

SURFACE VEHICLE INFORMATION REPORT

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(R) PREVENTION OF CORROSION OF MOTOR VEHICLE BODY AND CHASSIS COMPONENTS

Foreword—Prevention of corrosion is an important design consideration for metals used in body and chassis components. In some cases, corrosion resistance may be the dominating factor governing the selection of material or process; in others, it will be secondary to manufacturing feasibility, appearance requirements, and availability. 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 decade, corrosion problems have been recognized as ones of primary importance. Components experiencing the most severe corrosion are those exposed to road splash thrown up by the wheels. Salt and mud poultices 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 free from prolonged contact with salt and mud. Therefore, the owner can help prevent corrosion by washing the vehicle, including the underbody, particularly during periods of high salt exposure.

This report 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. 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 equally suitable for typical classes of parts, and the choice 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 establishing suitable specifications, process controls, and acceptance tests.

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

- a. Moisture
- b. Temperature
- c. Salt
- d. Galvanic Couples
- e. Abrasion

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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 severe 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 parts may be satisfied by a combination of the following:

- a. Selection of material
- b. Design considerations
- c. 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 required for 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 test.

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1. Scope—This SAE Information Report provides automotive engineers with the basic principles of corrosion, design guidelines to minimize corrosion, and a review of the various materials, treatments, and processes available to inhibit corrosion of both decorative and functional body and chassis components.

2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein. The latest issue of SAE publications shall apply.

2.1.1 SAE PUBLICATIONS—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE PAPER 912275—Proc. Automotive Corros. and Prevention Conference, Townsend, H. E., et al., 1991, p. 73

SAE Paper 912278—Lutze, F. and Shaffer, R. J., *ibid.*, p. 115

SAE Paper 912283—Petschel, M., *ibid.*, p. 179

SAE Paper 912284—Davidson, D. D. and Schumacher, W. A., *ibid.*, p. 205

SAE Paper 912285—Roudabush, L. A. and Dorsett, T. E., *ibid.*, p. 221

SAE Paper 912291—Roberto, O. E. and Hart, R. G., *ibid.*, p. 289

SAE Paper 950375—Simpson, T.C., Bryant, A.W., Hook, G., Daley, R.A., Swinko, R.J., and Miller, R.W.

2.1.2 ASTM PUBLICATIONS—Available from ASTM, 100 Bar Harbor St., Philadelphia, PA 19103-1187.

ASTM B 110—Dielectric Strength

ASTM B 117—Test Method of Salt Spray (Fog) Testing

ASTM B 136—Stain Resistance

ASTM B 137—Coating Weight

ASTM B 177—Practice for Chromium Electroplating on Steel for Engineering Use

ASTM B 183—Practice for Preparation of Low Carbon Steel for Electroplating

ASTM B 200—Specification of Electrodeposited Coatings of Lead and Lead-Tin Alloys on Steel and Ferrous Alloys

ASTM B 242—Practice for Preparation of High-Carbon Steel for Electroplating

ASTM B 252—Practice for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coating

ASTM B 253—Guide for Preparation of Aluminum Alloys for Electroplating

ASTM B 254—Practice for Preparation of and Electroplating on Stainless Steel

ASTM B 281—Practice for Preparation of Copper and Copper-Base Alloys for Electroplating and Conversion Coatings

ASTM B 320—Practice for Preparation of Iron Castings for Electroplating

ASTM B 322—Practice for Cleaning Metals Prior to Electroplating

ASTM B 368—Method for Copper-Accelerated Acetic Acid-Salt Fog Testing (CASS Test)

ASTM B 380—Methods for Corrosion Testing of Decorative Chromium Electroplating by the Corrodokote Procedure
 ASTM B 456—Specification for Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium
 ASTM B 487—Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross Section
 ASTM B 499—Test Method for Measurement of Coating Thickness by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals
 ASTM B 504—Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method
 ASTM B 530—Method for Measurement of Coating Thickness by the Magnetic Method: Electrodeposited Nickel Coatings on Magnetic and Nonmagnetic Substrates

2.1.3 SME PUBLICATIONS—Available from SME, P.O. Box 930, 1 SME Drive, Dearborn, MI 48121.

2.1.3.1 *SME Paper FC91-371* Jones, T.C., Proc. Finishing '91, 1991

2.1.3.2 Jones, T. C., The Finishing Line, SME, Third Quarter 1990, p. 1

2.1.3.3 User's Guide to Powder Coating, 2nd Edition," SME, 1987, Chapter 5, p. 55

2.1.4 OTHER PUBLICATIONS

2.1.4.1 Annual Statistical Report 1990, American Iron and Steel Institute, Washington, DC (1991), pp. 25–27

2.1.4.2 A. W. Bryant, L. M. Thompson, and W. C. Oldenburg, "U.S. Automotive Corrosion Trends at 5 and 6 Years," Automotive Corrosion and Prevention Conference Proceedings, P 228, L. Allegra, ed., Society of Automotive Engineers, Warrendale, PA (1989), p. 185

2.1.4.3 H. E. Gannon, ed., "The Making, Shaping, and Treating of Steel," 10th edition, United States Steel Corporation

2.1.4.4 H. E. Townsend, "Coated Steel Sheets for Corrosion-Resistant Automobiles," Materials Performance, October 1991, p. 60; National Association of Corrosion Engineers, Corrosion '91, Paper 91416, NACE, Houston, TX

2.1.4.5 Y. Miyoshi, "State of the Art in Precoated Steel Sheet for Automotive Body Materials in Japan," ISIJ International, 31, 1, 1991, p. 1

2.1.4.6 D. Quantin, D. Deparis, and J. C. Charbonnier, "Coated Steel Sheets for the Automotive Industry," Steel Technology International, 1990/1991, p. 245

2.1.4.7 K. Yamoto, T. Ichida, and T. Irie, "Progress in Precoated Steel Sheets for Automotive Use," Kawasaki Steel Technical Report, #22, May 1990, p. 57

2.1.4.8 "Cracking Down on Corrosion," American Iron and Steel Institute, Washington, DC, 1991

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2.1.4.10 L. W. Austin and J. H. Lindsay, "Continuous Steel Strip Electroplating," American Electroplaters and Surface Finishers Society Press, Orlando, FL, 1989

2.1.4.11 R. Baboian, "Causes and Effects of Corrosion Relating to Exterior Trim on Automobiles," Proceedings of the 2nd Automotive Corrosion and Prevention Conference, P-136, SAE, Warrendale, PA.

2.2 Related Publications—The following publications are provided for information purposes only and are not a required part of this document.

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- U. R. Evans, "The Corrosion and Oxidation of Metals," London, England, Edward Arnold, Ltd., 1960
- F. T. Laque and H. R. Copson, "Corrosion Resistance of Metals and Alloys," New York, NY, Reinhold Publishing Co., 1963
- N. D. Tomoshov, "Theory of Corrosion and Protection of Metals," New York, NY, Macmillan, 1966
- W. H. Ailor, Editor, "Handbook on Corrosion Testing and Evaluation," New York, NY, John Wiley & Sons, Inc., 1971
- "NACE Basic Corrosion Course," Houston, TX, National Association of Corrosion Engineers, 1971
- M. G. Fontana and N. D. Greene, "Corrosion Engineering," New York, NY, McGraw-Hill, 1967
- "Localized Corrosion—Cause of Metal Failure," STP 516, Philadelphia, PA, American Society for Testing and materials, 1972
- L. C. Rowe, "The Prevention of Galvanic Corrosion in Bimetallic Assemblies," SAE Paper 740101, presented at SAE Automotive Engineering Congress, Detroit, MI, 1974
- H. P. Godard, W. P. Jepson, M. R. Bothwell, and R. L. Kane, "The Corrosion of Light Metals," New York, NY, John Wiley & Sons, Inc., 1976
- H. Leidheiser, Jr., "The Corrosion of Copper, Tin, and Their Alloys," New York, NY, John Wiley & Sons, Inc., 1971
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- H. H. Uhlig, Editor, "Corrosion Handbook," New York, NY, John Wiley & Sons, Inc., 1948
- C. J. Slunder and W. K. Boyd, "Zinc: Its Corrosion Resistance," New York, NY, Zinc Institute, Inc., 1971
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- H. Suss, "Stress Corrosion—Causes and Cures," Materials in Design Engineering, 61, 102 (1965), April
- R. T. Knapp, J. W. Daily, and F. G. Hammitt, "Cavitation," McGraw-Hill, Inc., New York, NY, 1970

L. C. Rowe, "The Application of Corrosion Principles to Engineering Design," SAE Paper 770292 presented at SAE Automotive Engineering Congress, Detroit, MI, 1977

A. W. Bryant, "Designing Body Panels for Corrosion Prevention," SAE Paper 780916 presented at SAE Conference on Designing for Automotive Corrosion Prevention," Troy, MI, November 1978

Proceedings P-78, SAE Conference on Designing for Automotive Corrosion Prevention, November 1978

R. Dietz, "Design Characteristics and Constructional Features to Minimize Corrosion Sensitivity of Automobiles," NACE Paper 48 presented at NACE Corrosion 88, St. Louis, MO, March 1988

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R. Baboian, "Chemistry and Corrosivity of the Automotive Environment," in Designing for Corrosion Prevention, SAE, Warrendale, PA 1978.

R. Baboian, "Materials Degradation Caused by Acid Rain," American Chemical Society, Washington, DC 1986.

3. Definitions

3.1 Acid—Acids can be defined in several ways. For many purposes it is sufficient to say that an acid is a hydrogen containing substance which dissociates on solution in water to produce one or more hydrogen ions. The Bronsted concept states that an acid is any compound that can furnish a proton. The more general Lewis definition of an acid is anything that can attach itself to something with an unshared pair of electrons.

3.2 Acidic—For aqueous solutions, anything having a pH that is less than 7 is considered acidic.

3.3 Alkaline—For aqueous solutions, anything having a pH that is greater than 7 is considered alkaline.

3.4 Anodic Coating—A coating that is anodic to the underlying substrate. Anodic coatings offer sacrificial protection to the substrate.

3.5 Barrier Protection—A type of protection that relies on the coating preventing access of moisture or oxygen to the material being protected. Organic coatings often offer barrier protection to underlying substrates.

3.6 Base—Bases can be defined in several ways. For many purposes it is sufficient to say that a base is a substance which dissociates on solution in water to produce one or more hydroxyl ions. The Bronsted concept states that a base is any compound that can accept a proton. The more general Lewis definition of a base is anything that has an unshared pair of electrons.

3.7 Basic—For aqueous solutions, anything having a pH that is greater than 7 is considered basic.

3.8 Blister—A region of lifted paint typically caused by loss of adhesion within the paint system or between the paint and metal surface.

3.9 Cathodic Delamination—Type of corrosion damage caused by loss of adhesion between the paint finish and the metal.

3.10 Cathodic Coating—A coating that is cathodic to the underlying substrate.

- 3.11 Cavitation Corrosion**—Cavitation Corrosion occurs on the low pressure side of propellers and pump impellers where interruption in smooth flow causes vapor bubbles to form. When these bubbles collapse, they can destroy any protective coating and remove minute particles of metal.
- 3.12 Chromated**—Parts treated with chromic acid to improve their corrosion resistance.
- 3.13 Clearcoat**—A paint without pigment applied over a color basecoat to enhance the appearance and durability of the total paint system.
- 3.14 Cosmetic Corrosion**—Corrosion typically characterized by blistering and/or rusting that is aesthetically displeasing, but does not result in catastrophic failure of the item.
- 3.15 Creepback**—The undercutting or the separation of paint from the substrate at an edge, damage site, or a scribe line.
- 3.16 Current**—The "flow" of electricity expressed in amperes, milliamperes and microamperes.
- 3.17 Cyclic Testing**—Accelerated testing and simulation of service conditions by the use of controlled alternating exposures to at least two corrosive environments, such as salt or other chemical exposure, water immersion, temperature variations, humidity variations, ultraviolet (UV) light exposure, mud or clay contamination, gravel or shot blasting, and driving.
- 3.18 Current Density**—The current per unit area; generally expressed as amps per sq cm.
- 3.19 Deicing Salt**—Salts, typically NaCl and/or CaCl₂, applied to highways to aid in seasonal deicing.
- 3.20 Deionized Water**—Water that has had the charged species (Cl⁻, Ca²⁺, etc.) removed from it.
- 3.21 Diffusion**—The movement of one substance through another. Diffusion of contaminants into a paint system is often the cause of corrosion attack.
- 3.22 Differentially Zinc Coated**—A sheet (usually steel) with a zinc coating of a different thickness on one side than on the other side.
- 3.23 Dip-Spin**—A process using a perforated basket in which parts are placed to be dipped into an organic/inorganic finish, spun to remove excess coating then normally placed in an oven to cure the finish.
- 3.24 Electrochemical Reaction**—A chemical reaction which is driven by a difference in electrode potential from one site to another on the same or different parts.
- 3.25 Electrocoat, E-coat, ELPO**—A coating for metals deposited by the application of high voltages between an anode and a cathode in an electrolyte. Cathodic electrocoating is commonly used in the automotive industry.
- 3.26 Electrogalvanized**—Steel containing a zinc coating produced by continuously electroplating zinc onto the steel surface.
- 3.27 Electroplated Coatings**—Coatings applied in a low temperature continuous process where negatively charged steel sheet is passed between positively charged anodes. Metallic ions in an electrolyte bath are reduced and plated on the surface of the steel sheet forming the coating.
- 3.28 Flash Coating**—A very thin coating of paint or plating applied to provide limited corrosion protection or to improve the adhesion of subsequent coatings.

- 3.29 Hot Dip Galvanized**—Steel containing a zinc coating produced by immersion of the steel in a molten zinc bath.
- 3.30 Galvanneal**—Steel containing a zinc/iron alloy coating produced by the hot-dip process.
- 3.31 Gravelometer**—Machine used to cause consistent intentional paint damage to samples prior to or during laboratory corrosion testing. A gravelometer propels gravel or metal shot of a particular size and shape at the surface of a painted test specimen. The gravelometer is used to simulate the type of field paint damage caused by gravel or other road debris.
- 3.32 Hem Flange**—A method of joining two pieces of metal together in which the edge of one piece is folded tightly over the edge of the other.
- 3.33 Hot-Dip Coating**—A continuous process of applying coatings to steel in which the steel is immersed in a molten bath of the material to be coated.
- 3.34 Inside-Out Corrosion**—Corrosion that starts from the inside surface of a body panel and works outward.
- 3.35 Localized Corrosion**—Corrosion resulting in differential attack across a metallic surface. Localized corrosion is typically of a cosmetic nature, but can lead to catastrophic failure if a primary structural component is the site of severe attack.
- 3.36 Neutral**—In aqueous solutions, a substance having a pH of 7 is considered neutral.
- 3.37 Organic Coatings**—Coatings, primarily paints, applied to metallic or other substrates typically to provide corrosion protection and to improve aesthetic characteristics of the material.
- 3.38 Outside-In Corrosion**—Corrosion that starts from the outside surface of a body panel and works inward.
- 3.39 Perforation Corrosion**—Penetration of a panel due to corrosion. Perforation corrosion is usually associated with inside-out corrosion.
- 3.40 Phosphate Coatings**—Protective coatings formed by reaction of a metallic substrate with an acidic phosphate containing solution. The primary role of the phosphate coating is to enhance adhesion of the primer (electrocoat or other) to the metal. Phosphate coatings are typically Zn, Fe, Zn-Ni, or Zn-Ni-Mn phosphates.
- 3.41 Pitting Corrosion**—A type of perforation corrosion. Pitting corrosion is highly localized corrosion resulting in deep penetration at only a few spots.
- 3.42 Potential**—See electrochemical potential.
- 3.43 Poultice**—An accumulation of mud, sand, salt, and other road debris on the interior surface joints of body panels and structural components.
- 3.44 Pre-coated**—A material that has been coated prior to the manufacture of the ware or part.
- 3.45 Pre-treatment**—The treatment of a surface prior to the process of interest, for example: a phosphate coating is a pre-treatment for electrocoat or painting.
- 3.46 Proving Ground Tests**—Cyclical programs primarily conducted by the automotive companies to evaluate the effects of corrosive elements on the performance of fully assembled vehicles. Proving Ground Tests often combine on-road exposures with exposures in environmental chambers.
- 3.47 Reaction Cell**—A cell at which a chemical reaction is occurring.

- 3.48 Rust Proofing**—The application of coatings intended to prevent or greatly reduce the formation of rust on steel parts.
- 3.49 Saponification Corrosion**—Formation of a soap by the reaction of corrosion products with some organic coatings.
- 3.50 Scab Corrosion**—Cosmetic corrosion caused by break down of the surface protection system often preceded by blisters.
- 3.51 Scribe**—An intentional paint damage typically used for material evaluation during corrosion testing.
- 3.52 Sealers**—Products applied to joints or seams to prevent the entry of moisture or contaminants. Paint coatings applied to prevent the undesirable interaction of a subsequent coating with a previous coating or to enhance adhesion or corrosion protection.
- 3.53 Undercutting**—See Creepback
- 3.54 Uniform Corrosion**—Corrosion which occurs uniformly on the surface of a part. Uniform corrosion is not associated with joints and is not pitting.

4. Chapter 1—Principles of Corrosion

- 4.1 Electrochemical Theory**—Corrosion in the broad sense is accepted as the deterioration of any material because of a reaction with its environment, which means that materials such as plastics, ceramics, concrete, glass, and many others would be included in that definition. Most often, however, corrosion is associated with the deterioration of metals and alloys. The processes involved with corrosion of metals and alloys are predominantly electrochemical. An electrochemical process is one that involves a transfer of electrons in an oxidation-reduction reaction. Corrosion by direct chemical reaction (which does not involve a transfer of electrons) and hot corrosion (which involves high-temperature gases or molten salts) will not be discussed here.

The principle of electrochemical corrosion is the same as that involved with the functioning of a dry cell battery, which contains a graphite cathode¹ and a zinc anode in contact with a conductive solution (electrolyte). When the two electrodes are connected with an electrically conductive material, current will flow between them because of the difference in their oxidation-reduction (electrical) potentials. This current flow gradually destroys the anode. The degree of destruction depends upon the total amount of current flow. Faraday's law states it another way: "The mass of a substance liberated in an electrolytic cell is proportional to the quantity of electricity passing through the cell." These concepts of anode-cathode relationships and current flow are fundamental to understanding electrochemical corrosion.

The three essential parts of a corrosion cell are: (a) an anode, (b) a cathode, and (c) a conductive solution called an electrolyte. If any one part is missing, or if there is an interruption in the electrical path, current cannot flow and electrochemical corrosion cannot occur. Figure 1 shows how the current flows in a corroding system.

