

The Basics of Corrosion



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CORROSION -- WHAT IS IT?

It is appropriate to define the problem before proceeding to any presentation of a remedy.

Corrosion - the deterioration of a substance (usually a metal or its properties) because of a reaction with its environment; a natural consequence of a metal's temporary existence in a metallic form.

It might also be natural to think of corrosion as a simple, singular process or reaction that once understood could be turned off like a light switch or a faucet. This is not the case. In fact, there are many factors influencing the corrosion process and even more solutions or alternatives. These options, however, are not absolutes and are not able to totally eliminate or counteract the corrosion mechanism. The corrosion engineer deals in economics, material selection and coating treatment options, whose sum will "RETARD" the normal corrosion rate to a slower more controlled acceptable rate.

If cost and availability were not factors, we could select the very best materials and come close to eliminating the corrosion. But we have to eliminate consideration of materials like Platinum or Gold (the Noble metals) and think in terms of substances that we can afford to utilize.

Cost and availability have led to selection of practical materials like iron and steel, aluminum and copper alloys, plastics, ceramics, wood, stainless steels, stainless steel alloys and superalloys. They each have advantages and disadvantages: weight, working strength, heat transfer, etc.. Usually, a particular "best choice" has been chosen for a particular application. Very often the manufacturer cannot design a piece of equipment for a particular set of environmental and operating conditions, and he can only generalize for normal conditions. Subsequent installation may expose the metal surface to salt air, acid rain, and/or acidic industrial fumes.

We are all aware of the corrosion around us: the rusting of a nail, a discarded "tin can", automobile body panels. These are obvious examples

that are visually evident. There are also corrosive (deteriorative) situations where there is little or no external deterioration, yet the properties of the structure may be severely altered.

This introduction to the BRONZ-GLOW PROCESS is intended to acquaint individuals having little or no corrosion knowledge with the fundamentals of corrosion and common control practices - as these may add to a further understanding of aluminum alloys and like metal structures.

We will define terms as we move through this seminar. We have included a Simplified Glossary of Corrosion-Related Terms which we recommend you reference as the need arises. These are not "one and only" definitions.

INFLUENCING FACTORS

The previous Introduction began to unfold an understanding of "corrosion" and implied a few basis concepts:

Q. "In what environments does corrosion occur?"

A. "Just about any environment one can think of depending upon the material in question."

Q. "How many forms of corrosion are there?"

A. "Depending on what one means by "form," there are more than 50 specific types of corrosion, although there are only a few mechanisms which are common to all of them."

Of the 105 elements known to man about 80 of these are metals. Each element has different chemical, mechanical and physical properties, and while they can all corrode, they will differ from each other in manner and rate. In addition, about 40 of these metals have been combined in varying amounts to produce over thirty thousand (30,000) alloys.

In repetition, the fact that metals corrode should not be a surprise. It is a natural consequence that all refined elements will tend to revert to their natural "ore" state.

We normally become aware of corrosion by the surface layer formation, whether it is an oxide, carbonate, sulfate or other compound.

This layer is a naturally occurring boundary between a metal and its environment. In order to be effective though, it must be diffusion and

moisture resistant. Common boundary layers, such as "rust" on an iron nail, do not form a good barrier, as oxygen and moisture are allowed to penetrate the layer, rusting continues and failure will eventually occur.

Precautions to prevent iron and its alloys from corroding constitute a major effort in the corrosion field. Many methods are used, such as painting and electroplating, to form artificial protective layers over the iron surface.

Metals such as stainless steel, titanium and aluminum are frequently left unpainted. This is not because these metals are inert, but because the oxygen in the air helps to develop a protective surface layer of chromium oxide, titanium oxide which is invisible to the eye, their presence and protective effect can be verified.

In the case of the normally occurring protective oxide films, the corrosion problem is not the oxygen/oxide formation, but other aspects of the metal's environment which attack the oxide itself.

Some of the influencing factors of corrosion are summarized as follow:

1. Moist air is more corrosive than dry air.
2. Hot air is more corrosive than cold air.
3. Hot water is more corrosive than cold water.
4. Polluted air is more corrosive than clean air.
5. Acids are more corrosive than bases (alkalies).
6. Salt water is more corrosive than fresh water.
7. Corrosion will not occur in a vacuum.

While these are generally valid universal truisms, there are instances where every one of the above statements is incorrect. **There is an exception to every absolute.**

MATERIAL SELECTION

For a specific application, a certain alae may be superior to another, yet may compete for that same application because of factors other than corrosion. Cost is a major factor and has already been mentioned. Other factors may include one or a combination of the following:

1. Cost
2. Corrosion behavior

3. Solderability or weldability
4. Forming characteristics (bending, stretching, etc.)
5. Suitable mechanical properties (tensile strength, impact resistance, fatigue, etc.)
6. High or low temperature strength or ductility
7. Availability of material in proper form
8. Compatibility with other materials in proper form
9. Thermal or electrical characteristics
10. Unique characteristics such as low density, magnetism or nuclear radiation resistance

Let us repeat the first two:

1. Cost
2. Corrosion behavior

Knowing what substance to select is not a simple matter. In some applications wood is still the best; others may use, a plastic lined metal pipe or tank, or a ceramic-lined pipe; and often a special alloy is used. It is difficult to believe, but there are over 30,000 alloys in use today. It is useless to try to remember them all, but knowing where to look for them is sometimes important. We have included a brief look at various alloys and their properties in the appendix for your reference. The mechanical and corrosion resistance and properties of these materials vary widely and can be strongly affected by heat treatment.

CORROSION: WHY METALS CORRODE

The driving force that makes metals corrode is a natural consequence of their temporary existence in the metallic form. To reach this metallic state from their occurrence in nature in the form of various chemical compounds, called ores, it is necessary for them to absorb and store up for later return by corrosion, the energy required to release the metals from their original compounds. The amount of energy required and stored up varies from metal to metal. It is relatively high for some metals such as magnesium, aluminum and iron and relatively low for such metals as copper and silver. Table 2-1 lists some commonly used metals in the order of diminishing amounts of energy required to convert them from their ores to metal.

TABLE 2-1: Position of some metals in the order of energy required to convert their ores to metal.

Most Energy Required	Potassium
	Magnesium
	Beryllium
	Aluminum
	Zinc
	Chromium
	Iron
	Nickel
	Tin
	Copper
	Silver
	Gold
Least Energy Required	Platinum

A typical cycle is illustrated by iron. The most common iron ore, hematite, is an oxide of iron (Fe_2O_3). The most common product of iron, rust, has the same chemical composition. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the same compound. Only the rate of energy change is different.

The energy difference between metals and their ores can be expressed in electrical terms which are related to heats of formation of the compounds.

The relative difficulty of extracting metals from their ores in terms of the energy required and the consequent relative tendency to release this energy by corrosion is reflected by the positions of pure metals in a list (Table 2-2) where the energy involved determines its position. This is discussed later as the "electromotive series". In the case of aluminum, this element is most commonly found as Bauxite, and in pure hydrated oxide ($\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$).

FORMS OF CORROSION

Destruction by corrosion takes many forms depending on the nature of the metal or alloy, the presence of inclusions or other foreign matter at the surface. The homogeneity of its structure, the nature of the corrosive medium, the incidental environmental factors such as the presence of oxygen and its uniformity, temperatures, velocity of

movement, and such other factors as stress (residual or applied, steady or cyclic), oxide scales, (continuous or broken), porous or semi-porous deposits on surfaces, built in crevices, galvanic effects between dissimilar metals and the occasional presence of "stray" electrical currents from external sources.

