

The following explanation of alkaline and acidity, although elementary, will be adequate for the material contained in this text. The term "alkaline" (basic) pertains to compounds that yield hydroxide ions, OH^- , when dissolved in water. A compound that yields hydrogen ions, H^+ , or hydronium ions, H_3O^+ , when dissolved in water is called an "acid." If there is a predominance of hydrogen ions, H^+ , in a solution, then the solution is acidic. A predominance of hydroxide ions, OH^- , in a solution causes the solution to be alkaline, or basic. A balance of hydrogen ions and hydroxide ions results in a neutral solution. The pH of a solution is a dimensionless number which indicates the relative strength of the acidic or alkaline content of a solution and ranges from 1.2 to 12.8. Strongest acids (high H^+ concentration) correspond to lowest pH numbers, while strong bases (high OH^- concentration) are assigned the highest pH numbers. A neutral solution would have a pH number of 7.0. The surface layer of seawater is normally alkaline, with an approximate pH value of 8.0. However, in inshore areas where considerable microbiological activity exists, large quantities of hydrogen sulfide (H_2S) may tend to lower the pH, causing the water to become more acid. Conversely, a high photosynthetic activity of plants reduces the carbon dioxide (CO_2) content of the water, raising the pH and causing the water to become more alkaline. High water temperatures can also cause an increase in alkalinity as a result of CO_2 "boiling" off.

C. Summary

The foregoing should give a sound footing for understanding the fundamental mechanism of corrosion problems encountered in the marine environment. Briefly stated, for galvanic corrosion to take place the following statements must be satisfied:

1. Two or more metal areas must be involved which have different potentials. These can be different metals or different areas on a single piece of metal.
2. Electric continuity (conducting path other than electrolyte) must be established between the two or more metal areas.
3. The metal areas must be in contact with an electrolyte (usually seawater, but a drop of fresh water is also an electrolyte).

The Galvanic Series Table answers the question of which metal in a multimetal combination or alloy will act as the anode (sacrifice itself by corroding), and which will act as the cathode, (be protected). For example: A fitting made of 80-20 copper-nickel alloy is to be soldered into a 80-20 copper-nickel alloy pipe. Should the operation use a 50/50 lead-tin solder or a silver solder alloy? A glance at the Galvanic Series Table indicates that the 80-20 copper-nickel alloy is cathodic to the lead-tin solder but anodic to silver solder. If the lead-tin solder is used, it will corrode in its role as the anode and eventually disintegrate, leading to a joint failure. If silver solder is used, the fitting and pipe will be anodic, thereby protecting the soldered joint. The results of corrosion on the pipe and fitting should be negligible because of their large area as compared to the soldered joint.

III. FORMS OF CORROSION COMMONLY ENCOUNTERED

A. Uniform Attack

This form of corrosion (see Figure 5) is typically a chemical or electrochemical reaction that progresses in a uniform manner over unprotected surfaces exposed to the environment (2). Uniform attack is considered to consume more metal on a tonnage basis than any other form of corrosion. The mechanism by which uniform attack progresses can best be understood by considering a piece of sheet steel exposed to the elements. The steel will corrode fairly uniformly due to thousands of very small areas on its surface acting as cathodes, while neighboring areas act as anodes and corrode. These cathodic and anodic areas are constantly switching roles, and a fairly uniform corrosion process transpires as a result of this fluctuating mechanism. Alloying elements, heat treatment, surface conditioning, impurities, and other factors are thought to bring about this anodic/cathodic fluctuation. The corrosion due to uniform attack will continue as long as the material is exposed to an atmosphere with a relative humidity of 60% or greater, or if it is immersed in an electrolyte. The overall problems concerned with uniform attack are not considered to be very significant when compared to other forms of corrosion (2).

B. Galvanic Corrosion

As described in Chapter II, galvanic corrosion occurs between two or more metals which are electrically connected and in mutual contact with an electrolyte (Figure 4). The Galvanic Series Table lists many pure metals and alloys relative to their potential to corrode in a seawater environment. The table indicates which metal or alloy will be the more noble (cathodic) component of a multimetal galvanic system.

By employing this principle of galvanic coupling (electrically joining two or more metals), the more noble metal in the couple can be protected from corrosion. In this situation, the less noble material is corroded away deliberately to insure that corrosion does not take place on the more noble materials. The term "sacrificial anode" results from this cathodic protection technique. Cathodic protection will be discussed in detail in Chapter IV.

An important factor in galvanic corrosion is the area effect, or the ratio of cathodic versus anodic areas. Many rapid material failures have resulted from improper area ratios. One of the first such recorded failures happened in 1776 when the British Admiralty sheathed the bottom of the HMS Alarm with copper to prevent it from attack by teredo worms. The sheets of copper were in direct contact with most of the wrought-iron fittings, bolts, nails, and staples attached to, or protruding through, the hull, keel, etc. Within several months, it was found that most iron nails and staples had been corroded to a rusty paste. Also, all of the iron fittings and bolts contacting the copper had either failed or were severely corroded and in need of replacement (3). These failures resulted from placing a huge cathodic surface area (copper sheathing) in contact with the comparatively very small anodic areas (iron fittings, bolts, nails, and staples).

The amount of exposed, immersed surface area (cathodic or anodic) usually affects the resistance value, R , in Ohm's Law ($V=IR$). Circuit resistance, R , will generally be reduced as exposed surface area is increased. This reduction in circuit resistance forces an increase in the electron flow, I , necessary to maintain a fixed potential, V . A term for defining the quantity of electrons leaving or entering a specific amount of surface area is called "current density." Surface area is usually specified in square inches, in^2 ; square feet, ft^2 ; square meters, m^2 ; and so on. For example, if a current of 144 milliamperes (.144 ampere) was supplied to a 1-square-foot anode area, it would have a current density of 144 milliamperes per square foot, $144 \text{ ma}/\text{ft}^2$. Since there are 144 in^2 per 1 ft^2 , this value of current density could also be expressed as $1 \text{ ma}/\text{in}^2$.

This current density concept should become clear from the following explanation. A piece of copper is connected to a piece of zinc having a much smaller surface area (Figure 6a) (5). The voltmeter reading is about 0.68 volts (also from Figure 2) and will not vary as the surface areas are increased or decreased. In Figure 6a, the electron flow from the small zinc area must equal the electron flow into the larger copper area. Therefore, the current density on the zinc surface is much larger than the current density on the copper surface. This high current density occurring on the zinc is the result of many electrons leaving its small surface area. Hence, the zinc tends to corrode at a rapid rate. When the exposed surface area of zinc is increased (Figure 6b), the circuit resistance is decreased, and more electrons flow from the larger zinc surface. Although there are more electrons flowing from the zinc, its surface area has been increased, causing its current density to be lower than that of situation "a." By keeping the copper surface area the same and increasing electron flow to it (these electrons enter into reduction reactions on the copper surface), the current density is increased over the copper.

A further increase in zinc surface area (Figure 6c) will cause still more current flow, which may cause adverse effects around the copper. These effects will be discussed in the section on overprotection in Chapter IV. The current increase resulting from larger exposed surface areas of zinc will reach a limit dependent upon the surface of the copper. When this limit is reached, the copper surface has a maximum current density because its surface is supporting the maximum reduction reactions possible for the seawater-copper/zinc couple.

Another example of area effects can be seen in Figure 7 (2). Two pieces of steel are plated, one with zinc (galvanized) and one with copper. Each plate has a scratch in it which penetrates the coating down to the steel. Then both plates are immersed in seawater. Since copper is more noble than steel (see Figure 2), it becomes the cathodic surface (large area), and the steel exposed in the scratch is anodic (small area). In its effort to supply protective electrons to the copper surface, the steel corrodes rapidly, forming a deep elongated pit, which may lead to sudden failure. However, the other plate has a zinc surface which is anodic to the steel and only a small cathodic steel surface is exposed at the scratch. The exposed steel in the scratch receives its protective electrons from the zinc, and no steel deterioration takes place.

Figure 5 Uniform attack corrosion



Figure 6 Surface area vs. current density

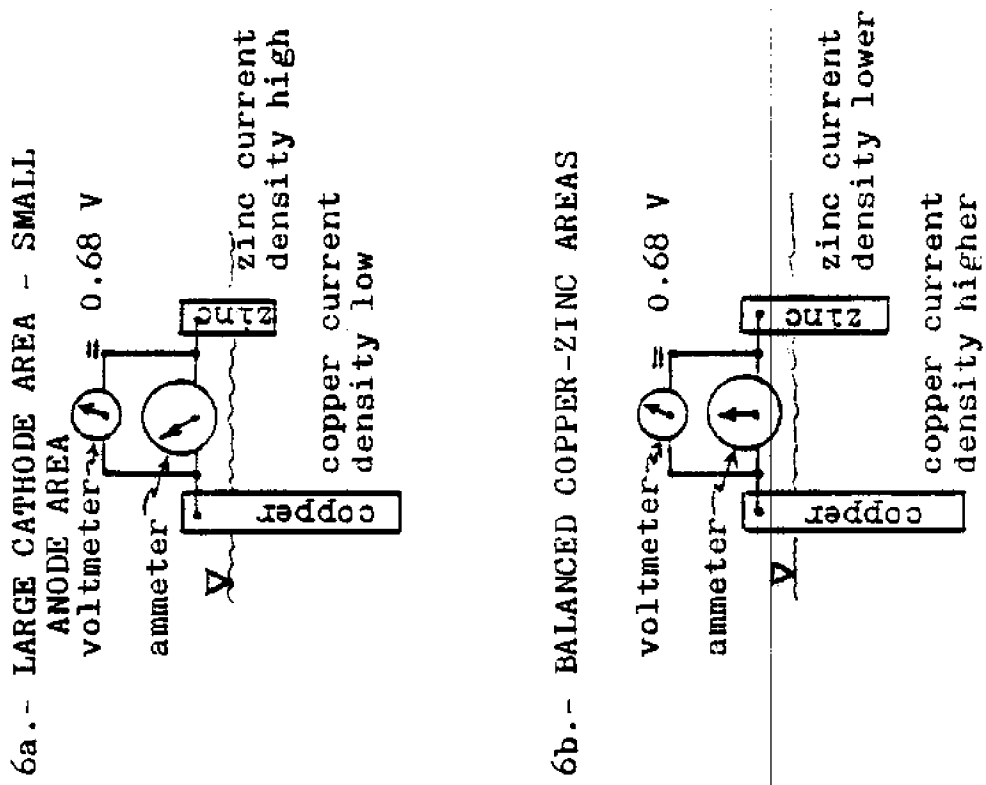
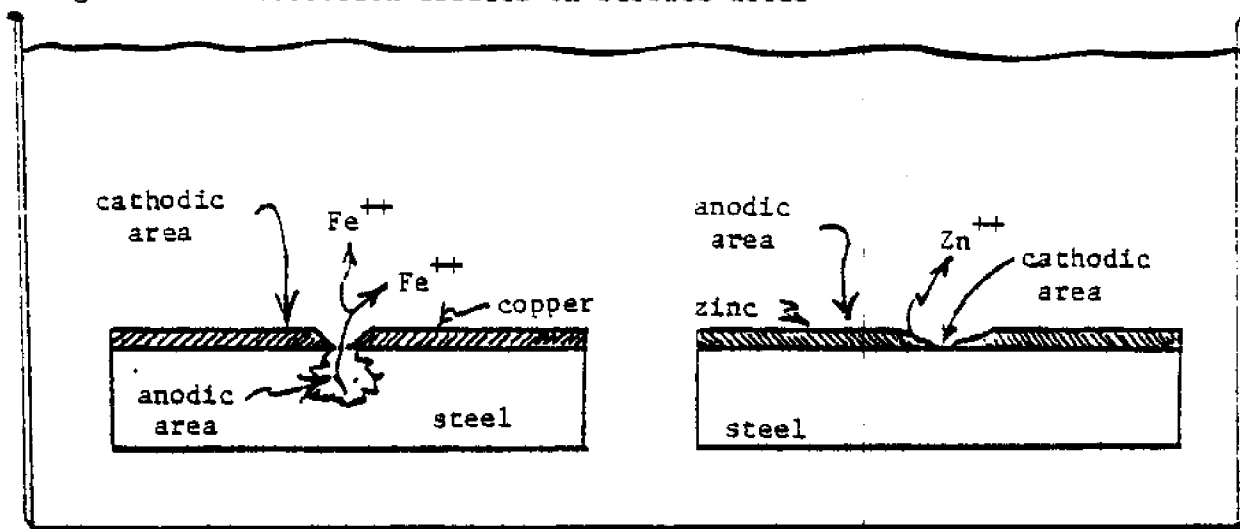


Figure 7 Corrosion effects on surface areas



As a last example of area effects, consider the following case. A large vessel has a damaged stainless steel shaft and requires that a small coupling be fabricated to replace the damaged section. The coupling is, as a last resort, made from a low alloy steel which is anodic to the stainless steel. The shipyard doing the repair work realizes that the steel is anodic to the shaft and puts several heavy epoxy paint coatings on the coupling for protection. When the vessel is launched, the large cathodic surface area of the stainless shaft begins its craving for protective electrons. The anodic couplings' external coatings say "No electrons here," but the unpainted, exposed small area in the internal keyway is quite capable of supplying electrons. The keyway will continue to corrode until there is a failure of the coupling. Painting the corroded coupling in this case was a mistake, because it reduced the surface area of the anodic coupling and forced electron flow to be generated from the critical keyway area.

An important rule to remember when one of two dissimilar metals in contact with each other is to be coated is that the more noble, or more corrosion-resistant, metal should be coated.

C. Selective Corrosion

The galvanic corrosion discussed so far has been concerned with two or more types of metals, such as copper and zinc, which are bonded together electrically. However, it is common to find that various solid metal alloys have undergone a corrosion mechanism in which one element of the alloy has been dissolved. This corrosion process is called "selective corrosion" or "selective leaching." Although selective corrosion is most commonly encountered with brasses (specifically termed "dezincification") and cast iron (termed "graphitization"), it can occur on many alloyed materials if conditions are suitable.

If copper and zinc are alloyed together, the result is brass. The varying percentage of zinc in the combination determines the quality and physical properties of the alloy. Common brasses range from about 60 to 85% copper, with the majority of the balance being zinc. The higher the percentage of zinc, the lower the quality of the brass.

