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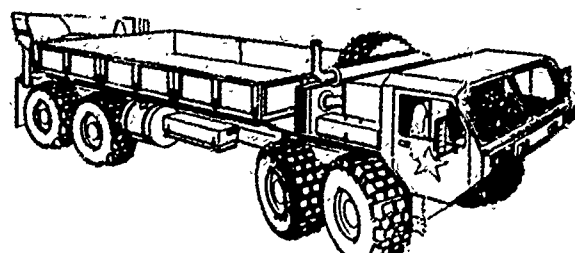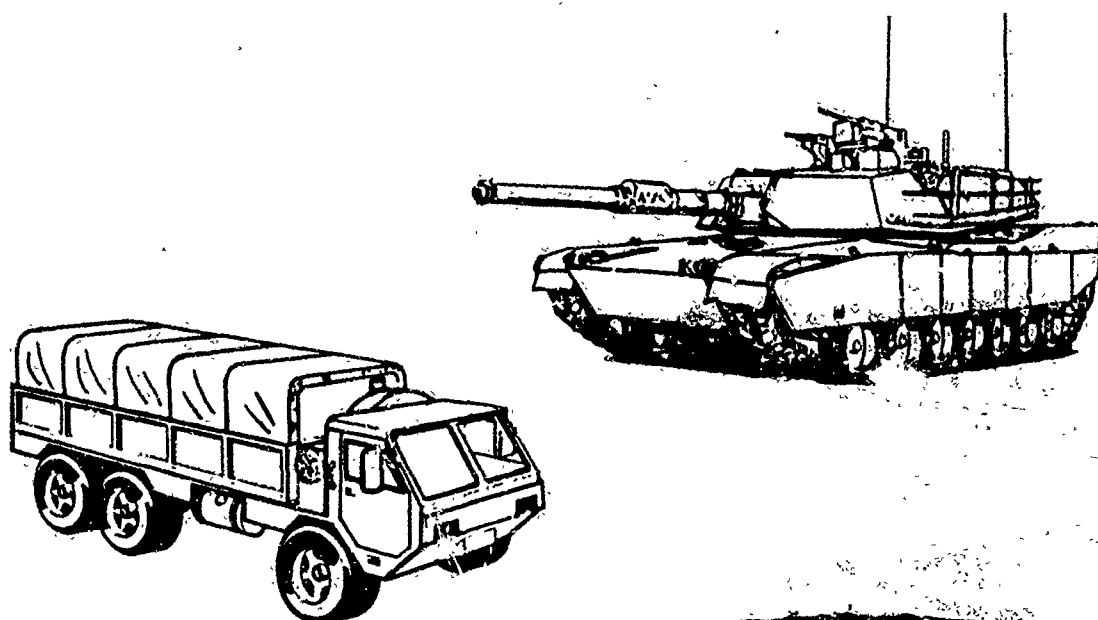# AD-A194 172

DESIGN GUIDELINES FOR PREVENTION OF CORROSION IN COMBAT AND TACTICAL VEHICLES

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DESIGN GUIDELINES FOR PREVENTION OF CORROSION
IN COMBAT AND TACTICAL VEHICLES

by

Mr. Alexander R. Kovnat, M.S.

US Tank and Automotive Command

March 1988

ABSTRACT

This report was prepared to provide guidelines for the military design engineer in developing improved corrosion control techniques for military combat and tactical vehicles. It covers basic corrosion theory, principles of proper design and protective coatings for metals. The common forms of corrosion are reviewed and specific approaches to control of each type are suggested.

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ACKNOWLEDGEMENT

PREFACE

Unintended destruction or deterioration of a material due to reaction with environment is defined as corrosion. Corrosion prevention is important due to its impact on cost, safety of operation of equipment, and conservation of valuable raw materials. It has been estimated that the direct and indirect total cost of corrosion is #30 -70 billion for the US and around #8 billion for the defense sector. However, there is a potential to save at least 35% of this cost with the application of existing knowledge of corrosion prevention and control.

As corrosion affects both economy and military preparedness of the Armed Forces, awareness and application of Corrosion Prevention and Control (CPC) techniques at all stages of design, fabrication, and maintenance become vitally important.

This publication is an updated version of a previously published CPC design guide, for Tactical Vehicles, published in 1981. Since then, the knowledge of CPC Techniques has developed substantially. New modern combat weapon systems are being developed at TACOM. It was therefore decided to publish a complete new design guide to advance CPC and to include coverage for both tactical and combat vehicles. This design guide document presents information and techniques primarily intended to improve the quality through prevention of corrosion. Also added is a new chapter titled 'Lessons Learned' which describes the corrosion problems experienced in fielded equipment, possible causes, and recommended solutions.

To accomplish this task, Mr. Alexander R. Kovnat, a Mechanical Engineer with a Master of Science Degree in Nuclear Engineering, who was the author of the previous CPC Design Guide was requested to research the state-of-the-art of CPC and prepare this new Design Guide for Combat and Tactical Vehicles. This new publication is the result. It is meant to be educational and informative to the reader. In preparation of this design guide the author has searched previously published literature on corrosion from various sources, papers, references and publications. Recognition and acknowledgements are herewith expressed to all those authors and publishers. Any opinions expressed within this design guide are those of the author and do not necesarily represent any official position of the U.S. Army Tank-Automotive Command.

This report may not be the last word on corrosion prevention, but rather a document which is intended to direct attention to a complex problem. The elimination and reduction of failures in Army equipment is a cooperative responsibility of Government and Industry. TACOM encourages recipients of this publication to review and inform this organization of any comments, suggestions and any new techniques or methods on prevention and control of corrosion which can be addressed in future CPC design guide publications. Please address CPC correspondence to:

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CHAPTER 1
INTRODUCTION

The purpose of this document is to address the problems of corrosion in military tactical and combat vehicles.

Corrosion of metals increases maintenance requirements and reduces the useful life of tactical and combat vehicles. In addition, a corroded body, frame, or propulsion system component is not conducive to safety, reliability, appearance or troop morale. Corrosion-related problems are imposing, in additional cost burdens to the Army, an estimated 2.0 to 2.5 billion dollars annually.