1. Because of convention, the graphite rod carries the "+" (positive) designation in the typical dry cell battery. Electrochemically, it is the cathode and carries the "-" (negative) designation.

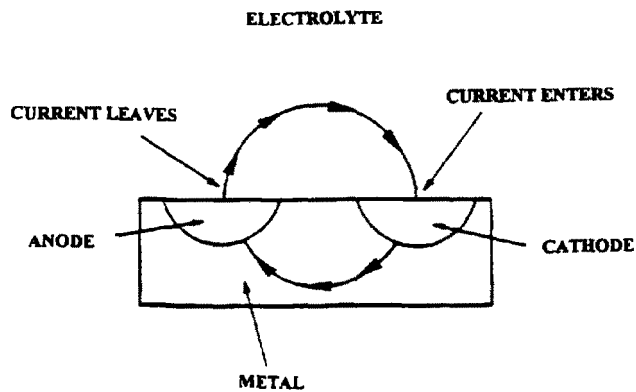
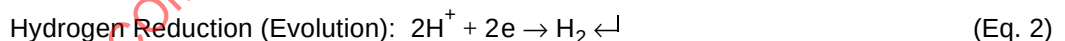


FIGURE 1—CURRENT FLOW IN A CORRODING SYSTEM

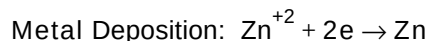
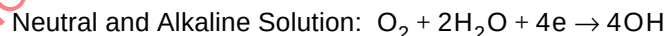
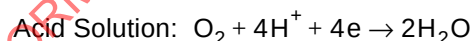
When a metal corrodes, oxidation occurs at the anode, which loses electrons, and reduction occurs at the cathode, which gains electrons. The direction of flow of electrons is the opposite to the current flow. The reactions at the anode and cathode are called half-cell reactions, and both must occur for corrosion to occur. They can occur on the same metal surface or on separated metal surfaces, provided there is some form of metallic contact between the surfaces and they share a common electrolyte. Some typical half-cell reactions for the anodic process are shown as follows:



When iron corrodes, ferrous ions (Fe^{++}) are found at the anode by the oxidation of the iron metal. Eventually, they are further oxidized at ferric ions that combine with oxygen and water to form hydrated ferric oxide (rust). The electrons lost at the anode are transported to the cathode, which allows the reduction reaction to take place. Half-cell reactions for the cathode process vary with the environment and involve consumption of electrons as shown as follows:



Oxygen Reduction



Hydrogen evolution is a very common cathodic reaction in acid solutions, and oxygen reduction can occur in any solution in contact with air. Metal ion reduction and metal deposition are less commonly associated with the corrosion process, but may be found in chemical process systems.

General chemistry uses the principle of an electrochemical corrosion reaction to produce hydrogen gas, H_2 . This occurs when zinc particles are added to dilute hydrochloric acid. The acid attacks the zinc metal forming zinc ions (Zn^{++}) and the zinc atom gives up two electrons (oxidation). This area becomes the anode. The electrolyte, dilute HCl, contains hydrogen ions (H^+) and chloride ions (Cl^-). The electrons leave the metal (this area becomes the cathode), are accepted by the hydrogen ions, and form a free hydrogen gas molecule (reduction). To complete the reaction, the zinc ion (Zn^{++}) joins with two chloride ions (Cl^-) and forms ZnCl_2 . The complete chemical reaction is:



The previous concept is illustrated in Figure 2.

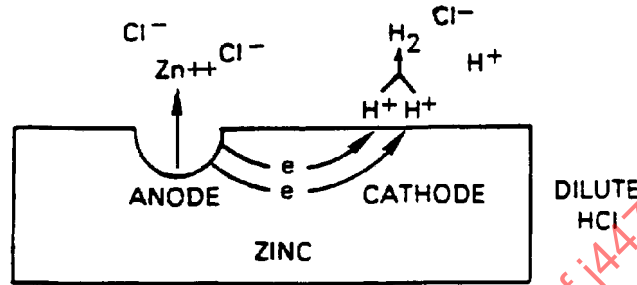


FIGURE 2—ANODIC AND CATHODIC REACTIONS WITH ZINC METAL IN DILUTE HYDROCHLORIC ACID

The possibility for corrosion to occur in a particular environment depends upon whether the free-energy change (ΔG) is negative in the following equation:

$$\Delta G + -nFE \quad (\text{Eq. 4})$$

where:

n = Number of electrons involved
 F = Faraday constant
 E = Cell potential

The cell potential (E) is the difference between the equilibrium potentials of the cathodic and anodic half-cell reactions, and can be determined from half-cell potentials that were measured under standard conditions. A list of such potentials is shown in Table 1. An example of how to determine the feasibility of a reaction between aluminum and moist air is as follows:

$$\begin{aligned}
 E &= \text{the potential of the cathodic reaction minus the potential of the anodic reaction} \\
 E(\text{O}_2/\text{OH}^-) - E(\text{Al}/\text{Al}^{+++}) \\
 E + 0.401 - (-1.662) &= 2.063
 \end{aligned}$$

The cell potential for this reaction is positive, and when substituted in the free-energy equation, it is found that the reaction can occur because ΔG is negative.

In summary, corrosion occurs when metal atoms are oxidized at the anode and enter the solution as ions, leaving behind an excess of negatively charged electrons in the metal. Electrons flow through the metallic circuit to the cathode, where positively charged hydrogen ions at the cathode surface are reduced to hydrogen atoms which combine to form hydrogen gas. When this reaction does not occur readily, oxygen is reduced and it combines with hydrogen ions or with water. The corrosion rate is dependent upon the ease with which these reactions occur and the driving force, or potential difference, between anodic and cathodic sites.

The essential requirement for corrosion is that a potential difference exist between two sites which are joined by an electrolyte and by an electrical path. Corrosion prevention is simply a means of interfering with the continuity of the circuit. The degree of success is determined by the extent of the interference.

**TABLE 1—STANDARD OXIDATION-REDUCTION (REDOX)
POTENTIALS (25 °C, VOLTS VS. NORMAL HYDROGEN ELECTRODE)⁽¹⁾**

Element	Electrode Reaction	Redox Potential
Gold	$\text{Au} = \text{Au}^{+3} + 3\text{e}$	+1.498
Oxygen (acid media)	$\text{O}_2 + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$	+1.229
Palladium	$\text{Pt} = \text{Pt}^{+2} + 2\text{e}$	+1.2
Platinum	$\text{Pd} = \text{Pd}^{+2} + 2\text{e}$	+0.987
Mercury	$\text{Hg} = \text{Hg}^+ + \text{e}$	+0.799
Silver	$2\text{Ag} = \text{Ag}_2^{+2} + 2\text{e}$	+0.788
Iron (ferric)	$\text{Fe}^{+2} = \text{Fe}^{+3} + \text{e}$	+0.771
Oxygen (neutral or alkaline media)	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} = 4\text{OH}^-$	+0.401
Copper	$\text{Cu} = \text{Cu}^{+2} + 2\text{e}$	+0.337
Tin (stannic)	$\text{Sn}^{+2} = \text{Sn}^{+4} + 2\text{e}$	+0.15
Hydrogen	$\text{H}_2 = 2\text{H}^+ + 2\text{e}$	0.000
Lead	$\text{Pb} = \text{Pb}^{+2} + 2\text{e}$	-0.126
Tin (stannous)	$\text{Sn} = \text{Sn}^{+2} + 2\text{e}$	-0.136
Nickel	$\text{Ni} = \text{Ni}^{+2} + 2\text{e}$	-0.250
Cobalt	$\text{Co} = \text{Co}^{+2} + 2\text{e}$	-0.277
Cadmium	$\text{Cd} = \text{Cd}^{+2} + 2\text{e}$	-0.403
Iron (ferrous)	$\text{Fe} = \text{Fe}^{+2} + 2\text{e}$	-0.440
Chromium	$\text{Cr} = \text{Cr}^{+3} + 3\text{e}$	-0.744
Zinc	$\text{Zn} = \text{Zn}^{+2} + 2\text{e}$	-0.763
Aluminum	$\text{Al} = \text{Al}^{+3} + 3\text{e}$	-1.662
Magnesium	$\text{Mg} = \text{Mg}^{+2} + 2\text{e}$	-2.363
Sodium	$\text{Na} = \text{Na}^+ + \text{e}$	-2.714
Potassium	$\text{K} = \text{K}^+ + \text{e}$	-2.925

1. Electrode potential values are given and are invariant (e.g., $\text{Zn} = \text{Zn}^{+2} + 2\text{e}$ and $\text{Zn}^{+2} + 2\text{e} = \text{Zn}$ are identical and represent zinc in equilibrium with its ions with a potential of -0.763 V versus normal hydrogen electrode.)

4.2 Factors Affecting Corrosion Rate—Among some of the more common parameters that affect the corrosion rate for a given metal or alloy are: (a) the chemical composition of the electrolyte, (b) temperature, (c) relative humidity, (d) surface conditions, (e) metal stress, (f) galvanic effects, and (g) ratio of electrode areas.

The effect of the chemical composition of the electrolyte is associated mostly with salt concentration, pH, and the nature of the ions. For a solution to be corrosive, it must be conductive; that is, it must have sufficient ionic strength to pass a reasonable amount of current. The acidity or alkalinity of a solution affects different metals differently. Such metals as zinc, aluminum, lead, and tin are soluble in acids as well as alkalis, but are more soluble when the solution pH is either very high or very low. Other metals, such as nickel, copper, cobalt, chromium, manganese, cadmium, magnesium, and iron are soluble in acids, but are generally insoluble in alkalis. Certain ions, particularly chloride ions, are highly mobile and have the ability to penetrate oxide films on the metal surface, which can lead to localized corrosion. Also, the species of salts in the electrolyte will often determine whether the corrosion products formed on the surface are adherent and protective or whether they are loose and permeable to the solution, allowing corrosion to continue.

Increasing temperature generally increases reaction rates, but it can also affect corrosion through its effect on films. It may increase their solubility or otherwise change their nature to make them less protective, or it can change the solubility characteristics of certain products and cause a precipitate to form that is protective. Temperature differential may also create an anode/cathode relationship on a given piece of metal; the part at elevated temperature may be anodic to the part at the lower temperature.

Relative humidity can have a very dramatic effect on the corrosion of metals, and for certain metals there is such a thing as a critical relative humidity above which corrosion will proceed at an accelerated rate. For example, the critical relative humidity for iron, copper, nickel, and zinc generally falls between 50 and 70%.

A dirty surface often exerts a very strong influence on the initiation and rate of corrosion. For example, dirt, debris, and hygroscopic substances can absorb and retain moisture, and also create local anodes and cathodes on a surface, which can initiate and prolong corrosive attack. Topographical irregularities and metallurgical variations and inhomogeneities at the surface are potential sites for initiation of corrosion. Surface films, particularly if they are discontinuous, can contribute to corrosion. Corrosion products can be very voluminous, and may accelerate corrosion by absorbing and retaining moisture.

Stressed materials often corrode faster than unstressed materials, and those under tension will corrode sooner and at a higher rate than the same material under compressive stress.

Galvanic effects result from the coupling of dissimilar metals and are particularly devastating when the electromotive (driving) force, or potential difference, between the metals is large. In addition, there is an area effect to consider because the corrosion rate of the more anodic member of the couple will increase almost in direct proportion to the cathode-to-anode area ratio. The worst case is when a large cathode is connected to a small anode. Besides the obvious situation where dissimilar metals are coupled, many galvanic effects result from dissimilar surface conditions discussed previously.

4.3 Forms of Corrosion—The forms of corrosion are broadly classified as: (a) uniform, or general corrosion; and (b) localized corrosion. Uniform corrosion occurs over the entire surface at about the same rate, which varies depending on the environment. In acids or other aggressive solutions, the attack may be very rapid, while in ordinary air atmospheres, the attack may be slow because of the formation of protective corrosion deposits. Uniform corrosion normally does not cause metal failures as rapidly as localized corrosion, but it is detrimental to appearance. Localized corrosion affects smaller portions of the metal surface, but the rate of penetration of the affected area can often be very fast, perhaps hundreds to thousands of micrometers per year. Some metals are more susceptible to one form of localized corrosion than to another. This type of information should be known before selecting a material for a particular application. The following brief descriptions of various forms of localized corrosion serve only as an introduction. More extensive information may be obtained from the literature.

4.3.1 **CONCENTRATION CELL CORROSION**—One of the most serious causes of localized corrosion is the concentration cell. This is a condition in which a local potential difference arises between two areas of metal exposed to different concentrations of dissolved ions in the same solution. Concentration cells are usually associated with crevices, recessed areas, scale, or surface deposits. The two major types of cells are: (a) the differential-aeration cell, and (b) the metal-ion cell.

The differential-aeration cell is formed as a result of a difference in the concentration of dissolved oxygen in the solution to which two areas of metal are exposed. The area that is exposed to the higher oxygen concentration tends to be cathodic, and the area exposed to the lower oxygen concentration tends to become anodic. These variations in concentration occur because oxygen is readily replenished at exposed areas of metal but not in stagnant areas. A typical differential-aeration cell is shown in Figure 3.

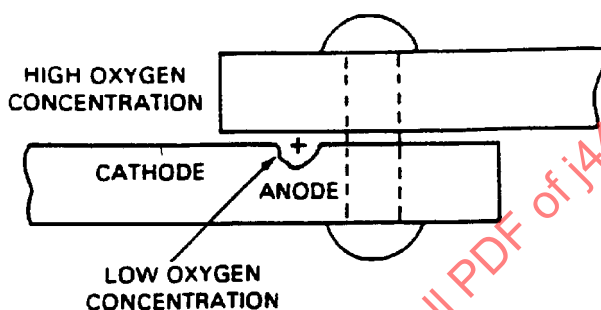


FIGURE 3—DIFFERENTIAL-AERATION CELL AT CREVICE FORMED WHEN TWO PARTS ARE BOLTED TOGETHER

A special case of the differential-aeration cell is called the active-passive cell. This type of cell is usually associated with metals, such as stainless steel, that require oxygen to retain their passivity. In the passive condition, these metals are very resistant to corrosion. If the film on the metal surface is damaged and cannot be reformed because of a lack of oxygen, the surface assumes a potential different from that of the surrounding passive surface, and a concentration cell is established. Because the anodic area is usually quite small, the attack can be very severe, developing deep pits in the surface. A typical example of this type of cell is that of attached trim molding. It is difficult for that area of aluminum or stainless steel in contact with painted body sheet metal to remain passive because air flow over it is slight, whereas the remainder of the molding surface is freely exposed to air, and it can remain passive. An active-passive cell is established between these two portions of the metal surface.

A metal-ion cell is formed when there is a variation in the concentration of metal ions at two different locations in a solution. Differences in metal-ion concentration result because open or exposed areas can have metal ions diffused or swept away more readily than when they are in stagnant areas. A difference of potential is found between these two locations, and current can flow. Corrosion occurs at the anode, which is the point where metal ions diffuse away from the surface. The area of attack in this case is opposite to that of the differential-aeration cell. An example of a metal-ion cell is shown in Figure 4.

Concentration cells can be set up by differences in temperature, agitation, illumination, liquid velocity, and other factors that affect solution homogeneity. This type of corrosion so often with crevices that it is frequently referred to as "crevice corrosion." When it occurs under deposits on the surface, it is sometimes called "poultice corrosion."

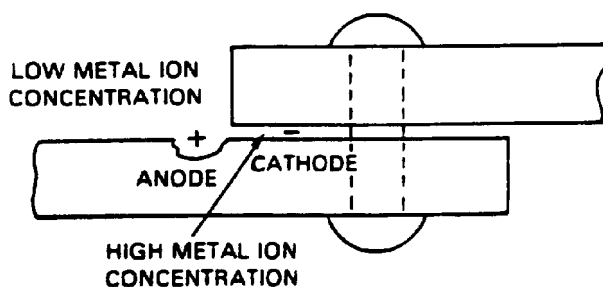


FIGURE 4—METAL-ION CONCENTRATION CELL AT CREVICE FORMED BETWEEN TWO PIECES OF METAL BOLTED TOGETHER

4.3.1.1 Prevention

- Use welded joints in preference to bolted or riveted joints.
- Caulk or seal unavoidable crevices effectively, using durable and noncorrosive materials.
- Minimize the contact between metal and plastics, fabrics, debris, etc.
- Avoid contact with materials which are known to contain corrosive elements or which are hygroscopic, since they may accelerate the cell effect. (Stainless steel has pitted when in contact with insulation containing only a few parts per million of chloride ion.)
- Avoid sharp corners, ledges, and pockets where debris can accumulate.

4.3.2 PITTING CORROSION—Pitting corrosion is a form of localized attack at a metal surface where small areas corrode preferentially. The rate of penetration is usually more rapid than it is in uniform corrosion. Some metals have a greater tendency to pit than others, but most metals will pit under some specific set of conditions. Metals such as aluminum or stainless steel, which form passive films, are especially susceptible to pitting corrosion.

Pitting should be considered a two-step process: one of initiation and the other of propagation. The exact cause of pit initiation is not well understood, but some differences must exist at the metal surface to account for the difference in potential which is necessary for corrosion to occur. Conditions which are usually associated with pitting are inhomogeneities in the metal surface, breaks in a protective film, deposits on a surface, and various kinds of imperfections. Pits vary greatly in size, depth of penetration, and frequency of occurrence. The increase in depth usually proceeds at a faster rate than the increase in width. Pits often have well-defined boundaries.

The environment has an important bearing on the initiation and growth of pits. Halides or halogen-containing ions contribute greatly to pitting; chlorides, bromides, and hypochlorites are considered to be the most aggressive. The chloride ion, for example, not only interferes with the formation of a protective film, but because of its size and mobility diffuses through weak points in the oxide film and enters into the corrosion reaction.

The auto-catalytic nature of a pit is responsible for its continued propagation at a fast rate. Chloride ions continue to migrate into the pit, and the solution within the pit becomes acidic. The acidity prevents the formation of a protective film, and the metal surface in the pit is kept in an active condition. As more metal ions are formed, more chloride ions diffuse into the pit, and the process continues.

4.3.2.1 Prevention

- Use materials with alloying elements designed to minimize pitting susceptibility, for example, molybdenum in stainless steel.
- Provide a surface as homogeneous as possible through proper cleaning, heat treating, and surface finishing.
- Reduce exposure to aggressive ions by shielding the part, coating the part, or by reducing the concentration of these ions.
- Increase the capability of the solution to make the metal passive. If the metal is immersed, use inhibitors or other additives.
- Minimize the effects of external factors on the design features which lead to localized corrosion; for example, the effects of differential aeration on crevices.