If brass is immersed in an electrolyte, selective corrosion begins on its surface, which is comprised of a matrix of copper atoms side by side with zinc atoms. Electrical continuity is guaranteed, and, as before, copper atoms act as cathodic areas and the zinc atoms begin to dissolve in true anodic fashion. As the mechanism proceeds, more cathodic surface area is exposed as the zinc continues to dissolve into the electrolyte, causing

increased corrosion rates. Equilibrium is established when the dissolution of zinc ions is slowed down in their attempt to migrate out of the brass through a maze of vacancies left by previously corroded zinc atoms.

The result of this dezincification process is that the brass loses its physical strength and will fail in service. Dezincified brass is readily observed by its spongy, dull-copper appearance (Figure 8). It is advisable to stay away from brasses unless specifications are supplied with them, as there are many that contain dezincification inhibitors.

Basically, copper, when alloyed primarily with zinc, is termed "a brass alloy." If copper is alloyed with significant amounts (5 to 15%) of tin or aluminum, it is termed "a bronze." Copper/nickel alloys are very numerous and have many trade names such as Cupronickel, Monel, and Nickel Silver. Although selective corrosion is possible on bronzes and copper-nickel alloys, they are much more resistant to this attack as compared to common brasses.

Graphitization is essentially the same process as dezincification, only it is used to describe the decay of gray cast iron. In this case, the alloy is primarily composed of iron and carbon (3 to 4.5%). When immersed in an electrolyte, the carbon becomes cathodic, and iron, which corrodes away, anodic. This corrosion process results in a very soft surface composed mainly of carbon (graphite) which retains original dimensions but has no physical strength. Many sudden failures in piping systems are the result of graphitization. Graphitization does not occur in modular, malleable, or white cast irons.

Many other alloys, such as bronzes, have selective corrosion mechanisms similar to those above, but have not had specific names attached to them. Figure 9 demonstrates selective corrosion of iron out of an inexpensive bronze propeller alloy. It should be remembered that a properly functioning cathodic protection system will protect these materials from corroding.

D. Cavitation Corrosion

Cavitation corrosion is really a two-component process comprised of corrosion taking place on a surface that has had localized surface cavitation damage. Cavitation corrosion is possible only on surfaces over which an adequate pressure drop is created, usually resulting from high-speed water flow over the surface. Figure 10 demonstrates the mechanism of cavitation damage as follows: (1) High fluid velocities cause localized low pressure areas adjacent to the surface film. (2) Fluid entering this low pressure area begins to "boil" (formation of vapor bubbles on the surface film due to low pressure) when pressure is low enough to equal the fluid's vapor pressure, point B. (3) Bubble collapses (implodes) against surface film and destroys it as high-pressure area is suddenly encountered, point C. (4) The exposed metal surface corrodes and forms a new surface film which can be removed by the next cavitation implosion to hit point C. Repetition of this process can result in deep holes and material failure.

Figure 8 Selective corrosion of brass



Figure 6 Selective corrosion of bronze

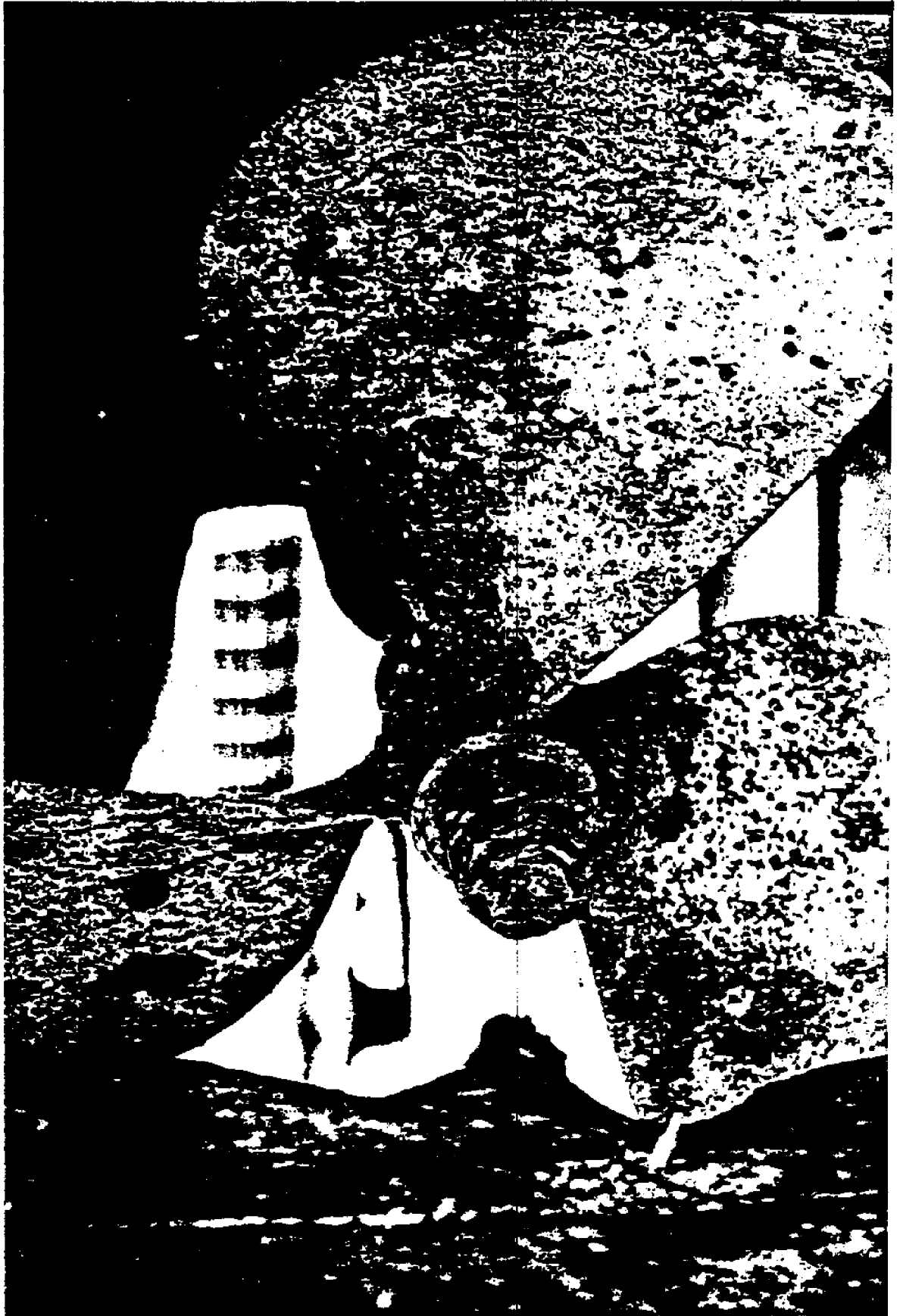
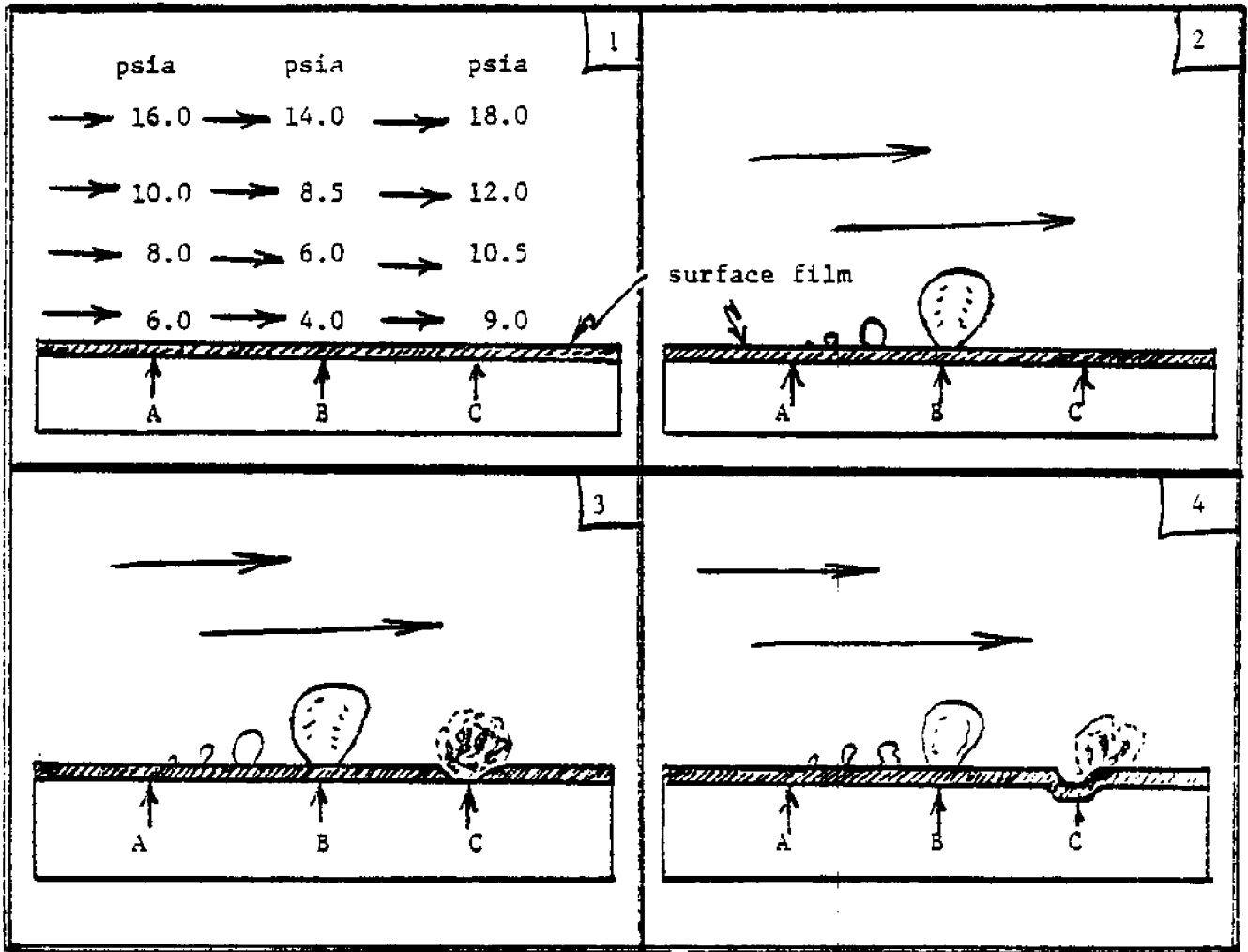


Figure 10 Cavitation mechanism



The shock wave produced by some cavitation bubble implosions can create pressures as high as 60,000 lb/in² (). This force can easily produce stresses well above the yield strength of many materials used for items likely to encounter cavitation conditions such as propellers, pump components, etc. In many cases, the force of an imploding cavitation bubble can tear metal particles away from the surface. The more a surface is roughened by cavitation damage, the more prone it is to further attack, because every rough point can serve as a nucleus for new cavitation bubbles.

Cavitation damage/corrosion is identified by a rough, pitted surface effected in a localized area which is subjected to high water velocities (see Figure 11). There are ways to prevent cavitation damage/corrosion: (1) The design can be modified to minimize hydrodynamic pressure differences. For example, if propeller cavitation is evident, then a change in propeller pitch and/or diameter may be necessary. (2) Use of higher strength materials such as stainless steels greatly improves resistance to cavitation damage. (3) Surfaces should be as smooth as possible, as smooth surfaces do not provide sites for bubble nucleation. (4) Cathodic protection systems may also reduce cavitation damage, possibly as a result of hydrogen bubbles forming on the metal surface and absorbing the shock from cavitation bubble implosion.

Figure 11 Cavitation damage on propeller



E. Concentration Cell Corrosion

If one part of a metal surface is exposed to a higher concentration of oxygen than another part of the surface, the higher oxygen area tends to become positive and the lower oxygen area negative (anodic). Thus, a piece of metal exposed to seawater with variations in oxygen content will tend to corrode in the low oxygen area (7). Also, any significant variation in ion concentration over the surface of a metal or component of a bonding system will tend to establish preferential anodic and cathodic areas. These concentration cells are not common, but they can be established in stagnant water situations, such as trapped pockets of bilge water or water-soaked wood.

F. Corrosion Resulting from Surface Coatings

Various paints and treatment solutions, when used improperly, can result in severe damage to hardware and hulls. The majority of all surface coating corrosion problems arise from paint systems applied below the waterline. The commercial coatings presently available on the market contain numerous metals and compounds derived from metals. Care must be exercised when selecting bottom paint for a vessel because the metallic content of some paints is often dense enough to permit current flow (Figure 12). If a bottom paint containing primarily copper compounds as the anti-fouling agent is applied to an aluminum hull, severe hull deterioration will occur. This is because the copper is more noble than the aluminum (seawater galvanic series) and therefore acts as a large cathode area, while scratches or holidays expose a small anode area (see Figure 13). Specially designed bottom paints containing the metal tin are well suited for aluminum hulls.

Copper-containing bottom paints can cause pitting on steel hulls and should be applied over a barrier coat of nonmetallic paint which insulates the steel from the copper-based paint. Some tin-based paints are well suited for application on steel hulls.

Selection of bottom paints for wood or fiberglass vessels does not present as many problems as does paint for steel and aluminum. However, an incorrect selection can cause serious damage. The total copper content of most non-commercial bottom paints ranges from 25 to 45%; this range includes all copper salts, copper oxides, and metallic copper. However, new and more potent antifouling paints have recently been introduced for the racing community, both sail and power. These paints contain about 70% copper and copper compounds supplied in a vehicle binder that has several percent of graphite thrown in to "toughen the coating" and form a "go fast" bottom.

A hull painted with one of these new bottom paints has a tremendous tendency to act as a large cathodic surface. The dense copper and graphite composition of the paints allows current to flow around the hull. Sacrificial anodes on vessels with this type of paint system can expect a life span of one to three weeks. Once the sacrificial anodes are gone, hull fittings, strut, propeller, shaft, and rudder are next in line. The only reason these items

Figure 12 Ingredients of several popular anti-fouling paints



- 65.5% Aromatic Hydrocarbons
 - 25.0 Copper Powder
 - 8.5 Epoxy Acrylic Ester
 - 0.4 Magnesium Oxide
 - 0.6 Resin
 - 2.5 Ni (tributyl) Oxide
-
- 100.0% Active Ingredients
 - 85.0% Copper Powder
 - 2.5 Ni (Tributyl) Oxide
 - 0.5 Inert
 - 100.0%

PETTIT
marine
 UNDERWATER GUARD
 ANTI FOULING
 FOR YACHTS AND BOATS

1922
 ATLANTIC
 CAUTION
 COMBUSTIBLE

32 FL OZ (1 QT.) 946 ml

ACTIVE INGREDIENT
 Ni (tributyl) Oxide 19.14%
 OTHER INGREDIENTS 80.86%

EPA Establishment No. 380-AL-1
 EPA Registration No. 38923-9-389

WARNING COMBUSTIBLE
 KEEP OUT OF REACH OF CHILDREN
 SEE BACK PANEL FOR ADDITIONAL
 PRECAUTIONARY STATEMENTS

PETTIT PAINT CO., INC.

