

# Prevention of Corrosion of Metals - SAE J447a

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## SCOPE

This Information Report is intended to provide automotive engineers with a guide to the principles of corrosion of metals and to methods dealing with its prevention.

## INTRODUCTION

Prevention of corrosion is an important design consideration for many applications of metals. In some cases, corrosion resistance may be the dominating factor governing the selection of material or process; in others, it will be secondary to economic considerations, physical properties, or the many other factors that are evaluated in the course of such selection. Means of preventing or retarding corrosion on specific parts may be important from the standpoint of assuring proper engineering function, contributing to service life, or producing and maintaining appearance. The designer should be familiar with the part that corrosion prevention plays in the selection of metal and/or treatment, so that the performance complies with the requirements.

With the use of salt for de-icing and dust control increasing at a rapid rate for the past several years, this corrosion problem has become recognized as one of primary importance. In addition, the adoption of extended warranty periods has made it mandatory that immediate steps be taken to reduce this corrosion problem.

Areas of most severe corrosion are those exposed to road splash thrown up by the wheels. Salt coatings built up in these areas hold moisture in contact with the metal parts and extend the periods of wetness, which in turn accelerate deterioration by corrosion. The best way to prevent corrosion is to keep these critical surfaces clean. Therefore, the owner can do a great deal toward preventing corrosion by frequent washings of the vehicle, particularly during periods of high salt usage on highways.

This section is intended to provide information covering the corrosion preventive methods commonly used for both ferrous and nonferrous metals. The particular practices discussed are those considered typical within the automotive industry, but are believed applicable to parts and products for many other applications. Metals used in marine, aircraft, and many other products and components will, of course, require protection selected for the particular exposure conditions or design requirements of such applications. Care has been taken to provide reliable data, but users should supplement this with their own experience and tests, to be assured of satisfactory results for their own specific requirements. Optional methods may be generally suitable for typical classes of parts, and the choice in different plants may vary, with acceptable results. In some instances, the preferred type of finish, coating, or treatment is indicated. Within the limits of whatever restrictions apply, after the selection is made, quality requirements are met by estab-

lishing suitable specifications, process controls, and acceptance tests.

The choice of corrosive preventive methods is greatly affected by the environmental and other conditions to which the part will be subjected in use, such as:

- |                     |                     |
|---------------------|---------------------|
| 1. Moisture.        | 6. Galvanic action. |
| 2. Sunlight.        | 7. Wear.            |
| 3. Temperature.     | 8. Abrasion.        |
| 4. Chemical action. | 9. Stress.          |
| 5. Salt.            |                     |

The applicable conditions of service should be evaluated and protection provided in terms of the expected life of the part. Also, the part design may have an important effect on prevention of corrosion in some environments, and should be considered in relation to the materials and/or treatments and coatings. Trapped moisture, lack of ventilation, crevices, and other design details or effects of design, may be significant.

In general, the corrosion preventive requirements of most automotive type parts may be satisfied by one or more of the following:

1. Selection of proper metal
2. Design considerations.
3. Use of inhibitors.
4. Choice of protective treatments and/or coatings.

The application of treatments or coatings to metal almost always requires some form of cleaning or other preparation for satisfactory results. Variations peculiar to the different coatings will be covered, where they are considered important to the results obtained.

A general discussion of the methods, characteristics of materials, and specific applications is given in subsequent text. References to related SAE Handbook Supplements and other SAE Information Reports are noted for those desiring additional or more detail knowledge.

## PRINCIPLES OF CORROSION

Corrosion is a destructive phenomenon which may be detrimental to the appearance of an object, or in extreme cases, may cause structural failure. It occurs in practically all environments, but is most often associated with those involving air and moisture. It is a complex process, which varies considerably with each set of conditions, and a thorough understanding of the subject is required to cope with it properly. This brief review can only generalize on the subject, and the reader is referred to SAE reports and other literature for more detailed information.

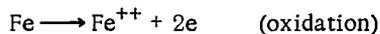
The rate at which corrosion proceeds is dependent upon the composition of the material, metallurgical treatment and fabrication of the product, and the exposure environ-

ment. Corrosion prevention may involve the use of corrosion resistant materials, the application of protective coatings, or control of the environment. The selection of a material or method of protection must be determined for each exposure condition and within prescribed economic limits. Laboratory testing serves as a guide in this selection, but exposure under actual conditions is considered necessary in many cases.

**MECHANISMS** - Corrosion is the destruction of metal or alloy by chemical or electrochemical change. Chemical change is usually associated with the formation of tarnish or oxide films by direct combination with gases. Most automotive corrosion involves an electrochemical reaction. This can be considered simply as the oxidation of metal at anodes and the reduction of a substance at cathodes. In order for these reactions to occur, certain basic requirements must be met:

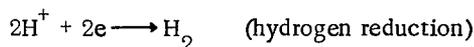
1. There must be a potential difference between adjacent sites on a metal surface or between alloys of a different composition.
2. An electrolyte must be present to provide solution conductivity and as a source of material to be reduced at the cathode.
3. An electrical path through the metal or between metals must be available to permit electron flow.

The corrosion of iron is a familiar case, and is therefore best as an example to describe these reactions. The oxidation process results in the formation of ferrous ions at the anode, as shown by the following reaction:

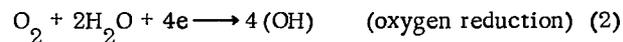


Ferrous ions move away from the surface and are oxidized to ferric ions, which combine with hydroxyl ions to form ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ). The corrosion product, identified as rust, consists of iron hydroxide or oxide in various states, depending on the degree of oxidation and dehydration.

The reactions in the reduction process at the cathode must take place concurrently for the corrosion process to continue. Several reactions are possible, and the one that occurs is determined by the environment. Hydrogen can be reduced by the excess of electrons at the cathode surface and evolved as molecular hydrogen by the following reaction:



When hydrogen is not removed from the surface, the cathodic reaction decreases, and the corrosion rate is reduced. In the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions are



Hydrogen evolution or oxygen reduction with the formation of water is more likely to occur in acid media, but oxygen reduction with the formation of hydroxyl ions is more dominant in neutral or alkaline media. In either case, there is an increase in the alkalinity of the solution at the cathode.

In summary, corrosion occurs when atoms detach themselves from the metal surface at the anode and enter the solutions as ions, leaving behind negatively charged electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solutions where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form water or hydroxyl ions, respectively.

The anodic and cathodic areas on a metal surface are formed by such variables as inhomogeneities in metal composition, differential surface conditions, metal stresses, or variations in solution concentration. Metal attack can be widespread or confined within a localized area, depending on the relative proportion of anodic and cathodic areas. When the areas are approximately equal, corrosion is usually uniform over the whole surface. However, when the cathodic area is large compared with the anodic area, the attack at anodic sites may be intensified.

There are several types of corrosion associated with a specific condition that effects the formation of anodic or cathodic sites, increases the potential difference between two areas, or effects the oxidation or reduction reactions. These types of corrosion warrant special consideration and are discussed in more detail in the following sections.

**CONCENTRATION-CELL CORROSION** - This localized type of corrosion is caused by variation in the concentration of the environment at various locations on the metal surface. A common form of this corrosion is referred to as "crevice corrosion." Variations in availability of air to the metal surface produces a similar result; metal at the area of low oxygen availability becomes anodic to other areas. Because the cathodic area is large compared with the anodic area, an intensified attack occurs at a small localized area. Concentration-cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, and similar parts.