4.3.3 GALVANIC CORROSION—This type of corrosion occurs when two dissimilar metals are coupled and exposed to an electrolyte. The intensity of the galvanic effect will be determined by the potential difference between the metals and the ratio of the cathode-to-anode areas mentioned earlier. The farther apart metals are in the electromotive series, the greater will be the accelerated corrosion of the least noble metals (anode).

The ratio of cathode surface area to anode surface area is important because it determines the current density on the anode surface. A large cathode area and a small anode area result in a high current density at the anode, whereas the reverse situation results in a low anode current density. In both cases the potential difference may be the same and the total current passing between two metals may be the same, but the rate of penetration is different because it is directly proportional to the current density. This effect, which is shown schematically in Figure 5, applies particularly to joints where rivets, screws, or bolts are used to join two pieces of metal together.

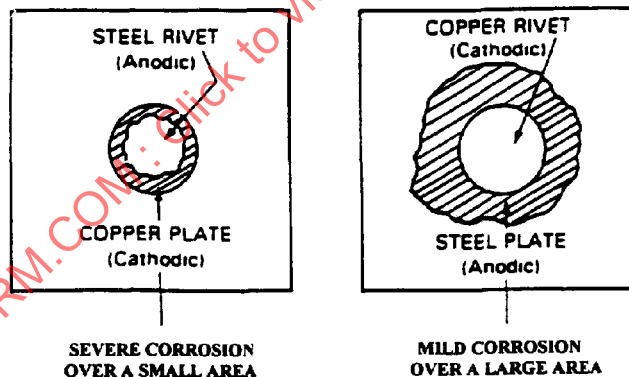


FIGURE 5—GALVANIC CORROSION BETWEEN STEEL AND COPPER (CORROSION OF STEEL IS SEVERE WHEN CORROSION IS CONCENTRATED ON A SMALL AREA)

Since the potential difference between two metals is so important to galvanic corrosion, a series, such as that shown in Table 2, is often used to estimate the likelihood of galvanic corrosion occurring and its magnitude. This series, based on a sea water environment, is at most a guide, since some variations are found in other environments. Ideally, a separate series should be determined for each environment, but this is hardly feasible. Alloys or metals which appear lower on the list corrode preferentially over those above them, when they are in galvanic contact. Metals are grouped together, and those in the same group should have little effect on each other.

TABLE 2—GALVANIC SERIES IN SEA WATER⁽¹⁾

Reactivity	Material
Cathodic (Noble)	Platinum
	Gold
	Graphite
	Silver
	Stainless Steel, SAE Types 30310, 30316 (Passive)
	Stainless Steel, SAE Types 30301, 30304 (Passive)
	Titanium
	Stainless Steel, SAE Types 51410, 51430 (Passive)
	67Ni-33Cu Alloy (Monel)
	76Ni-16Cr-7Fe Alloy (Passive) (Inconel)
	Nickel (Passive)
	Silver Solder
	Bronze
	70-30 Cupro-Nickel
	Silicon Bronze
	Copper
	Brasses
	76Ni-16Cr-7Fe Alloy (Active) (Inconel)
	Nickel (Active)
	Manganese Bronze
	Muntz Metal
	Tin
	Lead
	Lead-Tin Solder
	Stainless Steel, SAE Types 30310, 30316 (Active)
	Stainless Steel, SAE Types 30301, 30304 (Active)
	Stainless Steel, Types 51410, 51430 (Active)
	Cast Iron
	Wrought Iron
	Mild Steel
	Aluminum 2024
	Cadmium
	Alclad Aluminum
	Aluminum 1100, 3003, 5052, 6053
	Galvanized Steel
	Zinc
Anodic (Active)	Magnesium Alloys
	Magnesium

1. Modified from "Corrosion Resistance of Metals and Alloys," LaQue and Copson, 2nd Edition.

4.3.3.1 Prevention

- a. Avoid the use of combinations of metals which are widely separated in the galvanic series.
- b. Avoid combinations where the area of the anodic metal is small compared with that of the cathodic metal. Use more noble metals for rivets, bolts, and fasteners.
- c. Insulate joints of dissimilar metals when possible; even paint or plastic coatings will be helpful.
- d. Paint or coat all surfaces when possible. Avoid painting only the anodic metal, since corrosion may be accelerated at imperfections or breaks in the coating.
- e. Seal faying surfaces.
- f. Apply metallic coatings to reduce the potential difference between dissimilar metals.
- g. Avoid threaded connections if dissimilar metals that are far apart in the galvanic series must be used.
- h. Increase the thickness of replaceable sections of less noble metal.
- i. Attach sacrificial anodes such as zinc, magnesium, or aluminum to the metal to be protected, provided there is electrolytic contact.
- j. Use chemical inhibitors in solutions if possible.

4.3.4 STRESS CORROSION—Stress corrosion of a metal occurs when the metal is under the combined influence of sustained tensile stress, either applied or residual, and corrosion. Damage usually appears as localized cracks. The attack may be intergranular, transgranular, or a combination of the two. The conditions for stress corrosion are:

- a. A susceptible material
- b. An appropriate environment
- c. Stress
- d. Time

An example of intergranular stress corrosion cracking is shown schematically in Figure 6.

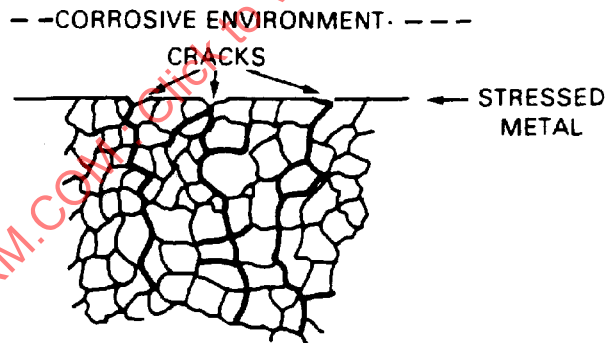


FIGURE 6—INTERGRANULAR STRESS CORROSION CRACKING

There is no known mechanism that explains all of the experimental evidence for stress corrosion. Three basic theories have been proposed: (a) electrochemical, (b) mechanical, and (c) surface energy. The electrochemical theory presumes the formation of fissures at grain boundaries because of either tensile stress or specific corrosion such as pitting or intergranular. Once the surface has been broken, the conditions are sufficient for accelerated corrosion, since film-free metal and grain boundaries are known to be anodic to film-covered metal and crystal faces, respectively. Regions of stress concentration develop after the onset of corrosion. When the stresses become sufficient, cracks develop and penetrate into the metal. Cracking stops when plastic deformation of metal, caused by strain and the cracking process, increases the energy necessary to propagate the crack. If a new film does not form over the freshly exposed metal, a new fissure starts at the notch of the crack by electrochemical corrosion, and the process is repeated.

The mechanical theory presumes that an electrochemical reaction may be necessary to initiate the crack, but mechanical effects are sufficient to propagate the crack. The surface energy theory is based on a lowering of surface energy by adsorption of specific ions. The reduction in atomic bond strength allows crack initiation and propagation to occur at abnormally low stresses.

Aging, heat treating, and tempering processes have an important bearing on the tendency of a material to crack; even slight variations in the hardness of a material have an effect on the stress level at which cracking occurs. A low concentration of certain impurities can increase the tendency of even pure metals to crack. The metallurgical condition of the metal is a determining factor in the susceptibility of the material to stress crack, but practically any material will undergo stress corrosion cracking under some condition of exposure. Some metals stress crack in very mild environments, while others require a more severe environment. Examples of various environments that produce corrosion of some of the common alloys are shown in Table 3.

Under some conditions the concentration of unfavorable species in the environment is increased at a localized area, or their effect is focused on sites that are susceptible to crack initiation. Some of these conditions are nucleate (surface) boiling, heat transfer, crevices, pits, cracks, voids, corrosion products, insulating materials, and splash zones. For example, water with only a few parts per billion of chloride can produce stress corrosion of sensitized stainless steel at pits; insulating materials with leachable chlorides at a concentration level as low as 2 or 3 ppm have caused cracking of stainless steel.

Although the environment has an important bearing on stress corrosion, its effects can be minimized by reducing stress concentrations and residual stresses which are introduced during fabrication of the material. Some of the factors that should be considered are: (a) discontinuities and sharp corners, (b) the effects of heat treatment, (c) galvanic couples and crevices that accelerate the effect of stress, (d) nonmetallic inclusions at or near the surface, (e) cold working without stress relief, (f) thermal gradients produced by quenching or welding, (g) welding defects, and (h) machining that leaves residual stresses.

4.3.4.1 Prevention

- a. Substitute more corrosion-resistant materials for the stress-sensitive material when possible.
- b. Design to minimize the factors that promote corrosion and residual or applied stresses. Avoid crevices, deep recesses, dissimilar metals, sharp corners, and notches.
- c. Alter the metallurgical structure of the metal by aging or tempering.
- d. Avoid designs that tend to concentrate specific effects or produce high thermal stresses.
- e. Include stress-relieving treatments when residual stresses are likely to occur. (One of the most effective treatments is the introduction of a counter compressive layer at the surface by surface rolling or shot peening.)
- f. Use protective coatings to reduce the incidence of stress corrosion; include organic as well as metallic coatings. (Coatings should be resistant to the environment and free of cracks or pores, since any opening in the coating might introduce a cracking problem that did not exist originally.)
- g. Modify the environment by changing the pH or reducing the oxygen content.
- h. Use inhibitors or cathodic protection, but only if appropriate for the conditions of use. (In case of cathodic protection, hydrogen is discharged, and it may increase the tendency for failure by hydrogen embrittlement.)

4.3.5 INTERGRANULAR CORROSION—Intergranular corrosion is the selective or localized attack of the grain boundaries or closely adjacent material without appreciable attack on the grain. An example of this type of corrosion is shown in Figure 7.

TABLE 3—ENVIRONMENTS WHICH HAVE SHOWN A TENDENCY TO PRODUCE STRESS CORROSION FOR CERTAIN MATERIALS⁽¹⁾

Alloy	Environment
Aluminum	Solutions of NaCl with or without H ₂ O ₂ Sea water Air
Copper	Ammonia vapor and solutions Amines Air, steam Mercury and mercury salts KOH or NaOH solutions
Inconel and Monel	KOH or NaOH solutions Organic chlorides Steam plus SO ₂ Mercury High-temperature steam and water
Magnesium	NaCl and K ₂ CrO ₄ solutions Rural and sea coast atmospheres Distilled water
Mild- and Low-Alloy Steels	NaOH or KOH solutions Acidic H ₂ S solutions Nitrate salts (Ca, NH ₃ , Na, and Ni) HCN solutions Chloride salts (Al, Mg, Ca)
Austenitic Stainless Steels	Pickling solutions (HCl, HNO ₃ , HF) Inorganic and organic chlorides KOH or NaOH solutions Sea water Steam condensate plus NH ₃ H ₂ S Sulfate solutions
Titanium	High temperature chloride HCl Chlorinated hydrocarbons NaCl solutions

1. Modified from "Stress Corrosion—Causes and Cures," H. Suss.

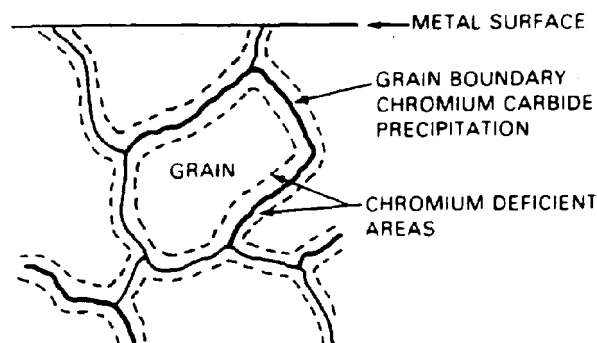


FIGURE 7—INTERGRANULAR CORROSION AT GRAIN BOUNDARIES DUE TO CHROMIUM DEFICIENCY

This type of corrosion is most often associated with austenitic stainless steels (e.g., SAE Type 30304). (Other alloys such as those of copper or nickel can be affected, too.) It appears to be related to the carbon content and perhaps to the nitrogen content. When stainless steel containing a significant concentration of carbon is heat treated in the sensitizing range of about 400 to 900 °C (750 to 1650 °F), carbon diffuses to the grain boundaries, where it combines preferentially with chromium to form chromium carbides. As a result, a small band of material on each side of the grain boundary becomes deficient in chromium. A potential difference is found between the chromium-deficient material in the grain boundaries and the grains. Since the grain boundaries represent a small surface area of anodic material compared with that of the grains, which are cathodic, the attack is usually accelerated.

Intergranular attack, often associated with arc welding, is sometimes referred to as "weld decay." It occurs some distance from the actual weld, because sensitizing temperatures are usually reached away from the weld. Spot welding is less susceptible to this effect because heating and cooling are more rapid, and hence there is less tendency for carbon diffusion to occur.

Several methods are used to prevent intergranular corrosion. The most obvious is the reduction of the carbon content (e.g., SAE Type 30304L). An alternative method is the addition of stabilizing elements, such as titanium (e.g., SAE Type 30321), columbium, or tantalum (e.g., SAE Type 30347). These elements have a higher affinity for carbon than does chromium, and chromium depletion is prevented. This type of corrosion can be prevented also by proper heat treatment. In the case of austenitic stainless steels, heat treatment in the temperature range of 1050 to 1100 °C (1920 to 2010 °F) is high enough above the sensitizing range to dissolve the carbides. This treatment is followed by rapid cooling to prevent the carbides from reforming. Ferritic stainless steels (e.g., SAE Type 51430) have a sensitizing range much above that of the austenitic steels, and they require heat treatment in a temperature range of 650 to 815 °C (1200 to 1500 °F), which is below the sensitizing range. When the problem cannot be avoided by any of these treatments, it is best to avoid the use of susceptible materials.

4.3.5.1 Prevention

- a. Use stainless steel alloys with low carbon content.
- b. Anneal the alloy at the proper temperature and follow with rapid quenching.
- c. Use stainless steel alloys that contain stabilizing elements such as titanium, columbium, and tantalum.
- d. Substitute an alloy that is less sensitive to intergranular corrosion.

- 4.3.6 **EXFOLIATION CORROSION**—This type of corrosion is considered to be a special form of intergranular attack in which delamination takes place parallel to the metal surface. Flakes of metal are peeled or pushed to the surface because of the internal stresses created by corrosion products. This form of corrosion is most common in rolled or extruded aluminum alloys in which grains are elongated or flattened. Susceptibility to exfoliation is associated with grain boundary precipitation and may be prevented by appropriate heat treatments.
- 4.3.7 **DEZINCIFICATION (DEALLOYING)**—Dezincification is a phenomenon associated with the preferential removal of zinc from brass alloys. It can be recognized by the pronounced copper color that appears, as opposed to the yellow color of brass. It may occur locally as a plug-type attack, penetrating the metal in a direction perpendicular to the surface, or as a layer type which affects broad areas of the surface. These two types are shown schematically in Figure 8.

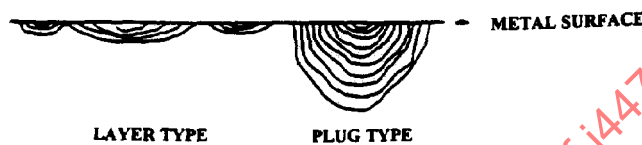


FIGURE 8—DEZINCIFICATION OF BRASS ALLOYS

Two possible mechanisms have been proposed for this type of attack: (a) the selective removal of zinc, leaving the copper behind, and (b) the dissolution of brass with the deposition of copper in the same area. In both types of attack, the metal is weakened as the result of the formation of a porous copper structure. The rate of attack increases with increasing temperature, increasing solution conductivity, decreasing solution flow and the accumulation of deposits on the metal surface. Dezincification is usually found to occur with brasses having a copper content below 85%. The plug type occurs more readily in low-zinc brasses and the layer type in high-zinc brasses. Dezincification can be avoided by using alloys which contain tin, antimony, or arsenic.

The effect of this type of corrosion is not much different from that of the graphitization of cast iron, where metal is preferentially removed and a porous mass of carbon is left behind. Similar types of corrosion are found with alloys of aluminum, cobalt, and nickel. In these cases it is referred to as dealuminification, etc.

4.3.7.1 *Prevention*

- a. Use copper alloys with the copper content above 85%.
- b. Use brasses alloyed with tin, arsenic, or antimony.
- c. Avoid environments where the solution becomes stagnant and deposits can accumulate on the surface of the metal.

- 4.3.8 **FRETTING CORROSION**—This type of corrosion is defined as damage that occurs at the interface of two contacting surfaces, at least one of which is metal, when they are subject to minute slippage relative to each other. This condition may be caused by vibration or by continuous slippage between two surfaces. Fretting corrosion is sometimes referred to as wear or rubbing corrosion, chafing corrosion, or friction oxidation. It is usually characterized by discoloration, formation of debris, and formation of deep pits. Fatigue cracks may be initiated at these pits.

The mechanism of fretting corrosion is not well understood. It is assumed that asperities on one surface rub clean the opposite surface. The fresh surface becomes oxidized immediately, and the oxide is removed when the surface is rubbed again with the asperity. The formation and removal of oxides occur continuously, increasing the local stress because of their larger volume. Mechanical removal of metal particles is also a factor, since these particles can be converted to oxides which increase the amount of debris. Fretting corrosion requires the presence of oxygen but not moisture. In fact, moisture may function as a lubricant and reduce the rate of corrosion. Damage can increase with a decrease in temperature and with an increase in load.

This type of corrosion can occur whether relative motion is intended or not. Parts which are quite often affected are bolts, suspension springs, flanges, king pins of steering mechanisms, keyed shafts and gears, ball and roller bearings, flexible couplings, connecting rods, electrical relay contacts, and many other parts of vibrating equipment. Parts fail because of fatigue, loss of dimensional stability, and damage of the surface.

4.3.8.1 Prevention

- a. Use a soft metal surface in contact with a hard metal surface; for example, tin, lead, or silver-coated metals in contact with steel.
- b. Roughen the surface to increase friction and reduce slippage.
- c. Increase the load to reduce relative motion. (If the load is not sufficient, damage can be increased.)
- d. Use low-viscosity lubricants in combination with phosphate-treated surfaces. (Molybdenum sulfide also decreases damage until it is displaced from the surface.)
- e. Increase the surface hardness of contacting metals.
- f. Use one material with a low coefficient of friction, if possible.