In 1985, the Commanding General of the Army Material Command (AMC) issued a Commander's Guidance Statement on Corrosion Prevention and Control (CPC). This statement directed all major subcommands within AMC to utilize state-of-the-art corrosion control technology in original equipment designs. The stated objective is to achieve corrosion-free design by utilizing design practices that address selection of materials, coatings, surface treatments, system geometry, material limitations, environmental extremes, storage conditions, packaging and preservation requirements, and rebuild/spare parts requirements.

In accordance with the Commander's Guidance Statement, the Corrosion and Materials Branch of Manufacturing Technology and Producibility Division of the RDE Center of the U.S. Army Tank-Automotive Command (TACOM) has been designated as the TACOM focal point for Corrosion Prevention and Control. Assigned responsibilities include establishing CPC programs for Tank-Automotive materiel. The Corrosion and Materials Branch also administers the training of personnel to develop awareness of the importance of CPC in TACOM-managed programs.

Because training of TACOM personnel is an essential part of CPC, the Corrosion and Materials Branch revised a report, <u>Design Guidelines for Prevention of Corrosion in Tactical Vehicles.</u> That report, originally written in 1980/1981, has been expanded to include combat as well as tactical vehicles, and to accomodate technical developments that have occurred since 1981.

The resulting revised document issued here, is intended for use by industrial contractors as well as project design groups within TACOM. This design guide can make a contribution to CPC by enhancing awareness of corrosion and stressing the technology that can be used to reduce its corrosion costs.

While this report concentrates on the problem of metal corrosion, the designer must keep in mind the possibility of replacing metals with polymers and polymer/fiber composites. The various aspects of design with composites will be addressed in a future report.

CHAPTER 2
THEORY AND BASIC PRINCIPLES OF CORROSION

2.1   Definition.   One can stimulate lively debate among students in a corrosion prevention course simply by asking what the word 'corrosion' means.

Many engineers will define corrosion as any chemical reaction between a metal surface and its surrounding environment. Obviously, corrosion occurs when steel surfaces rust. However, does corrosion occur when stainless steels react with atmospheric oxygen to form a self-limiting surface oxide layer? Can one speak of 'corrosion' when steel is subjected to phosphating solutions to form a layer of phosphate to serve as a paint base?

Furthermore, when various alloys exhibit stress-corrosion cracking, can one say that no corrosion occurred because very little metallic substance chemically combined with the surrounding environment? Corrosion will be defined, for the purposes of this document, as unwanted chemical reaction between a metallic material and its environment, resulting in deterioration of strength or other properties essential to the performance of a given item or system. In some instances, corrosion can also be defined as formation of unwanted reaction products which contaminate water, food, or other products. For example, a water storage tank is considered to have corroded if the water is rust (or other corrosion-product)-contaminated, even if the tank loses only a little of its inner surface. Also, corroded items can be unsightly (an 'eyesore'), even if enough metal is provided in its design to allow for corrosion during a specified timeframe.

The broader term material deterioration is used to describe phenomena whereby materials in general (i.e., rubber, plastics, wood) suffer loss of integrity, or contaminate other materials, because of environmental influences such as ultraviolet radiation, or presence of substances with which the material in question is not compatible. For example, polyvinyl chloride (PVC) can decompose when subjected to high temperature. Not only does the PVC lose its strength or insulating properties, but also, it generates vapors which can corrode metal components in the system in which the PVC was used. Ultraviolet radiation degrades polymers by breaking the molecular chains which are the essence of these materials. Ozone, present in the atmosphere at concentrations less than 1 part per million, causes embrittlement of rubber tires. Microorganisms cause materials such as wood or canvas to rot, and can also promote metal corrosion.

2.2   Fundamentals of Electrochemistry.

2.2.1   General Concepts.   Corrosion is nature's way of returning metals and alloys to their natural state, i.e., oxides or other chemical

compounds. Except for very few metals, most notably gold, a metal in uncombined form is unnatural if oxygen is around. Iron, for example, "wants" to be an oxide. This can happen in one of two ways: it can combine with oxygen directly, or indirectly via electrochemical processes* involving oxygen and an electrolyte, which will be discussed in subsequent paragraphs. The former process is mostly a high temperature (1000F or thereabouts) phenomena, while the latter can occur at normal environmental temperature.

Corrosion of motor vehicles and other metal structures of interest to the armed forces is essentially electrochemical, with four basic elements needed for the process to take place: 1) an anode, 2) a cathode, 3) an electrically conductive medium or electrolyte, and 4) an electrical connection between the anode and cathode other than the electrolyte.

Consider an electric battery (see Figure 1) consisting of a strip of zinc, a strip of copper, and a medium such as hydrochloric acid, sulfuric acid, or even a solution of common salt (sodium chloride). Note that the strips are not touching one another. If we connect a voltmeter to the strips, as shown in the figure, we measure an electrical potential or voltage. The zinc strip assumes a negative potential relative to the copper strip.
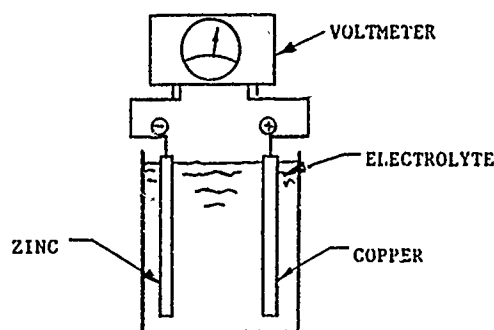
Fig. 1. APPARATUS FOR DEMONSTRATING THE
EXISTENCE OF CORROSION POTENTIAL

If the zinc is very pure (i.e., very little impurities which would cause local effects) and if the voltmeter draws very little current, no chemical reactions will occur. If any reactions do occur, they do so very slowly. Nonetheless, the electrical potential is still there, and can be measured by the voltmeter.

What this potential or voltage means, is that the zinc has a tendency to form ions, i.e.,

$$Zn \longrightarrow Zn^{++} + 2 \text{ electrons,}$$
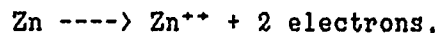
* Direct oxidation is theorized to be electrochemical, involving diffusion of oxygen ions through metal oxide films.

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and to push the electrons through the voltmeter to the copper strip. Since the two electrons have to be accounted for in one way or another, the zinc does not form ions at any significant rate unless current can freely flow from the zinc to the copper via an external circuit.