**GALVANIC CORROSION** - Galvanic corrosion occurs when two dissimilar metals are coupled and exposed to the same environment. The intensity of corrosion will be determined by the potential difference between the metals and the ratio of cathode to anode areas. The farther apart metals are in the electromotive series, the greater will be the accelerated corrosion of the least noble metal (anode).

As the electromotive proximity ratio of cathode to anode increases, the current density at the anode increases and the cathode is more effectively depolarized. Thus, large cathode areas to small anode areas should be avoided. When

a bimetallic couple cannot be avoided, or the metals cannot be insulated from one another, metals selected should be as close as possible to each other in the galvanic series or the smaller of the two parts should be made the more noble metal.

**PITTING CORROSION** - Pits occur as small areas of localized corrosion and vary in size, frequency of occurrence, and depth. Rapid penetration of the metal may occur, leading to metal perforation. Pits are often initiated because of inhomogeneity of the metal surface, deposits on the surface, or breaks in a passive film. The intensity of attack is related to the ratio of cathode area to anode area (pit site), as well as to the effect of the environment. Halide ions such as chlorides often stimulate pitting corrosion. Once a pit is initiated, a concentration cell is developed, since the base of the pit is less accessible to oxygen.

**STRESS CORROSION** - Either internal or applied stresses are involved in this type of corrosion. Internal stresses are usually the result of cold working, welding, or heat treatment. Stress may simply affect the corrosion behavior of the metal, or it may combine with an electrochemical reaction to produce cracks at an accelerated rate.

Cyclic stress results in a fatigue failure, which is accelerated by corrosive attack. The severity of stress corrosion for a given material depends, in part, on the degree of stress, concentration and nature of environment, and temperature. Common examples of stress corrosion are the seasonal cracking of brass, cracking of austenitic stainless steels in a chloride environment, and caustic embrittlement of steel. This type of corrosion can best be avoided by the use of appropriate heat treatment, selection of the proper alloy for a given environment, or the use of suitable protective coatings.

**INTERGRANULAR CORROSION** - Localized corrosion at grain boundaries of the metal or alloy is termed "intergranular corrosion." It is the result of a difference in potential between the anodic grain boundaries and the grains. Improperly heat-treated stainless steels are particularly susceptible to this type of corrosion, although other metals can be affected. This type of corrosion on stainless steel is thought to be the result of chromium carbide precipitation at the grain boundaries, with chromium depletion at areas immediately adjacent to the boundaries.

Intergranular corrosion can result in complete metal failure even though only a small portion of the metal is affected. The most effective means of prevention is that of proper selection of alloy and heat treatment.

**DEZINCIFICATION** - This form of corrosion is commonly associated with brasses. It is recognized by the formation of a pronounced copper color, rather than the yellow of brass. There are two types: one a uniform corrosion and the other a plug type that is localized.

Dezincification is thought to occur by either selective removal of the zinc, leaving the copper behind, or by dissolution of the brass and redeposition of the copper. The uniform type occurs more frequently on high zinc brasses and the plug type on low zinc brasses. The tendency to de-

zincification can be reduced by the addition of suitable elements to the brass. Rate of attack generally increases with an increase in temperature, increase in solution conductivity, and decrease in solution flow.

This category of corrosion is similar to graphitization of cast iron in which iron is removed, leaving a graphite mass with a porous structure. More recently, similar types of corrosion have been observed on other metals, and the tendency is to identify it by a similar nomenclature (for example, "de-aluminumification").

## METAL SELECTION

For many applications of ferrous metals, the base metal may have adequate corrosion resistance without the addition of special surface treatments or coatings. Nonferrous metals in some instances are even more likely to be suitable for use in the uncoated state. Therefore, designers should recognize the basic corrosion resistance of the metals intended for each specific application, in terms of the design function and the environmental conditions of operation, and consider the possibility of using the metal in the uncoated condition.

Uncoated carbon steels may be satisfactory in the absence of conditions that promote corrosion. These steels are frequently satisfactory when used in the presence of oils or other substances that tend to coat the surface and prevent oxidation, as on the inside of engine oil pans. However, when steel is exposed to moisture, even in the form of high humidity, surface corrosion can be expected to develop in very short time, and uncoated carbon steel should not be considered if the presence of rust is objectionable.

As environmental conditions become more corrosive, or as the standard of acceptability in terms of appearance or function is increased, changes in composition are needed. The addition of chromium, generally 16% (SAE 51430) or more for automotive applications, increases the degree of corrosion resistance. The composition covered by SAE 51434 (51430 modified with 1% molybdenum), for example, is used for bright exterior trim above the belt line. Austenitic stainless steels are normally used for applications at the belt line and below. Greater resistance to corrosion is achieved by austenitic compositions, which usually include substantial quantities of nickel in addition to chromium.

As exposure becomes still more corrosive, further composition modification of ferrous metals may be necessary. For extremely high temperatures, such as experienced on valves or on gas turbine components, additional alloying is indicated. Under certain environmental conditions substances, such as acid products of combustion and lead derivatives, which accelerate corrosion, may further limit the choice of appropriate materials. In such cases, the other functional requirements of strength, fatigue resistance, and hardness will also require consideration in addition to corrosion resistance.

Many nonferrous metals are less affected by ordinary exposure than the low alloy ferrous materials. The copper, aluminum, lead, nickel, tin, and zinc alloys are frequently acceptable without added protection. Examples include the use of copper and brass in radiators, aluminum castings or stampings in locations where appearance is not a factor, lead and tin in solder, lead in storage battery connections, and zinc die castings under conditions of mild exposure. Magnesium, however, is not generally considered acceptable without coating or treatment.

The designer should always keep in mind the inherent corrosion resistance of metals. The careful selection of an appropriate material can frequently lead to more satisfactory and economical results than those obtainable with coated metal.

DESIGN AIDS

Prevention of corrosion is one of the many important considerations in designing automotive products. The best corrosion protection is obtained by avoiding, or at least minimizing, exposure of metal surfaces to the continued service environments of water, salt, and other road contamination. The duration of wetness of each exposure and the frequency of exposure determines the degree of protection or the degree of corrosion resistance required for each component.

It is often more economical to provide good corrosion prevention by proper choice of design techniques than it is to use corrosion resistant materials or protective coatings. Sometimes the combination of both good design techniques and protective coatings is required to achieve the necessary protection for an anticipated corrosion problem.

Figs. 1-11 demonstrate the following principles to be observed in designing for corrosion resistance:

**Principle 1 - Fig. 1:** Keep underbody surfaces dry; avoid ledges, flanges, pockets, where dirt can accumulate and hold moisture. Horizontal flanges should be narrow and face away from line of travel. Flanges should slope downward to provide good drainage.

**Principle 2 - Fig. 2:** Where appearance is of primary

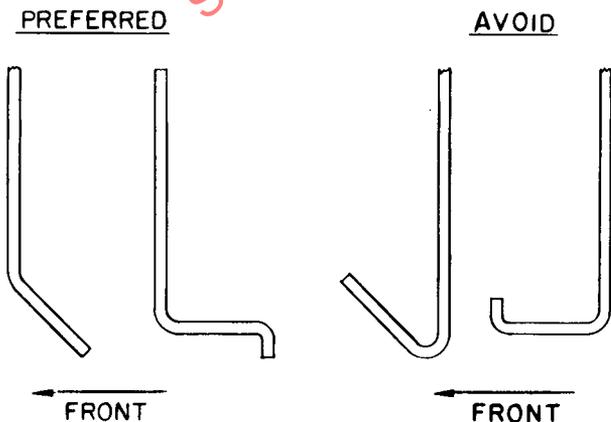


Fig. 1 - Principle 1

importance, use solder filled, double offset lap joint instead of mastic sealed coach joint or lap joint.