Except in rare cases of grossly improper choice of material for a particular service or an unanticipated drastic change in the corrosive nature of the environment or complete misunderstanding of its nature, failures of metals by very rapid general attack or wasting away are not often encountered.

Corrosion failures may be localized in the forms of pits, intergranular corrosion, attack within crevices and so on.

ELECTROCHEMICAL ASPECTS

While corrosion can take one or more of the several forms that have been mentioned, the mechanism of attack in aqueous solutions will involve some aspect of electrochemistry. There will be a flow of electricity from certain area of a metal surface to other areas through a solution capable of conducting electricity, such as sea water or hard water, or even condensed moisture containing soluble gases or salts.

The term "**anode**" is used to describe that portion of the metal surface that is corroded and from which current leaves the metal to enter the solution.

The term "**cathode**" is, used to describe the metal surface from which current leaves the solution and returns to the metal.

Table 2-2 Galvanic Series of Metals Exposed to Sea Water

ACTIVE END	Magnesium. Magnesium Alloys Zinc Galvanized Steel Aluminum 1100 Aluminum 6053 Alclad Aluminum 2024 (4.5 Cu. 1.5 Mg. .06 Mn) Mild Steel Wrought Iron Cast Iron 13% Chromium stainless steel Type 410 (Active) 18-8 Stainless Steel Type 304 (Active) 18-12-3 Stainless Steel Type 316 (Active) Lead-Tin Solders Lead Tin Muntz Metal Manganese Bronze Naval Brass Nickel (Active) 76 Ni - 30 Mo - 6 Fe alloy (Active) 60 Ni - 30 Mo - 6 Fe - 1 Mn Yellow Brass Admiralty Brass Aluminum Brass Red Brass Copper Silicon Bronze 70 - 30 Cupro Nickel G - Bronze M - Bronze Silver solder Nickel (Passive) 76 Ni - 16 Cr - 7 Fe Alloy (Passive) 67 Ni - 33 Cu Alloy (Morel) 13% Chromium Stainless Steel Type 410 (Passive) Titanium 18-8 stainless Steel Type 304 (Passive) 18-12-3 Stainless steel Type 316 (Passive) Silver Graphite
NOBLE	Gold
PASSIVE END	Platinum

The circuit is completed outside the solution through the metal or through a conductor joining two pieces of metal. The essential components are shown diagrammatically in Figure 2-1. The dots represent electricity (not electrons) flowing in the solution from the anode (-) to the cathode (+) and returning from the cathode to the anode through the metal wires.

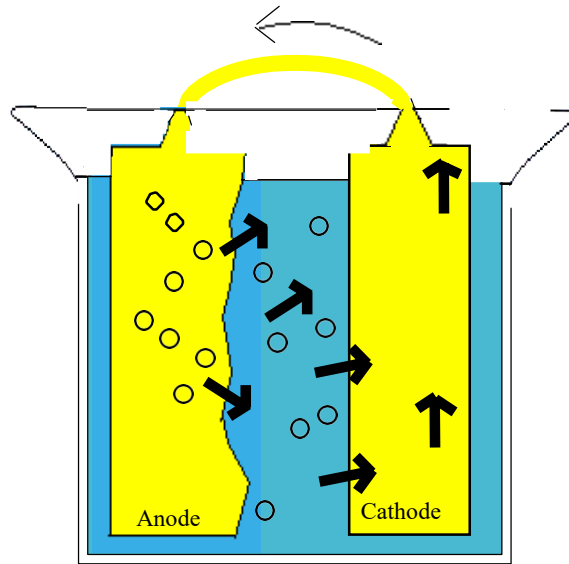
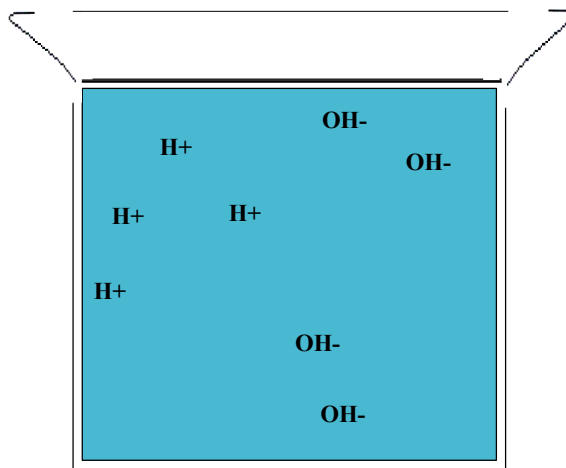


Figure 2-1 - Flow of electricity from metal to electrolyte to metal

A solution capable of conducting electricity is called an "electrolyte." Its ability to conduct electricity is due to the presence of what are called "ions". These are positively or negatively charged atoms or groups of atoms in solution. Pure water, sketched in Figure 2-2, contains positively charged hydrogen ions (H^+) and negatively charged hydroxyl ions (OH^-) in equal concentration.



**Figure 2-2
Hydrogen and hydroxyl ions contained in pure water**

The electrolyte forming a corrosive environment may be any solution, rain or even moisture condensed from the air. It can range from fresh water to salt water to the strongest alkali or to the strongest acid.

The anodes and cathodes involved in a corrosion reaction, like the zinc and graphite in a dry cell, are called electrodes. The electrodes may consist of two different kinds of metal or they may be different areas on the same piece of metal. The negative electrode, anode, is where corrosion occurs.

Let us consider what takes place at the anode when corrosion occurs. Positively charged atoms of metal leave the solid surface and enter into solution as ions. They leave their corresponding negative charges in the form of electrons which are able to flow through the metal or any external electronic conductor. The ionized atoms can bear one or more positive charges. In the corrosion of aluminum, each aluminum atom becomes an aluminum ion carrying three positive charges and generates three electrons. This is shown diagrammatically in Figure 2-3. These electrons travel through the metal or an external conductive medium to complete the reaction and consume these electrons.

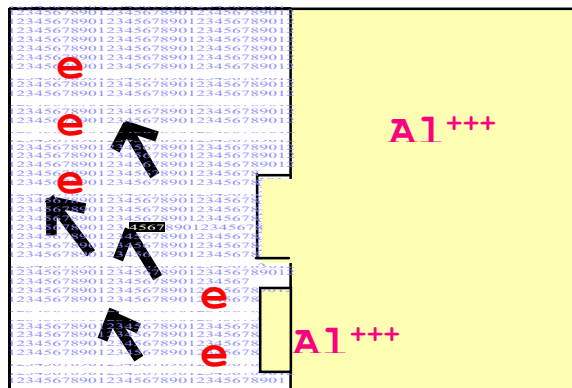


Figure 2-3
Formation of aluminum ions and release
of electrons in the corrosion of aluminum

What has been taking place at the cathode in parallel with what has been going on at the anode?