4.3.9 CORROSION FATIGUE—Corrosion fatigue is the cracking of a metal that has been subjected to the combined action of corrosion and alternating or fluctuating tensile stress. The initiation of cracks is generally associated with crevices at the metal surface produced during cyclic stress. Sometimes corrosion pits are formed at the metal surface first and provide sites for cracks to initiate. Unlike stress corrosion cracking, corrosion fatigue can occur with almost any material that is susceptible to corrosion. The damage that results usually exceeds the total amount that would be caused by corrosion and fatigue acting separately.

Corrosion fatigue cracks are generally, but not always, transgranular. For example, corrosion fatigue is apparently intergranular in lead. Also, in certain cases, the cracks in steel will follow grain boundaries for short distances if the boundary directions are oriented in the right direction.

A large number of aqueous environments can cause corrosion fatigue. Steel, for example, is susceptible in fresh waters, sea water, condensates from combustion products, and miscellaneous chemical environments. Generally, the resistance of a metal to corrosion fatigue is linked more closely with its resistance to corrosion than with its high mechanical strength.

4.3.9.1 Prevention

- a. Reduce stress by changing design.
- b. Shot peen the surface, or otherwise introduce compressive stresses.
- c. Improve corrosion resistance with metallic coatings, nitride coatings, or inhibited paint.
- d. Use corrosion inhibitors or cathode protection when exposure is in a solution.

4.3.10 CAVITATION-CORROSION—Cavitation is the formation of cavities or vapor bubbles in a liquid. This phenomenon occurs when the pressure of the liquid falls below its vapor pressure at localized sites in a given system. The formation of bubbles is known as boiling when caused by a temperature rise at constant pressure, but is known as cavitation when caused by a pressure reduction at constant temperature. The damage due to cavitation is caused primarily by the high impact collapse or implosion of the bubbles at or near the metal surface. The pressures generated by the collapse of a cavity have been calculated in some cases to be thousands of pounds (kilopascals) per square centimeter. However, there are at least two factors that contribute to the ultimate deterioration of the metal. One is the mechanical factor, which must always be present, and the other is corrosion. The relationship between the mechanical and corrosion components of cavitation damage is complex, but it is generally recognized that the collapse of cavities at the metal surface can destroy protective oxide films, and thus permit fresh metal to react with the environment. Hence, corrosion can accelerate damage initiated by the collapse of cavities.

Cavitation damage occurs typically on water pumps and pump impellers, on trailing faces of propellers and water turbine blades, and on the water-cooled side of diesel engine cylinders. It has been shown that there is considerable variation in the susceptibility of different alloys to cavitation damage. This variation extends also to different alloys with the same base metal. Such factors as surface hardness, metallurgical history, chemical composition, and, of course the environment are important to this difference. Nevertheless, the following list of alloys is offered as a general guide (but not as a specific use recommendation) to the selection of resistant materials. The alloy types are listed in order of probable decrease in resistance to cavitation damage:

- a. Stainless and high alloy steels
- b. Low-carbon steels
- c. Cast iron
- d. Brasses and bronzes
- e. Aluminum alloys

4.3.10.1 Prevention

- a. Design to minimize cavitation
- b. Select resistant materials
- c. Use appropriate corrosion inhibitors in recirculating systems

5. Chapter 2—Design Considerations

5.1 **Introduction**—Design is a major factor in corrosion prevention, but by itself cannot permanently preclude corrosion. It can minimize or eliminate pockets and ledges which tend to trap road debris and salt. It can provide drainage to minimize water retention or, alternatively, provide access holes for the introduction of barrier coats such as paints, sealers, and waxes. Appropriate selection of materials in the design stage can minimize galvanic couples or provide insulators to break the galvanic couple. Design can minimize susceptibility to stone pecking, shield unavoidable pockets, and locate electrical components in positions remote from corrosive environments.

Design also has a great influence in the application of protective coatings because to adequately coat bare steel components, the area must be accessible. The amount of access required is dependent on the material and application process chosen, but not to the extent that general guidelines cannot be developed or would not apply. The objective of this chapter is to suggest basic design guidelines.

5.2 **General Design Guide**—The design guidelines which follow are based on the fairly direct principles of (a) providing access paths for ingress and egress of protective coating materials and (b) preventing or reducing ingress of, and providing egress for, environmentally induced moisture and contaminants. The approach chosen is to show the application of this principle to major body components. In the process, areas of specific interest are highlighted.

5.2.1 HOOD ASSEMBLY—Figure 9 shows two basically different hood design approaches, the "hatch" hood, Section B-B, incorporating a grille opening panel (GOP), and the "conventional" hood, Section A-A, which does not utilize a GOP. For either approach the following aspects should be considered during the design process:

- All horizontal surfaces should slope toward drain holes. See Section 5.2.7.
- All primary drain holes should be located in the lowest outboard surfaces.
- A flat is generally required on the inner panel to accommodate the latch mechanism. This area should be carefully reviewed to provide drainage and eliminate pockets.
- In many cases, forming and/or appearance advantages are realized by use of a downstanding flange, for assembly of the hood inner and outer panels.

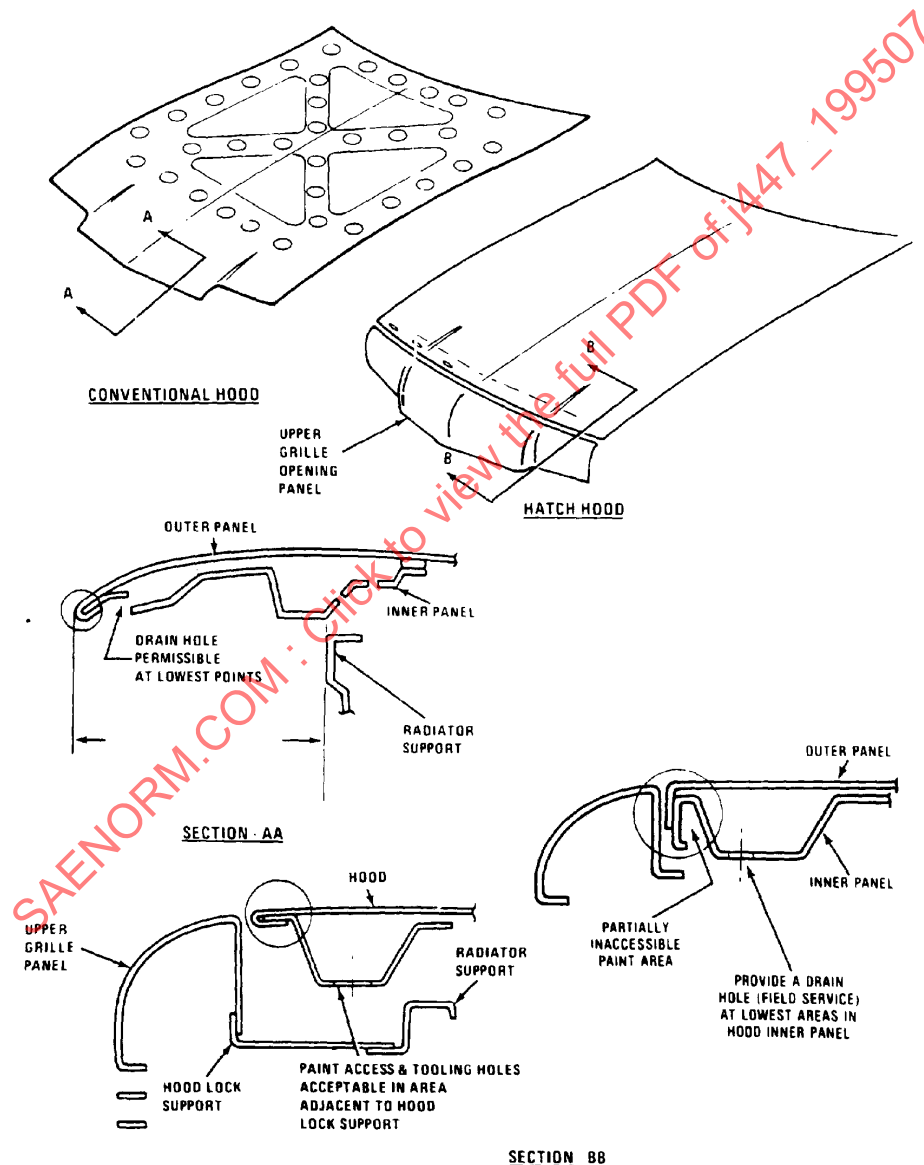


FIGURE 9—HOOD

5.2.2 FENDER ASSEMBLY—Figure 10 reviews some components of a typical fender assembly. For all designs, a full inner liner or apron is desirable to protect front components (headlamp housing, side marker lamps, etc.) and rear structure (fender reinforcement, door hinges, etc.) from road splash and possible abrasion. General comments for all designs are as follows:

- a. In Section A-A, the lower design is preferred since it generally allows a smaller metal-to-metal contact area.
- b. In Section B-B, fender extension, if welded in place as part of the fender assembly, should allow access for coatings.
- c. Section C-C shows various apron or splash shield approaches. If structurally possible, plastic is preferred for this component since this material is inherently noncorroding. In Section C-C, the rundown off the apron splash shield is directed away from the fender inner surface when splash shield is mounted outside the fender flange.
- d. In Section D-D, drainage can be accomplished by holes or offsets in the apron at lowest areas.

5.2.3 DOOR ASSEMBLY—Figure 11 typifies door inner and outer panel assembly conditions. In the overall view, the use of bolt on glass down stops or other bracketry is stated as preferred to a welded component. This design is preferred since a bolted component can generally be installed after protective coatings have been applied. General comments are as follows:

- a. Section A-A again calls for opening inner to outer panels as far as possible to allow access for protective coatings. This approach should be maintained along vertical edges. Along the leading edge, the inner panel will usually be pocketed outboard in the hinge mounting area. Although this is the typical situation, clearances should be maximized by careful review of hinge pillar, door inner panel, and hinge designs.
- b. View A and Section B-B show drainage provisions for lowest forward and rearward areas. Note in View A that outer panel hem flange is locally reduced to achieve a lower drainage point.
- c. Section B-B also highlights the previously stated rule of sloping horizontal surfaces toward drain points. This condition should be followed along the lower edge of the door inner panel (area "B").

5.2.4 QUARTER PANEL ASSEMBLY—Figure 12 shows a few typical construction areas in the quarter panel assembly. General comments are as follows:

- a. The forward lower edge of the quarter panel generally joins to the rocker panel. This joint should be sloped at least 15 degrees from the horizontal to provide drainage, Section C-C. Should this not be possible, as is often the case, or if an even more undesirable channel is formed, Section C'-C', a hot melt sealer may be placed in the area and allowed to flow. This will raise the level to that of the drain hole and allow proper drainage.
- b. Reinforcing ribs usually required on the wheelhouses would be indented inboard, as shown in Section B-B, to allow increased spacing between quarter and outer wheelhouse. As before, this enhances the ability to apply protective coatings. These ribs should also be designed to direct drainage toward drain holes in rocker and rear floor pan.
- c. Section A-A (preferred) shows the use of locating tabs for the quarter panel on the wheelhouse outer as a means of increasing space between the two panels. This design, although requiring removal of the tabs after assembly, has the benefit of reducing metal-to-metal contact.

Due to the great variation in quarter panel designs at quarter to rocker joints, lower back panel or quarter extension, and upper back or "tulip" panel, specific sections are not shown. These areas should be designed, however, using the drainage and coating access principles shown for other areas/panels.