**Principle 3 - Fig. 3:** Make joints watertight. Shingle lap joint to prevent entrance of water (point lap away from direction of travel or downward for best natural drainage).

**Principle 4 - Fig. 4:** Seal joints with mastic type compound and cover entire faying surface in riveted joint. Completely seal edges in welded joints to prevent entrance of moisture.

**Principle 5 - Fig. 5:** Provide protective flange for lap joint in line with wheel splash to prevent water and road contaminations from being driven into area of faying surfaces.

**Principle 6 - Fig. 6:** Avoid use of dissimilar metals in contact with each other when possible. To avoid galvanic corrosion if dissimilar metals must be used, observe:

- (a) Use large anode area (aluminum) to small cathode area (steel) to minimize galvanic effect.

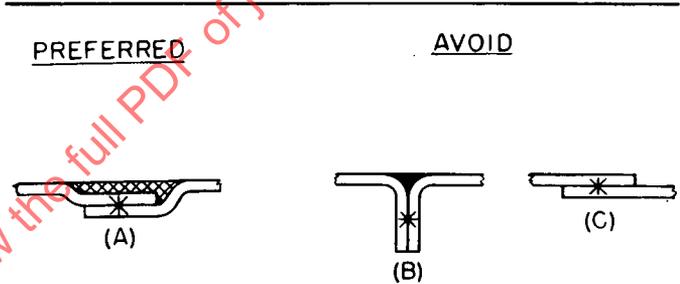


Fig. 2 - Principle 2

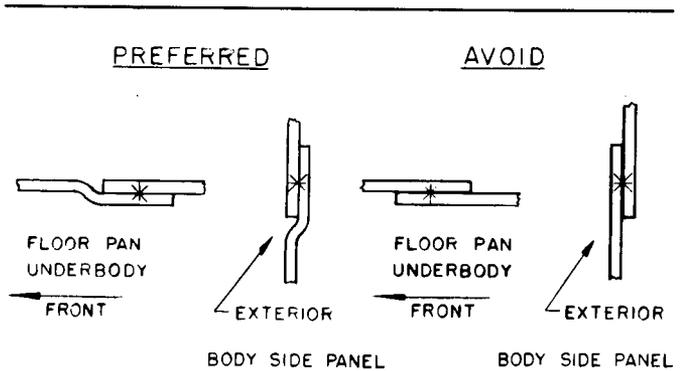


Fig. 3 - Principle 3

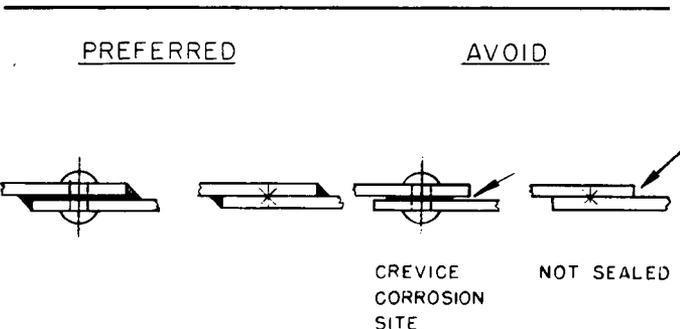


Fig. 4 - Principle 4

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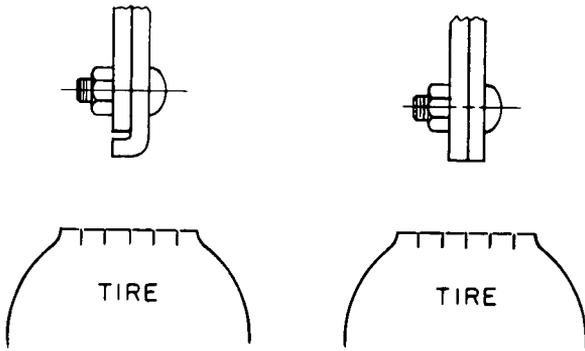


Fig. 5 - Principle 5

(b) Use metallic coating (zinc or cadmium) on cathode to reduce galvanic attack.

(c) Insulate joint. Use protective coating on both sections, especially on the cathode area.

(d) Keep joints watertight (use mastic sealer).

Principle 7 - Fig. 7: Use open construction whenever possible. Avoid box sections and enclosed areas in severe corrosion exposure. Proper application of protective coatings is difficult, and it is usually impossible to inspect for completeness of application in enclosed areas.

Principle 8 - Fig. 8: Provide adequate drainage in doors and in body areas having movable windows. Drain openings should be located to obtain best possible drainage. Openings must be large enough to avoid plugging and to per-

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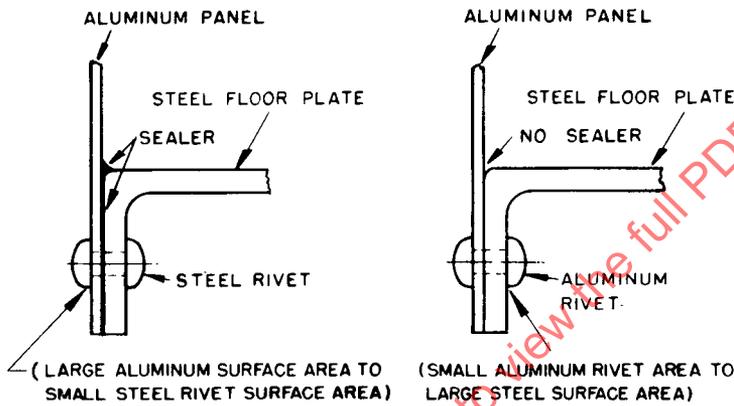
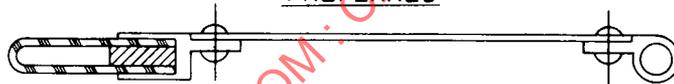


Fig. 6 - Principle 6

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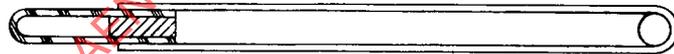


Fig. 7 - Principle 7

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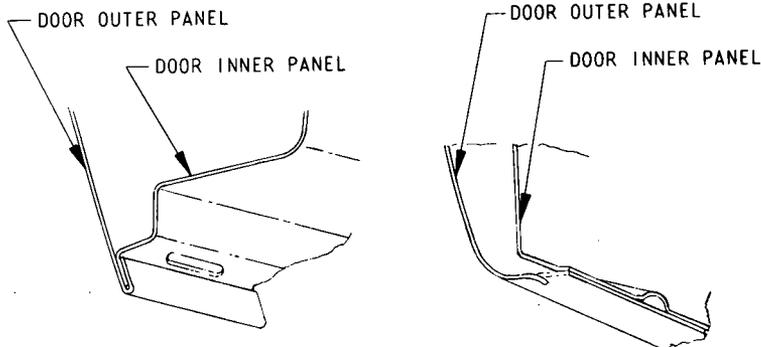


Fig. 8 - Principle 8

mit drainage flow equal to or greater than entrance flow.

**Principle 9 - Fig. 9:** When box sections or enclosed areas are used, provide sufficient openings for applications and drainage of protective coatings. Provision should be made for good ventilation and drainage such as fluted flanges, with flanges pointing downward and toward rear to minimize entrance of wheel splash and large enough to avoid plugging.