The electrons generated by the formation of metallic ions at the anode have passed through the metal to the surface of the cathode areas immersed in the electrolyte. Here, they restore the electrical balance of the system by reacting with and neutralizing positive ions such as hydrogen ions in the electrolyte. Hydrogen ions can be reduced to atoms,

and these often combine to form hydrogen gas by such reaction with electrons at a cathode surface. This reduction of hydrogen ions at the cathode surfaces will disturb the balance between the acidic hydrogen (H⁺)- ions and the alkaline hydroxyl (OH⁻) ions and make the solution less acid or more alkaline in this region. This is shown diagrammatically in Figure 2-4. This change in the concentration of hydrogen ions can be shown by the use of chemical indicators which change color with changes in hydrogen ion concentration and thus can serve to demonstrate and locate the existence of surfaces on which the cathodic reaction in corrosion are taking place.

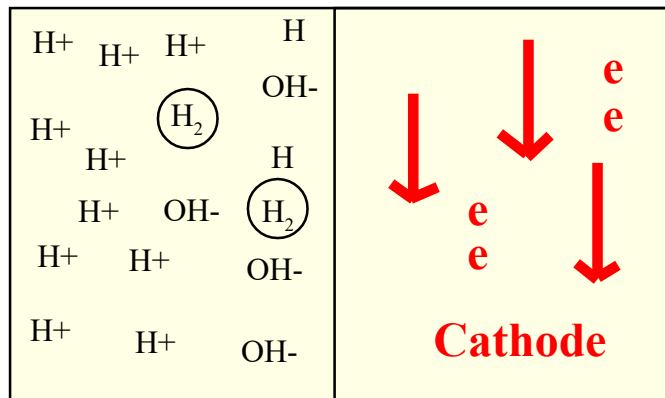


Figure 2-4 - Reduction of hydrogen ions at cathode to form hydrogen atoms and subsequently hydrogen molecules (gas). Hydroxyl ions also accumulate.

Briefly, then for corrosion to occur, there must be (1) a formation of ions and release of electrons at an anodic surface, where oxidation or deterioration of the metal occurs. There must be (2) a simultaneous acceptance at the cathodic surface of the electrons generated at the anode. This acceptance of electrons can take the form of neutralization of positive hydrogen ions, or the formation of negative ions. The anodic and cathodic reactions must go on at the same time and at equivalent rates. But corrosion occurs only at the areas that serve as anodes.

If we place a piece of mild steel in a solution of hydrochloric acid, we observe a vigorous formation of hydrogen bubbles. Under such conditions the metal corrodes very quickly. The dissolution of metal is occurring only at anodic surfaces.

The hydrogen bubbles are forming only at the cathodic surfaces even though it may appear that they are coming from the entire surface of the metal rather than at well-defined cathodic areas. The anodic and cathodic areas may shift from time to time so as to give the appearance of uniform corrosion.

If we could see this action through a suitable microscope, we would see many tiny anode and cathode areas shifting around on the surface of the metal. These areas are often so small as to be invisible and so numerous as to almost be inseparable.

If we could see just one anode and one cathode in a magnified view of a piece of aluminum in an acid solution, we would see electrons generated by the formation of aluminum ions flowing through the metal from an anodic area to a cathodic area. This is illustrated in Figure 2-5. At the cathode surface, the electrons would meet hydrogen ions, from the solution. One hydrogen ion would accept one electron and be converted into a hydrogen atom which could enter the metal and lead to hydrogen embrittlement, or as in most cases, it could combine with another hydrogen atom and become molecular hydrogen gas which would either cling to (Figure 2-6) or be released as a bubble from the cathodic surface. As this process continues, oxidation (corrosion) occurs at the anodic surfaces and reduction of hydrogen ions occurs at the cathodes. Note that the term oxidation is not necessarily associated with oxygen.

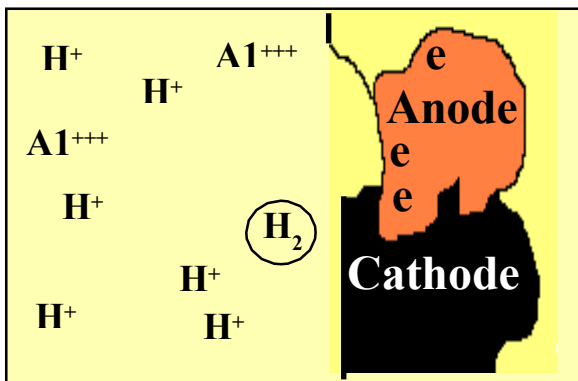


Figure 2-5 -
Formation of ions at an anodic area and release at a cathodic area surface in local cell on an aluminum surface.

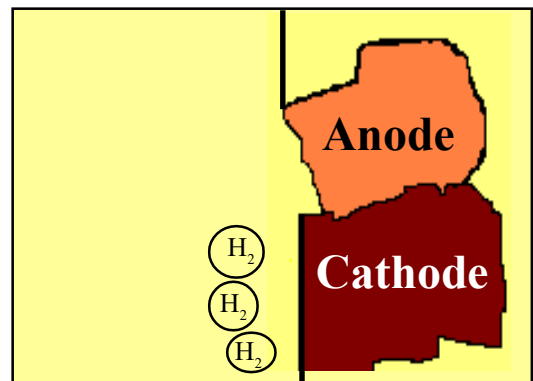


Figure 2-6
Accumulation of hydrogen on cathodic hydrogen.

This formation of hydrogen from hydrogen ions and its release as atoms or hydrogen gas are the principal reactions in corrosion by acids, but in neutral solutions such as sodium chloride, the evolution of hydrogen gas and its accumulation on the cathodic surfaces can slow down the cathodic reaction. This also slows the corrosive anodic process which cannot proceed at a higher rate than electrons can be consumed at the cathodic surfaces.

Such slowing down of cathodic reactions is called "cathodic polarization." Similarly, anything that directly slows down the anodic reaction is called "anodic polarization."

The products of the anodic and cathodic processes frequently migrate through the solution and meet to enter into further reactions that yield many of our common visible corrosion products. For example, with aluminum in water, the hydroxyl ions from the cathodic reaction, in the migration through the electrolyte toward the anodic surfaces, encounter aluminum ions moving in the opposite direction. These ions combine to form aluminum hydroxide ($Al(OH)_3$) which subsequently reacts further with oxygen in solution to form aluminum oxide [$(Al_2O_3) (nH_2O)$]. This is illustrated in Figure 2-7 and represents a form of corrosion with which we are all quite familiar.

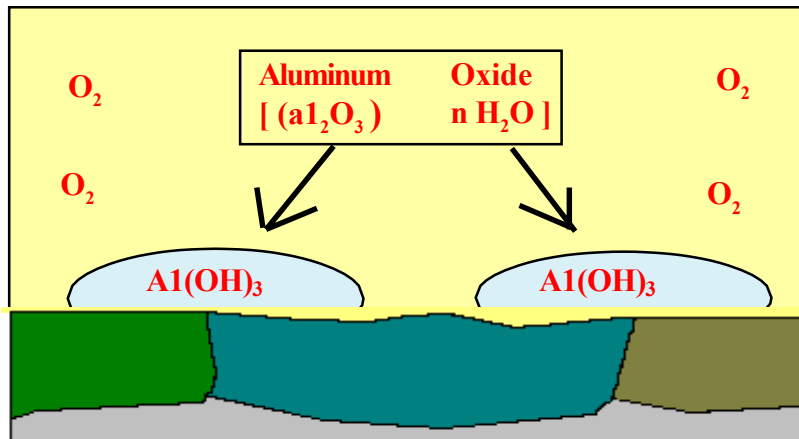


Figure 2-7
Formation of aluminum oxide by
interaction of products of anodic and
cathodic reactions.