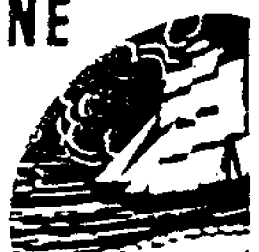
ONE QUART - U.S.A.

SPAR

toe Bottom Paint
 fouling B-44 Black

5 Liters

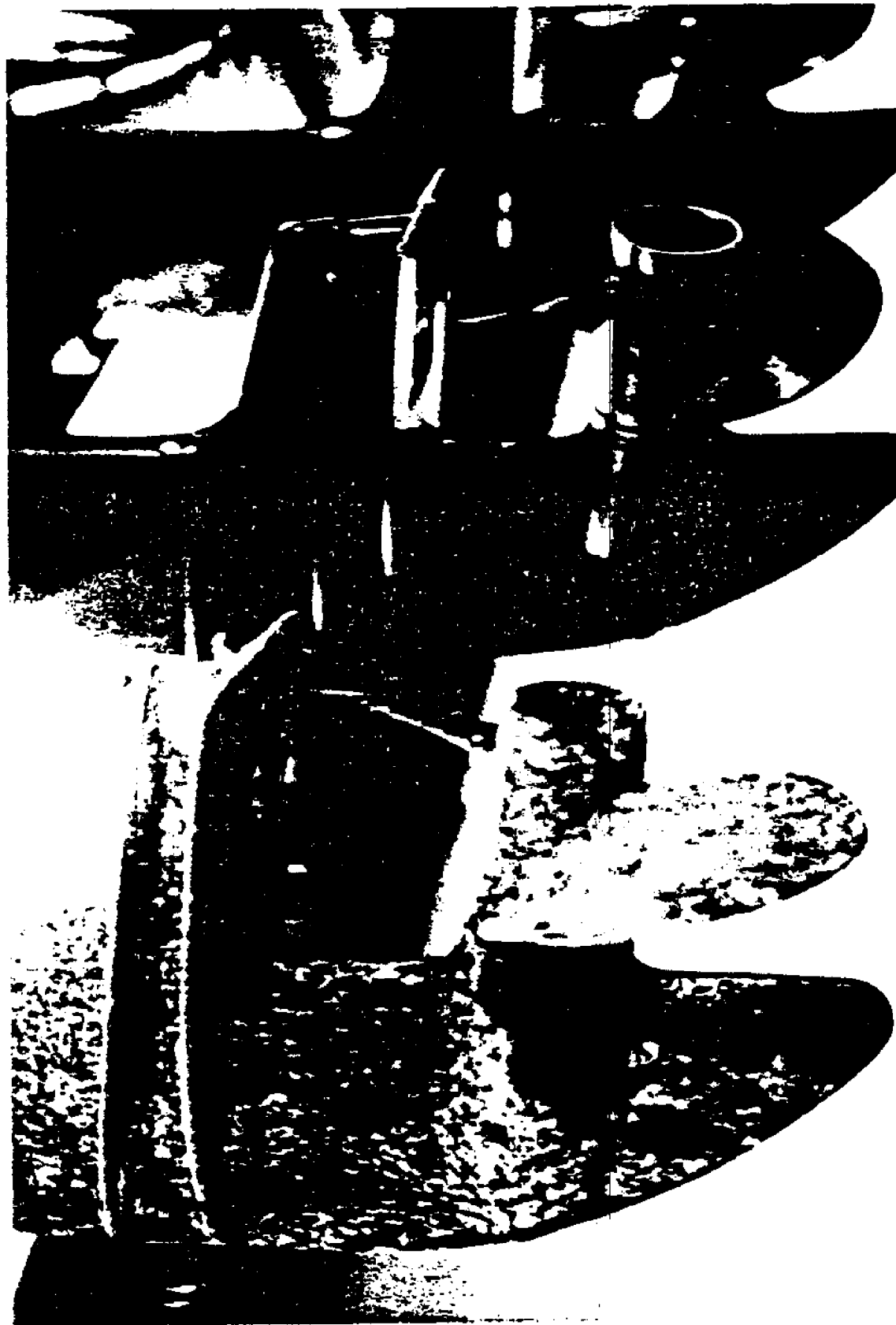
GLUCE
 SEA JACK
 MARINE



ANTIFOULING
 553-BLU

KEEP OUT OF REACH OF CHILDREN
 SEE BACK PANEL FOR ADDITIONAL PRECAUTIONARY STATEMENTS

Figure 13 Results of copper anti-fouling paint on aluminum in salt water



don't physically fall off the hull is that they are generally more noble than the copper paint film (seawater galvanic series). Good bronzes and stainless steels will be slightly cathodic to the bottom paint, but most brass fittings or fasteners will undergo varying degrees of dezincification.

There are real problems when a vessel with an aluminum outdrive unit is painted with a high copper content paint. If the outdrive is bonded to the hull through the bonding system, it will act as a sacrificial anode when immersed in the water. Several sailboats are manufactured with through-hull auxiliary drive units permanently mounted several feet aft of the keel. These drive units have a cast aluminum housing which lasts from five to seven weeks before corroding through when a high copper content bottom paint is applied to the hull (see Figure 14). Painting the aluminum housing with proper tin-containing paint will not retard the housing's destruction in this situation.

Careful analysis of bottom paints is a critical and often overlooked area that must be considered with corrosion control in mind. Treatment of wood used for vessel repairs should not arbitrarily be carried out without some forethought. Preservatives such as Cuprinol #10, which has 2% copper content, can pass current and allow fastenings to corrode galvanically. Wood gums and resins, under certain conditions, can pass current and further complicate the corrosion mechanism.

G. Crevice Corrosion

Significant portions of the following discussion and Figure 15 have been adapted from reference (2).

Intense localized corrosion frequently occurs in crevices and shielded areas on metal surfaces exposed to intermittent or continual immersion in an electrolyte. This type of attack is usually associated with small volumes of stagnant solution trapped by holes, gaskets, surface deposits, and crevices under bolt and rivet heads. To function as a corrosion site, a crevice must be wide enough to permit liquid entry but sufficiently narrow to maintain a stagnant zone. Therefore, crevice corrosion usually occurs at openings a few thousandths of an inch or less in width. It rarely will occur within grooves having a groove one-eighth of an inch or wider. Fibrous gaskets, which have a wick action, form an excellent stagnant solution in contact with the gasketed surfaces.

The crevice corrosion mechanism can be illustrated by considering two plates of steel bolted together and immersed in seawater (Figure 15a). Seawater has an inexhaustible supply of sodium ions (Na^+) and chloride ions (Cl^-). The initial reaction over the entire surface, including the crevice surfaces, involves the dissolution of steel (Fe^{++}) and reduction of oxygen to hydroxyl ions (OH^-). Every electron generated during metal ion formation (Fe^{++}) is consumed in the reduction of oxygen on the metal surfaces. After a short interval, oxygen within the crevice is depleted because of restricted diffusion, and therefore oxygen reduction ceases in the crevice area.

Figure 14 Corrosion of auxiliary aluminum drive unit



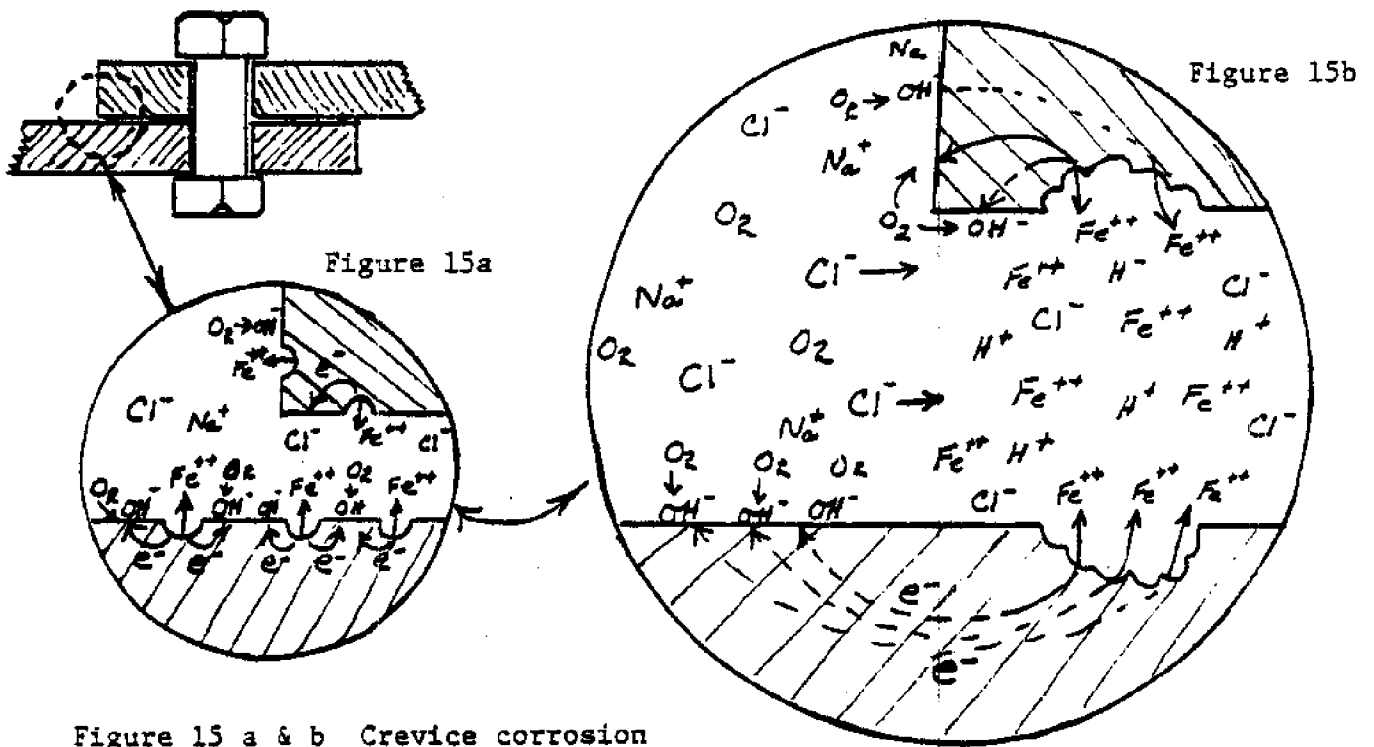


Figure 15 a & b Crevice corrosion

This oxygen depletion has an important indirect influence, which becomes more pronounced with increasing exposure. Although no more oxygen reduction occurs in the crevice, it does continue on other surfaces, allowing dissolution of steel to continue in the crevice, as shown in Figure 15c. This tends to produce an excess of positive charges (Fe^{++}) in the crevice solution, which are necessarily balanced by the migration of chloride ions into the crevice. Hydroxyl ions also migrate into the crevice, but they are larger and are less mobile than chloride ions and therefore migrate more slowly. This chloride ion migration results in an increased concentration of metal chloride within the crevice. This aqueous solution of a metal chloride disassociates water (hydrolyzes), allowing formation of an insoluble hydroxide and a free acid. Both chloride and hydrogen ions accelerate the dissolution rates of most metals and alloys. Since both ions are present in the crevice as a result of migration and hydrolysis, the dissolution rate of the steel is increased. The process is self-generating, rapidly increasing the dissolution of the steel.

The acid content of crevice corrosion cells has been found to contain a pH of 2 to 3. The increasing corrosion rate within the crevice causes increased oxygen reduction on the outer surfaces, which tends to cathodically protect the external surfaces. Crevice corrosion attack is limited to crevice-forming areas, while the surrounding surfaces suffer little or no damage.

Metals and alloys that are particularly prone to crevice corrosion are those which depend upon surface films for corrosion protection. These films are

destroyed by high concentrations of chloride or hydrogen ions. Anodized aluminum and stainless steels both depend on oxide films to form passive surface layers for the prevention of corrosion. Crevices formed by or around these metals may often become oxygen-deficient, and the self-generating mechanism of crevice corrosion will eventually begin. The time before attack may range from several days to several years, but once it begins, it proceeds at an ever-increasing rate.

For crevice corrosion to take place, an electrolyte is necessary. However, salt spray collected under a chafe rail or in the socket eyes of standing rigging will suffice. Crevice corrosion can be found under stainless steel bolts (see Figure 16), washers, screws, rub rails, wire rope swedge fittings, in the lay of stainless steel wire rope (see Figure 17), etc.

By the time crevice corrosion is visually observable, the damage can be well underway. Avoidance of crevice conditions should be strived for in all marine applications. Where crevices cannot be eliminated, the use of materials dependent upon surface films for protection should be avoided. Crevices should be sealed by welding, soldering, good caulking, or use of nonabsorbent gaskets such as teflon.

H. Pitting Corrosion

This type of corrosive mechanism is very similar to crevice corrosion. However, pitting can be initiated where no crevice exists. A pit can initially be formed by basic galvanic corrosion at an anode site. Scale products, produced by initial corrosion, coat the surface of the anodic area and thereby form a shield under which the crevice corrosion mechanism propagates. Surface coatings that are damaged or improperly applied may form crevice situations that promote accelerated pitting (see Figure 18a).

Pits can also develop in high fluid velocity areas as an impingement/corrosion erosion. Pits such as these are generally formed where metal impurities are located or the less noble metal of the alloy is preferentially sacrificed (selective corrosion).

I. Stress Corrosion

Usually, stress corrosion refers to a cracking process in a metal that is being subjected to a tensile stress while in a corrosive medium. The subject of stress-corrosion cracking becomes extremely involved with metallurgical terms that are beyond the scope of this text. Therefore, a brief overview will probably be of more benefit than an attempt at a detailed explanation.