**Principle 10 - Fig. 10:** Keep electrical connectors free from moisture:

- (a) Place dry locations preferably in passenger or luggage compartment.
- (b) When mounted externally, use location not exposed

to wheel splash and where road salt and dirt will not accumulate.

- (c) Protect externally mounted sockets and connectors with rubber boots.
- (d) Seal joints in lamp housings where moisture may enter. Use mastic type sealer.

**Principle 11 - Fig. 11:** Design fuel tank and other fluid containing components to eliminate solder joints requiring use of corrosive solder flux.

**INHIBITORS**

Corrosion inhibitors are substances that retard the rate of metal corrosion when added in small amounts to a cor-

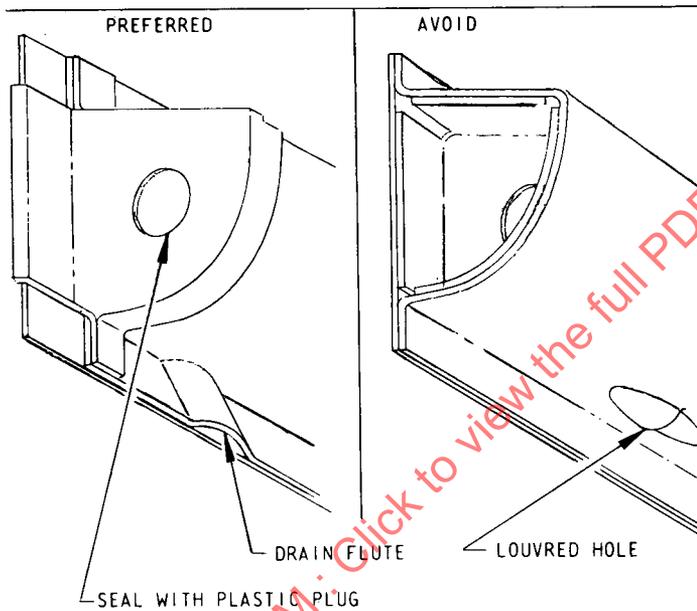


Fig. 9 - Principle 9

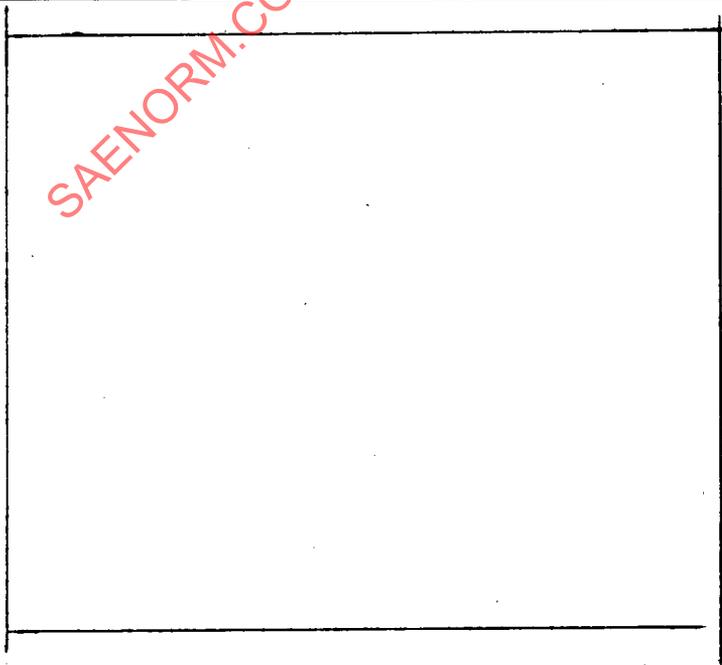


Fig. 10 - Principle 10

rosive environment. The successful application of inhibitors requires knowledge of corrosion processes involved in the system and the function of inhibitors under consideration. Inhibitors are often rather specific in their action, and the proper inhibitor or combination of inhibitors must be selected for each environment. An inhibitor may provide excellent protection in one system but aggravate corrosion in another. Additional information about inhibitors can be found in the SAE J814, "Engine Coolants."

Some substances function as inhibitors by adjusting the pH or preventing harmful deposition of undesirable products. Inhibitors generally function by contributing to the formation of insoluble protective films or by an adsorption process, resulting in a chemical or physical bond with the metal surface. In many cases it is likely that a combination of both reactions occurs.

Inhibitors can be broadly classified as anodic, cathodic, or general, depending on whether they polarize the anodic or cathodic reaction or both. There are any number of materials that function as inhibitors; they are primarily inorganic oxidants and alkalis or organic polar compounds containing oxygen, sulfur, or nitrogen.

**ANODIC INHIBITORS** - Anodic inhibitors function by the formation of insoluble protective films at anodic areas, or by adsorption. In the first reaction, anodic inhibitors may enhance oxide formation by oxygen or may contribute directly to the formation of oxides. In the second reaction, the physical or chemical adsorption of inhibitor anions leads to the formation of compounds of definite composition, but without surface metal atoms leaving their respective lattice positions.

Either of these reactions, or both, may be operative, depending upon conditions. Anodic inhibitors are sometimes called "passivators" because they render the surface passive. When used in adequate concentrations, anodic inhibitors may completely prevent corrosion. They tend to decrease the effective surface areas of anodes, and the ratio

of cathode to anode areas increases. Thus, at low inhibitor concentrations, it is possible to obtain intense localized corrosion, resulting in pits. For this reason, anodic inhibitors are sometimes said to be dangerous to use, although they are generally considered to be more effective than cathodic inhibitors. Some typical anodic inhibitors are the chromates, alkali phosphates, carbonates, hydroxides, silicates, nitrites, tungstates, and molybdates.

**CATHODIC INHIBITORS** - Cathodic inhibitors function by forming insoluble hydroxides at cathodic areas or by direct adsorption. Inorganic inhibitors containing metal cations, which form insoluble hydroxides, fall in the first category, whereas organic inhibitors are more likely to function by adsorption. In either case, the resultant effect is a decrease in hydrogen evolution, due to resistance to passage of electric current.

Although cathodic inhibitors are generally less effective than anodic inhibitors, they are considered safer to use because they do not produce the intensified attack at local anodes. Some of the more common inorganic cathodic inhibitors are salts of magnesium, zinc, nickel, manganese, arsenic, antimony, and chromium. Calcium salts may act as cathodic inhibitors by precipitation of carbonate ion in waters containing carbon dioxide.

**GENERAL INHIBITORS** - A number of materials interfere with both anodic and cathodic reactions and are termed "general" inhibitors. Some common examples are glue, agar, and gelatin. Many organic polar compounds are now considered to function by general adsorption. Inhibitors may be truly soluble or colloiddally dispersed. The inhibitor reduces the inherent activity of the metal by attachment to the metal. This attachment is normally through the polar groups containing oxygen, sulfur, or nitrogen. Under these conditions, the inhibitor can function as a barrier, increasing the electrical resistance, or can augment the oxide formation.