If the zinc and copper are connected (Figure 2), chemical reactions start happening. The zinc gives up two electrons per atom to form ions, which pass into the medium. The free electrons travel via the external circuit to the copper strip, where they re-enter the conductive medium in one or more reactions whose nature depends on the electrolyte involved.
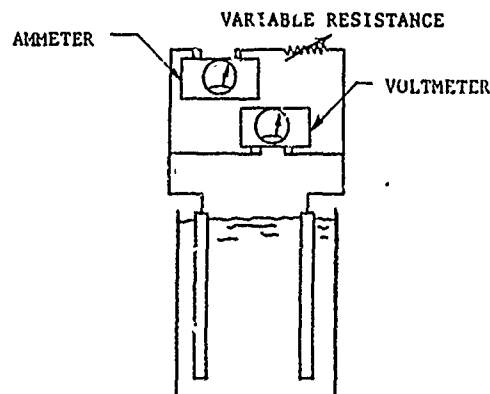
Fig. 2. AS ABOVE, WITH ADDITION OF VARIABLE
RESISTANCE AND AMMETER

In an acidic medium, hydrogen ions are present due to the tendency of acidic substances to disassociate when dissolved in water. Sulfuric acid in solution disassociates into hydrogen and sulfate ions, as follows:

$$H_2SO_4 \ \text{----}> \ 2H^+ + SO_4^{--}.$$
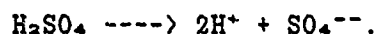
Likewise, hydrogen chloride, normally a gas, forms hydrogen and chloride ions in aqueous solution, while nitric acid forms hydrogen and nitrate ions, and similar reactions occur for other acids.

When the electrons from the zinc electrode reach the copper electrode in an acid medium, they combine with the hydrogen ions to form gaseous hydrogen:

$$2e + 2H^+ \ \text{----}> \ H_2$$
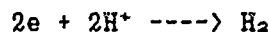
The sulfate (chloride, nitrate, etc.) ions remain in the aqueous solution, so that instead of pure zinc and hydrogen sulfate (chloride, nitrate, etc.), we now have hydrogen gas and zinc sulfate (chloride, nitrate, etc.).

In non-acid (neutral, or alkaline) media, the electrons turned loose by the zinc are consumed in other reactions, such as:

$$2e + 1/2 \ O_2 + H_2O \ \text{----}> \ 2OH^- \quad \text{or} \quad 2e + 2H_2O \ \text{----}> \ H_2 + 2OH^-$$

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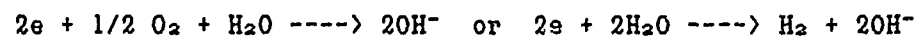
The OH, or hydroxyl, ions can combine with ions of zinc or other metal to form hydroxide, which may in turn break down to form hydrated oxides. The rusting of iron or steel is an example of indirect oxidation via formation of ions, reduction of oxygen to form OH ions, formation of hydroxide, and subsequent decomposition of the hydroxide to metal oxide and water.

In the example discussed above--zinc, copper, a suitable medium, and a physical connection between the metals--one can see the four basic elements that must be present for corrosion to take place. The anode is the metal, or area thereof, that corrodes. The cathode is a surface with lesser tendency to corrode, which therefore takes up electrons from the anode and completes the corrosion reaction. The electrolyte is a liquid, almost always an aqueous solution, which provides an ionic conduction path. The physical connection between anode and cathode (the fourth element) provides an electronic conduction path. In the above example, zinc sulfate (or other compound) is the corrosion product.

2.2.2 Corrosion rate, driving potential. In Figure 2, a voltmeter and ammeter are shown. If the variable resistance is set to infinity, (i.e., open circuit) a voltage will be displayed on the voltmeter. This voltage is a measure of the inherent driving force behind the overall reaction

$$Zn + 2H^+ ----> Zn^{++} + H_2 \quad or \quad Zn + 1/2 \; O_2 + H_2O ----> Zn(OH)_2$$
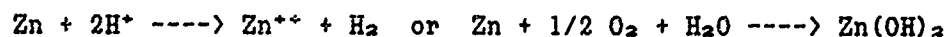
in the given media. The higher the voltage, the more the electrochemical reaction 'wants' to take place. The driving potential is linearly related to the difference in Gibbs free energy between initial and final products of the corrosion reaction. This, in turn, is the measure of the thermodynamic tendency of any chemical reaction to proceed. If delta G (G final - G initial) is less than zero, the chemical reaction will have a thermodynamic tendency to spontaneously go forward.

If a current flows, the voltage measured by the voltmeter will be less than the open-circuit voltage, and hence is not, at this point, an indication of the inherent driving force behind the reaction. The current measured by the ammeter is, however, an accurate measure (neglecting local effects at the anode) of the rate at which the anode is corroding. Each atom of zinc, for example, can only deliver two electrons. Hence current flow, measured in units of current per unit of anode area, is linearly related to corrosion rate in units of mass (or, volume) per unit area per unit time. For example, zinc (density 7.14 gram/cc., atomic weight

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65.38), when subjected to a corrosion current of 1 microampere per square centimeter, corrodes at this rate:

$$\frac{10^{-6} \text{ coulomb}^*}{\text{sec-cm}^2} \times \frac{1 \text{ gram-equiv.} \text{ of electrons}}{96,489 \text{ coulombs}} \times \frac{1 \text{ gram equiv. Zn}}{2 \text{ gram equiv. electrons}}$$

$$\frac{65.38 \text{ gram}}{\text{gm-equiv. Zn}} \times \frac{\text{cm}^3}{7.14 \text{ gram}} \times \frac{3600 \text{ sec}}{\text{hr}} = 0.171 \times 10^{-6} \text{ cm/hr.}$$

2.2.3 <u>Standard Electromotive Series.</u>   Each metallic element (pure iron, pure zinc, pure copper, etc.) has an inherent thermodynamic tendency to form ions when immersed in an aqueous medium.   Defining and measuring this tendency, however, needs some explanation.   First, neither anodic nor cathodic reactions can occur independently.   Accordingly, the tendency of a metal to form ions can only be defined and measured relative to a standard cathode reaction.   Furthermore, the behavior of a metal in contact with an aqueous solution varies with the concentration of its ions already in the solution.

Electrochemists define the <u>standard potential</u> of a pure metal by measuring its voltage relative to a hydrogen electrode, with the metal in contact with a solution of its ions at unit activity (1 gram-mole per liter, with an allowance for a correction factor called the activity coefficient).   If unit activity cannot be achieved, a correction factor can be applied to whatever concentration that can be achieved.   The hydrogen electrode is likewise surrounded by a solution with a unit activity of hydrogen ions, with hydrogen gas at 1 standard atmosphere feeding the electrode.   A suitable ionic bridge separates the two aforementioned solutions while providing ionic conduction, so that an electrical potential difference can exist and be measured.   The temperature is maintained at 25C.