During the phenomena of stress-corrosion cracking, the metal alloy is essentially unattacked over the majority of its surface but fine cracks propagate through it. Stress-corrosion cracks give the appearance of a brittle mechanical fracture, while in fact they are the result of highly localized corrosion processes (2). Cracking generally proceeds perpendicular to the applied stress. Increasing the stress in metal or alloy decreases the time before cracking will occur. Different materials have different "threshold" stresses below which no stress-corrosion cracking will occur in a given corrosive medium.

Figure 16 Crevice corrosion of stainless steel nuts.

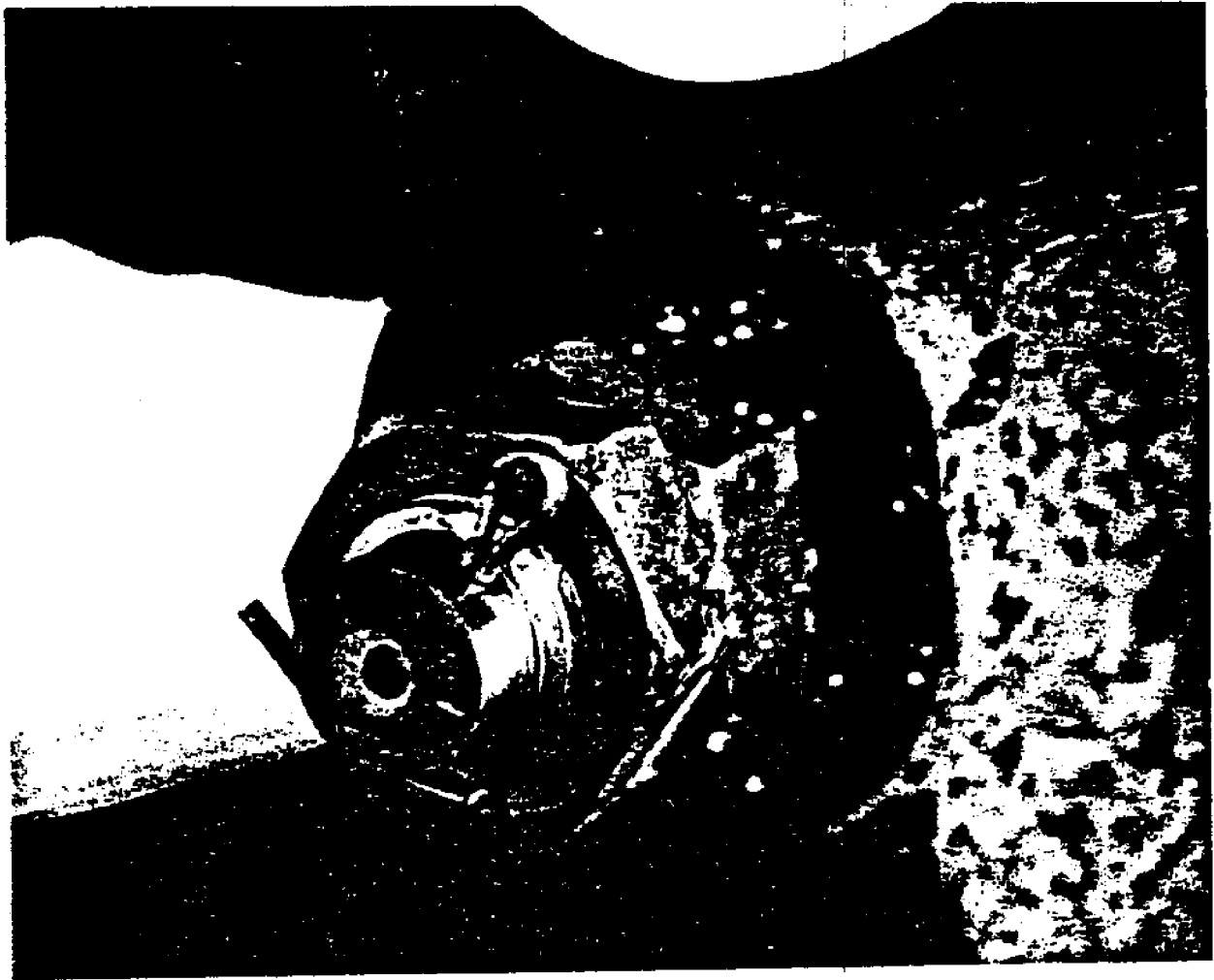


Figure 17 Crevice corrosion of stainless steel wire rope

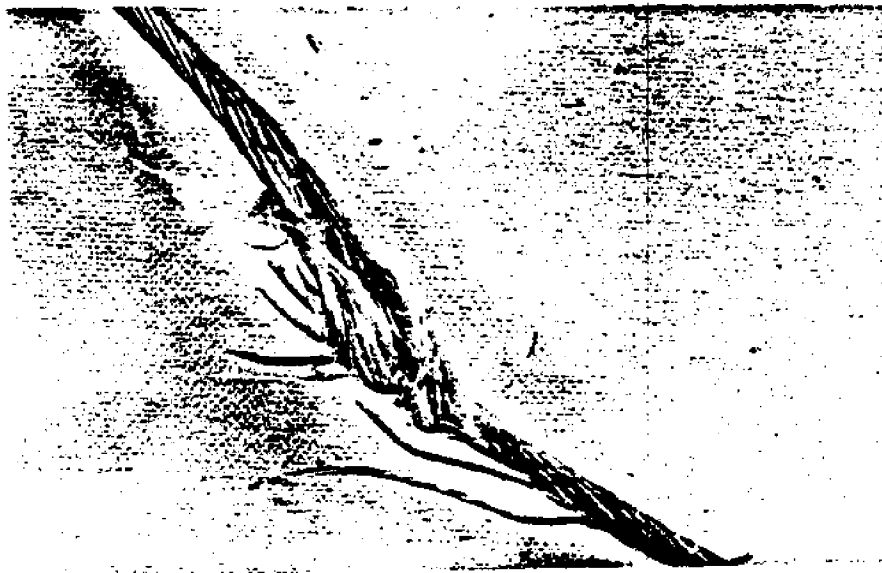


Figure 18a Severe pitting of steel plate



These "threshold" values are extremely variable and should be determined by careful tests for new materials or unusual environments.

In order for stresses to instigate stress-corrosion cracking, they must be of adequate magnitude and tensile (stretching) force. They may result from sources such as applied load, residual, thermal, or welding. Welding stresses often generate residual stresses near the yield point of the base metal. Stress-corrosion cracking is not unique to any specific corrosion medium. It can occur in aqueous mediums and nonaqueous, inorganic liquids as well as liquid metals and fused salts (2). Factors that can significantly effect the onset of stress-corrosion cracking are temperature, metal composition, stress, solution composition, and metal structure. It is generally accepted that pure metals are not susceptible to stress-corrosion cracking. Alloyed metals that are susceptible are stainless steels, brasses, mild steels, aluminum alloys, Monels, and magnesium alloys.

It is frequently observed that stress-corrosion cracks start at the base of microscopic pits. When the crack starts, the crack "tip" has a very small radius which causes high stress concentration, thereby allowing crack propagation to continue (2).

This type of corrosion is often difficult to identify and generally doesn't get much attention in small boatyard corrosion detection. But it does afford another possibility to consider for those unusual corrosion problems that may arise. In many cases, the common failure of hydraulic cylinders used on outdrive units can be attributed to stress-corrosion (Figure 13b). Also, the total failure of propeller shafting may be the result of stress-corrosion coupled with metal fatigue.

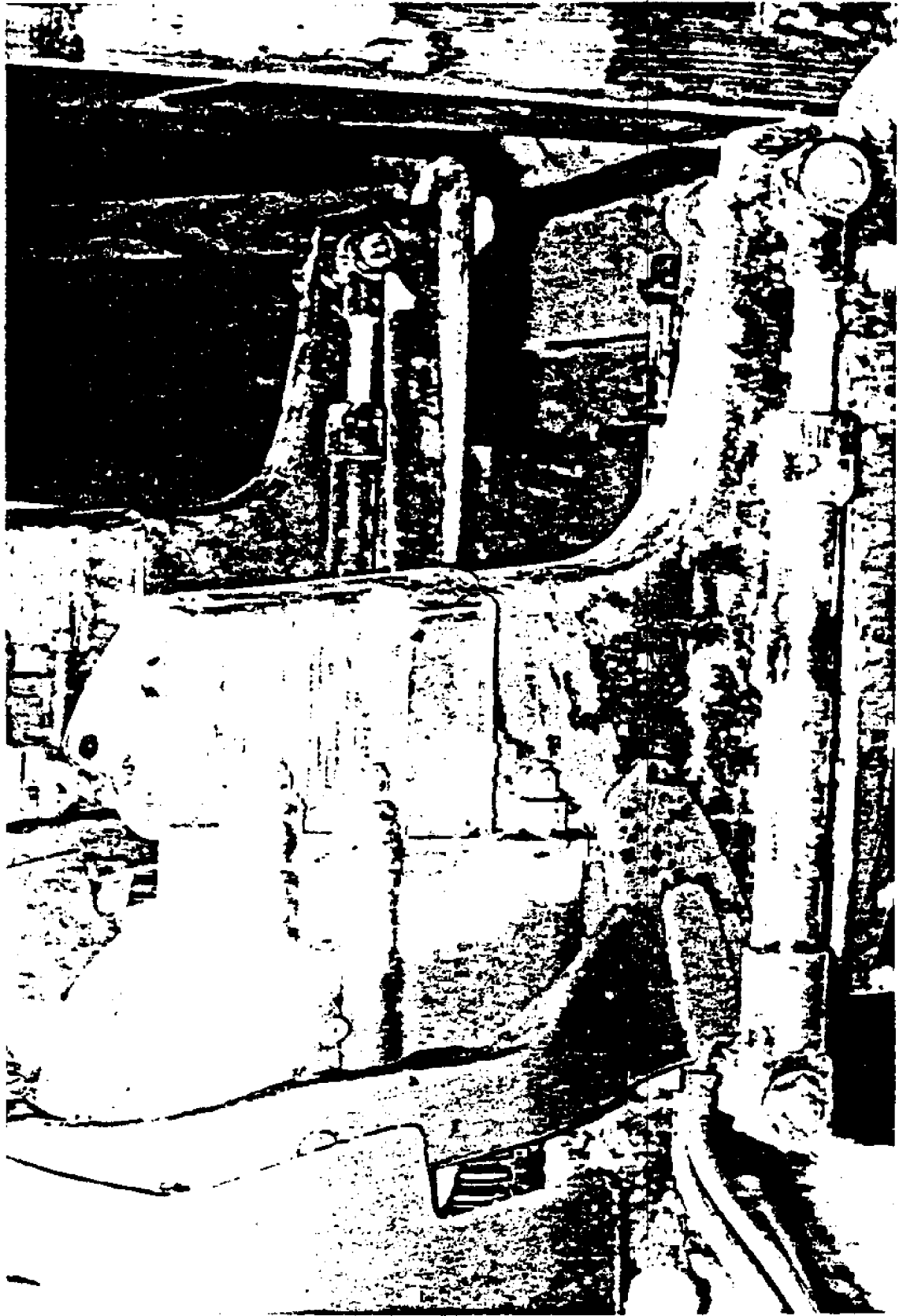
J. Stray Current Corrosion

This type of corrosion is recognized as having the greatest potential for creating extensive damage in a minimal amount of time. Stray current corrosion is caused by an electrical current, A.C. or D.C., that is being discharged improperly through a metal surface into an electrolyte. The surface through which the electrons are discharged into the electrolyte is electrically protected, while the surface through which the electrons re-enter the circuit is electrochemically dissolved. Almost all stray current problems are created from poor or inadequate wiring, damaged insulation, improper terminal mounting, or incorrect shore power connections.

D.C. stray currents can be propagated from numerous current-carrying items. Nearly all cases of D.C. current problems will be confined (cause and result) to individual vessels. If A.C. shore power is used to power a vessel's D.C. system, then the D.C. problems can be external to the problem vessel. When traced to the source, stray current problems inevitably are the result of inadequate or poor wiring situations.

It is an unfortunate but inescapable fact of life that while most boatyards and boatbuilders employ skilled craftsmen and mechanics, they come up short on qualified electricians. When a boat owner accepts delivery on his new or used vessel, chances are better than even that the wiring will be a jumbled

Figure 18b Stress corrosion of hydraulic cylinder on inboard/outboard drive unit.



array of uncoded wires running anywhere they are not visible. The average boat owner will scoop up any wires hanging in bilge water and try to secure them to anything that is dry except, it is hoped, the propeller shaft. Each year, a silent prayer is offered in an attempt to get through another season with no electrical problems; after all, it would cost a fortune to figure out where all those wires go and why. This situation becomes even more complicated with do-it-yourself electronic installations.

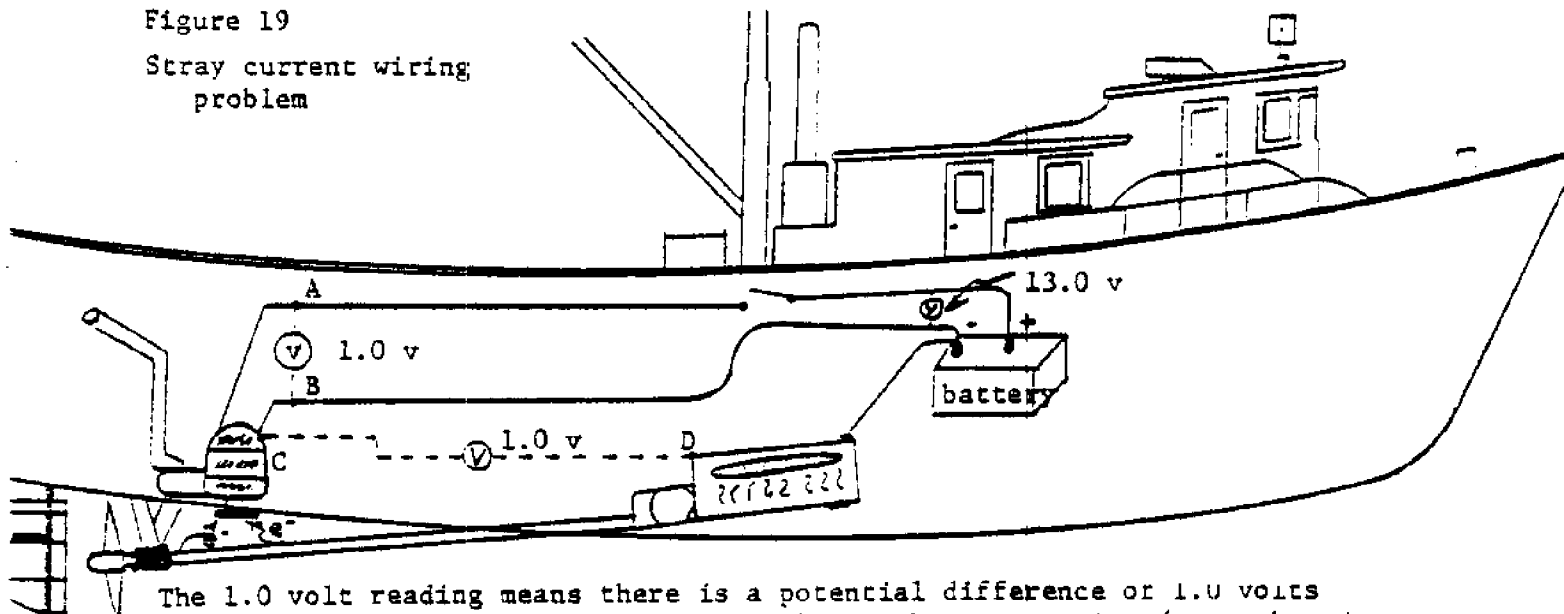
The two prime causes of D.C. stray current corrosion are the result of (1) reversed polarity on the ground side of electrical equipment or instruments, and (2) voltage drops in circuit lines creating potential differences. These two causes will be described in the following examples.