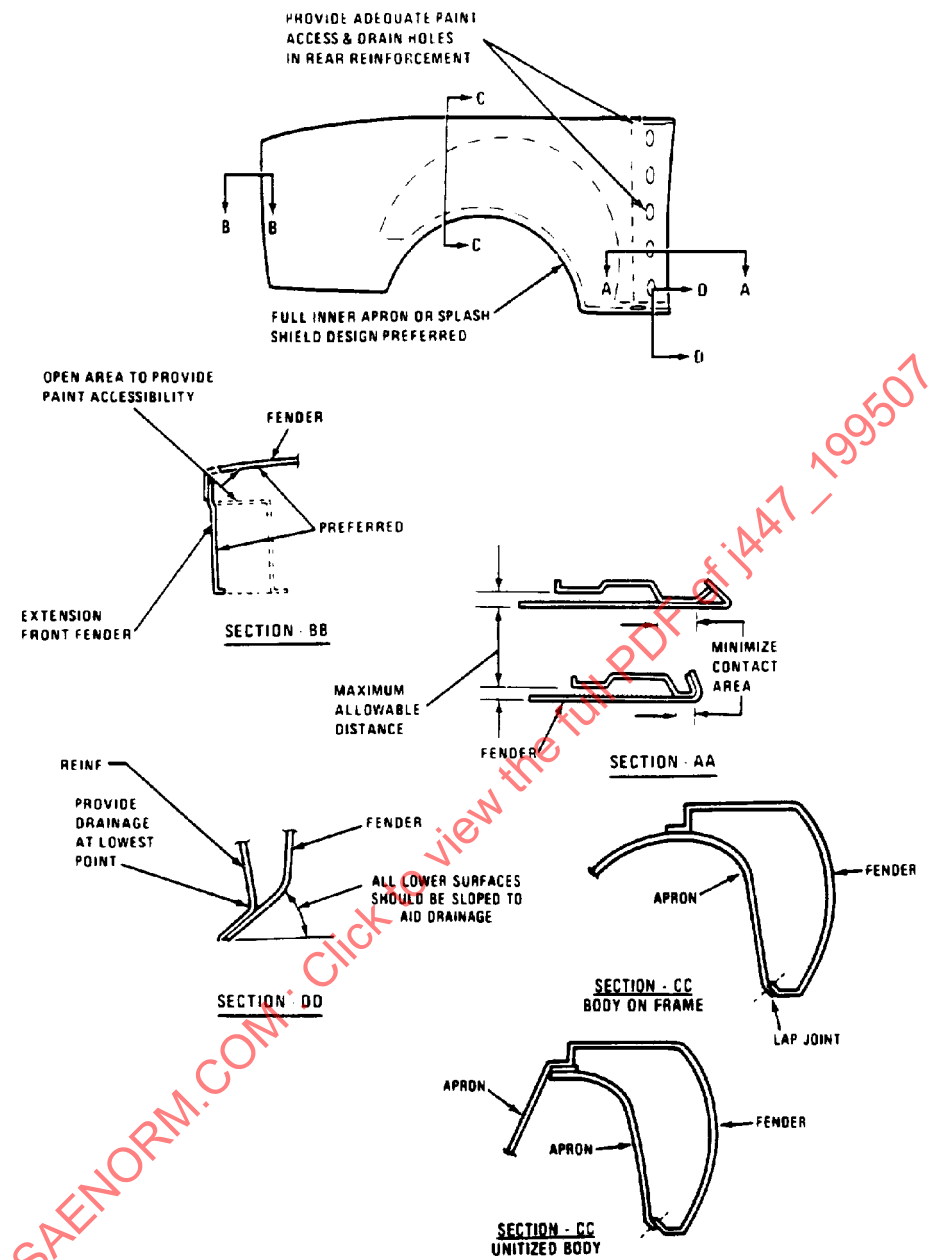


FIGURE 10—FENDER

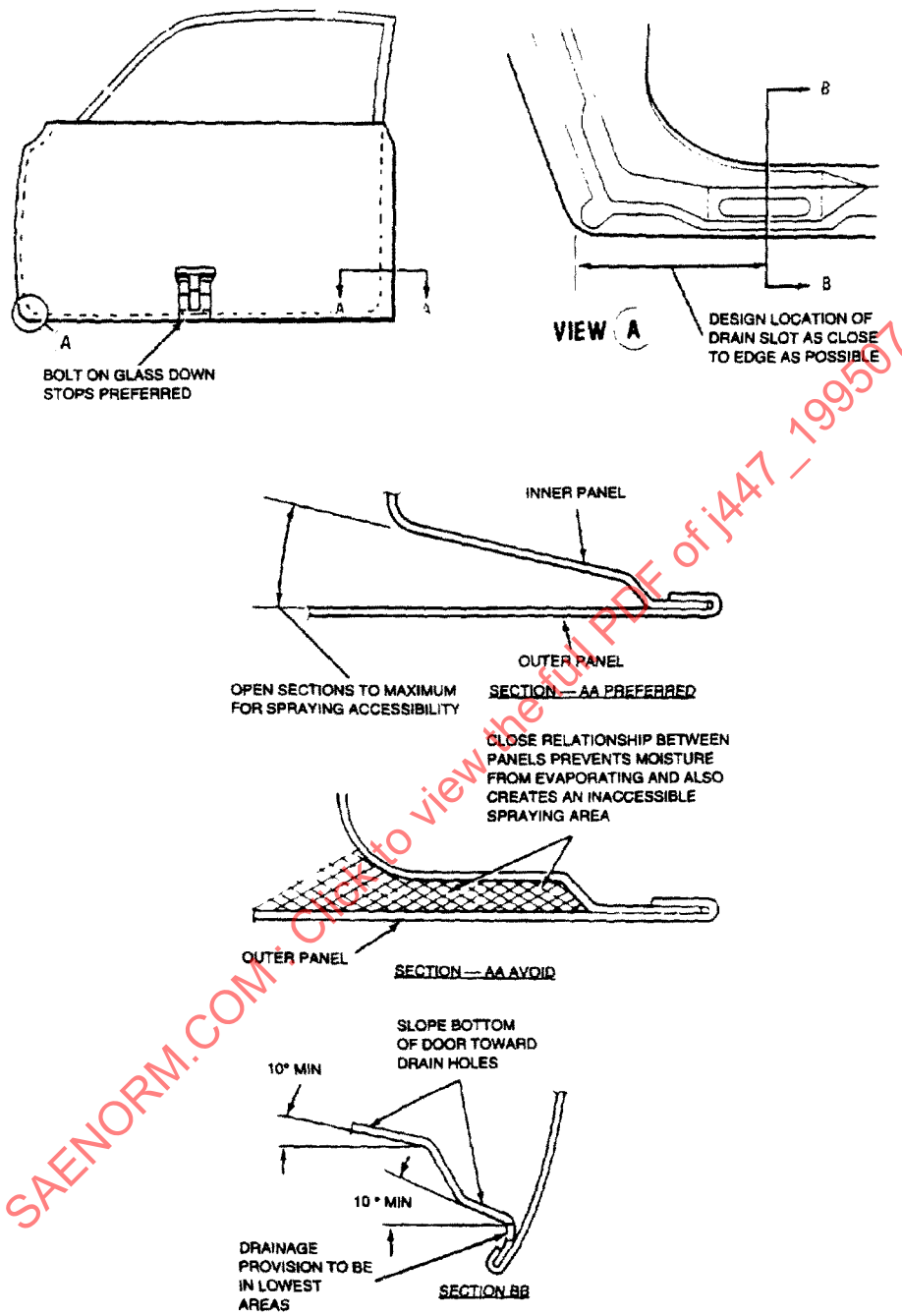


FIGURE 11—DOOR

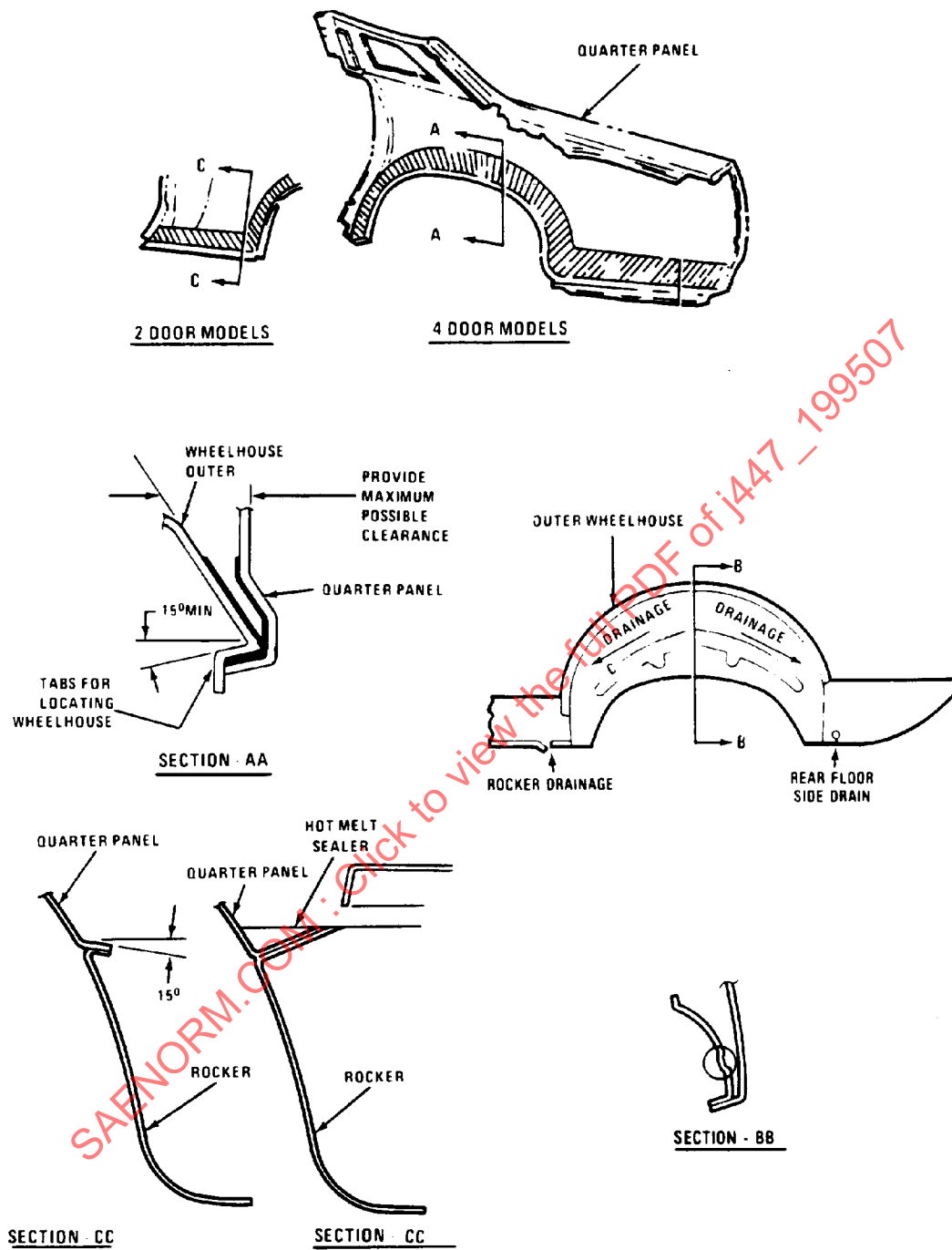


FIGURE 12—QUARTER PANEL ASSEMBLY

5.2.5 DECK LID ASSEMBLY—Figure 13 shows a typical deck lid assembly. Many of the same conditions shown for hood panels (Figure 9) hold true for deck lids with the exception of assembly by downstanding flange. In this light, the inner panel should have adequate paint access holes and flutes, and horizontal surfaces should be sloped toward drainage areas. The generally unique area on the deck lid is the rearward vertical surface shown in Section A-A.

- a. Section A-A (right hand) is occasionally used to accommodate appearance or other conditions. This is not the preferred approach due to generation of a high metal-to-metal contact area and inability to locate drain holes in lowest regions.
- b. Section A-A, preferred, shows a different approach which maximizes coating access area and allows effective drainage locations. This design approach should be considered at the earliest possible stage since it will generally affect the lower back panel configuration.

5.2.6 DRAINAGE—There are several aspects to consider regarding drainage from body sheet metal.

- a. All parts must be designed with the drain holes necessary to provide adequate drainage of water and contaminants during a lifetime of field usage. The placement and design of these drain holes in many panels have been discussed under previous headings.
- b. Figure 14 shows the drainage principle as it applies to location on the body. Joints should be "shingled" to reduce the possibility of moisture impinging directly into the lap as shown in the underbody section.
- c. Where not possible to shingle an exposed joint, as in some wheel splash areas, one panel should be turned to protect the joint as shown in the wheelhouse section.
- d. All drainage holes should be located in areas where contaminants and moisture will not be forced in when the vehicle is in forward motion. This condition is most critical in underbody areas such as the rocker panel and rear floor pan as shown in the field drain hole section.

Adequate drainage is also important during the cleaning, phosphating, and electrocoating of the sheet metal body in spray and dip systems.

- a. Where possible all horizontal surfaces such as floor pans and package trays should be sloped toward drain holes by at least 3 degrees. Due to surface tension, large amounts of liquid will fail to drain off horizontal and nearly horizontal surfaces.
- b. As many drain holes as possible should be used to avoid as much as possible the carryover of fluid from one tank to another. The loss of fluid from one tank is made even more costly by the need to filter it from the next tank. The use of drain holes that will require plugging must be balanced against the cost of plugging the holes.
- c. Provision must be made for sufficient ingress and egress of fluids when entering and leaving the various tanks to avoid floating the body on entry or dragging heavy amounts of fluid out upon exiting.

5.2.7 ROCKER PANEL—Rocker panels should be designed outboard of the door lower hem to protect the bottom edge of the door from stone abrasion and dirt accumulation Figure 15. The lower surface of the rocker panel should be sloped toward drain holes.

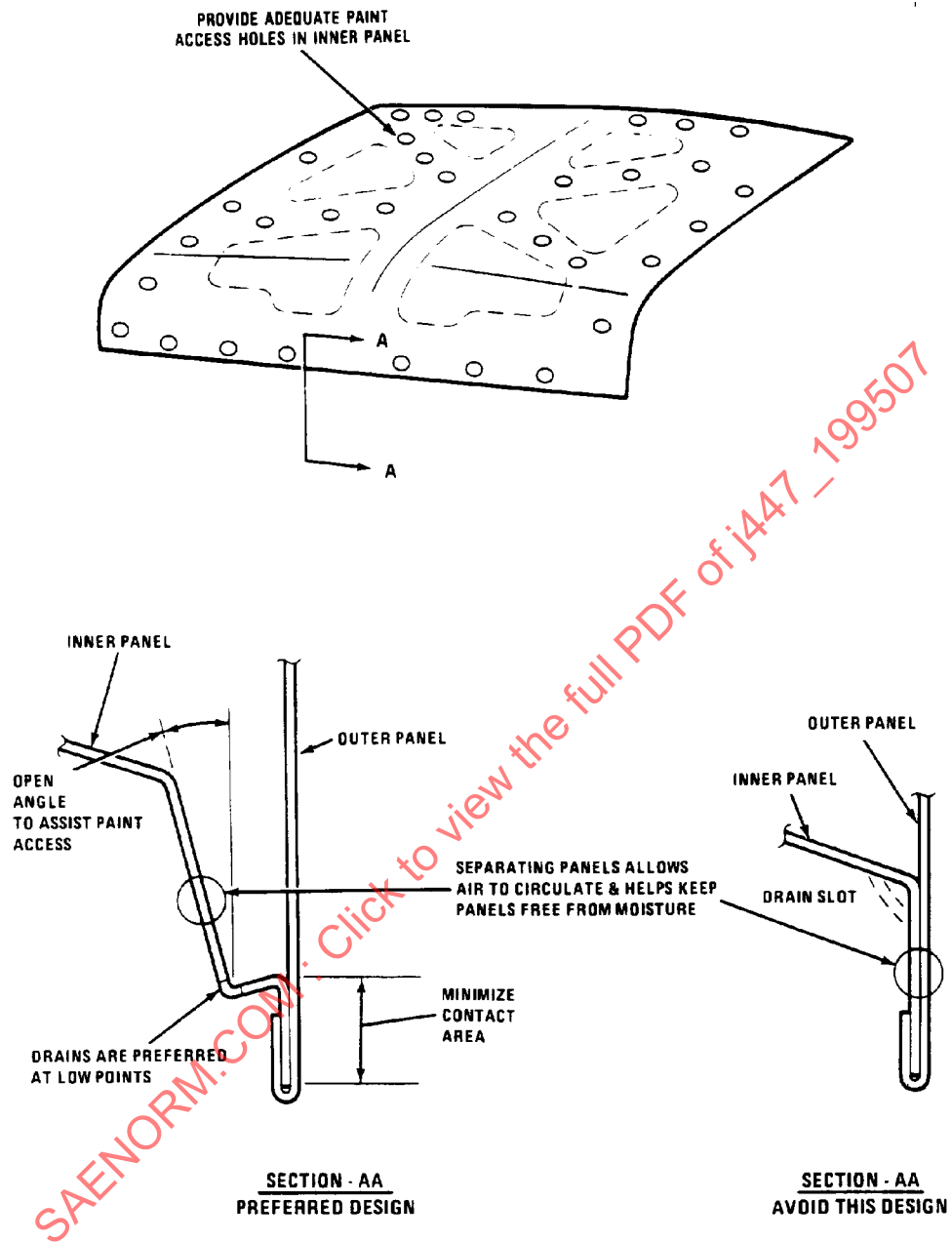


FIGURE 13—DECK LID

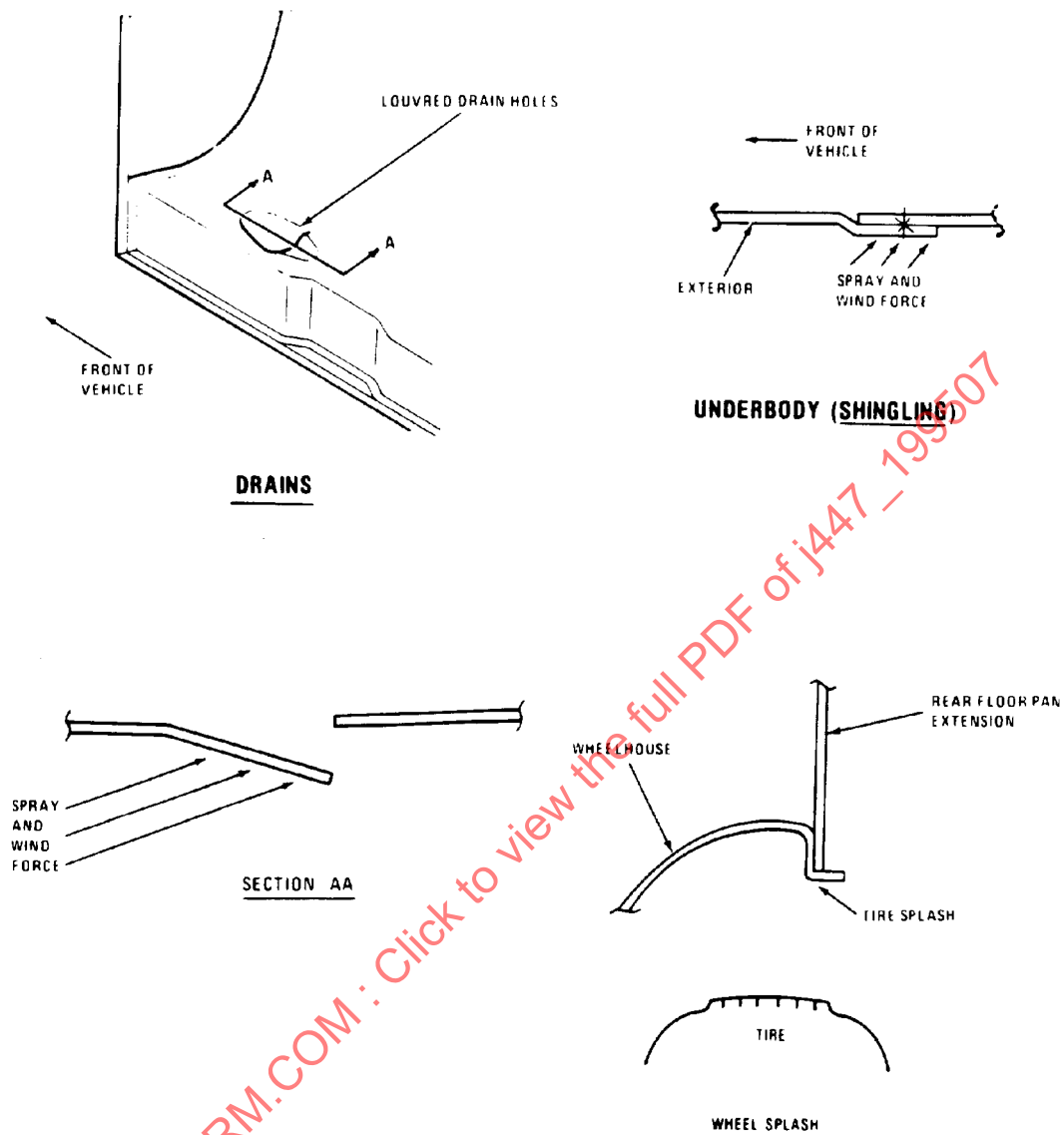


FIGURE 14—DRAINAGE

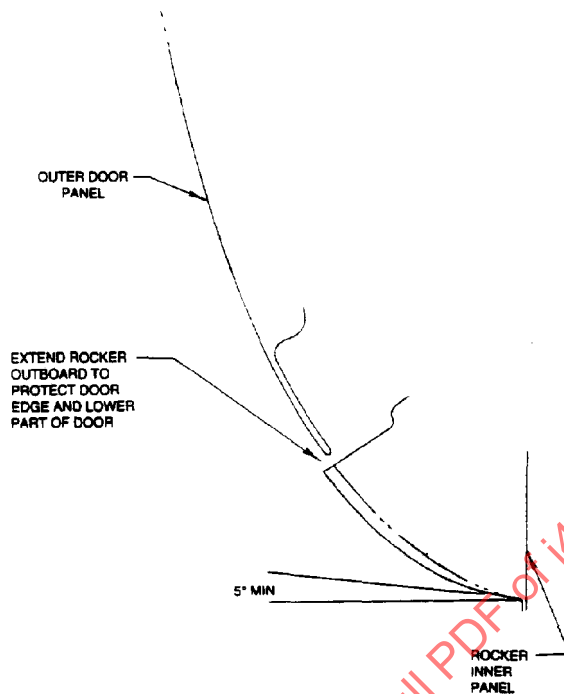


FIGURE 15—ROCKER PANEL

5.2.8 ELECTROCOAT PRIMER ACCESS HOLES—The holes required to permit the electrocoat priming process to function properly fall into three categories although in most cases the holes will serve overlapping purposes.

- a. Holes must be provided to allow the paint material to enter all box sections and closed off areas.
- b. Additional holes sometimes must be provided to ensure that the electrical plating process of the paint takes place on all the surface area. Due to the Faraday cage effect the throwing power, the distance into a closed chamber that the plating will occur, may not cover all the surface area between two access holes. When this happens additional holes are needed near the uncoated areas to allow plating of all the surfaces. Figure 9, Figure 10, and Figure 13 for examples of multiple holes in inner panels and reinforcements to improve throwing power.
- c. When a vehicle enters a dip tank there are some areas such as the wheelhouses that trap a bubble of air which prevents the fluid from contacting and, therefore, plating on the top surfaces. When this happens a small vent hole must be added to the top of the wheelhouse to relieve the air bubble. The hole must later be plugged. See the wheelhouse drawing in Figure 12.

5.2.9 FASTENERS—Sheet metal parts should be designed so that all holes for fasteners are stamped in the body panels. Less desirable is the drilling of holes in the body shop because of the metal chips created and the ragged edges that are hard to paint. These two methods do, however, allow for unbroken paint on a surface in conjunction with plastic inserts to act as insulation for metal screws or other nonmetallic fasteners Figure 16. The use of drill point screws or thread cutting screws must be avoided. These guidelines will prevent corrosion due to a broken paint surface.

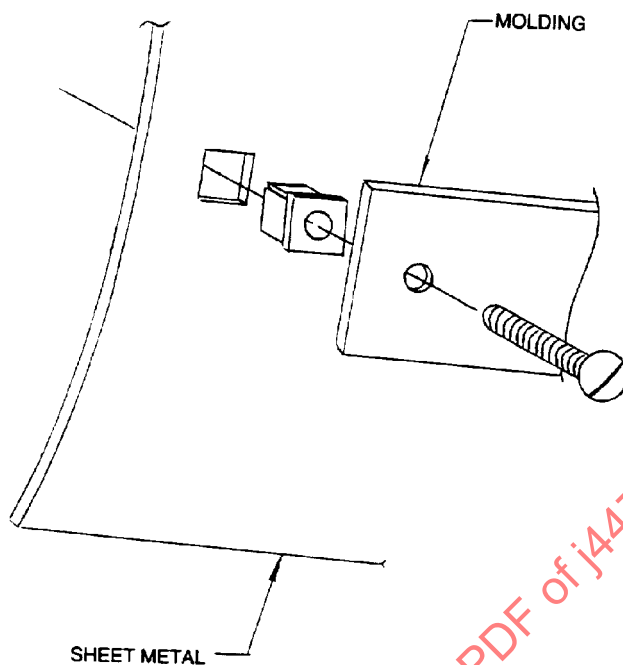


FIGURE 16—FASTENERS

5.2.10 DISSIMILAR METALS—The coupling of dissimilar metals should be avoided whenever possible. (See 4.3.3). In those instances where it cannot be avoided, steps must be taken to insulate the metals from each other. All metal molding and trim parts must be insulated from the painted sheet metal (unless bimetal trim is used), and the metal attachments should be insulated. Adhesive attachments for moldings and trim parts are preferred.