Under these conditions, the reaction

$$M \longrightarrow M^{n+} + n \text{ electrons}$$

will have an electrical potential relative to the hydrogen electrode reaction

$$H_2 \longrightarrow 2H^+ + 2 \text{ electrons.}$$

The potential of the hydrogen electrode is arbitrarily defined as zero volts.   Accordingly, since zinc, under standard conditions, measures -0.763 volts relative to the standard hydrogen electrode, its standard potential is stated as -0.763 volts.

* 1 coulomb = quantity of charge equivalent to 1 ampere for 1 second

A word about sign convention is in order here. Electricity is somewhat like a hydraulic fluid, with voltage being equivalent to pressure and current equivalent to flow rate. Since the basic carrier of electricity--the electron--is negatively charged by definition, the negative terminal of a battery or D.C. generator is the terminal where the electrons are under "positive pressure". In a corrosion cell, the electrons are under positive pressure at the anodic, or corroding metal, while at the cathodic metal they are under "suction", even though the former is labeled "-" and the latter, "+".

Under the same conditions, iron has a standard potential of -0.440 volts. Magnesium has the highest standard potential of all structural metals, -2.37 volts. In all instances where the standard potential is negative, the metal tends to go from the pure state to ions in solution, while at the hydrogen electrode, the hydrogen ions tend to absorb electrons and become hydrogen gas.

Noble metals, such as gold, do not form ions in non-oxidizing environments. If the standard potential of gold is measured, we find that the hydrogen would be the "corroding" electrode, while the gold would actually deionize, i.e.,
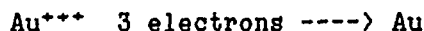
$$Au^{+++} \quad 3 \text{ electrons} \quad \text{----} > \quad Au$$

The hydrogen would have a thermodynamic tendency to form H^+ ions, and the electrons thus detached would be under 1.50 volts "pressure" relative to the gold electrode. Accordingly, with the sign convention described above, the standard electrode potential for gold is +1.50 volts.

The electromotive force series (see Table 1) is a relative ranking of the tendency to form ions under standard conditions. Hence if one were to prepare the setup in Figure 3, the iron (standard potential -0.440 volts) will have a tendency to corrode, while the copper (std. pot. +0.337 volts) will deionize. The overall reaction would be

$$Fe \quad + \quad Cu^{++} \quad \text{----} > \quad Fe^{++} \quad + \quad Cu.$$
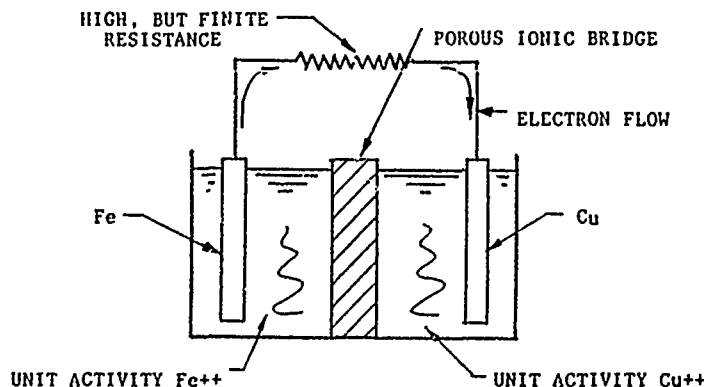
Fig. 3. APPARATUS FOR DEMONSTRATING DIFFERENCE IN STANDARD POTENTIAL BETWEEN IRON (Fe) AND COPPER (Cu)
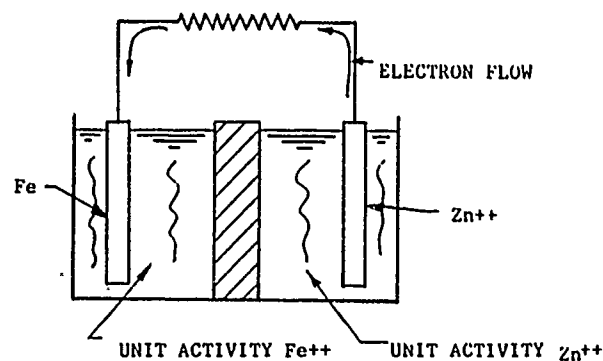
Fig. 4. AS ABOVE, EXCEPT FOR (Zn) IN PLACE OF COPPER (Cu)

On the other hand, the iron electrode in Figure 4 (again, -0.440 volts std. pot.) will be protected while the zinc electrode (std. pot. -.763 volts) will corrode. This is, in fact, what happens in the real world when mild steel is galvanically protected by zinc coatings. In the case of copper and iron, it likewise so happens that copper in contact with steel in sea water results in accelerated corrosion of the steel.

TABLE 1

Mg ---->	Mg++	+	2e-	-2.370 volts
Al ---->	Al+++	+	3e-	-1.660 v
Zn ---->	Zn++	+	2e-	-0.763 v
Fe ---->	Fe++	+	2e-	-0.440 v
Ni ---->	Ni++	+	2e-	-0.250 v
Sn ---->	Sn++	+	2e-	-0.136 v
Pb ---->	Pb++	+	2e-	-0.126 v
H2 ---->	2H+	+	2e-	0.000 v
Cu ---->	Cu++	+	2e-	+0.337 v
Hg ---->	Hg++	+	2e-	+0.854 v
Pt ---->	Pt++	+	2e-	+1.200 v
Au ---->	Au+++	+	3e-	+1.500 v

2.2.4 Galvanic Series. The standard electromotive series must not, however, be used as a design guide, because it does not reflect real world conditions. In actual engineering situations, metals are not surrounded by unit activities of their ions. Engineers dealing with corrosion situations involving coupling of dissimilar metals would be better to consult a galvanic series, which ranks various metals and alloys when coupled to a standard electrode in sea water, or saltwater of a given concentration, and with given flow velocity. A galvanic series for sea water is given in Table 2.