The role of oxygen in increasing corrosion is easily demonstrated by placing a metal such as aluminum or iron in two flasks filled with water. Oxygen is allowed to bubble through the water in one flask to supply it with oxygen. The water in the second flask is saturated with nitrogen to help eliminate dissolved oxygen. After the gasses have bubbled for several hours, one will observe that the metal in the oxygen-free solution has remained bright, but the metal in the oxygen rich water has already begun to rust or tarnish.

PROTECTIVE OPTIONS

CATHODIC PROTECTION

Since it has been demonstrated that electrochemical corrosion results from, or is accomplished by, a flow of current between anodic and cathodic surfaces, it should be possible to prevent corrosion by controlling the flow of corrosion currents. The ultimate objective is to suppress all current flowing from the anode in a corrosion cell. This can often be accomplished by applying current from an external source so that current will be made to flow to, instead of from the original anodic surface. This will result in a cathodic rather than an anodic reaction on these surfaces.

To accomplish this, the source of the protective current must be at a higher potential than that of the anodic surface to be protected.

Cathodic protection can be illustrated by a simple experiment using two iron nails and a piece of zinc. If one iron nail is immersed in water, but in contact with the zinc, it will not corrode. The nail by itself will corrode. This is why galvanized iron (zinc-coated steel) is so widely used.

A simple experiment can be conducted using iron nails with half their surfaces coated with copper and with one of these being connected to a piece of zinc. As would be expected, the unplated half of the first iron nail would become anodic to the copper-coated half and corrode promptly. In the case of the partially plated nail connected to the zinc, the galvanic corrosion of the iron half would be suppressed and a cathodic reaction would be made to occur along both the bare iron and copper plated surfaces.

In normal corrosion, the amount of current (rate of electron flow) required by the cathodic reaction that is occurring is supplied by the

electrons generated by corrosion of the anodic surfaces. By means of artificial cathodic protection, this quantity of electrons can also be provided by an external source.

PASSIVITY AND PROTECTIVE FILMS

Up to now, for the sake of simplicity of discussion, we have ignored effects of corrosion products and other surface films that can have profound effects on the corrosion behavior of metals.

Oxide films which form naturally upon most metals when they are exposed to the air can provide substantial protection against further attack by many environments. If it were not for such films, many of our common metals near the top of the electromotive series would corrode rapidly in ordinary air and water. This would be the case, for example, with magnesium and aluminum.

Other corrosion product films or scales are also protective. For example, insoluble films of lead sulphate are responsible for the resistance of lead to corrosion by sulfuric acid. The base films that form on copper alloys in sea water contribute greatly to their durability. The extent to which these films are able to adhere, resist removal by turbulence effects or be restored rapidly if broken, largely determines the relative merits of the copper alloys in resisting velocity effects.

The effect of oxygen and other oxidizing agents on corrosion is variable and complex. Oxygen can accelerate corrosion by participating in cathodic reactions; oxygen and other oxidizing agents can sometimes retard corrosion by forming protective films. Metals, like iron, may carry very thin invisible oxygen or oxide films; if so, they are said to be rendered "massive" by such films. Passivity is exhibited by iron, stainless steel and other metals if its measured potential resembles that of platinum, rather than the potential of the unfilmed metal. It can be demonstrated, also, by a resistance to corrosion orders of magnitude greater than that of the unfilmed or unpassivated "active" metal.

Iron can be made temporarily passive by a film developed by immersing the metal in concentrated nitric acid. When pieces of iron and platinum are immersed in concentrated nitric acid, a potential difference of about 300 millivolts will be measured with the iron anodic. If the measurement were to be made in hydrochloric acid, which destroys any

passive film on the iron surface, the potential difference would be 700 millivolts in the same direction. The 400 millivolt shift in the potential of the iron was due to the passive film developed on the iron surface by the oxidizing effect of the nitric acid. However, the passive film that can be formed in this way on iron by nitric acid is very frail and can be easily destroyed.

The existence and fragility of the passive film formed in this way on iron can be demonstrated by an experiment using nitric acid and a solution of copper sulfate. We know that when bare iron is immersed in copper sulfate it will become coated with copper deposited electrochemically on the iron by the plating process previously described. If, however, we first dip the piece of iron in concentrated nitric acid to form a passive oxide film and then dip it into the copper sulfate solution, no copper will plate out immediately. But if, when we remove this filmed piece of iron from the copper sulfate solution, we simply tap it, the passive film on the iron will be destroyed and copper will plate out from the copper sulfate solution clinging to the iron surface. Copper deposition will start at the point where the iron specimen is tapped and spread in seconds to the rest of the surface.

By alloying iron with sufficient chromium and nickel, and sometimes with other elements as well, the ease with which it can be made passive by an oxide film and the ability of such passive films to survive both mechanical and chemical stress can be increased. The result is the family of stainless steels which have added so greatly to our list of materials able to withstand severely corrosive environments. Environments of an oxidizing nature tend to preserve rather than destroy the passivity of stainless steels. However, they aggravate the corrosion of ordinary iron or other metals with which oxygen accelerates corrosion.

In the absence of a passive film, the addition of chromium and nickel to iron would not be expected to change its potential in a direction towards that of noble platinum. In fact, the greater activity of chromium, which is considerably higher than iron in the electromotive series should cause a shift in potential in the opposite direction in the absence of a passive film.

Under circumstances where there may be limited access of oxygen to a stainless steel surface, passivity may be destroyed on such surfaces while the remainder of the stainless steel surface will remain

passive A difference in potential between the active and passive

stainless steel surfaces will be created. This will set up a powerful galvanic cell between the active and passive stainless steel surfaces and result in serious corrosion of anodic areas.

The difference in potential between the active and passive states of stainless steels, and some other metals and alloys that develop passivity, will account for the dual locations of these materials in positions representing either their active or passive states in the galvanic series shown as Table 3-3. Active-passive cells are primarily responsible for the severity of pitting and crevice corrosion of stainless steels under circumstances in which such attack occurs.

Restoration of passivity within pits or crevices is frequently prevented by the acid nature of corrosion products when they can accumulate within the pits and crevices. Low flow velocity and gravity aid in the accumulation of acid products within these spaces and consequently, will promote the most severely localized corrosion.

The power of a cell between an active surface created within a crevice and a large passive surface of stainless steel outside the crevice can be demonstrated by a simple experiment.

PROTECTIVE LAYERS AND COATINGS

Ordinary steels exposed to moist atmospheres eventually develop relatively thick oxide layers (rust) which are often loose and much less protective than the very thin, almost invisible films that are responsible for the passivity and corrosion resistance of stainless steels, aluminum, magnesium, titanium, and other metals.

The chemical and physical nature of the rust layers that develop on ordinary iron and steel, and the extent to which such rust coatings become effective in retarding further corrosion are affected considerably by the composition of the steel. Sulfur in steel causes the rust layers to be non-protective; the presence of small amounts of copper may offset the bad effect of the sulfur. The further addition of small amounts of nickel and chromium or both enables steel to develop rust coatings that are quite protective and become even more protective with time. These effects can be illustrated by comparing the low alloy steel with ordinary steel

and very low copper steel exposed near the seashore to the same atmospheric conditions.