5.2.11 GENERAL COMMENTS—Figures 9 through 16 show general application of desirable design conditions for major body panel assemblies. Not all designs are considered but the principle exemplified should be and generally can be incorporated in variations not discussed.

As suggested at the beginning of this chapter, design is only one aspect of the many considerations in maximizing corrosion resistance. The corrosion considerations reviewed should be considered during the early design stages and should be carefully balanced with other considerations such as:

- a. Structural requirements
- b. Manufacturing and assembly feasibility
- c. Cost and weight objectives

It is seldom, if ever, possible to achieve a perfect design. Because of this, design considerations other than corrosion may require concessions not optimal for application of protective coatings. When this occurs, areas exposed to the external environment which are inaccessible after component assembly should be reviewed for application of protective materials prior to assembly.

6. Chapter 3—Chemical Conversion Coatings

6.1 Introduction—Chemical conversion coatings such as phosphate, oxide, or chromate are universally accepted in industry to enhance corrosion resistance. Phosphate coatings are also used as aids for wear prevention or cold forming, as a substitute for paints, and as matrices for the retention of oils, waxes, or lubricants.

Metal surfaces must be rendered free of shop soil, oil, grease, lubricant, and rust to provide a surface condition receptive to the formation of a uniform, adherent chemical film or coating. The method of cleaning varies greatly with the metal to be treated and the type of chemical coating to be applied. Cleaning preparation may vary from mechanical methods such as flat polishing or abrasive blasting to vapor or solvent degreasing through the more generally used immersion or spray aqueous phase cleaners.

6.2 Phosphate Coatings—Phosphate coatings are the most widely used preparation in the automotive industry and are of four basic types:

- a. Modified zinc or iron phosphate coatings to produce a corrosion resistant base for paint retention on steel, zinc, or aluminum surfaces.
- b. Heavy zinc phosphate coatings for rust preventive oil retention.
- c. Manganese or zinc phosphate coatings for wear resistance or break-in on bearing surfaces.
- d. Zinc phosphate coatings in conjunction with soap films as an aid to cold forming.

The phosphate coatings function as an adsorptive crystalline nonmetallic matrix for retention of oil or lubricants for corrosion resistance, wear resistance, or forming dies. As a substrate for paint films, the phosphate coatings may enhance paint bonding and act as a nonmetallic barrier between corrosive elements and the base metal.

6.2.1 PHOSPHATE COATINGS FOR CORROSION PROTECTION—Heavy coatings of either zinc or manganese phosphate, when treated with corrosion inhibiting oils, result in a synergistic effect. Zinc phosphate and manganese phosphate, when oiled, are used to protect underparts of automobiles, such as nuts, bolts, brake pedal assemblies, accelerator levers, master cylinder plugs, accelerator brackets, hood latch yokes, hydraulic cylinder covers, etc.

All these heavy coatings are produced by immersing the cleaned articles in the hot processing solution for 5 to 15 min, depending on the bath chemistry. The weight of the coatings produced depends upon the manner in which the articles are cleaned, immersion time cycle, the composition of the processing bath, and the analysis and previous history of the metal. Most coatings, however, that are used for corrosion protection have weights between 8.6 and 32 g/m² (800 and 3000 mg/ft²) of surface area.

6.2.2 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 1.6 to 3.2 g/m² (150 to 300 mg/ft²) of surface area. The solutions used are mainly zinc and other divalent metal dihydrogen phosphates (like nickel or manganese) containing various accelerating agents and producing phosphate coatings not only on steel but also on zinc and aluminum. Methods of application are by spray, dip, and brush at temperatures from 20 to 100 °C (70 to 210 °F) and processing times from 45 s to 5 min.

Automobile bodies and sheet metal parts are coated with a zinc phosphate coating prior to spray or electrophoretic painting. (Processing times generally vary from 45 s to 2 min with temperatures ranging from 45 to 60 °C (115 to 140 °F).) Dip treatment is preferred since inner surfaces of the bodies are phosphate coated in contrast to the partial coating (primarily exterior) achieved by spray treatment. Coatings obtained by dip processing generally have smaller crystals and tend to be more corrosion resistant than the larger crystals obtained by spray processing.

The iron oxide/iron phosphate coatings are relatively light in weight and range from 0.3 to 1.0 g/m² (25 to 90 mg/ft²) 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 may be processed by this type of treatment.

Both iron and zinc phosphate coatings are usually given a chromium containing or, more recently, a chrome free rinse (post rinse) prior to final water rinses and paint application.

- 6.2.3 PHOSPHATE COATINGS FOR WEAR RESISTANCE—Phosphate coatings, particularly manganese phosphate, consisting mainly of the mineral hureaulite $[\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}]$, 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, camshaft, gears, and the like. Corrosion resistance is also imparted to these items by this heavy phosphate treatment.
- 6.2.4 PHOSPHATE COATINGS AS AN 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, or reactive soap, to aid in the cold forming and extrusion of these metals. Zinc phosphate is commonly used. Some automotive parts produced by this means are bumper bars and guards, tubing, truck wheels, transmission driveshafts, housing, piston pins, and gear blanks.

6.3 Oxides

- 6.3.1 BLACK OXIDE ON STEEL—The black oxide type of surface treatments are 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 components. The coatings are 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 alkali/nitrate method. The clean metal is immersed in a strong alkaline solution containing oxidizing agents and other additives, which at temperatures up to approximately 150 °C (300 °F), produces the blackening effect.

A lower temperature method for forming the black oxide uses a weak acid solution containing neutral nitrate salts and other additives. The clean metal part is immersed in an agitated solution at 100 to 105 °C (210 to 220 °F), and the coating formed is chemically equivalent to that using the hot alkaline solution.

- 6.3.2 ANODIC COATINGS ON ALUMINUM—The purpose of anodizing is to produce an oxide coating on aluminum under controlled conditions to enhance the durability and/or appearance of the parts. Anodizing is applicable to wrought, cast, or extruded aluminum alloys. The following types of functional and decorative aluminum parts are often anodized:

- a. Pistons and hydraulic cylinders
- b. Automotive moldings
- c. Bumpers and grilles

The electrolytic finish on aluminum, produced by an anodic treatment is a dense durable aluminum oxide which offers good abrasion and corrosion protection after proper sealing. These films possess excellent absorption qualities for paints, dyes, and electrolytic coloring processes which are often applied after anodizing but prior to sealing. When paint is applied to anodized aluminum, the seal is omitted unless the parts are used for decorative purposes.

After appropriate cleaning and/or bright dipping, the anodizing process is continued 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. The porous oxide film produced by either of these processes must be sealed by immersion in hot water, chromate, nickel acetate, or silicate solution to increase the barrier properties of the oxide. Combinations of these seals, such as nickel acetate followed by hot chromate or hot water [100 °C (210 °F) min], have gained increasing acceptance by the entire automotive industry for decorative parts. Anodic treatment of pure aluminum gives the best protection. Alloying constituents to aid in manufacturing and improve mechanical properties generally degrade the corrosion resistance of the coating.

All aluminum must be properly prepared to insure complete coverage and image clarity to the finished part. Recommended practices are detailed in the Aluminum Association publication "Designation System for Aluminum Finishes," Table 2, Chemical Finishes.

Various ASTM and automotive standards exist specifying various anodic thicknesses for specific service conditions or use. Descriptions of the anodic coatings are contained in Table 1 of ASTM B 580-73.

Coatings on the order of 8 μm (0.0003 μin) are generally specified for automotive exterior moldings and other decorative parts. Parts subsequently exposed to temperatures over 100 °C (210 °F) in various stages of assembly (paint repair ovens, etc.) have a tendency to craze. The thicker the anodic coating, the more pronounced the crazing.

The most common quality control tests are:

- a. ASTM B 117—Salt Spray Test
- b. ASTM B 136—Stain Resistance
- c. ASTM B 137—Coating Weight
- d. ASTM B 368—CASS Test
- e. ASTM B 110—Dielectric Strength
- f. ASTM B 487—Microscopical Thickness Measurements

Other tests could include the Acid Dissolution Test and Thickness Measurements by Light Section Microscope.

- 6.3.3 OXIDE-CHROMATE COATINGS ON ALUMINUM—Coatings for aluminum produced in short immersion or spray times have been developed for sheet, castings, forgings, and 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 often 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.

6.4 Chromates

- 6.4.1 CHROMATE COATINGS FOR ZINC AND CADMIUM—Chromate coatings 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 a basic chromium chloride.

Chromate coatings tend to become harder and more adherent during rinsing and subsequent exposure to the environment. Films are thin, iridescent, and produce 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.

- 6.5 Coatings for Magnesium**—In general, two classes of treatment are used for preparation of magnesium alloy surfaces for painting: chemical treatments, class I; and anodic treatments, class II. The class II treatments are more protective. Generally, these coatings are applied to very clean surfaces.

Cleaning methods include mechanical (abrasive) treatments, solvent cleaning, alkaline solution treatments, and acid pickles not resulting in protective conversion coatings. Cleaned surfaces will withstand only mildly corrosive indoor exposure. When greater corrosion protection is desired, as in many outdoor environments, surface preparation by one of the conversion classes is necessary. ASTM D 1732 describes the treatments and methods available.

- 6.6 Evaluation Tests**—Accelerated laboratory tests commonly used for evaluating chemical surface treatments are salt spray, humidity, cyclic corrosion, and water soak tests. Some of the ASTM test methods are given in Table 4.

TABLE 4—EVALUATION TESTS

Test Method	Specification
Salt Spray, 5% NaCl	ASTM B 117
5 or 20% NaCl	QQ-M-151 ⁽¹⁾
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	TT-P-141-B ⁽¹⁾

1. Federal Specification

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 evaluated for corrosion resistance 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.

7. Chapter 4—Organic Primers and Topcoats

- 7.1 Introduction**—Corrosion protection for metals is often obtained by the use of an organic coating or paint. This method of corrosion protection has been used from the beginning of recorded paint technology and the recognition of corrosion as a phenomenon of nature.

The basic components of a paint are resin, pigment, and usually a carrier or solvent. This technology has evolved from a simple mixture of materials found in nature, such as ores and natural gums or resins, to a complex chemistry of numerous specific pigments dispersed in synthetic polymers with a variety of solvents having carefully controlled properties.

Painting to control corrosion of metals is often done because it is a cost-effective method of achieving protection and may also provide decorative characteristics. Paint achieves corrosion protection primarily as a barrier coat. It prevents or retards the electrochemical reaction of corrosion by stopping or slowing down the charge transfer at the metal-solution interface. Specific resins provide properties of good adhesion to metal and good corrosion resistance under a variety of corrosive environments.

Examples of resin polymers are epoxies, epoxy esters, polyesters, alkyds, vinyls, acrylics, oils, and others. Usually the thicker the coating, the greater its corrosion resistant properties. Primers are normally applied at 10 to 30 μm . Additional coats can increase the total film thickness to 100 μm or more, as needed.

A variety of pigments are also utilized to achieve corrosion resistance. Specific pigments such as the family of chromates, provide unique properties of corrosion inhibition. Others, such as molybdates, lead, or zinc-containing pigments also provide some corrosion-resistant characteristics when dispersed in the paint.

Some paints are formulated to be sacrificial coatings which contain pigments less "noble" in the galvanic series (Table 2) than the metal to be protected. Corrosion protection is obtained from the pigment, such as zinc metal, being electrochemically consumed as the sacrificial anode. This coating has a specific protective life related to the corrosive environment in which it is used.

There are a wide variety of paints which may provide corrosion protection for specific situations. The evaluation of these paints may require a complex, environmentally specific testing procedure. The most common accelerated non-cyclic, QC type test for paints is the ASTM B 117 salt fog exposure. There are a variety of other more field relevant cycle tests which can be used [SAE Papers 912275, 912278, 912283, 912284, and 912285]. It is important that any accelerated test be related to intended end use.

Material selection is influenced by the method of application. Often the application method is as important with regard to cost and protection desired as the paint to be used. The variety of methods used and their characteristics are described to provide a basis for selecting a process to obtain the necessary paint properties.

Due to environmental restrictions, the use of water-borne coatings is increasing. With the addition of nonmetallic materials (e.g., plastics) as parts of automotive components and assemblies, lower cure temperatures 65 to 110 $^{\circ}\text{C}$ (150 to 230 $^{\circ}\text{F}$) are desired.

Coating lines for body assemblies require a high degree of sophistication in the control of paint chemistry and application.

7.2 Spray Application—The application of organic primers and topcoats with the various types of spray equipment available is a proven and well-defined process. This equipment effectively acts upon a stream of paint, solvent or water-borne, and by various means disperses the paint into a cloud of finely divided particles. This cloud of atomized paint particles is then deposited on the intended surface forming a protective or decorative coating. Atomization is desirable to produce surface smoothness and, in the case of metallic topcoats, uniform metallic flake orientation.

Spray application provides considerable flexibility in processing methods and procedures. Some of the advantages are as follows:

- a. A variety of shapes can be coated with reasonable uniformity.
- b. Spraying is still the only practical method of applying the very popular metallic topcoat finishes. Good atomization of the paint stream and uniform application are essential to proper orientation of the metal flake.
- c. In general, spray application provides greater latitude in the type of paint formulation that can be used. For example, it is very difficult or impractical to use dip application methods with highly pigmented products.
- d. Spraying provides the opportunity to apply different products to accomplish very specific goals. Guide coat primer systems, primers of contrasting color applied wet-on-wet, are very common where subsequent sanding is done to signal the operator to stop prior to exposing the substrate.
- e. High-fill primers for rough metal, corrosion-inhibiting primers for high-corrosion areas, and low-gloss black-out topcoats for special styling treatments provide further examples of instances where spray application is particularly appropriate.

- f. Variations in paint thickness are possible as specific areas can be increased without the expense and problems associated with higher thicknesses all over.
- g. The ability to change products quickly and at generally less expense is also an advantage associated with spray application. Spray systems usually utilize lower paint volumes than typical dip or flow-coat installations. Higher volumes can produce significant disposal costs should it become necessary to change products because of new technology, a change in processing requirements, or possibly a failure related to the paint formulation itself.
- h. Many different substrate materials can be painted simultaneously by spraying.

A few drawbacks do exist with spray painting, as with any system, with the most important being:

- a. Efficiency—When compared with most dip, flow coat, electrocoat, or autodeposition operations, the amount of coating actually being deposited in relation to the total amount used is lower with spray application. This is accounted for by the loss of overspray or the atomized paint particles that get blown beyond the work by the atomizing air. This can be controlled somewhat by electrostatic application equipment.
- b. Health—Potential health hazards do exist since the spray principle requires the fine atomization of coating material. Inhalation of some of the paint ingredients could be harmful and should be controlled with the proper equipment and precautions.
- c. Labor—Spraying is generally more labor intensive than other coating methods and requires some degree of operator skill. Automatic spray equipment reduces these requirements.
- d. Application Control—The cost of controlling the spray environment can become considerable. The human element requires that high volumes of fresh air (for safety and health reasons) be supplied at a comfortable working temperature. Water-borne materials generally must be applied in a humidity-controlled atmosphere since very little can be done to change the evaporation rate. And finally, spray booth maintenance is a very important aspect of spray application. The cleaning of filters and exhaust stacks and the removal of waste overspray require close attention.

7.3 Dip Application—This process is a method of dipping the part into a bath of paint, draining the part, and force drying or baking the part. Dip coatings are used throughout industry for many primer and one-coat finishing systems.

The selection of a coating type and color is directly related to the end use intended for the finished part. Water-borne dip coatings provide fire resistance and desirable ecological properties. The use of a dip-coating system does affect properties of appearance, quality, cost, and other factors.

Some of the advantages are:

- a. Simplicity—Minimal manpower and equipment for painting are required.
- b. Low Cost—Paint utilization is relatively high on properly operated systems. Paint drippings are recovered and returned to the system.
- c. Ease of Control—A minimally skilled operator can maintain proper solids, viscosity, and other factors to maintain acceptable application properties.
- d. Good Coverage—A dipped part receives a complete coating, except for air bubbles or pockets, on all areas immersed in the paint.
- e. Consistency—Each part coated receives an identical coating similar in appearance and film build; i.e., the process is not operator dependent.

Some disadvantages are:

- a. Nonuniform Film Coating—The coating on a dipped part tends to be wedge-shaped with a thin film at the top and thicker at the bottom. There can also be flow lines or sags around any openings and a bead at the bottom of the part.
- b. Part Design and Hanging—A part must be hung properly. Parts may trap and carry out paint or have air bubbles trapped in some inaccessible areas preventing paint from coating these areas. Some parts do not lend themselves to dip application.
- c. Solvent Washing—Solvent evaporating from warmer areas may condense on colder areas "washing" the paint off the colder wall, leaving some areas unpainted. Oven curing increases this tendency.
- d. Labor—Proper part hanging in loading and unloading may be labor-intensive.
- e. Product Change—Changing product requires extensive cleaning and recharging of the tank or having multiple dip tanks with a relatively large paint inventory.
- f. Flammability—Special fire protection is required for solvent-borne dip primers. Water-borne primers reduce this problem.
- g. Foam—Solvent-borne paints usually have fewer foaming problems than water-borne paints. Foam can cause a flaw in the paint film which adversely affects appearance and quality.

Dip-spin application of organic coating is used primarily on smaller stampings and fasteners. Organic or inorganic/organic finishes are applied over phosphated, plated, or mechanically cleaned surfaces. After application, the dip spin method is baked at temperatures ranging from 90 °C to over 315 °C (200 °F to over 600 °F). However, other colors are available and color matches can be obtained.

Organic/inorganic coatings have provided the newest generation of corrosion resistance performing in most cases better than electroplated/chromated finishes. Providing salt spray corrosion resistance (ASTM B 117) from 240 h to over 1000 h. They also provide excellent resistance to galvanic corrosion. Being less conductive, they can be coupled with stainless steel, aluminum, and carbon steel.

Coatings with PTFE (Polytetrafluorethylene) can act as a replacement for cadmium plated parts where required for lubricity and where range of torque must be controlled for clamp load.

Some advantages of the process are:

- a. Excellent coating utilization (low cost) could be in the high 90's percent. Coating only goes onto product not into air spray.
- b. Minimal manpower requirements.
- c. Good part coverage, skilled operations can maintain the proper RPM's, viscosity and proper solids to attain the coatings acceptable application properties.
- d. Some coating types can withstand operating temperatures up to 648 °C (1200 °F).
- e. Can be applied to ferrous or nonferrous substrates.
- f. Normally provide longer life corrosion resistance than standard electroplated parts.