1. Reversed Polarity. A small fiberglass sailboat had a compass mounted on its tainless steel wheel stand in the cockpit. The bonding system consisted of connecting the auxiliary engine to a keel bolt by means of a 12-gauge wire; no other bonding was attempted. The compass light was wired up, with one wire connected to the insulated terminal and the other to the light casing, which contacted the metal wheel stand. The wires were fed down through the stand, where a cockpit on/off switch was installed in one of the two wires. The wires were then brought forward, and one was connected to the fused panel and the other to the negative busbar. After several months in the water, the rudder had disappeared. Haul-out revealed a deteriorated rudder post stub, which was originally cast in the fiberglass rudder. Wiring was checked and revealed that (a) the negative lead was connected to the insulated light terminal, while the positive lead was grounded to the casing; (b) the on/off switch was installed in the negative leg of the circuit, leaving the positive leg closed to the light casing; (c) the casing was secured to the stainless steel wheel stand and thereby supplied it with a continual positive charge. This charge was transferred to the rudder post via the stainless steel steering cable. This resulted in electrons, supplied by the vessel's battery, to exit from the propeller, which was negatively grounded to the engine. These electrons traveled back to the narrow, exposed band of the rudder post between the hull and rudder top, where severe corrosion occurred leading to failure.

2. Voltage Drops in Circuit Lines. In Figure 19, an unbonded vessel has an aft seawater-circulating pump connected via a bronze seacock to the bronze through-hull fitting. When the pump was wired, inadequate wire size was used (too small). This introduces additional resistance, R , into the circuit when the pump is running. The additional resistance creates a voltage drop over each leg of the wire. For the purpose of this example, assume that each leg of the circuit has sufficient resistance to create a 1.0 volt drop over its length, and any voltage drop due to the pump motor resistance will be neglected. Therefore, the positive leg has a 1.0 volt drop and the negative return has a 1.0 volt drop when the pump is running. The negative return lead is jumped to the pump casing to meet typical backyard electronic codes for grounding. If, while the pump is running, a voltmeter is connected between

"A" and "B", a reading of 11.0 volts is obtained. If the meter is connected on the casing at "C", which has the same value as "B", and to "D", a reading of 1.0 volts is obtained. No resistance is encountered between "D" and the negative battery terminal because of heavy battery cable connection.

Figure 19
Stray current wiring
problem



The 1.0 volt reading means there is a potential difference of 1.0 volts between the engine (shaft and propeller) and the pump casing (seacock and through-hull fitting). Therefore, when the pump is running, electrons will flow from the propeller shaft through the water and will enter the bronze hull fitting, causing it to corrode.

The same condition could exist internal to the hull with a bilge pump, using the bilge water as the electrolyte. It should be noted that voltage drops cannot be read unless the circuit is closed.

The previous examples demonstrate two problems that can arise in vessels that do not have a proper bonding system. More about bonding in Section A of Chapter IV. Had a bonding system been installed on the sailboat, the wheel stand and rudder post would have been bonded and a direct short would have resulted upon wiring the positive leg. This would have tripped a breaker or blown a fuse but would also have indicated that something was drastically wrong. If the through-hull pump fitting had been bonded, it would have had the same potential as the engine and no voltage drop would have appeared between "C" and "D". However, this would mean that while the pump was operating the bonding system would carry some of the pump's electrical current. Although this is undesirable, it is better than having a boat sink because of the corrosion failure of a through-hull fitting.

Proper wiring techniques, continuity of polarity, and adequate wire size to handle the current are important factors to remember when wiring a vessel. Many times during electrical installations, wire that is "on hand" is used and assumed to be adequate to handle the electrical current.

This often leads to undersized wiring, which can produce significant voltage drops and may damage electric motors and cause stray current corrosion. The following equation will allow proper copper wires sizes to be calculated for boat wiring. This equation can be used for both A.C. and D.C. wiring and has been formulated to allow a maximum voltage drop, due to wire size, of 0.250 volts at the electrical unit.

$$D = 43 \times I \times L$$

D = wire size in circular mils

I = current in amperes drawn by electric unit

L = length in feet of wire run from power source to unit

Once "D" has been calculated, Figure 20 can be used to find the corresponding A.W.G. (American Wire Gauge) copper wire size. Since it is unlikely that practical application of this equation will result in values of "D" corresponding exactly to a certain wire size, the next largest wire size should be used. The following example demonstrates the use of the wire size equation. The seawater-circulation pump of Figure 19 is to be wired up, using proper wire size. The pump is located 30 feet from the power supply, and, according to the manufacturer, it draws 5 amperes at full load. Hence:

$$D = 43 \times 30 \times 5$$

D = 6450 circular mils

Figure 20 shows that 6450 cir-mils is slightly less than #12-gauge wire (6530 cir-mils). Therefore, the pump should be installed using a minimum copper wire gauge of #12.

Stray current can also result from bad A.C. power connections or improper shore power wiring. Many marina complexes have had tremendous growth over the past 20 years. A dock holding 20 slips 15 years ago may have 30 to 40 slips today. In many cases, outlets with overload protection have been added to existing wiring. A situation like this can result in A.C. voltage drops all along the dock because of inability of the older wiring to supply adequate current.

A practice commonly encountered on many older docks is a two-wire system with no safety ground wire. In Figure 21 (5) two boats, B + C, have their ground and neutral wires interconnected in the shore power receptacle. The boats' bonding systems are tied into the ground wire of each boat's shore cable, under the assumption that ground and neutral are separate.

FIGURE 20

<u>Circular Mils</u>	<u>AWG#</u>	<u>Circular mils</u>	<u>AWG#</u>
101	30	10,380	10
160	28	16,510	8
254	26	26,250	6
404	24	41,740	4
642	22	66,370	2
1020	20	83,690	1
1620	18	105,500	0
2580	16	133,100	00
4107	14	167,800	000
6530	12	211,600	0000

If the dock wires are subjected to heavy current draw from boat "C" or other vessels further down the dock, they may not be adequate to carry this current without creating a significant voltage drop. With the neutral wires of each boat connected to their bonding systems, a voltage difference equal to half the total voltage drop at "C" will be applied between the vessels. This voltage difference, which can amount to 5 or 10 volts, also exists between the vessel and sediment (ground), steel bulkhead, etc. A.C. current will flow between the vessel and the closest object having a different potential. This current flow will cause corrosion damage to the submerged hardware of both vessels.

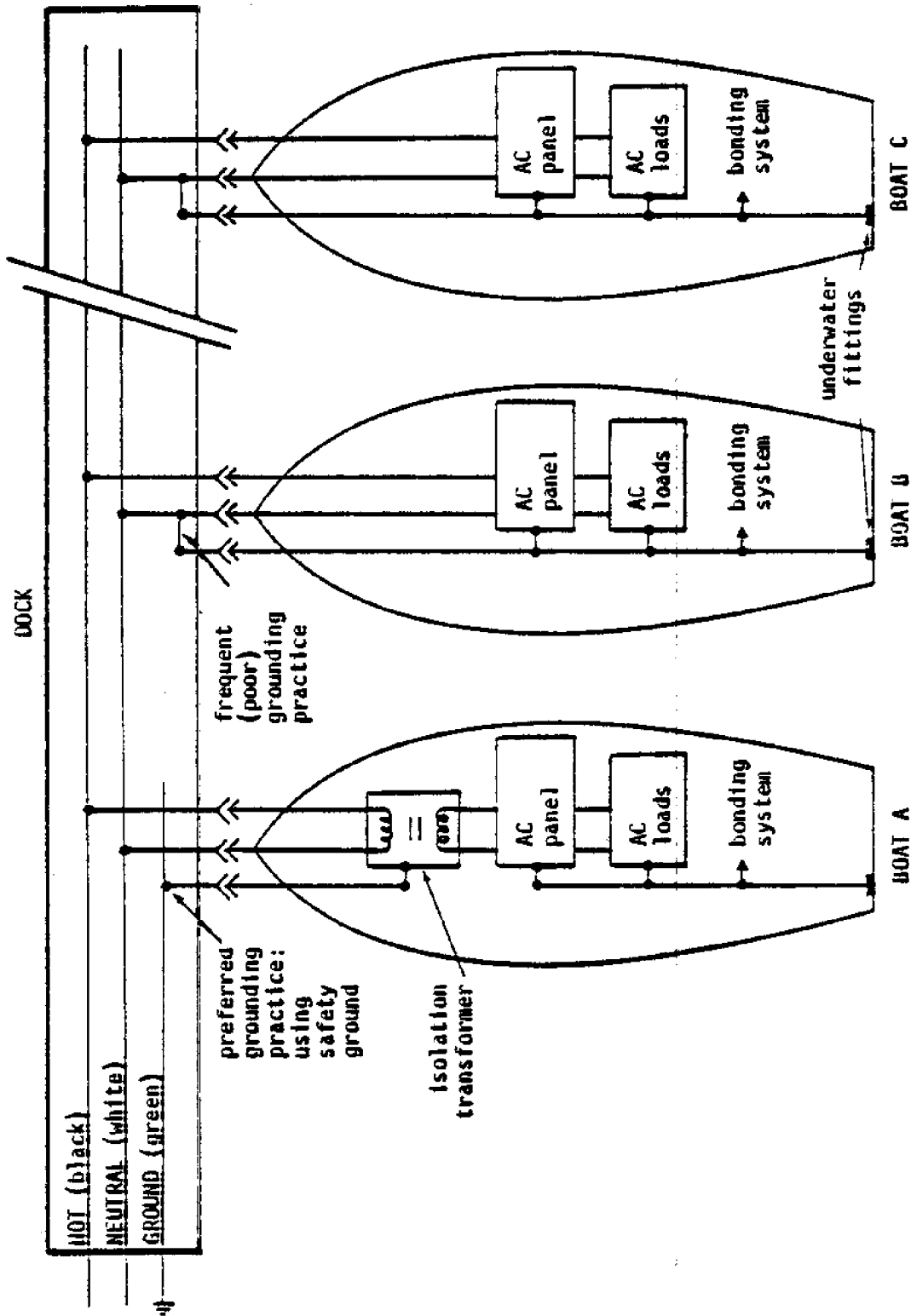
The corrosion damage would be most severe on the fittings closest to the vessel or to the object that the current is exchanged with. However, if many vessels are encountering small voltage drops, the resistance of seawater may be high enough to prevent destructive current flow.

Three wire dock systems are safer, and minimize the chance of stray currents due to voltage drops on the dock. The third safety grounding conductor would tend to tie all the bonding systems together at a common ground potential. This is a solution for dock wiring problems, but shore power connectors and a vessel's internal wiring can also allow A.C. stray current.

An isolation transformer is a wise investment for vessels connected to shore power on a regular basis. Within the transformer a primary winding receives shore current and, by magnetic induction, causes voltage and current flow to be established in the secondary winding (Figure 21, Boat A). The secondary windings supply the vessel with current at the vessel's potential. The two windings are totally insulated (isolated) from each other, thereby eliminating any problems from bad marina wiring, reversed polarity, or bad wiring of the adjacent boat.

Another device, an Isolater, which is manufactured by Mercury Marine, can be installed in the grounding safety conductor. This separates the boat's bonding system from shore ground potential and the accompanying problems that may arise. Wire-to-wire contact is still maintained between current carrying conductors with this system.