This self-protecting quality of low alloy steels containing nickel, chromium and copper, has led to the increasing use of these low alloy steels without any protective coatings whatever for buildings, towers and other structures exposed to atmospheric corrosion.

COATINGS FOR CORROSION PROTECTION N. E. Hamner

The concept of placing a protective barrier between materials and their environment is so ancient that its origin is lost in the mist of history. As can be expected with a concept so old, its materials, methods and qualifications are numerous and diverse. Furthermore, some uses of a barrier, while originally satisfactory, are now obsolete or obsolescent in the light of new discoveries about the properties of matter and because the merits of individual components of barrier systems are better understood now.

There are three main kinds of compositions of barriers: Inert or essentially inert, inhibitive and sacrificial. Various combinations of these types are found in coating systems designed to use some or all of the several protective advantages provided. It must be remembered, however, there is no such thing as a "perfect" coating in a practical sense so none of these types or any combination can be expected to give perfect protection. The properties of materials being what they are, none are so inherently stable that they will permanently resist attacks by the environment.

Thus, practical coatings are a compromise between the maximum protection that can be extracted from a system and how much is available to pay for them. With respect to economics it probably would be as expensive to achieve a "perfect" coating as it is to make anything else perfect. The longer the effective life of a coating system, usually the greater the cost of the coating.

From another aspect, coatings protect by one or more of the following mechanisms:

¹NACE Corrosion Handbook

1. Prevent contact between the environment and the substrate.
2. Restrict contact between the environment and the substrate.
3. Release substances which are inhibitive of attack by the environment on the substrate.

4. Produce an electrical current which is protective of the substrate.

The effectiveness of a coating system is directly related to the degree to which it effectively interposes itself between the environment and the substrate or reduces attack by the environment. This concept applies equally well to both cathodic and anodic (electrical) protection, both of which in an absolute sense are coatings in that they interpose barriers between the environment and the substrate. In a similar way, such methods as peening to produce compressively stressed surface material resistant to attack also are coatings in an electrochemical sense. These will not be discussed further here.

CONVERSION COATINGS

For the purposes of this chapter it will not be necessary to list or discuss all of the numerous methods whereby conversion coatings are applied or material used to produce them. Many of these methods are highly specialized; others produce properties which are not necessarily a protective function of barriers between the substrate and the environment and so on. It is sufficient to list a few of the most commonly used as follows.

ANODIZING

This process involves deposition of a material from an aqueous bath, usually under the impetus of an electrical current, which produces a tightly adherent surface coating integral with an interface layer consisting of a complex between the deposited and the base material. This process is commonly used on aluminum or reactive metals such as magnesium.

The resulting coating may be smooth or matte, contingent on its function and often is brightly colored. Thicknesses are commonly on the order of 4-7 mils. Anodized coatings are characterized by their hardness, tight adherence to the base and the speed with which they can be applied in uniform thickness on a wide variety of surfaces of varying cross sections and complexities.

Anodized coatings are resistant to a wide variety of corrosives. Those which are produced by acids on aluminum have a hardness approaching that of corundum. The films produced by acids are oxides, which vary according to the kind of bath in which they are formed. They are tenacious but tend to crack on bending.

A conversion coating is an adherent reaction product layer on a metal surface formed by a suitable chemical, such as an iron phosphate film on iron developed by phosphoric acid.

PHOSPHATIZING

There are three principal phosphatizing compositions: Iron, zinc and manganese phosphate. All are applied by essentially the same method and have similar resistances. Phosphatized coatings usually are applied from a hot aqueous bath, but also may be applied cold. Phosphoric acid, the active ingredient in the solutions, reacts with the substrate surface to produce a coating which consists almost entirely of a crystalline complex of the phosphoric acid, iron, zinc or manganese component.

Phosphoric acid is the active ingredient also in many materials usually applied cold, such as "wash primer" which may include, in addition to phosphoric acid, inhibitors such as chromates. In these materials, usually applied to freshly cleaned metal surfaces, the primer functions as a binder between the substrate and subsequent coatings which are selected to resist the external environment. The chromate, or other' components, (lead, for example) functions as an inhibitor (or passivator) helping to protect the substrate either by its rejection of water, affecting pH or by preventing disbonding of the surface coatings, or all three.

Phosphate coatings can be applied with precision at high rates using assembly line methods. Because they are deposited from aqueous solutions, they can be applied uniformly to surfaces with widely varying cross sections, etc. ***They require good surface preparation and precise controls of composition, time and temperature. They make a good base for application of top coats*** and are compatible with almost every commonly used paint formulation.

ALUMINIZING

Aluminum coatings are commonly applied two ways:

1. To sheets and shapes of uniform cross sections, or
2. Sprayed on surfaces, usually in a maintenance operation.

The first method consists of immersing the metal in molten baths of aluminum, often as a terminal operation in production of strips. In this method of application, the resulting interface phase and surface produced is much the same as that produced in similar baths applying zinc, to

produce hot dip galvanized surfaces.

Unlike galvanizing, which will be discussed later, aluminum does not, in most environments, convey electrical or sacrificial protection to

the surfaces to which it is applied. Because of its high resistance to attack by atmospheric corrosives and hot gases, aluminized materials are gaining wide acceptance. The surfaces corrode at

As a maintenance coating, aluminum is applied in two ways:

1. As a component dispersed in a liquid, usually an organic binder, and
2. After being melted by a hot gas flame (such as oxygen-acetylene or oxygen-butane) and impelled against a surface. The molten drops of aluminum flatten and solidify on the surface. This is known as flame-spraying.

When used as a so-called pigment* in solution coatings, tiny flakes of aluminum are deposited with the vehicle in which they tend to align themselves parallel to the substrate surface. In this configuration they present a series of barriers to corrodents.

Both "leafing" coatings as described above (1) and hot sprayed coatings (2) have characteristics in common: They are resistant to comparatively high temperatures (up to 1200 F (649 C) in some environments), have high reflectivity and usually resist the destructive effects of actinic rays in sunlight. Flame sprayed aluminum coatings, because they are porous are especially effective after they are sealed with topcoats compatible with the aluminum and the environment. They frequently are used as an intercoat for this reason.

CALORIZING

Of the many coatings applied by use of heat and/or reactive chemicals only a few will be discussed here. Because they are reasonably typical aluminum coating will typify the class. A principal use of calorizing is to confer resistance at high temperatures to oxidizing or corrosive gases, often moving rapidly. Because gases commonly attack materials by diffusing into their surfaces, the function of calorizing is to limit this diffusion and interpose a layer of material which retains its integrity at high temperatures.

Similarly, surfaces may be nitrided or carburized to confer resistance under roughly similar conditions. Various metals, oxides and

processes are used to create and fix coatings of this type to base materials. Surfaces so coated are commonly used in processes involving hot gases or liquids moving at rapid rates.

Cementation coatings, of which carburized is one type, are formed by diffusion when the coating metal and base metal are exposed at temperatures sufficient to diffuse one metal into the other, sometimes with the help of halogens. They usually are harder and more brittle than pure metal coatings.

Some of the other coatings often, but not always, termed "conversion" include:

OXIDE COATINGS

Black, brown or similar coatings can be formed on the surface of steel (magnetic oxides such as those formed inside boilers by exposing freshly cleaned surfaces to certain chemicals are one example) and on aluminum and other metals by several methods including at least one proprietary method.