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Noble or cathodic ↑	Platinum Gold Graphite Titanium Silver ⌈Chlorimet 3 (62 Ni, 18 Cr, 18 Mo) ⌊Hastelloy C (62 Ni, 17 Cr, 15 Mo) ⌈18-8 Mo stainless steel (passive) ⎪18-8 stainless steel (passive) ⌊Chromium stainless steel 11-30% Cr (passive)
	⌈Inconel (passive) (80 Ni, 13 Cr, 7 Fe) ⌊Nickel (passive)
	Silver solder
	⌈Monel (70 Ni, 30 Cu) ⎪Cupronickels (60-90 Cu, 40-10 Ni) ⎪Bronzes (Cu-Sn) ⎪Copper ⌊Brasses (Cu-Zn)
	⌈Chlorimet 2 (66 Ni, 32 Mo, 1 Fe) ⌊Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
	⌈Inconel (active) ⌊Nickel (active)
	Tin Lead Lead-tin solders
	⌈18-8 Mo stainless steel (active) ⌊18-8 stainless steel (active)
	Ni-Resist (high Ni cast iron) Chromium stainless steel, 13% Cr (active)
	⌈Cast iron ⌊Steel or iron
	2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
Active or anodic ↓	Cadmium Commercially pure aluminum (1100) Zinc Magnesium and magnesium alloys

2.2.5 <u>Polarization and Corrosion Potential.</u> When a corrosion situation such as Figure 1 is set up, the corrosion rate at the anode (in mass or volume per unit area per unit time) is directly proportional to current density at the anode. The current flow, in turn, is limited by the resistances of the electronic conduction path, the solution, the interfaces between solution and anode, and solution and cathode. In an engineering corrosion situation, one must conservatively assume that the electronic and ionic conduction paths offer negligible resistance to current flow. The only phenomena holding back the current is <u>polarization</u> at the anode, the cathode, or both. At the anode, ions of dissolved metal can act as a sheath, partially blocking further dissolution. Layers of corrosion products can also hinder further dissolution. At the cathode, electrons can only be disposed of as fast as the kinetics of hydrogen reduction and discharge, or oxygen diffusion and reduction, will allow.

Refer to Figures 5 and 6. The electrochemical potential of both anode and cathode are measured relative to a reference electrode, such as the mercury/mercurous chloride reaction. At infinite external resistance (no

current flow), the anode will possess one characteristic potential E_{ao}, and the cathode will likewise possess a characteristic potential, E_{co}. The difference between E_{ao} and E_{co} is the characteristic driving force behind the corrosion reaction. When current is drawn, the potential of the anode E_{ao} becomes less negative (or more positive) due to anode polarization. The cathode potential E_{co} becomes less positive (or more negative) due to cathode polarization.
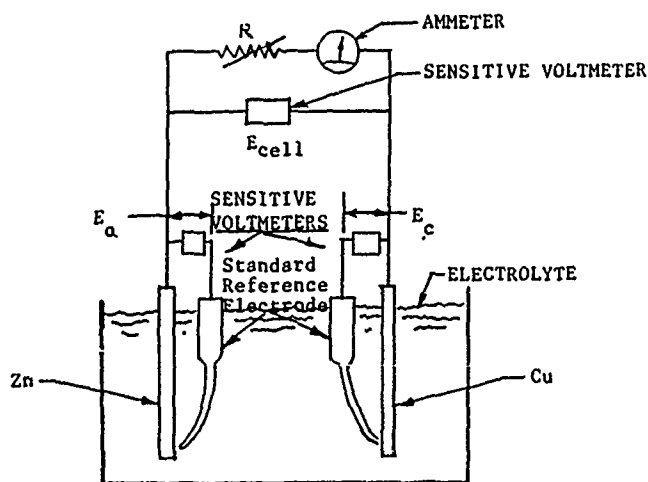
Fig. 5. APPARATUS FOR MEASURING POLARIZATION
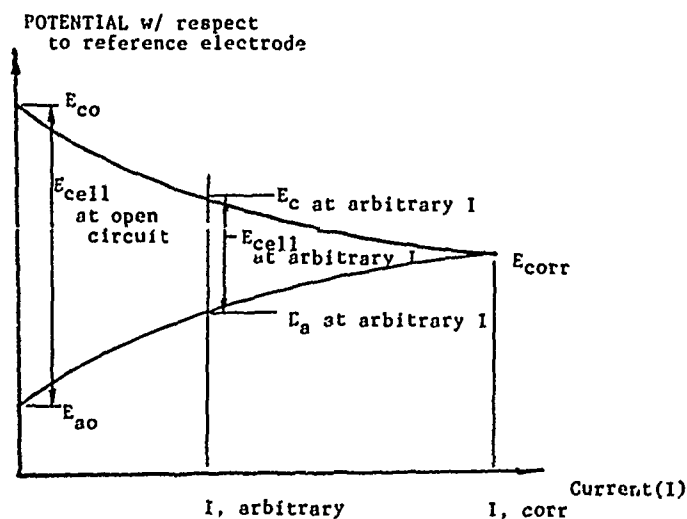
Fig. 6. POLARIZATION CURVES

At zero external resistance (short circuit), current flow is limited entirely by polarization, neglecting electrolyte resistance. The anode and cathode will now have the same potential E_{corr} relative to the standard electrode. This is the underline corrosion potential of this particular system. The corrosion current, I_{corr} normalized to anode area, is linearly related to corrosion rate, as explained earlier.

2.2.6 <u>Anode/Cathode Polarization, and Relative Area Effect</u>. If the potential of the anode E_a changes greatly as current increases while cathode potential E_c changes very little, the corrosion current at short-circuit will be limited by anode polarization (see Fig 7a). The corrosion process is then said to be under anode control. Likewise, if the cathode polarizes readily while the anode does not, the corrosion process is said to be under cathode control.