Figure 21 Example of stray current corrosion due to inadequate AC wiring



boats B and C have voltage difference, and thus corrosion, due to decreasing voltage along dock neutral

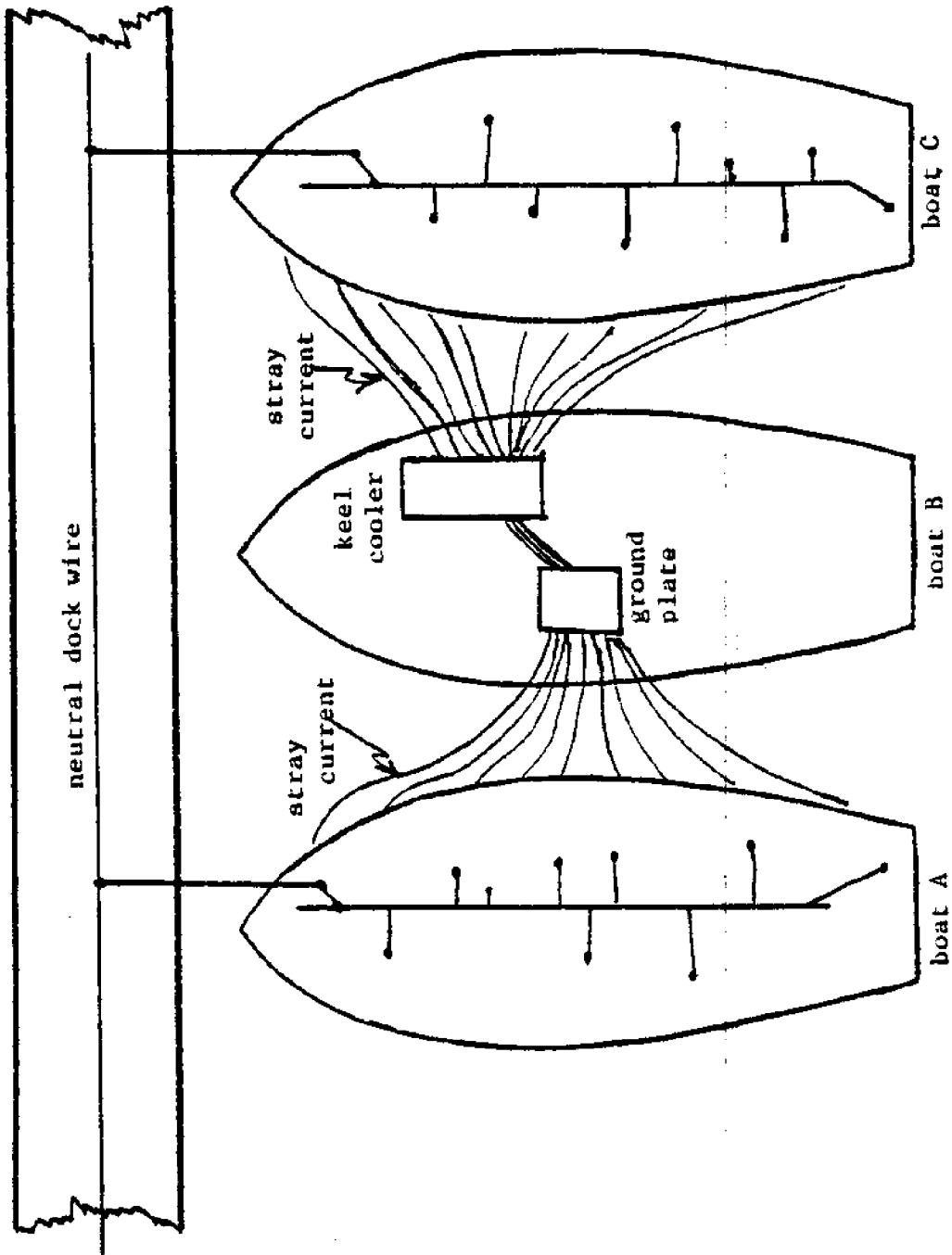
Tremendous corrosion rates can be achieved by using an autotransformer type of battery charger. The primary and secondary windings in these units are electrically linked and the transformed low A.C. voltage is rectified to D.C. When hooked to the battery, the negative side of the battery charger is essentially tied into the propeller via the negative ground on the engine. Very strong stray currents can result from this type of system.

After all the careful wiring, the installation of an isolation transformer, and a thorough bonding system throughout, stray current corrosion can still be a problem. It can result from current fields, flowing through the water surrounding the vessel (Figure 22) (5). These flowing currents will attempt to pass through the least resistive material in their path. The bonding system of a wooden or fiberglass boat, or hull of aluminum or steel boats, is less resistive than seawater. Therefore, a well-protected vessel can act as a "jumper wire" for flowing currents and develop stray current corrosion as an innocent bystander. In the case described in Figure 22, all three vessels will display corrosion problems.

Welding machines have been responsible for large vessels sinking at the dock as a result of welding current corrosion. In order to save time and effort, some welders may attach the welding ground (work) lead to a steel bulkhead or piling. With this system, they have only to string one heavy cable onto the vessel, since the seawater forms the other current-carrying leg. This system will function adequately and the vessel's hull will be undamaged except for paint loss, if the welder is using a D.C. machine and welding with straight polarity. However, the bulkhead or piling will be rapidly consumed in the process. Damaging problems can arise using this poor practice if (a) the welding leads get reversed (welding with reversed polarity), which will cause the hull to corroded away; or (b) another vessel gets between the ship being welded and the welding machine's ground leg. Welding currents traveling through the water will enter and exit from the vessel's hull as a result of its lower resistivity. The tremendously high currents used in welding will make short work of mild steel plate if they are applied improperly.

Should corrosion problems arise and stray currents are suspected, there are several simple tests that can be achieved dockside. Hull potential measurements at several locations should be made using a portable reference electrode. This technique will be explained in detail in the section on cathodic protection. The potentials measured should not differ by more than about 10 millivolts, 0.010 volt (5). Significant variances in hull potential readings would indicate potentially damaging electric fields in the water. Shore power polarity should be investigated (1) (6). This can be determined either by measurement with a multimeter or by using a polarity indicator (5). This precaution will prevent accidental reversal of the shore power, which under some circumstances could cause the hot conductor to be carried to boat ground. Only high-resistance polarity indicators should be used; the American Boat and Yacht Council (ABYC) requires that these devices have an impedance of at least 100,000 ohm (1). Otherwise, they can draw appreciable current and give rise to stray current corrosion (5).

Figure 22 Electrical current fields in water



IV. CORROSION PREVENTION

A. Cathodic Protection

In the section on galvanic corrosion in Chapter III, there was a description of how multimetal systems can be galvanically protected by bonding them electrically to a less noble metal. The less noble, anodic, metal is corroded away intentionally in order to supply electrons to the protected metals. This protection process is termed "cathodic protection" and the anodes are called "sacrificial anodes," since their function is to self-destruct during the liberation of electrons.

Sacrificial anodes used in marine service have been primarily constructed from a pure zinc, since it is anodic to nearly all metals used in marine applications. Magnesium, as indicated by the seawater Galvanic Series, is less noble (more anodic) than zinc. However, the availability of magnesium anodes, their fairly rapid consumption, relative expense, and need of frequent maintenance generally makes them less desirable than zinc. Certain aluminum alloys are becoming more and more accepted as sacrificial anodes, especially as zinc anodes continue to rise in cost. Aluminum anodes have approximately the same galvanic potential as zinc anodes. An anode alloy of zinc and aluminum, trade name, Galvalum, is used on many steel offshore structures.

With this knowledge, it becomes obvious how sacrificial anodes can be employed to prevent a boat's underwater hardware from corroding. This corrosion control is more efficient if the vessel has been thoroughly bonded. A bonding system ties all significant metal components together electrically with a heavy, low-resistance conductor (copper bar, #8 insulated wire, etc. The bonding system is not intended as a ground system, but should be tied into the ground system.

The absence of a bonding system makes corrosion protection virtually impossible for intake and discharge fittings, transducers, exhaust ports, etc. However, a bonding system allows sacrificial anodes to be employed for the protection of all underwater hardware. In most cases, the bonding system should be connected to an appropriate anodes located a little aft of amidships and close to the keel. Larger or deep-keel vessels may require an anode on both sides of the keel for adequate protection. The anode should have a piece of rubberized or other insulative gasket material insulating it from the outer hull surface to prevent a localized reaction with the bottom paint. This location of anodes keeps them central to the bonding wire network and optimizes the protection afforded by the anodes to all underwater hardware.

An important rule of thumb to be kept in mind when installing any cathodic protection system is that anodic protection will tend to follow a line-of-sight path." In other words, if the anode can't see the object to be protected, then protection will be minimal or nonexistent. Also, the protective power of the anode diminishes as separation distance between it and the protected object increases. Bonded objects beyond a radius of 10 to 12 feet from the anode will receive minimal protection.

In addition to the bonding system's protective anodes, it is advisable to install individual anodes on items such as propeller shafts, rudders, and radio ground plate. These supplemental anodes compensate for accelerated anode deterioration resulting from high water velocities encountered around propellers, shafts, and rudders.

It should be noted that for a zinc or aluminum anode to function correctly, it must be corroding (Figure 23). Therefore, if after a season's use the appearance of the anodes shows little or no deterioration, then they have not been working (Figure 24). There are three primary causes for anodes not functioning properly: (1) poor electrical contact, such as shaft or rudder anodes put on over paint; (2) anodes painted after installation; and (3) too many impurities in the anode which cause extensive surface build-up on the anode and eventually insulate the anode surface from seawater. The appearance of impure zincs generally show up as hard, tenacious, dark gray or black surface films. Good zinc anodes require a minimum of 99.20% pure zinc content, as indicated by the following military specifications, MIL--A--18001 (5):

Lead (max.)---0.006%	Cadmium---0.025-0.15%
Iron (max.)---0.005%	Aluminum---0.100-0.50%
Copper (max.)---0.005%	Zinc remainder
Silicon (max.)---0.125%	

If a zinc anode contains more than 0.005% iron, it will be rendered ineffective. Recycled zinc will almost always contain unacceptable levels of iron, due to the melting and recasting process. Therefore, if recycled anodes are to be used, proof of composition should be obtained prior to installation. The scale formed by high iron content can actually be cathodic to steel and thereby accelerate corrosion of adjacent steel surfaces (5).

Zinc anodes are available in various shapes and sizes. The most efficient manner of anode attachment is by use of cast-in brackets which, on steel hull use, are welded on the hull, insuring positive electrical contact. If a nut/bolt arrangement is used for securing the bonding system to the hull anodes, corrosion products (scale) can build up between the anode and bolts in a short period of time. This scale can increase circuit resistance to the point of isolating the bonding system from the anode, rendering it useless. Since zincs with cast-in bolts are not available, one method of securing bolts is to drill a hole in each end of the steel cast-in place straps and braze or silver solder a bronze or galvanized bolt in place.

Determination of the exact amount of protective anode is more black magic than art. There are predicted rules employing surface area ratios--i.e., surface area of protected material versus anode surface area--but most initial systems are based on an educated guess. Variables such as contour of hull, paint system applied, combination of metal types to be protected, seawater conditions at mooring, and amount of time underway all have a significant role in determining the proper amount of anodes.

Figure 23 Properly corroded zinc anodes.