The concentration of inhibitor needed to protect a metal

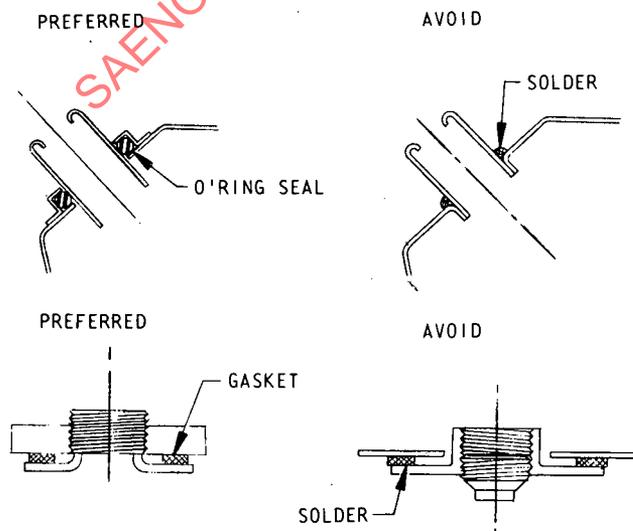


Fig. 11 - Principle 11

or alloy in a given environment depends upon such variables as the composition and temperature of the environment, velocity of the liquid, and presence or absence of galvanic couples. The concentration may vary from a few parts per million to several percent. Caution should be used with galvanic couples because passivation of one metal may increase the corrosion rate of the other, either through a change in cathode to anode ratio or a reversal in polarity.

A general inhibitor, which adsorbs to both cathodic and anodic areas, should be effective with galvanic couples. Crevices need special attention because replenishment may be more difficult. Corrosion deposits on the metal may screen the metal surface from the inhibitor and must be considered. Organic inhibitors should be stable both chemically and physically, in addition to being effective at low concentrations.

Inhibitors are used largely to protect ferrous metals and alloys, but are also effective for the protection of aluminum, magnesium, copper, brass, lead, zinc, and many other metals. Some of the principle uses for inhibitors are the protection of water supply systems, circulating water systems for cooling or air conditioning, steam condensate lines, metals exposed to acid solutions, engine cooling systems, and packaged metal products. Some of these applications are discussed in more detail in the following sections.

**WATER SYSTEMS** - The composition of water is one of the most important variables affecting the corrosion process in a water system. High concentration of dissolved materials can increase the conductivity of the solution, and certain ions interfere with the formation of protective films and the activity of the inhibitor.

Water systems may be open or closed recirculating systems or "once through" systems. Because the latter system uses considerably more water, it is not employed extensively. The type of system will govern to a degree the choice of method of corrosion prevention and the type of inhibitor.

Some of the commonly used inhibitors are sodium and potassium chromates, phosphates, and silicates. A high initial dosage is usually required in an open system when treatment is first started. This dosage may be reduced as a protective film develops on the metal surface. A higher dosage can be maintained in a closed system because none of the solution is lost.

Soda ash, caustic soda, lime alkaline phosphates, silicates, borates, and ammonia are materials used to neutralize acidity or control pH, but they do not necessarily eliminate corrosion. Sodium sulfite is sometimes used to remove traces of oxygen.

Sodium silicates are anodic inhibitors that provide protection by the surface action of metal ions with the silicate anion or by precipitation of negatively charged colloidal particles at anodic sites. Silicates effectively reduce flocculent rust and inhibit dezincification of brass. Although they require close pH control, they often provide effective inhibition.

Chromates function as anodic inhibitors and passivate the metal surface by aiding in the formation of an iron-oxide

film, which also includes some chromium oxide. Some organic chromates are also used, and they function in a similar manner.

Phosphates are anodic inhibitors that produce an iron phosphate at local anodes to assist in maintaining the oxide film. Polyphosphates, through their softening and sequestering action, prevent deposition of substance that might create potential differences at the metal surface. Thus, it helps to reduce pitting and tuberculation of steel pipes.

Polyphosphates are cathodic inhibitors in that positively charged colloidal particles migrate to cathodic areas and are neutralized. Consequently, they are effective with many galvanic couples. Polyphosphates can revert to orthophosphates, which are less effective and tend to produce sludge in the system. These inhibitors find many applications in boiler feed waters, cooling towers, and other processing operations.

Nitrites are used in some systems, but often in combination with another inhibitor. Nitrates are sometimes recommended for the protection of aluminum and stainless steel. Although organic inhibitors are effective, they are often disregarded because of their higher cost. Small amounts are sometimes used in combination with inorganic inhibitors, and they improve the efficiency by synergistic action. In any case, a balanced treatment is required for effective prevention of water system corrosion under the variety of conditions that exist.

**ACID SOLUTIONS** - Acid solution inhibitors belong to the group that functions as cathodic polarizers. They are used to control the rate of attack in pickling solutions, such as those used to remove mill scale and corrosion products in preparation for finishing. They are also effective with acid compounds used to clean boiler tubes, engine blocks and heads, heat exchangers, condensers, and industrial equipment.

Most commonly used materials are polar-organic compounds such as amines, mercaptans, aldehydes, unsaturated alcohols, and thioureas. The inhibitor may be soluble or dispersed, such as gelatin or glue. Size, shape, and degree of polarity of the molecule affect the degree of inhibition.

The effectiveness and type of inhibitor to be used will vary with the acid and with the metal to be protected. The acids must retain the ability to dissolve oxides or scale while at the same time reducing the rate of attack on the metal. In some acid solutions, inorganic inhibitors containing chromium, arsenic, or antimony function as effective inhibitors.

**PACKAGING INHIBITORS** - For many years the most commonly used materials were rust preventive compounds consisting of pastes, waxes, greases, and oils, which were applied by spraying, brushing, or "slushing." These materials function as barriers by excluding moisture from the metal surface, although many of the polar compounds incorporated in the formulated product are adsorbed by the metal surface and function by other inhibitive processes.

Typical examples of this type of material are alkaline earth metal salts of sulfonated petroleum derivatives, lead soaps or compounds, sorbitan monooleate, barium petroleum

sulfonates, alkenylsuccinic acid, and high molecular weight carboxylate salts.

In recent years the use of vapor corrosion inhibitors has become more widespread. These material permit immediate use of an object without necessity of removing oil or grease preservatives. They are thought to function by slow vaporization and transport of the vapor to the metal surface, where it is adsorbed or condensed. It is then available to be dissolved in moisture that may contact the surface and to function as a typical inhibitor. The method of vaporization and transport is somewhat in question. It has been claimed that the salt hydrolyzes and the products of hydrolysis vaporize and recombine during deposition.

Typical vapor inhibitor materials are amine salts of weak inorganic acids and amine-organic acid complexes. Examples are dicyclohexylammonium nitrite, dicyclohexylamine carbonates, and organic esters of carboxylic acids. VCI inhibitors are available for use in many forms: crystalline solids, alcohol solutions for spray applications, coatings on paper and other packaging materials, and in oil solution.

The inhibitors are most commonly used in closed systems, although they have been used in storage bins and in water rinse solutions for temporary protection. It is recommended that the inhibitor be no farther than 12 in. from any part of the metal surface to be protected. The effective life of these inhibitors depends on the rate of air flow over the inhibitor surface and temperature. These inhibitors are not effective against all contaminants nor even against fingerprints. They often have a detrimental effect on metals and alloys of zinc, magnesium, copper, brass, and cadmium. Although they are primarily used for the packaging of ferrous products, they have been sprayed into interior engine chambers for storage protection, and have been used as an additive to lubricant oils, to protect metals in the system during vehicle transport.

More recently, coated papers have become available for protection of nonferrous metals such as copper, aluminum, and silver. These metals do not normally function as vapor inhibitors, but must be in contact with the metal or act as a barrier. They often react with air contaminants to prevent their contact with the metal.