One proprietary compound which deposits a silicone on the surface of a variety of ferrous and nonferrous metals forms a bond to the base so tenacious it can be removed only by special solvents or abrasives. It is resistant to heat and to many corrosive liquids and gases.

Oxide coatings on aluminum as hard as Rockwell C70 are used for resistance to salt water and other corrosive media.

CHROMATE COATINGS

These include, among others, at least one proprietary material which benefits not only from the passivation effect of the chromate ion but also from the barrier effect of the coating itself. Coatings of this type may be used on surfaces which previously have been phosphated or galvanized, or alone on freshly cleaned surfaces.

INORGANIC (NON-METALLIC) COATINGS

Inorganic include numerous classes of materials, among them the hydraulic cements, ceramics and clays, glass, carbon, silicones and silicates and others. On a volumetric basis, hydraulic cements are most common. So commonly used are these cements that they often are not identified by many as coatings at all.

HYDRAULIC CEMENT

Cements are used to coat pipe inside and outside, especially pipe that is to be buried or submerged, as are water or sewer lines. Cast iron pipe may be coated at the mill by a process during which the pipe is spun on the center of its longitudinal axis while a mortar mixture is sprayed onto the inside surface in a uniform, dense layer. After proper curing, provided the pipe is handled carefully, this coating effectively protects the pipe interior against attack by water and many other liquid and gaseous corrosives.

A cement coating on steel of any configuration is protective to the steel because the alkaline reaction of hydraulic cement maintains a pH at the steel surface which effectively prevents corrosion. This it does when encasing reinforcing steel, for example, where it functions both as a strength component and as a protective.

Cement is applied to external surfaces of pipe to protect them from soil or water in which the pipe is buried or submerged. In the case of underwater piping to transport gas or liquid hydrocarbons, for example, it may be mixed with barite or other heavy materials, to confer negative buoyancy. It may be used also in mixtures of organic materials where its ability to maintain a noncorrosive pH at the surface of steel is exploited.

CERAMIC (CLAYS)

These also may be used in much the same way as are hydraulic cements, but they usually are applied to confer resistance to heat and/or attack by hot high velocity gases. Thus, they are used in exhaust passages emitting hot gases such as rocket nozzles, furnace linings and other similar applications.

GLASS

A material now being produced in a variety of new and interesting formulations, glass usually is applied as slurry, nearly always in a production line, but seldom for maintenance purposes. Once applied and as long as protected from mechanical abuse, glass surfaces are highly resistant to -acidic and many mildly alkaline corrosives (especially the new types), are easily cleaned, but difficult to repair.

Glass lines and coated pipe, valves, pumps, vessels of all kinds are widely used in the chemical, pharmaceutical and food industries.

It would be correct also to include under this category coatings such as those involving silicones which were covered previously. Silicon also can be applied by pack cementation methods as can beryllium and other metals, to produce surfaces with varying properties of hardness and resistance to corrosion.

METALLIC COATINGS

Any metal that can be electrically, chemically or mechanically deposited can be used to produce a barrier. One way to consider metals as coatings is to divide them into anodic (or sacrificial) and cathodic (or non-sacrificial) categories.

(a) Sacrificial coatings, for the purpose of this discussion, are those which are electrically sacrificed to protect the substrates to which they are attached. While this relationship can be true for almost any two metals, the most commonly used anodic metal is zinc, which, because of its galvanic relationship to steel in most natural environments, has long been the most common coating of this type. Zinc, which may be applied by immersion, hot gas flame, or applied by pack cementation is used on a wide range of flat materials, wire, castings and other items. The protection conferred by zinc is a function of its thickness.

CONVERSION COATING TREATMENTS

Conversion coating treatments, which rose to prominence during World War II, were developed primarily by metal producers and by manufacturers of chemical specialties as a result of the growing need for improved corrosion resistance and paint adherence over that of untreated metals.

Chromate conversion coatings are essentially amorphous compounds consisting of both hexavalent and trivalent chromium, the metal being

treated, and, to some extent, include salts and oxides of other constituents of the treating solution. Films on such metals as zinc, cadmium, aluminum, magnesium and their alloys, and to a lesser extent, tin, copper and silver and their alloys, can be produced by immersion, brushing or spraying. Electrolytic treatments, formerly popular, have given way to simpler non-electrolytic treatments. Chromate conversion treatments for ferrous materials have been the subject of many patents; however, their commercial development has been relatively unsuccessful in comparison with the more widely accepted phosphate treatments.

Colors, depending on the metal being treated, may be clear, iridescent, yellow, green through olive drab or brown to black. Little abrasion resistance can be ascribed to the coatings, although aging tends to harden the films. Heating to about 200 F can cause dehydration and slight cracking, but little impairment of film quality. Exposure to higher temperatures can cause undesirable cracking and adversely affect film quality. By comparison with most anodic coatings, on aluminum for instance, the film has greater flexibility where working or fabrication after treatment is necessary.

The prime function of chromate films is to provide some measure of passivation in the case of clear films, or with the more colored films much improved corrosion resistance either for protection alone or as an improved base for organic finishes. Some clear finishes serve as decorative finishes or, in the case of copper and its alloys, as an improved brightening treatment before chromium plating. Also, some of the clear treatments for cadmium and zinc serve as bright dips in that they produce an appearance more closely resembling a virgin metal surface and to some extent exhibit a chemical polishing effect. The amorphous, absorptive character of freshly applied coatings permits dyeing; usually for indoor or moderate exposure. Performance of dyed chromate coatings in bold exposure is improved by lacquering.

Thickness of films produced varies upward to 0.00002" and in some cases up to 0.0001", and is indicative of the extent of the attack on the metal treated. For this reason treatments for cadmium and zinc plate (depending on the type) require a certain plate thickness. Corrosion protection afforded increases with coating thickness. However, the character rather than thickness of the coating is more important in this respect. Generally, the more colored films offer superior corrosion resistance.

Chromate conversion treatments are mostly acidic, and to a lesser extent, alkaline solutions based on chromic acid, sodium or potassium dichromate or chromate. In a few cases, other less soluble chromates have been considered. Normally dichromate and chromate in pure solution are inhibitive to most metals (as in chromic acid to some materials), requiring that activators be added to promote chemical attack of the metal with attendant reduction of chromium and film formation. Fluorides, chlorides, nitrates, sulfates, phosphates, and usually simple organic acids (such as formic, acetic, trifluoroacetic), derived from acids or salts have been used. Trivalent chromium, silver or manganese salts serve to impart color or otherwise alter the character of the coatings. A continual surge of development to improve quality or for varying film qualities has been the basis of considering a variety of many other organic and inorganic materials. Commercial formulations are available as either dry solution mixes for simple makeup to appropriate strength. Addition of other acids may also be required.

THE BRONZ-GLOW DIFFERENCE

The Bronz-Glow Dip Process coil coat is a patented single component resin formula that buffers corrosive atmospheres and airborne contaminants from depositing on the fin tube and causing corrosive attack. Bronz-Glow Coil Coat is the only single component coating to provide full pH range (1.0-14.0) protection.