POTENTIAL vs STANDARD ELECTRODE

E_c

E_a

CURRENT DENSITY

I_{corr}
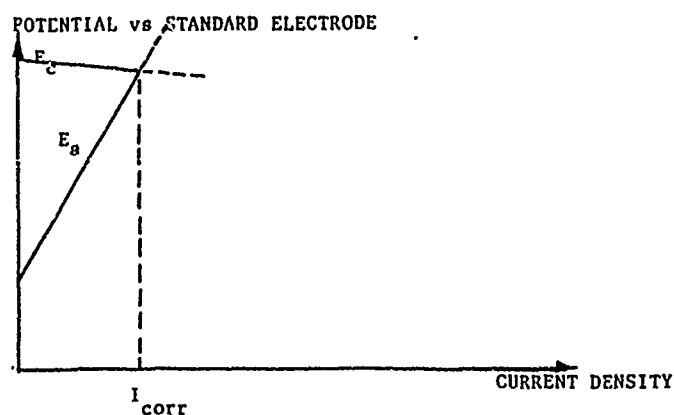
Fig. 7a. CORROSION UNDER ANODE CONTROL

E_c

E_a

I_{corr}
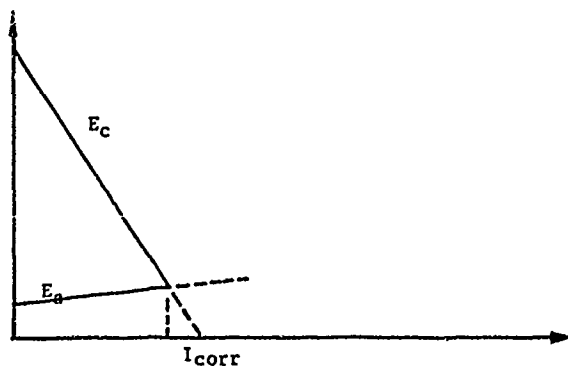
Fig. 7b. CORROSION UNDER CATHODE CONTROL

The preceeding paragraphs assumed equal anode and cathode areas. If the areas are not equal, the <u>current densities</u> at anode and cathode will be unequal. However, the total current will be the same at both anode and cathode, because every electron transferred in an anodic reaction must be accounted for in a cathodic reaction.

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In engineering corrosion situations involving dissimilar metals, the relative areas of anode and cathode are important in determining the corrosion rate at the anode. If the cathode area is much less than that of the anode, any given corrosion current results in a much higher current density at the former than at the latter. If cathode polarization is an important factor (it usually is, because of the kinetics of the oxygen reduction reaction $1/2\ O_2 + H_2O + 2$ electrons $----> 2OH^-$), total corrosion current will be limited to a low value because, at that value, the cathode current density is as great as the kinetics of cathode reactions will allow. In addition, the low total corrosion current is distributed over a large anode, resulting in a low rate of corrosion in terms of metal loss per unit area. With a large cathode and small anode, cathode polarization is less pronounced, because for any given total current the cathode current density is low. And even a low total corrosion current will result in a high corrosion rate in metal lost per unit area per unit time, because there is less anode area over which to distribute the loss. This is why large cathode/anode area ratios should be avoided in engineering design.

2.3 <u>Thermodynamics vs Kinetics</u>. The diagrams shown in Figures 6 and 7, known as Evans diagrams, can also be used to illustrate the distinction between <u>thermodynamics</u> and <u>kinetics</u>. Figure 8a is an Evans diagram of a corrosion situation where there is a strong thermodynamic driving force, as represented by the large difference between anode and cathode potentials. Fig. 8b illustrates a small driving potential. Note that in Fig. 8a the corrosion rate is low because of pronounced polarization effects. The reaction in 8a is favored thermodynamically but not kinetically. In 8b the reaction does not have a powerful thermodynamic driving force, but proceeds more rapidly because there is little polarization. This means that rate-limiting kinetic factors are not strongly manifested in Fig. 8b. In Fig. 8a, kinetics constitutes the dominant factor. Figures 8a and 8b illustrate how kinetics can override thermodynamics in determining corrosion rates.

LARGE DRIVING
POTENTIAL

Icorr
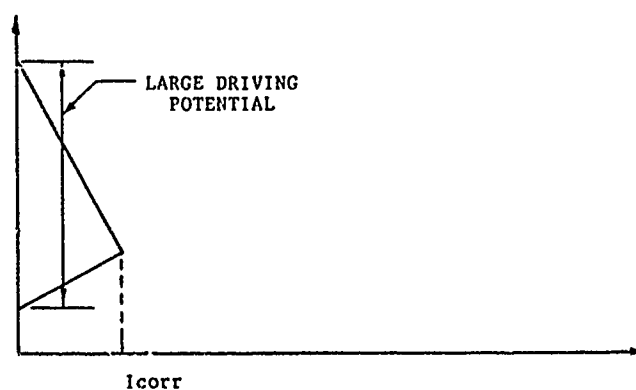
Fig. 8a.
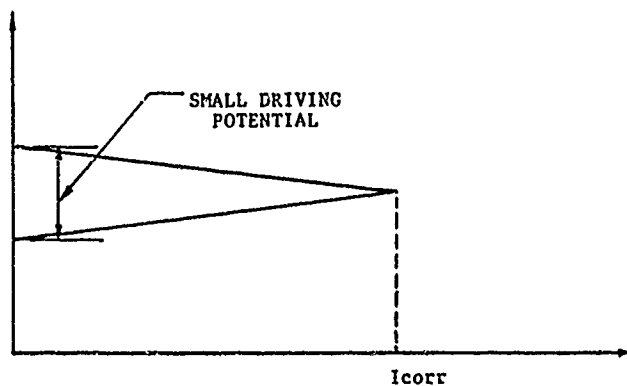
Fig. 8b.

Fig. 8. EVANS DIAGRAMS SHOWING HOW KINETICS CAN OVERRIDE
THERMODYNAMICS IN DETERMINING CORROSION RATE

2.4 Real-World Corrosion Effects. Corrosion caused by dissimilar metals in contact with one another is an important problem in real-world engineering design. However, a bimetallic couple need not be present to set up an electrochemical cell. If a strip of mild steel is placed in an acid solution, different regions on the metal surface will become anodic and cathodic, shifting from time to time, because of non-uniformities in the steel's microstructure. Particles (i.e., carbon) can act as cathodes, setting up small electrochemical cells. Exposing a metal surface to an electrolyte where the concentration of metal ions varies from one location to another, will set up an electrochemical differential concentration cell (often referred to simply as a concentration cell). In metal structures with joints, crevices can be formed by overlapping surfaces at welds, or at bolted or riveted joints. Metal within crevices can become anodic due to differential aeration effects, resulting in localized corrosion. When a metal is exposed to an electrolyte, any phenomenon that creates an electrochemical potential difference between one location and another will cause the anodic area to corrode.

2.5 Forms of Corrosion. Corrosion manifests itself in a variety of forms. It can cause uniform wastage of metal, or it can manifest itself as intense metal dissolution over a small area. A summary of the forms of corrosion encountered by the design engineer is given as follows.