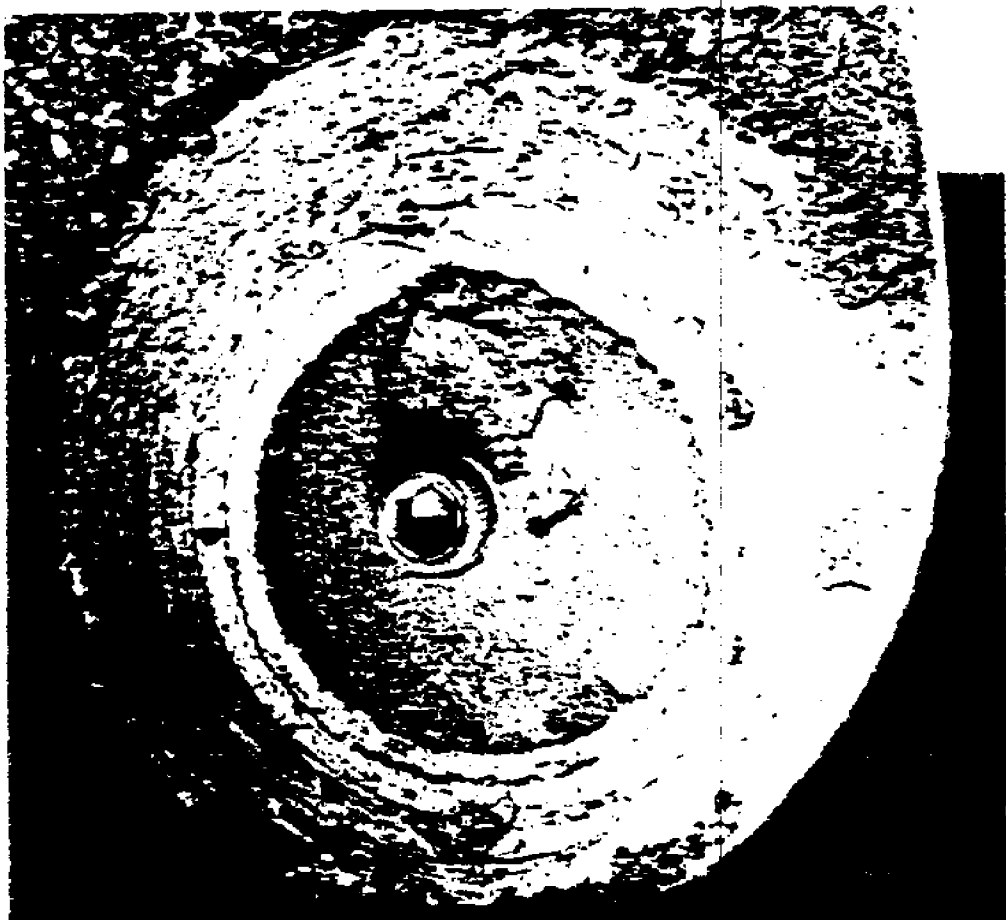
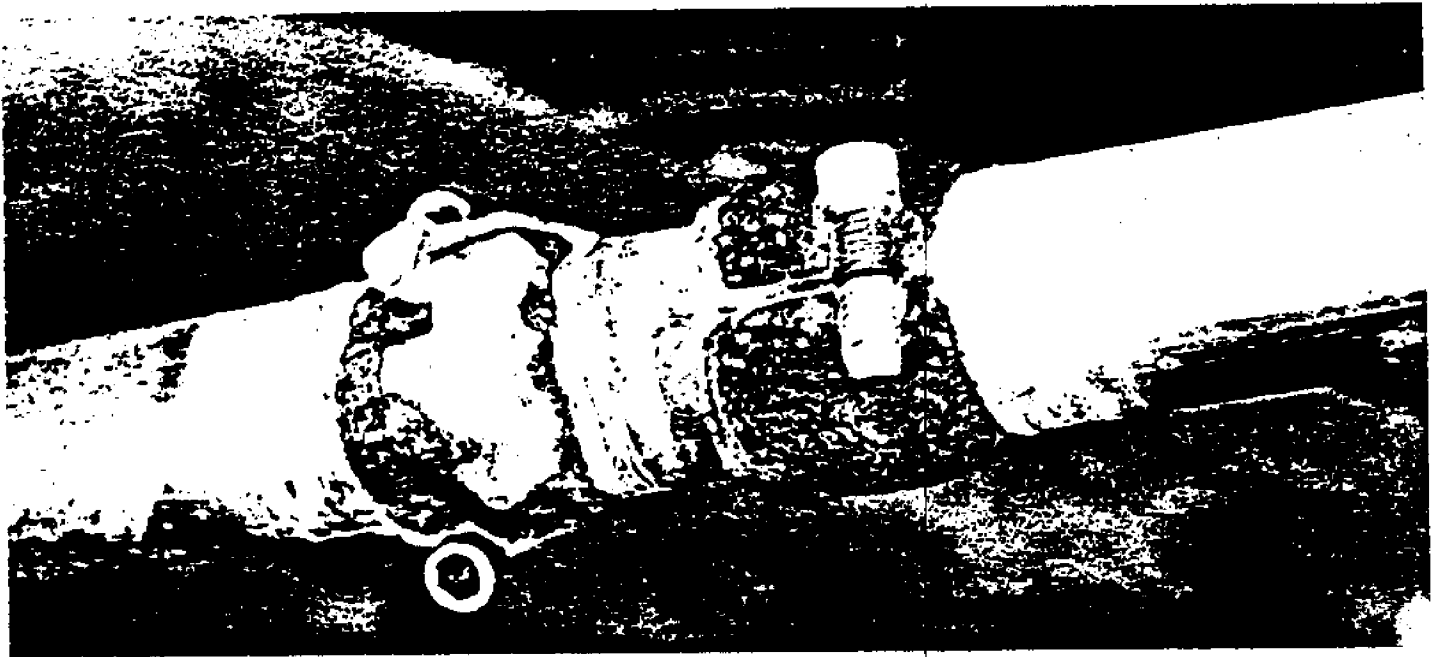
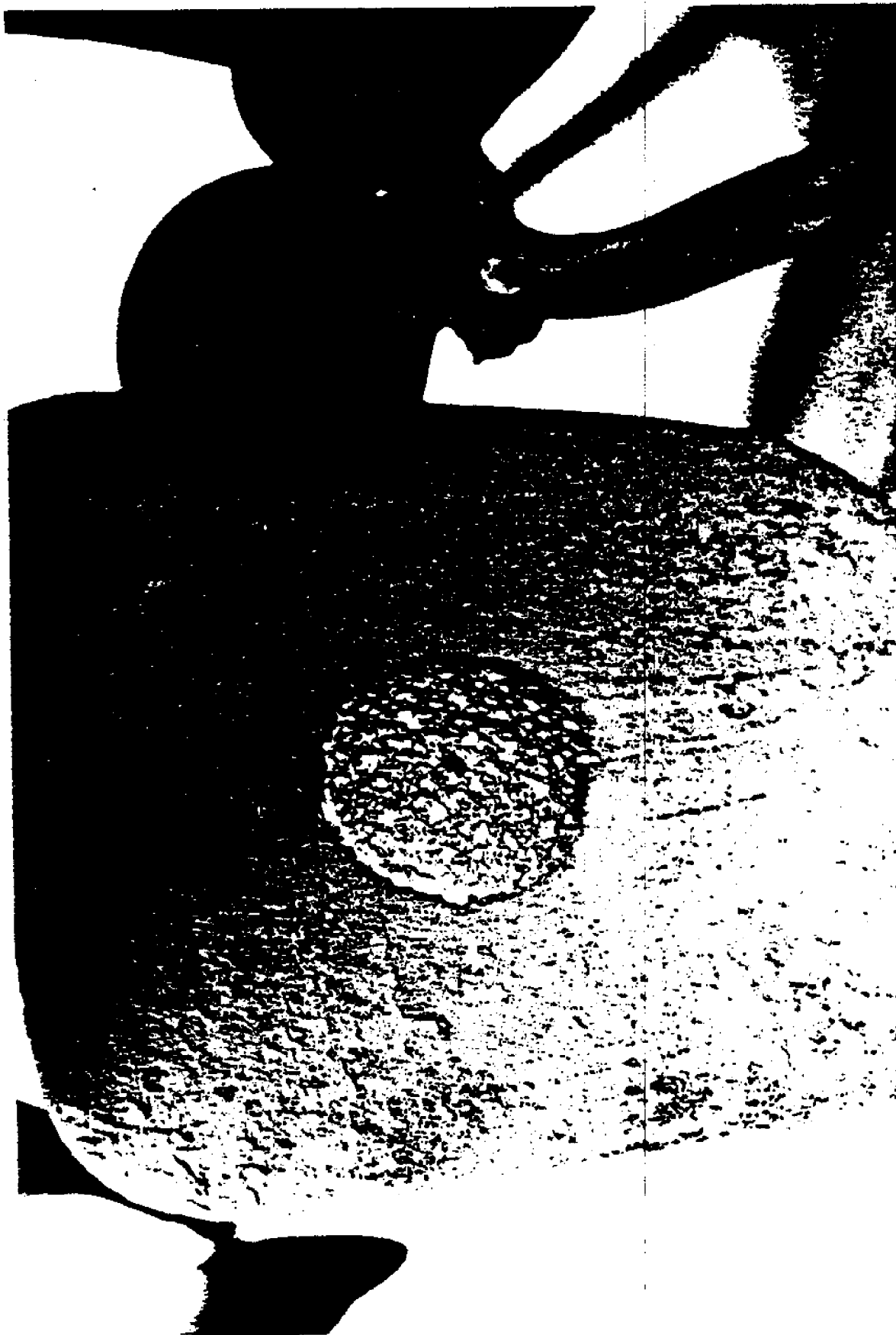


Figure 24 Zinc anode not corroding properly.



In applying any cathodic protection system, care must be taken not to over-protect (use too many anodes). The concept of "If a little zinc is good, then a lot of zinc will be much better" is totally incorrect. A first attempt system should be estimated, based on past experience (successful!) or the ratings listed in Figure 25 (5).

Figure 25 Summary estimates of zinc weight for vessel class

Hull	22' Cruiser	30' Cruiser	32' Sailboat	40' Cruiser	48' Cruiser	58' Cruiser	78' Dragge
Wood or Fiberglass	1.5 lb	16 lb	3.6 lb	35 lb	44 lb	68 lb	93 lb
Steel	31 lb	81 lb	53 lb	128 lb	185 lb	290 lb	458 lb
Aluminum	23 lb	38 lb	44 lb	64 lb	100 lb	162 lb	281 lb

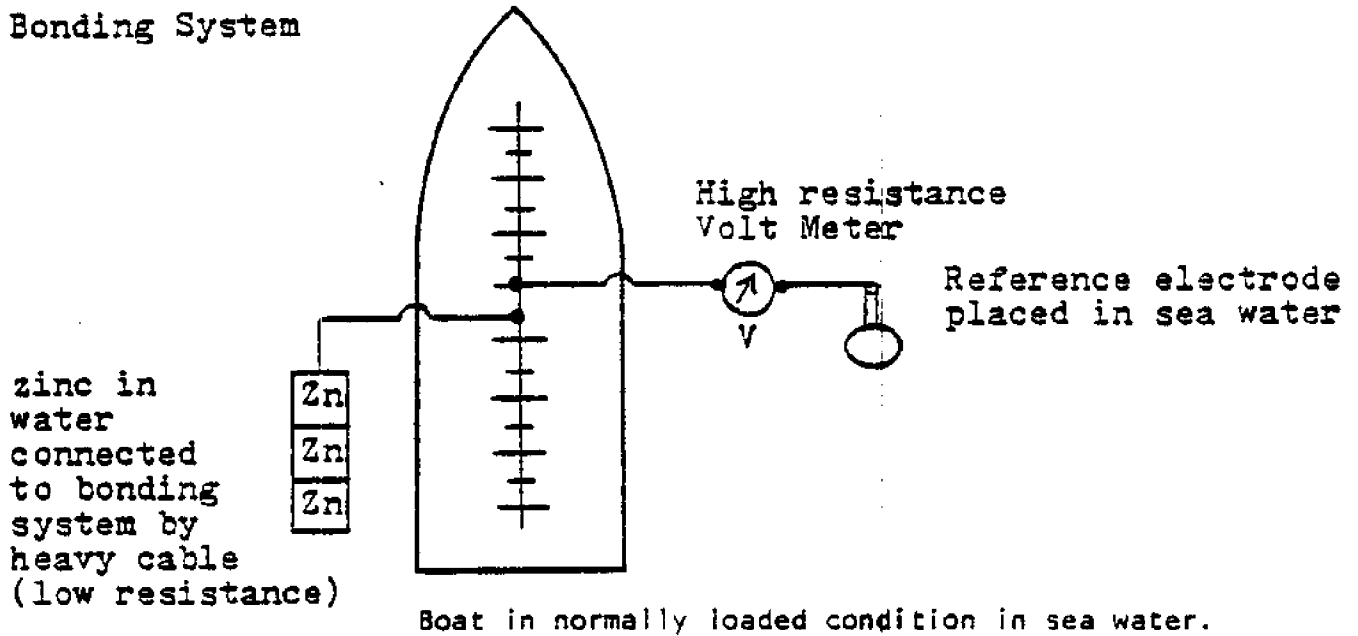
Weight of zinc in pounds using 11 lb rectangular anodes.

A more exact method of determining the quantity of anodes requires the use of a reference electrode (usually, a silver-silver chloride or copper-copper sulfate). Using this method, the hull potential (potential of the bonding system for fiberglass or wooden boats) is measured relative to the reference electrode. This potential is then adjusted by adding zincs until a hull potential of the correct voltage is obtained (see Figures 26,27). The hull potential should be checked several times each season to insure that the proper potential is maintained. Many expensive vessels carry their own reference electrode for frequent monitoring. Ideal hull potentials, to be maintained for effective corrosion control, vary according to hull materials. A steel hull should be maintained between 800 and 900 mV, an aluminum hull between 940 and 960 mV, and fiberglass or wood with a predominance of bronze hardware between 575 and 650 mV. These potentials are all relative to a silver-silver chloride reference cell.

In order to get accurate potential readings during hull potential adjustments, the anodes being added should be placed as close to their prospective fixed locations as possible. Also, the hull potential adjustment should be made after all individual anodes have been installed (collar, rudder, ground plate, etc.). The vessel should be allowed to sit overnight in the water to allow the cathodic surfaces to stabilize before making potential adjustments. The reference electrode should be moved to several different locations around the hull to ensure that the hull potential is fairly uniform. Furthermore, anode surfaces which will not be exposed to seawater in their installed state should be taped so that these surface areas will not affect hull potential measurements.

Figure 26 Schematic of hull potential measurement.

Bonding System



It should be noted that it is the surface area of the anodes that shift the hull potential and not the anode weight. The weight is only indicative of the anode's lasting power. Therefore, if hull potential is adjusted with all sides of an anode exposed and then the anode has one side covered by the hull when it is installed, the hull potential will shift.

Hull potential will vary considerably whether the boat is underway or dockside. The fast water velocities encountered while underway swiftly carry reaction products away from cathodic surfaces. This process allows the cathodic reaction to accelerate, creating a greater demand for current that must be supplied by the anode. Hence, if the hull potential is adjusted for dockside mooring, the vessel may very well be underprotected while underway. Conversely, if the hull potential is adjusted for underway conditions, the vessel may be overprotected at the dock. For vessels that remain at dockside most of the season, the small amount of time running underprotected should create no significant corrosion, and hull potential should be adjusted for dockside. Commercial vessels present a different problem, which can best be solved with installation of an electronically controlled instrument which regulates current flow between the anodes and the bonding system. These systems employ a reference electrode permanently mounted underwater on the hull as well as a control box which automatically adjusts hull potential to compensate for varying conditions. Basically, the system is set up with enough anodes to provide adequate current protection while the vessel is underway (which normally would overprotect the vessel at dockside). However, the electrical lead from the anodes is not connected directly to the bonding system but to a control device which regulates the current flow between the anodes and bonding system. The control device continually compares the hull potential (determined by its permanently mounted reference electrode) with the desired pre-set potential and regulates current flow to maintain a balance between them. These units extend the useful life of the anodes by insuring minimum, yet adequate, current flow to the protected components. Such devices are manufactured by Bartell Corporation, Newport Beach, California, and Electro-Guard Corrosion Control Systems, San Diego, California. Note that these are not impressed current devices (devices employing D.C. current from an

Figure 27 Vessel hull potential measurement.



external source such as batteries or a generator) but are current-regulating devices. Impressed current devices will be discussed in Section C.

B. Overprotection Problems

Just as severe corrosion problems arise from large cathode-small anode situations, overprotection problems can arise from large anode-small cathode situations. Overprotection generally results from galvanic protection systems or impressed current systems that are not properly adjusted. Impressed current protective systems will be discussed in Section C. In many cases, overprotection can be more damaging than insufficient protection, especially on wooden or aluminum vessels.

Overprotection results when the cathodic areas receive an excess of electrons, forcing increased reduction reactions on the cathode surface. In seawater these reactions cause an excess generation of hydroxyl ions (OH^-). If the cathodic surface is exposed to open seawater, then the reaction product of hydroxyl ions does not buildup and introduce problems. However, in an overprotected situation the current flow is generally large enough to force reduction reactions on all surfaces of the cathodic object which have sufficient electrolytes surrounding them. Damp wood is a suitable electrolyte and therefore major damage is incurred by overprotection on wooden boats.

Figure 28 depicts a heavy bronze exhaust port secured through the transom of a boat. The dockside water level is approximately one-third of the fitting height. In good fashion, the fitting has been secured to the bonding system, which is connected to the anodes. When too much anodic surface area is used (too many zincs), the hull potential is raised to its maximum and high current rates begin to flow through the bonding system. At the exhaust fitting these currents cause reduction reactions on the outer surfaces exposed to seawater, which cause no problem because their products are dissipated in the water. However, the reduction reactions taking place at the fitting's interface with wood that is soaked with salt water cause a buildup of hydroxyl ions (OH^-), which permeate the wood. These hydroxyl ions actually attack the wood fibers, destroying their strength. The appearance of this alkaline attack on the wood is very similar to that of dry rot (Figure 29).