The Bronz-Glow Process includes a protective impalpable chemically bonded coating which passivates the metal preventing further oxidation and promotes superior adhesion for subsequent coatings applied to the surface of the base metal. The patented Bronz-Glow Husky Coil Coat having superior moisture resistance, 300% elasticity and full pH range protection is then applied. The final result is a highly corrosion and abrasion resistant coating that protects against acids, alkalies, salt water, acid rain, chlorine vapors, hydrogen sulfide gases and mists. Bronz-Glow's Husky Coil Coat protects against a host of aggressive natural, commercial and industrial corrosion promoting atmospheres.

BRONZ-GLOW is a patented process specifically developed to aid in establishing an economical means of protecting aluminum fin tubes from the costly effects of corrosion. Unlike phenolic coatings, BRONZ-GLOW is highly flexible, eliminating the potential of the coating cracking, chipping or flaking when the coils are installed or the fins bent. This prevents the development of openings to the bare metal where corrosion can start. BRONZ-GLOW has minimal effect on heat transfer coefficients. Unlike paints it resists the tendency to blister, crack or flake and seals out moisture, one of the major ingredients in the corrosion process. It also prevents air borne contaminants from depositing on the metal surface. Coils are cleaned in a spray washer with an environmentally safe mild detergent, specially formulated for the Bronz-Glow Process, to remove stamping and drawing oils as well as shop soils.

The BRONZ-GLOW PROCESS is a multistep process consisting of a preliminary detergent wash of the surface to remove loose dirt and fabrication oils, then an acidic solvent wash to remove oxides, condition the metal surfaces, and apply the impalpable chemically bond coat. The acidic solvent wash is an important step in preparing the substrate metal with corrosion inhibitor qualities. Since there is no metal loss in the cleaning and deoxidizing process, no minimum material thickness is required.

The application of the BRONZ-GLOW corrosion inhibiting conversion coating yields a protective base on the aluminum fin and at the interface of the fin and tube which inhibits corrosion at this galvanic cell area. Extensive laboratory testing has demonstrated superior corrosion protection. The impalpable chemically bonded corrosion inhibitor coating applied under the Bronz-Glow Husky Coil Coat produces the highest quality corrosion resistant coil coating for an aggressive corrosive atmosphere.

City Testing Laboratories Salt Spray Test (available upon request) protective coating and also have excellent UV ratings. To our knowledge no

other company which coats coils practices this technology of metal cleaning and conditioning plus applies four distinctly formulated corrosion resistant coatings and corrosion inhibitors in the protection of aluminum, such as is used in fin tube evaporators and condensers. The BRONZ-GLOW PROCESS provides our manufacturer representatives, licensees, distributors, and dealers with the highest quality corrosion resistant coating on the market today.

WHY DO WE LEAD THE FIELD?

Because we did not just formulate a coating; we engineered a process and a system. A system, which includes not only our patented in-house dip process but several types of mobile BRONZ-GLOW application field rigs. The specially engineered BRONZ-GLOW field rigs were developed to provide manufacturer representatives, distributors, licensees and their customers a full-service program at a highly competitive price. We not only coat the coils but more importantly we prepare the metal first to be more corrosion resistant, prior to applying a substrate coating and one of our selected moisture barrier synthetic resin coil coatings.

HOW DO WE TREAT THE METAL?

1. We remove the grease, oils and oxides from the surface that would hinder coating adhesion.

2. When conditioning the metal surface we remove the impurities in the surface of the metal which if left would aid in accelerating corrosion.

3. Our BRONZ-GLOW metal conditioner while removing impurities deposits protective salts on the surface of the metal and at the interface of the fin and tube which act as a corrosion inhibitor.

THEN WHY THE IMPALPABLE CHEMICALLY BONDED COATING? What does it do?

1. Our impalpable chemically bonded coating molecularly bonds itself to the surface of the metal, and through its unique blend of non-toxic chemicals which once applied provides a highly corrosion resistant protective coating.

2. The impalpable film with its passivating effect prevents oxidation and improves the corrosion resistance of the aluminum.

WHAT IS THE POLYELASTOMER COIL COAT?

1. Bronz-Glow's patented Husky Coil Coat is a synthetic resin base formulation that creates a moisture barrier and blocks out atmospheric pollutants such as acid rain, salt air, chlorine, hydrogen sulfide, condensation, etc. from reaching the fin tube surface.

2. BRONZ-GLOW coil coatings were formulated to provide the best of several protective qualities.

a. Flexibility - to prevent cracking, chipping, and flaking of the coating. Further with its +300% of flexibility it is the only coil coating we know that will expand and contract at the same rate as the fin and tube.

b. Chemical resistance - to provide corrosion protection in the full pH range of (1.0-14.0) which includes the most harsh chemicals found in industry as well as more common corrosive pollutants as those identified in #1 above. (See the partial list at the end of this section).

c. Moisture barrier - to create a unique single component film that prevents moisture from penetrating to the metal surface where an anodic cell can be created. Husky Coil Coat inhibits against corrosive attack caused by moisture.

d. Repairable - to develop a coating that could be repaired in the field for easy repair of damage caused by installation services or where severe wind abrasion may occur. This allows for a complete "PM" program and often saves the cost of removing the coils and early replacement from corrosive attack on the damaged area.

e. The Bronz-Glow coil coatings do not support combustion, making tube repair safer.

f. Bronz-Glow Coil Coat does not give off hazardous or toxic gases once coating is dry.

g. Single Component coating to reduce waste and unnecessary disposal cost.

WHY HAS THERE BEEN SUCH A WIDE ACCEPTANCE?

1. Because we did not stop at developing a quality coating, we went one step further and took into consideration the needs of the industry and those HVAC suppliers that serve the industry.

a) Cost effective and cost efficient process (Automated & Quality controlled).

b) Extremely competitive pricing (Volume Discounts).

c) Prompt turnaround of orders (3-10 days).

d) Flexibility of application (In-house dip or field spray).

e) Meaningful warranty (5 years).

f) Follow-up service programs and coating maintenance kits.

WHAT DO WE MEAN BY FLEXIBILITY?

1. The BRONZ-GLOW dip process has been modified to provide the customer quality service in the field similar to that process applied at one of our licensed in-house facilities.

2. Coils may be spray coated in the unit or dip coated at a Bronz-Glow licensed facility. It is, however recommended that to ensure 100% coverage coils should be dip coated. Rarely can a coil of three rows (3 inches deep) or more be coated 100% when in a unit. In most such cases the coating does not penetrate the coil, even when sprayed from both sides of the coil. The rare exception is if a coil has only a few fins per inch.

3. Bronz-Glow licenses issues the customer a written warranty and a written Certification of Process which identifies the process (spray or Dip) used to coat the coil.

HOW DO WE SAVE OUR CUSTOMERS COST?

1. We give a high quality coating at a competitive price.

2. Coils may be treated in a new unit already installed, saving the cost of removing, shipping and replacing the coil after coating, not to mention saving down time.

3. Because of the flexibility of the BRONZ-GLOW PROCESS we can save you the time of waiting for special order coil coatings we can coat a stock unit making you more competitive on price and delivery.

4. Available through the "Field Applicator" are annual coil cleaning and inspection contracts in local service areas of our licensees or Bronz-Glow Technologies, Inc... These contracts are at competitive rates.

Our Husky coil cleaners are environmentally friendly and biodegradable; there are no harsh caustics or acids such as nitric and hydrofluoric acid used in many coil cleaners. This makes them safer to apply for the technician.