2.5.1 Uniform corrosion. This happens when a metal surface, upon exposure to the atmosphere or an electrolyte, forms minute anodic and cathodic regions which shift about as corrosion progresses. Rusting of iron or steel is the most familiar example.

2.5.2   Pitting.   Pitting is a localized phenomena where small areas corrode preferentially, forming cavities (pits) in a metal surface. This type of corrosion occurs when metals that form passive oxide layers (i.e., stainless steels) are exposed to environments containing certain ions, notably chloride. The corrosive ions penetrate weak points in the normally protective oxide layer, creating localized corrosion cells. The localized corrosion site, or pit, is the anode, while surrounding uncorroded metal is the cathode. Pitting is a very destructive form of corrosion, because the pits tend to rapidly become deeper until perforation of a component (i.e., tubing) occurs.

2.5.3   Crevice Corrosion.   This occurs in locations such as joints or recesses (see Figure 9). One mechanism accounting for crevice corrosion is differential aeration, where metal within the crevice is subjected to less oxygen than the surrounding metal. The greater availability of oxygen outside the crevice sets up an electrochemical cell, with the crevice as the anode. Once metal dissolution begins, the corrosion process becomes autocatalytic (as in pitting), resulting in intense localized corrosion.
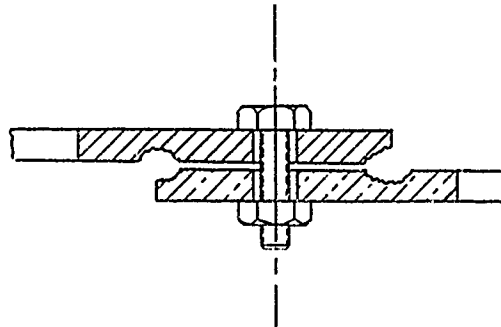
Fig. 9.   CREVICE CORROSION

2.5.4   Poultice corrosion.   This occurs when deposits of mud or other debris hold stagnant moisture in contact with a metal surface. As with crevices, differential aeration sets up an electrochemical cell which initiates corrosion in oxygen-starved locations. In addition, such deposits absorb moisture from the atmosphere. They also tend to prolong the presence of moisture which would otherwise drain away or evaporate. This invariably increases corrosion difficulties.

2.5.5   Galvanic Corrosion.   All forms of corrosion are 'galvanic', because differences in electrochemical potential between anodic and cathodic metals, or regions of the same metal, drive the process forward. When engineers speak of galvanic corrosion, they are referring to corrosion of one metal brought about by (or accelerated by) electrical contact with a different metal, which acts as a cathode when both metals are subjected to an electrolyte.

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Galvanic corrosion of a sacrificial metal can be used to forestall corrosion of a metal one wants to protect. Steel storage tanks located underground in conductive soil can be protected by placing sacrificial anodes of zinc or magnesium in proximity to the tank, with an electrical connection between them. Zinc coatings on steel are beneficial because the former corrodes sacrificially, protecting the latter at pores, scratches or other discontinuities in the coating.

2.5.6 Stress-Corrosion Cracking. (SCC) can happen when a metal or alloy, susceptible to a given corrosive agent, is exposed to that substance while simultaneously under tensile stress. Brass cartridge cases were at one time susceptible to 'season cracking' during the monsoon season in India, due to presence of ammonia in the local atmosphere. SCC affects a number of alloys including stainless steels, and alloys of aluminum, magnesium, and titanium. A related phenomena, hydrogen embrittlement, is a problem with high strength steels.

Plastics can suffer stress-corrosion cracking. Some polymeric materials (i.e., polycarbonates) will 'craze', or develop a pattern of surface cracks, when exposed to certain chemicals.

2.5.7 Intergranular Corrosion. This is preferential corrosive attack along grain boundaries, arising from electrochemical potential differences between grains and grain boundary precipitates. Intergranular corrosion is a problem with austenitic stainless steels subjected to improper heat treatment, unintentionally, during welding. Chromium carbide precipitates form at grain boundaries, leaving adjacent grains depleted in chromium and hence vulnerable to corrosion.

2.5.8 Exfoliation, or layer corrosion, is a problem with high strength aluminum alloys. It occurs when a vulnerable alloy is rolled so as to form an elongated grain structure. Upon exposure to an electrolyte, corrosive attack proceeds along subsurface paths parallel to the surface. The corrosion products occupy a larger volume than the alloy itself, and therefore delaminate layers of uncorroded metal.

2.5.9 Dealloying, or Parting Corrosion. In certain alloys, a corrosive medium may selectively dissolve one or more alloying elements without dissolving the whole alloy. A familiar example is dezincification of brass. Cast iron is susceptible to a form of dealloying corrosion whereby the corrosive medium leaches away the metallic portion of the cast iron structure, leaving behind a porous mass of carbon.

2.5.10 Fretting Corrosion. This occurs when two surfaces, at least one of which is metal, are in contact with relative movement between them, in the presence of a corrosive medium. The result is pitting, or stress-corrosion induced cracks. One mechanism involved in fretting corrosion may be wearing away of protective films, leading to the damage described above.

2.5.11 Corrosion Fatigue. This is a premature failure caused by repeated stress cycling in a corrosive environment.

Ordinary fatigue is characterized by loss in strength of a test specimen as a result of stress cycling a given number of times. The fatigue characteristics of a given material can be expressed in graphical form by plotting strength remaining as a function of the number of test cycles. (see Figure 10). When a corrosive agent is present, the remaining strength after a given number of cycles will be less than the corresponding strength when no corrosive agents are present.
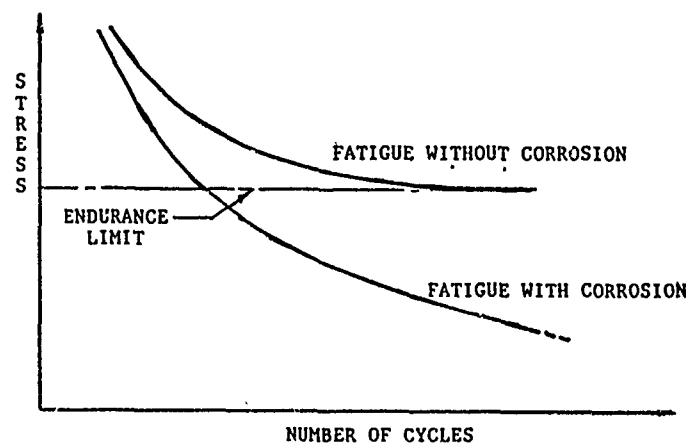
Fig. 10. CORROSION-FATIGUE

2.5.12 Impingement, or Erosion, Corrosion. This occurs when a corrosive fluid stream impinges on a metal surface, resulting in localized erosion. This type of corrosion is encountered mainly in fluid systems such as heat exchangers.