**ENGINE COOLANTS** - Coolant solutions used in the automotive engine are either water or a solution of water and an antifreeze. The antifreeze provides a suitable carrier for the inhibitor, but in its absence, the inhibitor must be added separately. The type of inhibitor used in the formulated antifreeze may vary substantially from that used for water inhibition. The choice of inhibitor for an antifreeze often depends upon its solubility in the concentrate.

The number and variety of metals involved in a cooling system require the use of more than one inhibitor to provide protection for all metals. Sodium nitrite is an excellent inhibitor for ferrous metals, but tends to accelerate the corrosion of solder; thus, other inhibitors must be added to complement its action and protect solder.

Typical examples of inorganic salts used for inhibition are sodium metaborate or tetraborate, sodium arsenite, so-

dium phosphates, sodium silicate, sodium benzonate, and sodium nitrite. Salts other than sodium salts are often used to increase the solubility in the antifreeze concentrate. Polar oils are sometimes used. They consist of a suitable mineral oil, containing an emulsifier, and polar type organic agents such as soaps, sulfonates, or sulfated fatty oils. The polar group is adsorbed by the metal surface, permitting the oil to function as a barrier. An organic compound, which is widely used in many formulations, is sodium mercaptobenzothiazol (NaMBT). It offers some protection to other metals, but is most specific for copper and brass.

The impurity level of chloride, sulfate, bicarbonate, cupric, and other ions in water used in automotive service can affect the concentration and type of inhibitor required as well as the life of the inhibitor. Corrosion products in the system lead to more rapid inhibitor depletion because of adsorption. For effective protection of an engine cooling system, good and continuous inhibition is essential.

**MISCELLANEOUS CORROSION INHIBITORS** - Air conditioning systems have used chromates, nitrites, orthophosphates, carbonates, and benzoates as inhibitors. These materials are anodic inhibitors and must be used in sufficient concentration to passivate all metals. Inhibitors are very often used in combination, such as silicate plus complex phosphate or hexametaphosphate plus chromate. It is necessary to maintain the pH within an appropriate range.

Steam condensate lines are protected by adjusting the pH with caustic soda or soda lime. Waste sulfite liquors (lignin) are sometimes used in these systems. Frequently, film forming amines are used, such as octadecylamine with ammonia or quaternary ammonium salts. A volatile amine such as morpholine has been used successfully. It is stable at high temperatures and vaporizes at low concentration in boiler water, condensing with initial condensates. Morpholine is also alkaline and neutralizes acidic compounds. Ethylenediamine and morpholine or ammonia and cyclohexylamine have been used in combination. Glucosates have also been used for boiler water treatment.

Inhibitors play an important part in priming paints. Zinc chromate pigment is used extensively. It is slightly soluble in water. Moisture that diffuses through the paint film dissolves some of the pigment, producing a concentration of chromate ions at the metal surface. Other corrosion inhibiting pigments are compounds of lead or zinc. Red lead is considered to inhibit by its alkaline nature. Other pigments include basic lead sulfate, white basic lead carbonate, basic lead chromate, zinc tetroxy chromate, zinc oxide, calcium plumbate, and combinations of these.

Sodium chromate and sodium nitrite have been used in the transport of gasoline, to protect the system against corrosion by condensed moisture. More recently, commercial oil-soluble corrosion inhibitors have been made available for this purpose.

#### CHEMICAL SURFACE TREATMENTS

The coating of metallic surfaces with a chemical surface treatment such as phosphate, oxide, and chromate has be-

come accepted commercial practice as a means of providing an increase in corrosion protection of the metal surface, either unpainted or as a base for paint.

In general, the metal surfaces should be cleaned prior to application of chemical surface treatment. The surface treatment must produce a coating or film that is continuous and adherent to the base metal, to provide the corrosion resistance of which it is capable. In order to obtain the maximum benefits of these coatings, soil such as grease, oil, wax, shop dirt, soldering and welding fluxes, and corrosion products such as rust, abrasives, scale, drawing compounds, active salts, and the like must be removed.

The soil removing operations, with accompanying rinses, are usually a part of the sequence of operations in the production of satisfactory chemical surface treatments. For more detailed information on chemical surface treatments see SAE Information Report, "Automotive Painting Practices -- SAE J761."

**PHOSPHATES** - Phosphate coating of metal surfaces is now widely used to

1. Provide rust resistance of iron and steel when used in conjunction with rust inhibiting oil.
2. Produce a corrosion resistant paint base for iron, steel, zinc, and aluminum.
3. Reduce wear and obtain corrosion resistance on bearing surfaces when used with lubricating oils, particularly during break-in of new parts.
4. Aid in cold forming of steel and aluminum in combination with organic lubricants.

**Nonmetallic** coatings of zinc, manganese, or iron phosphates are produced on clean metal surfaces from aqueous solution by spray or immersion. The main objective is to form a stable nonreactive coating chemically combined with the base metal which, by its absorptive crystalline nature, aids in providing a mechanical bond between the metal and oil, lubricant, or paint finish. When used with paint, it must retard spread of corrosion from breaks in the paint film and minimize paint blistering by forming a barrier between the metal and corrosive agents.

**Phosphate Coatings for Corrosion Protection** - Heavy phosphate coatings, when treated with corrosion inhibiting oils, give a synergistic effect in that the protection afforded by the combination is greater than that obtained by the sum of the two used separately. Zinc phosphate and manganese phosphate, when oiled, are used to give adequate protection for underparts of automobiles, such as nuts, bolts, brake pedal assemblies, accelerator levers, master cylinder plugs, accelerator brackets, hood latch yokes, hydraulic cylinder covers, and so forth.

All these heavy coatings are produced by immersing the cleaned articles in the hot processing solution for the required length of time. The weight of the coatings produced depends upon the manner in which the articles are cleaned, the composition of the processing bath, and the analysis and previous history of the steel or iron. Most coatings, however, that are used for corrosion protection have weights between 800 and 2500 mg/sq ft of surface area.

**Phosphate Coatings as Paint Base** - Conversion of metallic surfaces to phosphate coatings prior to application of paint finishes constitutes the major use of these coating materials. Two types of coatings are used as paint bases, namely, zinc phosphate and iron oxide/iron phosphate.

The zinc phosphate coatings are of medium weight, with coating weights in the range of 150-800 mg/sq ft of surface area. The solutions used are mainly zinc phosphate, containing various addition agents, and produce phosphate coatings not only on steel but also on zinc and aluminum. Methods of application are by spray, dip, and brush, at temperatures from 70-210 F, and processing times from 10 sec to 10 minutes. Most automobile bodies and sheet metal parts are coated with the zinc phosphate type of coating prior to painting.

The iron oxide/iron phosphate coatings are relatively light in weight and range from 25 to 90 mg/sq ft of surface area. They are thin and dense, with an amorphous structure. Steel surfaces may be both spray cleaned and coated in the same solution by combining a synthetic detergent with the coating material. Auto interior trim parts such as instrument panels or steering posts, and truck cabs, fenders, and hoods, represent items that are processed by this type of treatment.

**Phosphate Coatings for Wear Resistance** - Phosphate coatings, particularly manganese phosphate, reduce wear on bearing surfaces by acting as a medium to hold lubricating oils in a continuous film between moving metal parts. Parts that are representative of this type of application are pistons, piston rings, cylinder liners, valve tappets, camshafts, gears, and the like. Corrosion resistance is also imparted to these items by this heavy phosphate treatment.

**Phosphate Coatings as Aid in Cold Forming of Metal** - Another important field of application, although not primarily for corrosion resistance, is the phosphate coating of steel and aluminum, subsequently treated with an organic lubricant to aid in the cold forming and extrusion of these metals. Zinc phosphate is commonly used. Some of the automotive parts now being produced by this means are bumper bars and guards, tubing, truck wheels, transmission drive shafts, housing, brake drums, and frames.