Some disadvantages of the process are:

- a. Most present coatings are solvent, not water-based.
- b. Cannot throw coating into deep or blind holes.
- c. When not applied properly, can fill fastener and stamping recesses and shallow holes.
- d. Expensive to coat flat parts.

7.4 Flow Coat Application—Flow coating is an automatic operation in which the product to be painted is conveyed through a chamber equipped with low pressure nozzles that completely flood the product with paint. There is no atomization as with spray painting. This process is especially adapted to painting large articles which would require large dip tanks if finished by dipping and are of such shape that spray painting would not be practical because of high material losses.

Coatings that are formulated as flow-coat primers may be chemically similar to their spray- or dip-applied counterparts. They are normally modified to provide for better oxidation stability, improved flow, and increased hiding. The selection of a coating formulation is influenced by the environmental factors to be encountered during storage, the end use intended for the part, and coating cost.

Some disadvantages of the process are:

- a. **Good Paint Utilization**—Material utilization can be as high as 97% depending on the product being flow coated. Since excess paint can be collected and reused, material utilization varies only slightly from product to product.
- b. **Versatility**—Practically any type of part can be flow coated provided it can be properly drained.
- c. **Good Coverage**—Since the parts are completely flooded with the coating material, a complete coating is obtained on all exposed surfaces.
- d. **Labor Savings**—Manpower requirements are minimal for flow coating. The principal need is for loading and unloading. With automatic viscosity and make-up control, very little labor is needed to control the bath during operations.
- e. **Low Paint Inventory**—The quantity of paint in use at any time is only about 10 to 15% of the bulk volume of material normally required for dipping the same quantity of work.
- f. **Minimal Health Hazard**—As with other automatic coating processes, the exposure of personnel to a potentially hazardous environment is minimized because the coating is applied and cured in more or less isolated enclosures.

Some disadvantages of the process are:

- a. **Nonuniform Coating**—Because of flow-out immediately following coating, film thicknesses will be somewhat heavier at the bottom of the product than at the top. However, as with dip coating, film thickness characteristics and appearance are very consistent within a given set of control parameters based on viscosity, total solids, solvent balance, paint temperature, and paint application pressure.
- b. **Part Configuration and Hanging**—The method of hanging is important in obtaining proper coating on all surfaces. When parts are improperly hung, problems can occur from excessive paint carry-out or carry-in of pretreatment chemicals and from lack of proper flow-out. As a result, loading labor is critical.
- c. **Solvent Washing**—Solvent evaporation from inner areas during flow-out may condense on adjacent cooler areas resulting in washing off the coating from the colder surface leaving the surface unpainted.
- d. **Foam**—Foam can cause appearance and protection problems on parts. If the foam is not rapidly dissipated, cratering or film discontinuities will occur. Foaming is more prevalent in water-borne coating than in solvent-borne. Foaming can be controlled by a well-formulated paint containing defoaming agents.
- e. **Clean-Up and Maintenance**—Clean-up and maintenance costs are generally higher with flow coating than with competing processes.

Following shutdowns, the flow-out tunnel must be flushed down, the flow coat piping, headers, nozzles, and heat exchangers must be flushed, and bath agitation must be started. Since a number of mechanical components are an integral part of the flow coating process, maintenance can be a significant portion of the operating costs.

7.5 Electrocoating—Electrocoating is a dipping process where the piece to be painted is immersed in a tank containing paint solids dispersed in water and then electrically energized with a direct current potential that causes almost water-free paint solids to deposit on an electrically conductive surface. For safety purposes, no one is allowed within the coating enclosure while the system is in operation.

Paints used in this process are electrically ionizable and can be formulated to deposit at either the anode or the cathode. Although a wide range of resins including alkyds, epoxies, polybutadienes, acrylics and polyesters have been used in electrocoat paint formulations, not all organic resins are currently used in this process. Pigment composition, size, and purity are critical. Water soluble organic solvents (e.g., the monoalkyl ether of ethylene glycol) and water insoluble solvents (e.g., naphtha) are used in electrocoat paints.

The electrocoat process is used to apply primers and single-coat enamels. Some of the advantages of using this process are:

- a. The coating process is completely automatic.
- b. A relatively uniform film can be obtained over all surfaces.
- c. All sizes and shapes of parts can be coated in the same tank.
- d. Paint drawaway from sharp edges during coating and baking is minimized.
- e. The coating formed is usually free from runs, sags, and similar surface defects.
- f. Compared to conventional spray or dip applications, the process is capable of providing improved coverage over hidden and recessed areas such as coach joints, automobile rocker panels, and structural steel sections.
- g. The deposited coating is relatively free of solvents. Solvent washing is not a problem.
- h. Through the use of ultrafiltration and reverse osmosis equipment, electrocoating can be made into a closed-loop system reducing pollution problems.
- i. Paint utilization in this process approaches 100% of theoretical.

Some of the drawbacks of the electrocoat process are:

- a. Facility and equipment costs are relatively high.
- b. A large volume of paint is required.
- c. Energy costs may be higher than on other processes.
- d. Coverage is dependent on voltage, the length of the tank, and the speed of the conveyor.
- e. Adequate access and drainage holes must be provided in parts for the paint and electrical energy to enter to allow the coating process to occur.
- f. Maintenance of electrocoating tanks is important to ensure proper operating conditions.
- g. "Cratering" can occur when painting some metals.
- h. Thermal distortion of plastic components (of an assembly) can occur due to the (relatively) high cure temperature.

7.6 Autodeposition [SAE Paper 912291 and 2.1.3.1, 2.1.3.2]—Autodeposition is a coating process in which a combination organic-inorganic film is deposited on metal surfaces. Only four steps are usually employed, including cleaning, autodeposition coating, a final sealing rinse, and oven curing. This process precludes the need for a conventional phosphate pretreatment process prior to painting. Curing is achieved by standard convection ovens, infrared radiation, or by a heated "immersion cure" aqueous final rinse stage.

Coating occurs via a chemical oxidation-reduction reaction similar to those that occur in electroless plating of metals. The autodeposition painting bath comprises a 4 to 7% by weight dispersion of an organic latex emulsion, dilute (0.2%) hydrofluoric acid, and an oxidizing agent. In the autodeposition process, metallic iron is oxidized by the acid to the ferrous cation which dissolves into solution at the work surface. Subsequently, the metal cation coprecipitates with the anionically-stabilized organic latex onto the work surface. The coating reactions are not exothermic so that neither the solution nor the part to be coated are heated. A final reaction rinse is typically employed to impart additional corrosion resistance to the coating.

The autodeposited coating is uniform, usually 12 to 25 μm in thickness, low in gloss, and suitable for items requiring good corrosion protection.

Some advantages of this process are:

- a. Few process stages are required, minimizing capital and floor space requirements.
- b. No coating build-up on hangers.
- c. The coating process relies on chemical reaction allowing coating of all hidden or recessed areas with even coverage.
- d. Reduction in expended energy is realized by the elimination of the phosphate pretreatment process.
- e. The coating does not pull away from sharp edges, coats evenly over machined surfaces (e.g., threaded fasteners) and is free from runs, sags, orange peel, and similar defects.
- f. Very low maintenance is required.
- g. The process is environmentally benign with low or no VOC emission and heavy metal effluent. No fire hazards are present.

Some of the drawbacks of the autodeposition process are:

- a. Current applications are for ferrous and galvanized surfaces only.
- b. The coating can exhibit some patterning and is topcoatable by only selected finishes.
- c. Waste paint generation may be higher than some other coating systems unless an ion exchange reclamation unit is employed.
- d. Color availability is limited at present.

7.7 Powder Coating—Powder coating is a process which has had recent developments of new coating materials and new application techniques. In this process, dry plastic powders are applied to a clean/treated surface. After application, the coated object is heated, fusing the powder into a smooth continuous film. Today, plastic powders are available representing a wide range of chemical types, coating properties, and colors. The most widely used types include acrylic, vinyl, epoxy, nylon, polyester, urethanes, and cellulose. They are finely ground, free-flowing powders with generally higher molecular weight polymers than those used in solution finishes.

It is because of the high molecular weights that the coatings may be formulated to have good durability, toughness, and abrasion resistance. Powder coatings and the means of applying them offer some distinct advantages over conventional painting processes.

- a. The most significant advantage, from an environmental point of view, is the elimination of organic solvent carriers. The powders are applied as 100% solids and are virtually free of pollutants.
- b. The 100% solids nature of powder offers conservation advantages. The fact that the coating is a powder, means that the overspray can be collected, separated, and reused.
- c. With powder, spray-coating efficiency is high; as much as 90% can be retained on the parts, especially if recovery of overspray is used. The complete coating can be applied with one coat as compared to the two to four coats often necessary with conventional systems. Smaller more compact spray areas can be used, saving space and energy.
- d. Powder coating operations are much simpler. Unskilled labor can be used to apply these coatings. Many operations can be automated.

Some of the disadvantages of powder coatings are:

- a. The majority of the exterior automotive topcoat colors sold in the U.S. today are metallic finishes. A special process is available in which metallic flakes are blended into the powder coating and sprayed onto a part; however, the clarity of the finish is not currently equal to that produced by the conventional basecoat/clearcoat paints. Powder suppliers must match existing standards or automotive styling must sell a different "metal appearance" to the public.
- b. Color matching is more difficult to achieve initially and may be more difficult to correct in production.
- c. High baking or high application temperatures are required for these materials.
- d. Some parts with recessed areas may be difficult to coat electrostatically because of loss of electrical attraction to inner or recessed areas.
- e. Equipment for spray-powder coating is relatively complex and expensive in order to provide color changing, powder recovery, and safety.
- f. Film thickness control at low film build is difficult.

7.7.1 POWDER APPLICATION TECHNIQUES [SEE 2.1.3.3]—Modern application techniques for applying powders fall into three basic categories: (a) Fluidized Powder Bed Process, (b) Electrostatic Fluidized Bed Process, and (c) Electrostatic Powder Spraying and other electrostatic application methods, including Discs and Powder Coating Tunnels.

7.7.1.1 *Fluidized Powder Bed Process*—The fluidized bed is essentially a chamber or box with a porous bottom through which air is introduced. When the flow rate of the air is properly adjusted, the powder behaves like a fluid. The object being coated is then preheated and immersed in the bed of fluidized powder. The heat causes the powder particles to adhere to the object. The powder is then fused into a smooth continuous coating in an oven. Coated parts can then be air-cooled or water-quenched. Film thicknesses, ranging from 254 to 1270 μm can be obtained. Low film thicknesses are not normally achieved as film thickness control is difficult.

7.7.1.2 *Electrostatic Fluidized Bed Process*—Electrostatic fluidized bed process combines features of both the fluidized bed process and the electrostatic spray process. The preheated or cold electrically grounded object is immersed into or suspended over a cloud of charged particles. The particles are post-heated in order to fuse them into a continuous film suitable for small parts.

7.7.1.3 *Electrostatic Powder Spray Coating*—In this process, the electrically conductive and grounded object is sprayed with charged, nonconducting powder particles. The charged particles are attracted to and cling to the substrate until the charge is dissipated (several days), thus allowing time for the particles to be oven-fused into a smooth continuous film. Coating thicknesses ranging from 25 to 126 μm are obtained. Control of low film thickness is difficult. A spray booth and collection system can recover all overspray. This powder can be separated and reused.

8. Chapter 5—Protective and Decorative Post-Applied Metallic Coatings

8.1 **Introduction**—Various types of metallic coatings can be applied to ferrous and nonferrous metallic and nonmetallic substrates after forming. These coatings are used to provide corrosion protection and/or a decorative appearance. Some coatings are chosen because they are anodic to the base material and offer sacrificial protection. Others offer barrier type protection. The choice of a particular coating material is dependent on the environment it is exposed to and the function it is to perform.

8.2 Application of Metallic Coatings—Metallic coatings can be applied by different processes. The most common method of application is electroplating. This process deposits coating material to the substrate metal (or conductive nonmetal) by applying an electrical potential between the part (cathode) and a suitable anode while immersed in an electrolyte. Mechanical plating is a process which uses finely divided metal powder. The powder is cold-welded to the part by tumbling the powder, the part, and a suitable media such as glass beads in an aqueous solution. Autocatalytic application is an electroless plating system where the metal coating is deposited on a part by way of a chemical reduction reaction in the presence of a catalyst. Hot-dip coating is a process where the part is immersed in the molten metallic coating material. The coating is usually of greater thickness than that produced by other processes.

The following are descriptions of the more common metallic coatings:

- 8.2.1 **ZINC**—A common corrosion-resistant coating used to protect metallic parts. Because of its position in the electromotive series, zinc offers sacrificial as well as barrier protection to iron and steel substrates. Zinc alloy coatings, such as zinc/nickel and zinc/iron, are gaining popularity for their improved corrosion resistance. Zinc coatings are most commonly deposited by electroplating. Mechanical plating is often used when parts may be subject to hydrogen embrittlement. Mechanical plating is limited to relatively small parts that can be tumbled. Zinc can also be applied by hot dipping. This process develops a coating thickness in excess of that of electro- or mechanical-plating. The appearance of a hot-dipped (galvanized) part is not as good as either electro- or mechanical-plated parts due to the increased thickness and spangle associated with this process. Zinc-coated parts are almost always used with a conversion coating applied after plating to retard the formation of white-corrosion product, or to act as a paint base.
- 8.2.2 **CADMIUM**—This coating material is very similar in appearance and corrosion protection to zinc. It can be applied by electroplating and mechanical plating. It can be alloyed with other materials such as tin to increase its corrosion resistance. This is generally done by mixing the cadmium/tin powders for the mechanical process. Once popular and used interchangeably with zinc, cadmium is now becoming very scarce due to environmental concerns. Cadmium is considered very toxic and has been outlawed in some European countries. Because of its excellent predictable torque tension relationship, it is still used in critical fastener application and areas where its lubricity is necessary. Like zinc, cadmium is usually supplied with a chromate conversion coating applied after plating to retard the formation of white-corrosion product.
- 8.2.3 **LEAD**—Lead is commonly applied to metals to provide protection from corrosive chemicals such as battery acid. It is also used in the fuel system on parts like metal filler neck tubes. However, lead is attacked by alcohol, and its use in alternate fuel systems must be controlled. Lead coatings are applied by the electroplating and hot-dipped methods. Lead coatings are barrier-type coatings, and offer no sacrificial protection to iron and steel parts.
- 8.2.4 **NICKEL/CHROMIUM**—One of the most common metallic coating systems used in the automotive industry is copper/nickel/chromium or nickel/chromium in either bright, satin, or brushed finish. Because of their durability and appearance, these coatings are widely used on a variety of substrates to provide an attractive corrosion resistant metallic surface. Common substrates for these coatings include: steel (both low and high strength), aluminum, zinc, and plastic. While this coating offers barrier-type corrosion protection to the substrate, the different layers react galvanically with each other.
- 8.2.4.1 **Steel**—After proper cleaning, parts are electroplated with a layer of copper (this step is optional in many specifications). A layer of semi-bright nickel is then applied followed by a layer of bright nickel. A very thin layer of chromium is then applied. The chromium layer is usually microdiscontinuous (microporous or microcracked). Pore count or crack density is closely controlled. Different methods are used to produce the microdiscontinuous chromium layer. The typical solutions used for the chromium layer are the hexavalent type. Due to environmental concerns, use of hexavalent chromium salt baths may be eliminated or reduced.

8.2.4.2 *Aluminum*—There are two major pre-plate systems used to produce decorative chromium-plated aluminum parts. These are the Zincate and Alstan processes. Modifications of the processes are used by different platers. Modifications sometimes include a layer of electroless nickel after the pre-plate treatment. The remainder of the plating process is similar to that described for steel except the copper layer is required.

8.2.4.3 *Plastic*—Different types of plastic are being plated. Most end users have internal specifications governing the process and performance of the plated part. An initial pre-plate system is used to apply a conductive coating to the part. The remainder of the plating process is similar to that described for steel. As with the aluminum substrate, the copper layer is required for plated plastic parts.

8.2.4.4 *Zinc*—Many zinc parts are plated with decorative chromium. These include both die cast and wrought zinc substrates. The plating process is similar to that described for steel, except copper layer is required.

8.3 **Hard Chromium**—This electrodeposited coating is a hard, durable abrasion resistant finish. Smooth hard chromium surfaces have a very low coefficient of friction. Coating thicknesses vary depending on the intended use. Thin coatings are usually plated to size and buffed to remove microscopic roughness. Parts with thicker coatings are usually overplated, then ground to size.

8.4 **Precious Metal**—Gold and silver plating are sometimes used to coat such things as electrical contacts. Due to the high cost of the plating material, systems have been developed to selectively plate areas of a part. Many of the plated parts are supplied as part of module assemblies.

8.5 **Specifications**—The following is a list of specifications that deal with metallic coatings:

ASTM B 117—Test Method of Salt Spray (Fog) Testing

ASTM B 177—Practice for Chromium Electroplating on Steel for Engineering Use

ASTM B 183—Practice for Preparation of Low Carbon Steel for Electroplating

ASTM B 200—Specification of Electrodeposited Coatings of Lead and Lead-Tin Alloys on Steel and Ferrous Alloys

ASTM B 242—Practice for Preparation of High-Carbon Steel for Electroplating

ASTM B 252—Practice for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coating

ASTM B 253—Guide for Preparation of Aluminum Alloys for Electroplating

ASTM B 254—Practice for Preparation of and Electroplating on Stainless Steel

ASTM B 281—Practice for Preparation of Copper and Copper-Base Alloys for Electroplating and Conversion Coatings

ASTM B 320—Practice for Preparation of Iron Castings for Electroplating

ASTM B 322—Practice for Cleaning Metals Prior to Electroplating

ASTM B 368—Method for Copper-Accelerated Acetic Acid-Salt Fog Testing (CASS Test)

ASTM B 380—Methods for Corrosion Testing of Decorative Chromium Electroplating by the Corrodokote Procedure

ASTM B 456—Specification for Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium

ASTM B 487—Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross Section

ASTM B 499—Test Method for Measurement of Coating Thickness by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals

ASTM B 504—Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method

ASTM B 530—Method for Measurement of Coating Thickness by the Magnetic Method: Electrodeposited Nickel Coatings on Magnetic and Nonmagnetic Substrates

9. Chapter 6—Coated Steels for Corrosion Resistance

9.1 Introduction—Coated-sheet steel typically refers to steel overlayed with a protective coating applied in a continuous process. These materials provide the traditional advantages of steel, such as strength and formability, with the cost-effective durability and corrosion resistance of the coatings.