Figure 28 Exhaust fitting through transome overprotection

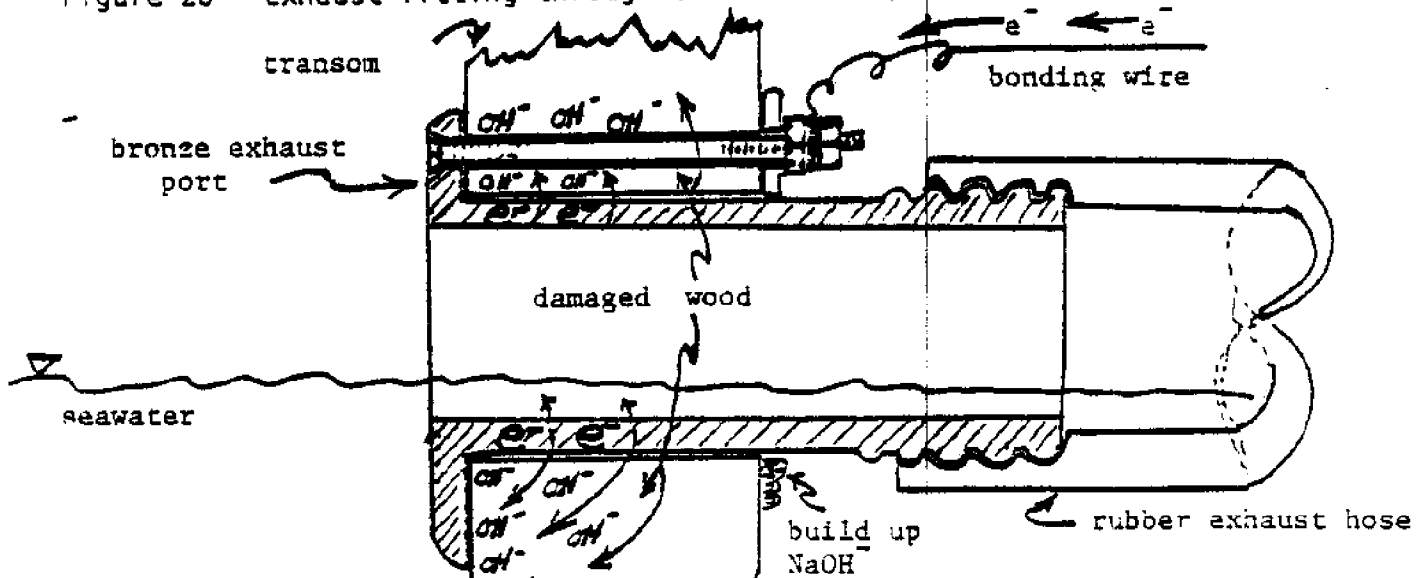
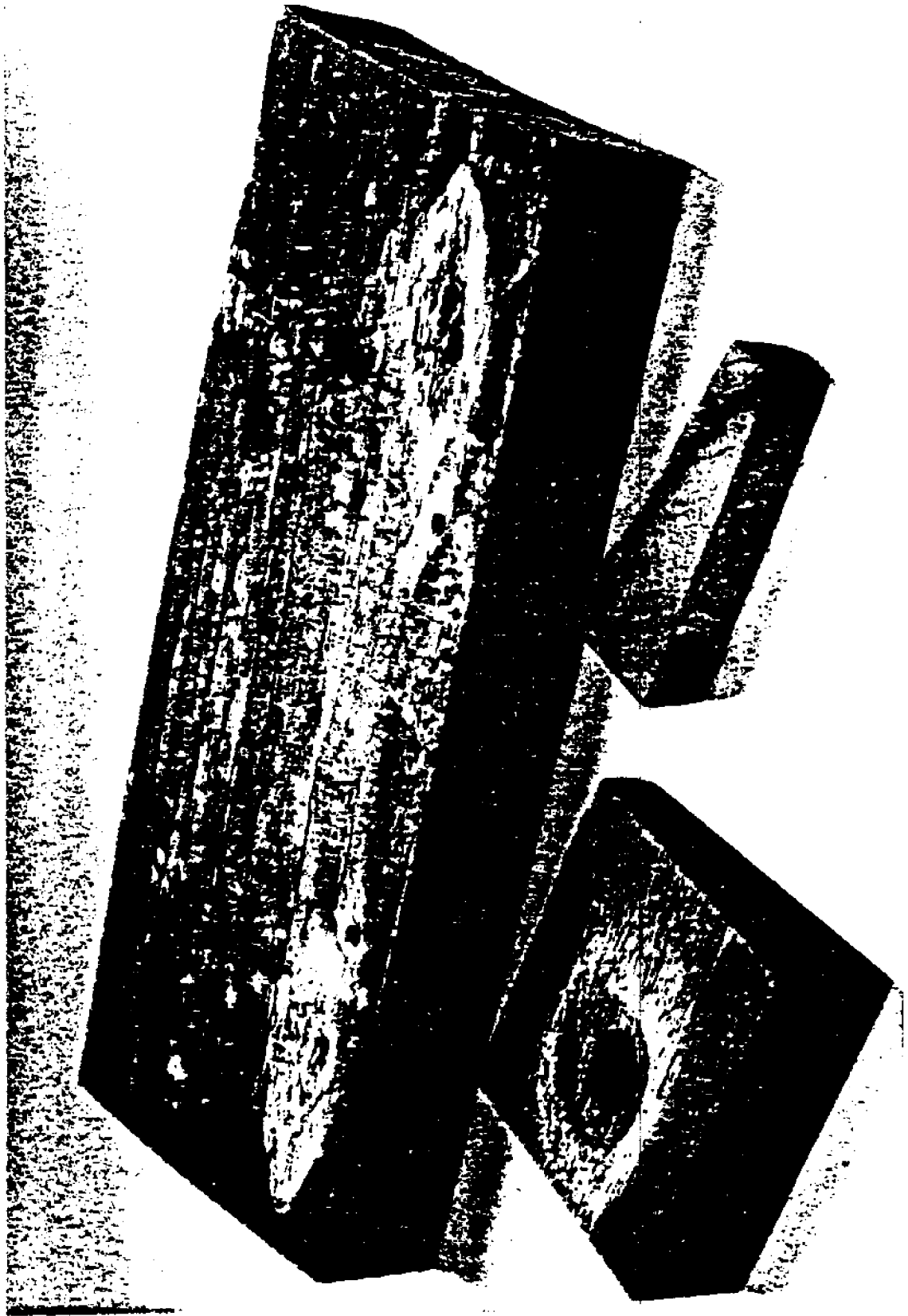


Figure 29 Overprotected wood.



Generally, wood deterioration due to overprotection leaves a white deposit around the fittings on the inside of the hull. This substance is generally composed of several compounds that have precipitated out of the water-soaked wood as a result of the overprotection reactions. Compounds such as calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium carbonate (CaCO_3), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), and, in severe cases, sodium hydroxide (NaOH) are present in the white deposit. The deposit will have a bitter taste compared to the salty taste of sodium chloride (NaCl). These deposits can also appear on metal surfaces that are overprotected such as offshore steel structures. The coatings that result on the protected steel actually act as a corrosion barrier. These deposits can be neutralized by ample washing with distilled white vinegar.

Also the generation of large concentrations of hydroxyl ions by overprotected surfaces can create other problems. Oil-base paints on wood, fiberglass, and metal vessels can be broken down chemically and eroded away. Aluminum becomes extremely susceptible to corrosion when exposed to high concentrations of hydroxyl ions. Overprotected aluminum hulls will display varying degrees of corrosion depending upon the amount (potential) of overprotection. Therefore, quality cathodic protection monitoring is critical for proper maintenance of aluminum vessels.

Overprotection can also generate free hydrogen (H_2), which can build up between the protected surface and the paint film, causing it to blister. This is most evident on steel hulls, and can be identified by blisters with clean, uncorroded metal beneath. If the blistering is caused by excess hull anodes, no significant corrosion problems should be encountered until the anodes are nearly exhausted. At this point, many paint blisters may have been sloughed off, leaving the exposed metal to fend for itself. This metal may corrode at a slow rate due to uniform corrosion or may itself begin to act as a sacrificial anode if the hull is connected to a nobler metal such as bronze.

It is also possible to generate atomic hydrogen (H) at cathodic surfaces as a result of overprotection. Atomic hydrogen can severely damage certain steels by a mechanism called hydrogen embrittlement. Although mild steels are not susceptible to embrittlement problems, many high strength steel alloys and stainless steels are.

Mild steels, in areas of atomic hydrogen generation, can be severely damaged by hydrogen blistering. In addition to the possibilities of hydrogen embrittlement and blistering around overprotected cathodic areas, there exists the chance that caustic embrittlement may damage mild steel. Caustic embrittlement more truly is a type of stress-corrosion cracking, accelerated by a caustic (high OH^-) environment (2).

Hydrogen embrittlement, hydrogen blistering, and caustic embrittlement are types of corrosion damage that are very rarely seen in local boatyards. They are only mentioned as an attempt to inform the reader of their existence and to allow avenues for further study.

C. Impressed Current Protection

These devices cathodically protect metal surfaces by forcing D.C. electrons to flow from the protected cathodic surface to special anodes (Figure 30) (5). The polarity of the system forces the protected cathodic surface to polarize to the point where localized, galvanic activity on the surface is eliminated and corrosion does not occur. The anodes of impressed current systems are composed of inert material, such as platinized titanium, and do not enter into the electrochemical reactions; i.e., they don't corrode away.

Many large vessels, oil drill rigs, production platforms, offshore terminals, etc., have some type of impressed current system for corrosion control. These systems constantly monitor hull potential and maintain the correct electron output from cathodic surfaces. Anodes generally need no replacement, except when they are physically damaged, but may require cleaning if precipitated reaction compounds build up around them. Factors determining electron flow are (1) dimensions of submerged area requiring protection; (2) speed of the vessel or water current around stationary unit; (3) the condition of the surface coating covering the protected area since a good coating requires minimal electron flow; and (4) conductivity of water (fresh, brackish, or salt).

An impressed current system is generally composed of four major components (5):

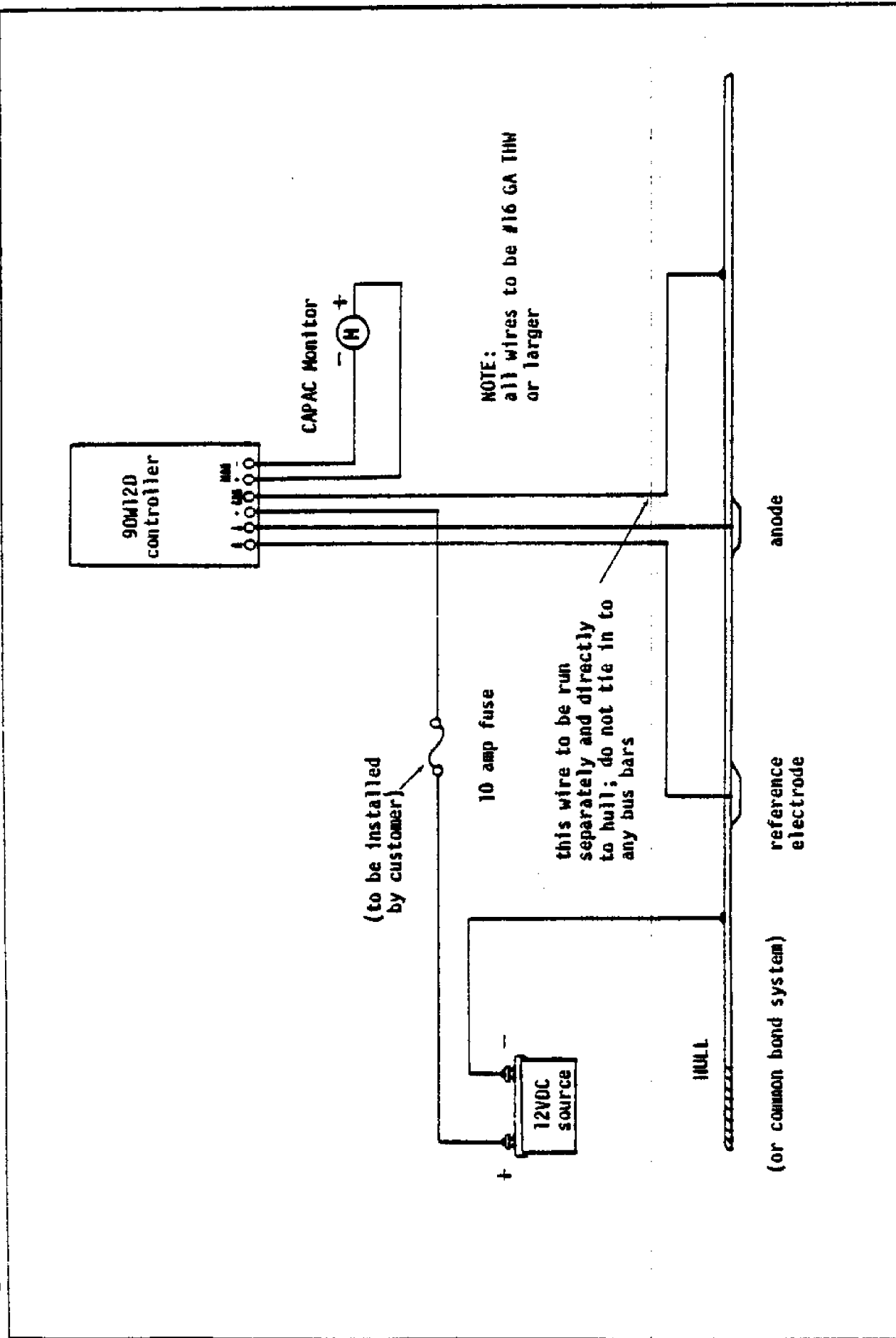
1. A controlling device which automatically varies D.C. electron flow to the cathodic surface. It does this by comparing the hull's potential to a pre-set value.
2. A permanently mounted reference electrode which continually monitors the hull potential for comparison by the controlling device.
3. An anode or series of anodes permanently mounted in the hull and electrically insulated from it. Anode faces are usually recessed in the hull to prevent damage from debris in the water, or from entanglement with lines. Electrons from the protected surface flow through the water and enter the impressed current circuit through the anode.
4. A monitoring device which allows system parameters, such as hull potential and electron flow, to be easily observed on meters of digital readout.

These systems are not inexpensive and require a knowledge of their workings to make them reliable and efficient. On smaller vessels, used only intermittently, the current draw can drain battery banks over a period of several weeks. A small system can be purchased from Mercury Marine or OMC to protect in/out drives or outboards.

It should be remembered that if an impressed current system is installed incorrectly, the vessel's hull and/or hardware can be forced to act as an anode. This will cause rapid corrosion of the hull and/or hardware, resulting in very costly damage.

In this section the term "electron flow" appears throughout the discussion. This wording is employed to maintain continuity within the text because the term was adapted in Chapter I. To repeat from Section B of Chapter I: current flow is always opposite to electron flow.

Figure 30 Impressed current system



Schematic for an Impressed Current System (courtesy, Engelhard Industries)

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