#### OXIDES

**Black Oxide on Steel** - The black oxide type of surface treatment is used to produce an attractive black appearance on steel articles, with little increase in corrosion resistance. The oxide coating can be produced with slight dimensional change of the part being treated. This coating has a property of holding oils and waxes, and may be suitable for a variety of applications, including bearings, gages, aircraft engine parts, and machine compounds. They are now used in the automotive field on spark plug shells, bolts and nuts, and bearing separators or retainers.

The most commonly used method of forming the coating is the aqueous alkali/nitrate method. The clean metal part is immersed in a strong alkaline solution containing oxidizing agents and other additives, which at temperatures up to approximately 300 F produces the blackening effect.

**Anodic Coating on Aluminum** - The electrolytic oxide finish on aluminum, produced by an anodic treatment, is a dense, thin, durable aluminum oxide on the metal surface, which offers good abrasion and corrosion protection. These films possess excellent absorption qualities for paints and dyes.

The process of anodizing is carried on by making the aluminum the anode in an electrolyte that yields oxygen upon electrolysis. Chromic and sulfuric acid anodizing processes are the most commonly used in industry. The porous oxide film produced by either of these processes must be sealed by immersion in hot water, chromate, nickel acetate, or silicate solutions, to increase the protective value of the oxide. Anodic treatment of pure aluminum gives the best protection. Anodized hydraulic cylinders, pistons, grills, and window moldings illustrate the use of the anodic treatment in the automotive field.

The anodic coating may be dyed and then sealed, to produce colored aluminum. Films produced from the sulfuric acid process are most satisfactory for dye treatment.

**Oxide-Chromate Coatings on Aluminum** - Short time treatments for aluminum have been developed for sheet, castings, forgings, extruded, and rolled structural forms.

These films produce good corrosion resistance for unpainted surfaces, and are also bases for paint. The coatings, which are thin and iridescent, are formed at room temperature without electricity by spray, immersion, or brush application. These amorphous oxide-chromate films are flexible and can withstand moderate draws without trouble. There is no appreciable dimensional change in the article being treated. Coated metal parts can be both arc and spot welded.

#### CHROMATES

**Chromate Coatings for Zinc and Cadmium** - Chromate coatings materially aid in preparation of zinc and cadmium as bases for paint. Nonmetallic chromates prevent the metal from reacting chemically with the fatty acids in the paint vehicles. Chromate treatments are also used to retard "white rusting" of unpainted metal and to color the surface for decorative purposes.

Most of the commercial processes are applied by immersing the cleaned metal in the chromate bearing solution for a short time at room temperature. The gelatinous film that is deposited is considered to be a basic chromium chromate.

It tends to become harder and more adherent during rinsing and subsequent exposure to its environment. The film is thin, iridescent, and produces very little change in dimensions of the article treated. Abrasion resistance is usually low.

Zinc die cast carburetors, lock cylinder assemblies, and fuel pumps illustrate automotive items that may be chromate treated.

**COATINGS FOR MAGNESIUM** - In general, two classes of treatments for preparation of magnesium alloy surfaces for painting are in current use: chemical treatments, class I; and anodic treatments, class II. The class II treatments are considered the more protective of the two. Generally any of these coatings are applied to surfaces previously freed from all contamination.

The various cleaning methods include mechanical (abrasive) treatments, solvent cleaning, alkaline solution treatments, and acid pickles not resulting in protective conversion coatings, and are suitable preliminary treatments. Such cleaned surfaces will stand only mildly corrosive indoor exposure. When the highest degree of corrosion protection is desired, as in many outdoor environments, surface preparation by one of the conversion coat classes is necessary.

ASTM designation D 1732-60T "Preparation of Magnesium Alloy for Painting," describes the treatments and methods available.

**Evaluation Tests** - The accelerated tests, which are most commonly used for evaluating chemical surface treatments, are salt spray, humidity, and water soak, all at physical and outdoor exposure at selected locations. Government and ASTM methods that cover the conditions of these tests are given in Table 1.

Proper chemical control of all surface treatment solutions and good maintenance of equipment are prerequisites to obtaining satisfactory results. Painted articles in particular should be checked in salt spray and humidity on a frequent and regularly scheduled basis, to detect both improper operation of the chemical surface treatment system and contamination of the coated surface prior to application of paint.

#### PAINTS, LACQUERS, AND ENAMELS

In the protection of iron and steel against corrosion, probably the most important item is the organic coating generally referred to as "paint."

Paint may be divided roughly into three classifications: paint, lacquer, and enamel. While these three names originally were descriptive of three definite types of materials, modifications in formulation to improve properties has removed any fine line of distinction among the three.

Originally, paint was made from natural gums and oils, with pigments added to give the desired color. It dried to a hard film by oxidation. Today, paint is made using a number of different resins, both natural and synthetic, including asphaltic type materials and latex.

The first lacquers were based almost entirely on nitrocellulose, with some natural gum added. They dried by sim-

Table 1 - Conditions of Evaluation Tests

Salt Spray, 5% NaCl	ASTM B 117
20% NaCl	ASTM B 117-49T
5 or 20% NaCl Federal Specification	QQ-M-151
Water Immersion	ASTM D 870
Conical Mandrel	ASTM D 522
Preparation of Steel Panels for Testing	ASTM D 609
Conducting Exterior Exposure Tests	
of Paint on Steel	ASTM D 1014
General Testing	Federal Spec. TT-P-141-B

ple evaporation of the solvents. Improvements were made in nitrocellulose lacquers in the middle 1930s, by substituting synthetic resins for the natural resins. Although they dried to the touch in a matter of minutes, they obtained best durability by force drying at moderately elevated temperatures for a short time. Acrylic lacquers are the newest type of lacquers and are extensively used by the automotive industry because they exhibit excellent durability, both in the pigmented and unpigmented state. The acrylics require that the undercoat be of such a nature that it will not permit or promote migration of the plasticizer from the acrylic into the undercoat.

Oldtime enamels were made from natural gums or resins so formulated that they would dry with a high luster. Pigments were added for color. Hours were required for drying. Enamels in use today are made from synthetic resins, and for best durability, they should be baked at somewhat higher temperatures and for a longer time than lacquer.

All three types of organic coatings are used in protecting the iron and steel parts on automobiles. For example, asphaltic base paints are used on frames and chassis parts that are not easily seen and therefore need not be decorative in quality.

Enamels and lacquers are used in approximately equal amounts for protecting and beautifying the exterior parts of motor cars produced in the United States. There are advantages and disadvantages in both types of materials.

Enamel requires a higher baking temperature for a longer time than lacquer. This shows to a decided advantage for lacquer when masking and taping for two-tone painting operations on bodies. Since lacquer dries to the touch in a few minutes, it can be taped and the second color applied without a baking operation. The rapid drying of lacquer and the fact that most of the drying of lacquer comes from evaporation of solvents, rather than by oxidation, makes repair operations, both in the plant and in the field, much simpler.

Lacquer dries with a lower luster than enamels, and therefore must be polished to produce the desired gloss. This adds to the cost. However, this polishing removes the "orange peel" or rough appearance present in all sprayed films. The polishing of lacquer can produce "thin spots," which lack the durability of a normal film. Recent improvements made in acrylic lacquers makes it possible to produce a high initial luster (without polishing) by baking the acrylic lacquer at elevated temperatures.