With coated steel, the responsibility of applying the coatings is dealt with prior to the delivery of the steel. The cleaning and coating of the steel are the responsibility of the supplier. These coatings on steel are often applied with more efficiency and uniformity than is possible with post-applied coatings, and this can translate into lower "per part" costs. Another benefit to the user of coated sheet is minimization of environmental concerns over coating application. Although coated steel can be used without any additional coating, coated steel for automotive applications will typically receive an organic coating after assembly. This requires the same types of cleaning and/or chemical pretreatments as uncoated steel substrates to ensure good paint adhesion and field performance.

Coated steel may be especially useful for preventing "inside out" or perforation corrosion. Perforation corrosion in automotive bodies usually starts on the interior surfaces of the body panels. This often occurs on interior areas that are difficult, if not impossible, to coat after assembly. Coated steel also offers all the advantages of typical anti-corrosion systems: acting to increase the life and value of a product; allowing the use of thinner steels to reduce weight and increase fuel economy; and increasing vehicle safety by reducing corrosion damage to critical load bearing parts.

The use of coated steel products in the U.S. has increased dramatically over the last ten years. Figure 17 graphically represents an 83% increase in North American shipments of all coated steel products between 1982 and 1989 [2.1.4.1]. The primary reason for this increase was the movement by the automotive industry toward coated sheet to combat corrosion. During this period, a significant decrease in the incidence of automotive corrosion was also witnessed throughout the industry. Figure 18 shows the results of five SAE parking lot surveys of 5 and 6 year old cars with model years ranging from 1980 to 1989 and SAE Paper 950375. A significant decrease in both the number and severity of defects occurred during this period. Although design modifications, improved pretreatments, and paints also played a role in this decrease, the movement to coated sheet body panels is probably the key factor responsible for this decrease.

The corrosion resistance of coated steel products is afforded by the coatings which can be either barrier, sacrificial, and/or inhibitive coatings. Barrier coatings separate the steel from corrosive environments. A barrier coating owes its protective value to its own relative chemical inertness to the environment in which it is exposed.

Sacrificial coatings offer electrochemical protection to the exposed steel surfaces. When two pieces of dissimilar metal are electrically or galvanically coupled and exposed to an electrolyte, there is a flow of electrons between the metals accompanied by chemical reactions on their surfaces. The difference in the electrode potentials of the two metals produces the flow of electrons from the more active metal (the anode) to the less active metal (the cathode). This results in an accelerated rate of corrosion of the more active metal while corrosion of the less active metal is prevented. Sacrificial coatings are anodic with respect to steel and in the presence of an electrolyte (e.g., moisture films containing conductive ions) will tend to protect exposed steel surfaces at breaks in the coatings. It is important to note that the effectiveness of a sacrificial coating depends upon both the corrosive environment and the type and thickness of the coating. A coating that offers sacrificial protection in one environment may not do so in another. If there is no exposed base steel, sacrificial coatings act as barrier coatings, although such coatings are subject to chemical attack and oxidation in contrast with true barrier coatings. This is not a problem for coatings such as zinc, however, which has a corrosion rate that is approximately 1/10th that of iron in atmosphere.

Inhibitive coatings contain substances that act to inhibit the corrosion of steel. Chromates are often used for this purpose [2.1.4.3].

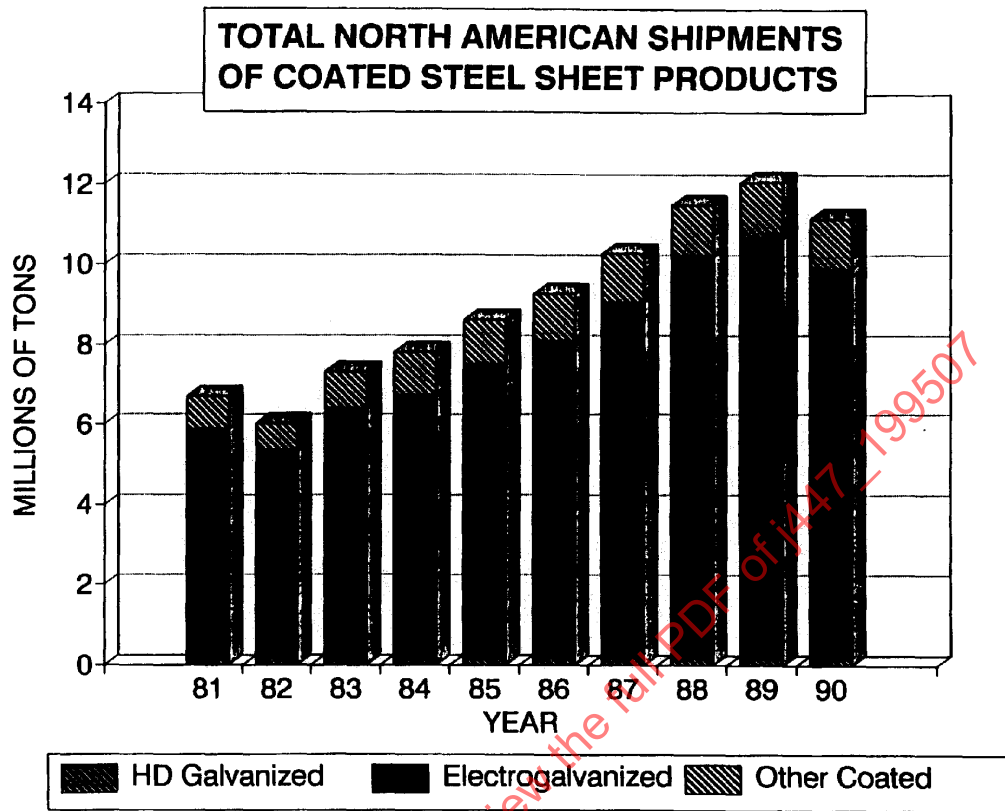


FIGURE 17—NORTH AMERICAN SHIPMENTS OF COATED STEEL SHEET PRODUCTS

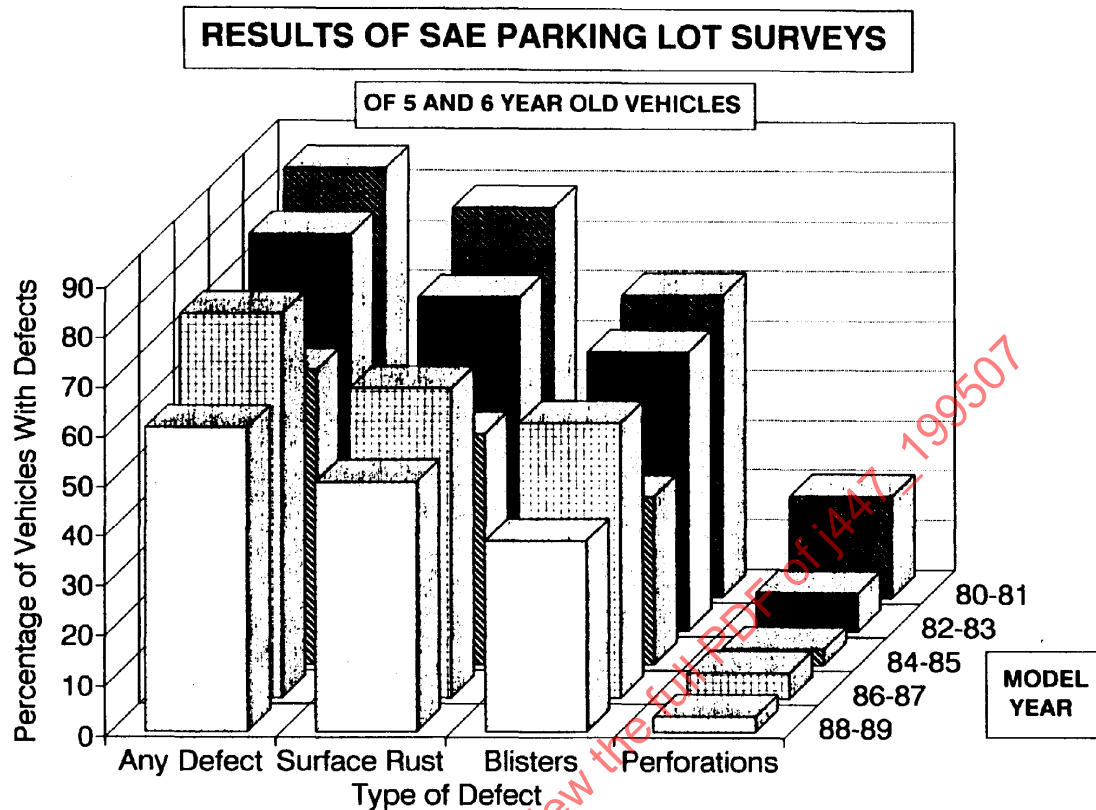


FIGURE 18—RESULTS OF SAE PARKING LOT SURVEYS

Coated sheet products are usually prepared by one of two techniques: hot-dipping or electroplating. The most commonly used commercial coated sheet products and the relevant processes of application are described in the next few pages. The reader is also referred to several recent review articles that describe coating microstructure, preparation, and properties in further detail [2.1.4.4-2.1.4.8].

9.2 Hot-Dip Coated Steel Products—Hot-dip coated steel products are produced by a continuous process of immersing properly cleaned and (inert gas) annealed steel strip into a molten bath of the desired metal coating. The hot-dip process is the most cost effective method of producing corrosion resistant coatings on a steel substrate.

Several new hot-dip coating facilities began supplying the North American automakers in 1993 and combined with planned new European and Japanese lines, hot-dip zinc capacity is increasing at a faster rate than electroplated steel sheet. A schematic of a typical continuous hot-dip coating line is shown in Figure 19.

The principal types of hot-dip coated steel currently available are: zinc coated (galvanized), zinc-iron coated (galvanneal), aluminum coated, aluminum-zinc alloy coated (Galvalume®), and lead-tin alloy coated (terne). Characteristics of these products are described later in this chapter.

9.2.1 GALVANIZED STEEL—Hot-dip galvanized steel (HDG) is produced by dipping the steel strip into a bath of molten zinc containing 0.1 to 0.2% aluminum. Although both, one- and two-side galvanized steel can be produced, the automotive industry predominantly uses two-side coated HDG for parts designated as hot-dip coated.

HDG may be produced with a wide range of coating weights depending on the automotive specification. Table 5 shows the minimum and maximum coating limits per side for a variety of coating classes typically used by car makers. The automotive industry is moving away from coating designations previously specified as oz/ft² to the international designation of g/m².

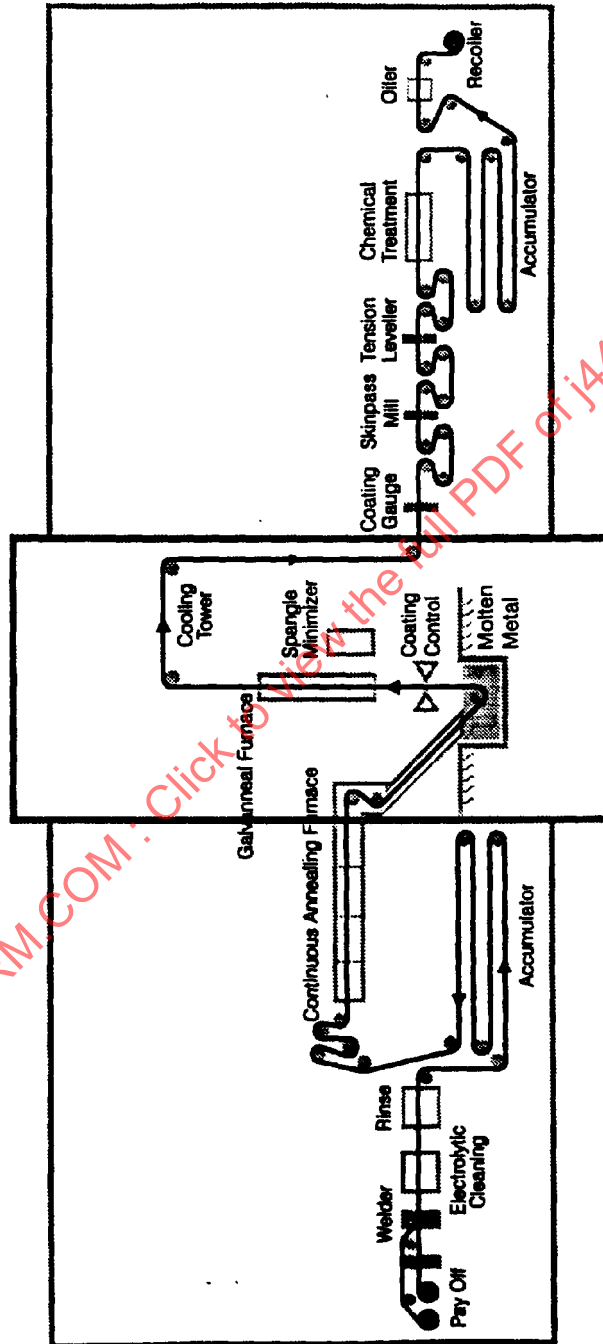


FIGURE 19—CONTINUOUS HOT-DIP LINE

TABLE 5—TYPICAL AUTOMOTIVE COATING WEIGHTS FOR HOT-DIP GALVANIZED STEEL

Coating Designation	Minimum Check Limit Single Spot Test/Side (g/m ²)	Maximum Check Limit Single Spot Test/Side (g/m ²)
0G	0	0
20G	20	60
60G	60	110
70G	70	120
90G	90	140
98G	100	160
100G	100	140

NOTES

- 60G0G refers to one-side coated galvanized steel: 60 to 110 g/m² on one side and 0 g/m² on the other side.
- 100G100G refers to two-side equally coated galvanized steel: 100 to 140 g/m² on each side.
- 90G70G refers to differentially coated galvanized steel: 90 to 140 g/m² on one side and 70 to 120 g/m² minimum on the other side.
- Some North American car makers have more restrictive limits than shown above. Others have limits based on triple spot test measurements.

A variety of strength and formability levels are available ranging from commercial quality, drawing quality, deep-drawing quality, extra-deep drawing quality, as well as 240 to 825 MPa (35 to 120 ksi) minimum yield strength, high strength, low alloy galvanized.

Zinc is anodic to steel under most exposure conditions and will offer sacrificial protection to exposed steel surfaces. Hence, zinc coatings will continue to offer protection to the base steel after the coating is penetrated by corrosion or mechanically damaged or at cut edges. Zinc coatings will protect steel at moderate temperatures, but zinc-coated steels should not be used above 260 °C (500 °F).

Zinc-coated steels are subject to damage from humid storage stain caused by adverse storage or shipping conditions. The product may be rendered more resistant to humid storage stain by the application of a "ship-out" oil. However, the protection afforded is temporary.

Zinc coatings are ductile and can be stamped, roll or brake formed, deep drawn, spun, or lock formed.

Zinc-coated steel can be welded by electric resistance, metal arc, laser and seam welding, although the processes must be adjusted to allow for the peculiarities of the material. Arc welding produces a zinc oxide vapor which requires ventilation. Resistance welding requires higher currents, higher pressures, and longer cycle times than for uncoated steel. Zinc-coated steel is readily solderable with low melting point solder.

Although zinc-coated steels are paintable with a variety of paints readily available from most paint suppliers, a conversion pretreatment (such as zinc phosphate) is required for good paint adhesion.

- 9.2.2 HOT-DIP GALVANNEAL—Zinc-iron alloy coatings (galvanneal = GA) are produced by heating zinc-coated strip during the continuous galvanizing operation immediately after hot dipping. Preparation of GA coatings begins by dipping the steel strip in a bath of molten zinc that also contains aluminum (0.1 to 0.2%) to control the extent of iron/zinc alloying. Coating weight is controlled by blowing off the excess zinc using air knives after the strip exits the bath. The strip is then reheated to start the diffusion of iron from the steel substrate into the zinc. The strip temperature is maintained to allow the iron to diffuse to the coating surface and then the strip is rapidly cooled to stop the diffusion process.

GA is a zinc-iron coating consisting of approximately 8 to 18% iron and the balance zinc. Unlike pure zinc coatings, which have a silver, reflective appearance, the GA coating has a dull grey color. The GA coating also "feels less smooth" due to its microporous surface. This microporous surface can also result in retention of applied lubricants during subsequent cleaning processes. Although the bulk iron concentration in the coating is 8 to 12%, the coating typically contains several different zinc-iron phases ranging from 5 to 21% iron. The iron concentration and phase variations occur due to the diffusion process by which GA is made.

Zinc-iron coatings provide less sacrificial protection of exposed steel compared to free zinc coatings. Also, due to their iron content, the corrosion products of GA are reddish-brown, whereas the corrosion products of free zinc coatings are white. However, alloying zinc with iron improves the corrosion resistance by lowering the corrosion rate of the coating.

Zinc-iron alloy coatings are also more weldable and offer better paint adhesion than free zinc coatings. They are, therefore, well suited for exterior skin panels, inner closure panels, and structural components. However, GA coatings are more susceptible to coating adhesion problems, such as powdering and flaking, compared to HDG steel.

Typical coating weights of automotive GA are shown in Table 6. As with HDG coatings, a variety of formable and high-strength grades are widely available.

TABLE 6—TYPICAL AUTOMOTIVE COATING WEIGHTS FOR HOT-DIP GALVANNEAL STEELS

Coating Designation	Minimum Check Limit Single Spot Test Side (g/m ²)	Maximum Check Limit Single Spot Test/Side (g/m ²)
30A	30	60
40A	40	80
50A	50	90
60A	60	90

NOTES

- a. Some North American car makers have more restrictive limits than shown above. Others have limits based on triple spot test measurements.

Other types of hot-dip coated steels are used in automotive applications other than body panels. These include aluminum-coated steel, aluminum-zinc alloy-coated steel, and tern-coated steel.

- 9.2.3 **ALUMINUM-COATED STEEL**—Aluminum-coated steel is produced by dipping cleaned and inert gas annealed steel strip into a molten bath of aluminum alloy containing 8 to 12% silicon. Coating weight is typically 120 g/m² total both sides based on triple spot measurements.

The enhanced high temperature corrosion performance makes this product well suited for making parts of the automotive exhaust system including intermediate pipes, mufflers, and tail pipes.

- 9.2.4 **ALUMINUM-ZINC ALLOY-COATED STEELS (GALVALUME®)**—Aluminum-zinc alloy coated steel is also produced by dipping cleaned and inert gas annealed steel strip into a molten bath of aluminum alloy containing 55% aluminum, 43.5% zinc, and 1.5% silicon. The coating consists of an aluminum rich matrix with zinc rich interdendritic areas. Coating weight is typically 150 g/m² total both sides based on triple spot measurements.

Automotive applications for this product are similar to those for aluminum-coated steel; i.e., requiring high-temperature corrosion resistance. Typical applications include heat shields, gas tank shields, mufflers, and under hood parts.