5. Lack of corrosion through proper coating, means dollar savings through more efficient unit operation. Less wear on the compressor and other motor drives.

WHAT OPTIONS TO CORROSION PROTECTION ARE THERE?

OPTIONS AVAILABLE ARE:

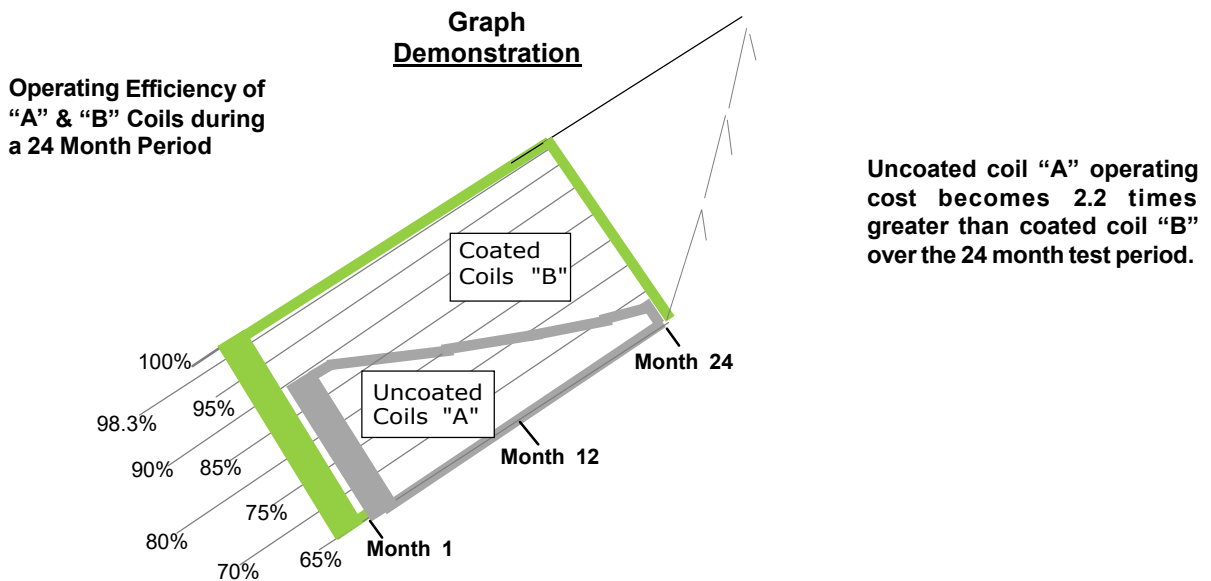
1. Ordering of special alloy fin tubes. This is many times more costly and often results in long delays in delivery of a unit. Even copper fins are subject to corrosion (patina) and chloride embrittlement in salt air atmospheres.

2. The most likely and cost effective option is to select a versatile high quality coil coating. There are several types available. They range from poor to excellent in protective quality when subjected to specific corrosive atmospheres, or environments. Bronz-Glow licenses evaluate the condition under which your equipment will operate, and suggest the treatment options available, for the operating environment, under our quality coating processes.

THE ADVANTAGE IS OBVIOUS!

Cost savings through efficient operations.

Based on the results of U.S. Navy Test N-1560 performed by Whirlpool Laboratory and Florida Power & Light kilowatt hour and use rate charge, the following operating cost defining the benefit of Bronz-Glow coated coils over uncoated coils highly significant. As much as 55% energy savings and two to three years coil life.



The declining operating efficiency of the uncoated coil "A" lost over a third of its heat transfer efficiency. The coated coil "B" on the other hand maintained 98%+ of its heat transfer efficiency, resulting in a 46-63% (Average 55%) better operating efficiency than the uncoated coil "A".

**BRONZ-GLOW QUICK REFERENCE
CORROSION RESISTANCE GUIDE
FOR ITS HUSKY BRAND COATINGS**

CHEMICAL

Acetic Acid
Aluminum Nitrate
Ammonium Carbonate
Ammonium Hydroxide
Ammonium Monobasic
Arsenic Acid
Barium Nitrate
Brine Solution
Calcium Hypochlorite
Chlorine
Chromic Acid
Copper Sulfate
Formic Acid
Haptenic Acid
Hydrofluosicic Acid
Hydrogen Peroxide
Lactic Acid
Maleic Anhydride
Nickel Chloride
Phosphoric Acid
Potassium Hydroxide
Potassium Fluoride
Sodium Chlorate
Sodium Cyanide
Sodium Hypochlorite
Sodium sulfate
Stearic Acid
Titanium Oxide
Water (sea)

CHEMICAL

Aluminum Chloride Aluminum
Sulfate
Ammonium Chloride Ammonium
Nitrate
Ammonium Sulfide Barium
Hydroxide
Borax Solution
Calcium Chloride
Caustic Liquor
Copper Chloride
Ferric Chloride
Ferrous Sulfate
Glucose
Hydrochloric Acid
Hydrogen Sulfide
Hydroxy Acetic Acid Magnesium
Chloride Nickel Acetate
Nitric Acid
Potassium Bromide
Propionic Acid
Sodium Carbonate
Sodium Chloride
Sodium Hydroxide
Sodium Phosphate
Sodium Thiosulfate
Sulfuric Acid
Water
Zinc Chloride

This partial reference guide is based on atmospheric environments of vapors, mists, and airborne particulate not immersion applications. Inquire about Bronz-Glow Coatings available for specific applications above or not specified. Further data will be released as additional corrosives are tested.

WHAT TO CONSIDER WHEN SELECTING A COATING COMPANY

When selecting a coating or coating company for corrosion protection of your temperature control system more than the company behind the coating is equally as important as the coating selection. Here are some of the considerations that you as a specifying engineer, owner, or contractor should consider.

1. How long has the coating company been in business.
2. Type of corrosion resistant testing has been performed on their coating.
3. Are independent test results on their brand of coating available.
4. How is it applied - spray or dip.
5. How is the metal surface prepared prior to coating.
6. Can they provide references of installations similar to your environment for your firm to check their success of treatment.
7. Will they let you visit and tour their facility.
8. What procedure do they employ for dip coating or spray coating.
9. What is the extent of their training in coating application or dismantling of a unit and reconstruction of a disassembled unit.
10. Do they provide or issue a written "Coating Compliance Certificate".
11. Do they issue a written 5 year coating warranty.
12. Do they provide field coating repair service on warranty.
13. Do they provide field coil cleaning & touch-up programs.
14. Are their coil coatings specifically formulated for fin tube coils.
15. Can their coating be repaired in the field.
16. Do they have local representation in your area.
17. How does their warranty claim program work
18. What type of records are developed and kept in performance of work on your equipment.
19. What is their program for multi-facility accounts.
20. What is their program for high volume accounts.
21. Do they have a customer service department.
22. Do they have ongoing training for their technicians.
23. What is their pricing structure.
24. Will they give a fixed or not to exceed price.
25. Is their coating toxic or fire retardant.
26. Does the coating company blend its own formula or whose product do they apply.
27. Is their product or process patented.

One or all of these questions may apply to the owners concerns or interests. Bronz-Glow encourages owners, specifying engineers and contractors to be prudent when selecting a coating company for themselves or their customer.

The proper coating is an effective economical means of protecting your equipment, extending its useful operating life and preventing undue energy cost caused by inefficient operation.