It is not good practice in painting exterior parts where long time protection is required to apply either lacquer or enamel directly to bare metal. To gain good adhesion, a primer should be used. Primers can be oleoresinous or synthetic resin type. Baked primers perform better than air dried primers.

Where rough metal is used and a smooth finish is desired, a surfacer or glaze must be used over the primer. This, too, can be oleoresinous or synthetic resin type and should also be baked. The surfacer is sanded before the application of the lacquer or enamel. In some cases the properties of the

primer and surfacer are combined in one material known as a primer surfacer.

All metal to be painted must be free of dirt, oil, grease, drawing compounds, soldering flux, or other contaminants. Coating the metal with a phosphate coating gives added protection.

Care should always be taken in all painting operations to prevent operators from placing hands on parts in process. Perspiration and grease from the hands can cause serious failures in service.

Many special types of paints, such as wrinkle and spatter finishes, are used, but these generally fall into the class of enamels or lacquers, and should be treated as such.

More complete information on automotive painting practices can be obtained by referring to SAE J761, "Automotive Painting Practices."

## METALLIC COATINGS

**ELECTROPLATED COATINGS** (See also SAE J474, "Electroplating Practice") - Ferrous and nonferrous metals may be protected against corrosion by the application of thin films of metals more resistant to corrosion than the base metal. Electroplating is generally the method used for applying such films after forming or fabricating the part. Pre-plated sheets are also finding increased applications.

In many applications it is difficult to separate the protective and decorative functions of such electrodeposited coatings. On any components that are visible, a pleasing appearance of lasting quality is a prime requisite. Many such articles are also subject to wear and abrasion in varying degrees. Thus, the physical properties of the film are important in selecting the proper combination for maintaining appearance under varying conditions of wear and corrosion.

Protective and Decorative Coatings - Combinations of copper, nickel, and chromium are the electroplated coatings most widely used for protection against corrosion and wear when a bright appearance is also required. These coatings protect by providing a barrier that prevents contact of underlying metal with corrosive elements. In some combinations one layer may be sacrificial to another, but the net effect is to have an impervious barrier for the base metal.

The production of these films involves many factors, such as preparation of base metal; composition, thickness, and adhesion of each film; the physical properties of the layer (brittleness, crack pattern, and so forth).

While thickness of film is still used in specifications, it is not in itself sufficient to ensure satisfactory performance. The degree of protection depends on the particular combination; thus, duplex nickel is better than most single films of nickel at the same thickness. The type of chromium and whether it is used as a single or duplex coating is also important. The specified thickness usually refers to a minimum required on significant areas. The thickness of the

film on other areas may be greater, owing to inherent characteristics of plating processes.

While these films usually fail by pitting, some have a tendency to blister. The blisters may form between the base metal and the deposited coating, or they may form between the layers of the deposited coating. Typical components using copper-nickel-chromium and nickel-chromium are bumpers and bumper guards, grills, handles and knobs, bezels and locks, lamp rims and housings, and hub caps and wheel discs.

Originally, chromium was used on stainless steel only to improve the color match with plated parts, but service experience has shown that it increases corrosion protection. Typical components for this application are wheel discs, mouldings, and window channels.

Protective Coatings - Many functional components must be protected against corrosion without the need for pleasing appearance. In some cases sufficient protection can be obtained by electroplating zinc, cadmium, tin, or lead. Zinc and cadmium protect steel by a different mechanism than does copper-nickel-chromium alloy, because they are anodic to the underlying metal and prevent corrosion adjacent to the coating by sacrificial action. This effect, plus the fact that zinc and cadmium are plated more uniformly, makes it possible for thin coatings to give good protection in mild and moderately severe corrosive environments.

Although these coatings may be deposited with a bright pleasing appearance, they tend to become dull and dark on exposure. Cadmium shows less tendency than zinc to do this. This tendency can be overcome to some extent by the application of chemical surface treatments, but the permanence of appearance is not comparable with that of a chromium finish.

It is difficult to deposit zinc on cast and malleable iron and high carbon steel surfaces; cadmium is therefore preferred for such applications. Zinc plating process are much more prone to cause hydrogen embrittlement of high carbon steel components, such as springs. When such articles are plated with zinc or cadmium, a baking operation is necessary to relieve hydrogen embrittlement.

Zinc is sometimes applied to stampings, to which an organic coating is subsequently applied. Chemical surface treatment of the zinc surface is necessary to ensure adhesion of the organic coating. Since zinc is usually cheaper to plate than cadmium, it is generally preferred. When plated in equal thicknesses, the protective values of the two metals are approximately equal except in marine exposures, where cadmium is superior.

The following list includes typical components on which zinc and cadmium are used:

1. Nuts, bolts, screws, and miscellaneous fasteners.
2. Hinges.
3. Concealed lock parts.
4. Concealed mechanical linkages.
5. Ash tray boxes.
6. Lock washers (cadmium preferred).
7. Springs (cadmium preferred).

8. Electrical contacts (cadmium).

9. Floating vibration dampeners (cadmium).

10. Electrical equipment parts and housings.

11. Closed section doors (zinc plated mill stock).

12. Steel, copper, and brass parts used in contact with aluminum (cadmium preferred).

Electrodeposited lead coatings must be classed as purely protective. Lead coatings have been used on fasteners as an alternate to zinc and cadmium, but they are particularly adaptable to parts located in the immediate vicinity of a lead storage battery, such as copper battery connector cables. A minimum thickness of 0.001 in. is suggested.

Tin is electroplated for protection of certain fuel system parts because some plated coatings catalyze gum formation. It is also plated on steel backed bearing shells for temporary protection. Tin or cadmium plate may be used where both protection and solderability are of importance.

Tests for Electroplated Coatings - Two new accelerated corrosion tests have been developed by AES Research Committee, Project 15, and have been adopted as standards by ASTM. These are the CASS test (ASTM B368) and the CORRODKOTE (ASTM B380). These have generally replaced the neutral salt spray test (B117) for rapidly evaluating copper-nickel-chromium electroplated coating systems over steel and zinc base die castings. These two tests have been valuable for revealing effects of variations in plating practices. Results are obtained in 24 hr or less instead of over 100 hr for neutral salt spray. Good correlation has been obtained in comparing the results of the CASS and CORRODKOTE tests to results obtained on copper-nickel-chromium plated parts of automobiles driven in the Detroit area.

For methods of measuring local thickness, refer to ASTM 219, "Method of Test for Local Thickness of Electrodeposited Coatings."

Cost and Design Considerations - Mechanical, chemical, or electrochemical finishing of an article to be plated may be a large part of the total finishing cost. Many of the metals discussed can be plated bright, and surface roughness can be decreased by the use of certain copper and nickel plating processes. However, in general, the appearance of a plated coating is largely dependent on the surface prior to plating. The smoother the finish, and the greater the protection required, the more costly is the finishing operation.

Design of an article to be plated can have a tremendous effect on the ability to deposit a given minimum thickness of plate and on the associated finishing costs. Avoidance of holes, deep recesses, and sharp internal angles on significant surfaces is a prime requisite.

**CHEMICALLY REDUCED METALLIC COATINGS** - Metal coatings can be deposited from solution by chemical reduction. A familiar example is the silvering of mirrors.

A process for the deposition of nickel by chemical reduction has limited use. The specific advantage of the process is that the thickness of the metal coating is uniform, regardless of the contour of the article being coated. Surfaces of holes, interiors, and recesses that would be impractical