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CHAPTER 3
BREAKING THE CORROSION CYCLE

3.1   <u>The Theoretical View.</u>   Corrosion of metals (other than high temperature oxidation) involves four basic elements: anode, cathode, electrolyte, conduction path.   The electrochemical potential difference necessary to create an anode and cathode may be due to dissimilar metals, multiple phases within an alloy's microstructure, surface defects or contaminants, or design details such as crevices.   Knowing the fundamental causes and forms of corrosion, one can move on to the study of methods of breaking the corrosion cycle.

Looking at corrosion from the theoretical viewpoint, one can interrupt the corrosion process at one or more of the four basic elements, as follows.

3.1.1   <u>The Anode.</u>   One can inhibit the overall corrosion reaction by interfering with the anodic reaction

$$M \longrightarrow M^{+n} + n \text{ electrons.}$$

This can be accomplished by coating the anode with a physical barrier (i.e., gold plating on electrical contacts), or by using a corrosion inhibitor which attaches itself to anodic sites in a metal/electrolyte interface.

3.1.2   <u>The Cathode.</u>   Excepting high temperature oxidation, corrosion cannot occur without cathodic reactions.   One can interfere with cathodic reactions with one or more of these approaches.

Eliminate the cathode.   This means avoiding the presence of metals or other materials (i.e., graphite in lubricants) that are cathodic with respect to the metal to be protected.   Impurities in various alloy systems (i.e., copper, iron, or nickel in magnesium alloys) can form local cathodes.   When using materials that are sensitive in this regard, quality control standards must be maintained.

Reduce the cathode/anode area ratio.   If the cathode is reduced in area relative to the anode, the rate of cathodic reactions will be reduced.   The overall corrosion cycle will likewise be diminished, because the rates of electron transfer at anode and cathode must be equal.

Coat the cathode.   If a separate cathode (i.e., the more `noble` metal in a bimetallic couple) is coated, cathodic reactions cannot occur.   One could use a physical barrier, such as an organic coating, or (for bolts, rivets, etc.) plating with a metal more compatible (less cathodic) with the structure to be protected.

In some closed systems involving a liquid, inhibitors can be used to reduce the rate of cathodic reactions.   An example is inhibitors used in acid pickling baths, so that the acid dissolves oxide layers while the

base metal is protected. Such inhibitors work by inhibiting the hydrogen discharge reaction at local cathodic sites.

3.1.3   The Electrolyte.   An electrolyte is necessary for virtually all corrosion of engineering importance. Accordingly, one can reduce corrosion of metal structures by eliminating the electrolyte, or rendering it less harmful. The engineer can design an article or system so as to eliminate "sump" areas where moisture could accumulate, or provide drain holes at the lowest points of such areas.

3.1.4   The Conduction Path.   In any electric battery, the metal "fuel" does not "burn" (corrode) when no current is drawn. Or, if it does, it does so very slowly. The reason? When a radio, flashlight, et cetera, is not turned on, there is no electronic conduction path between the battery's anode and cathode. The functioning of any battery is simply galvanic corrosion, deliberately induced in a controlled manner to harness the energy released when a metal, such as zinc, goes from the pure state to a chemical compound.

In design situations where dissimilar metals are in proximity in the presence of an electrolyte, one can prevent an unwanted short-circuited "battery" by not having physical contact which would provide an electrical connection between the anode and cathode. When joining dissimilar metals, the joint should provide for adequate transmission of mechanical forces but not electrons. The designer can achieve this by specifying insulating sleeves, washers, gaskets, and so forth, to break the electrical short circuit that would otherwise exist.

3.1.5   Alternate Approaches.   There are approaches to reducing corrosion that are not covered by the above categories. Zinc coatings on steel, or sacrificial anodes to protect steel structures underground (or underwater) are examples of using the forces of electrochemistry to work in one's favor. A variation of this approach is rendering a structure artificially cathodic by impressing an electrical potential between it an an inert anode, using an external power source. In fact, metals that "passivate" (form protective oxide layers) can be protected in some electrolytes by rendering them artificially Anodic!

3.2   Design Engineer's View.   Real-world corrosion situations do not involve a physically separate anode and cathode, except for those involving dissimilar metals. Accordingly, approaches to fighting corrosion from the engineer's viewpoint (as opposed to the theoretical viewpoint) should also be examined. These approaches are as follows:

1. Select the right material for the job.
2. Apply protective coatings.
3. Use proper design techniques.
4. Modify the environment.

3.2.1 **Material Selection.** The first approach means avoiding, if possible, materials that are unsuitable for the operating environment. An example is aluminum alloys for aircraft. At one time, aircraft engineers used alloys such as 7075-T6 extensively, because of their superior strength. However, 7075-T6 is very vulnerable to corrosion, compared to the same alloy with a modified heat treatment, i.e., 7075-T73.

When using multiple materials, the engineer must consider compatibility. Combinations of materials which are vulnerable to deterioration of one of the materials should be avoided if one can use acceptable alternative combinations. As an example of compatibility, many aluminum alloys are acceptable in typical atmospheres. Copper alloys, such as bronze or brass, also resist atmospheric corrosion. However, the combination of aluminum in contact with copper (or its alloys) is vulnerable to corrosion of the aluminum, because of galvanic effects.

3.2.2 **Protective Coatings.** Closely related to the above approach is application of protective coatings to isolate a vulnerable material from corrosive agents. It would be uneconomical to use stainless steel for the bodies and frames of tactical trucks. Hence plain carbon or low-alloy steels, adequately protected with zinc and organic coatings, are the best remaining choice right now. Aluminum alloys, plastics, and composites deserve consideration for new designs. (See Chapter 9 for aluminum design considerations.)

3.2.3 **Design Techniques.** Students of corrosion and design engineers would agree that getting rid of electrolytes is one way to interrupt the corrosion process. Many of the design principles recommended in SAE literature and articles are based on the fact that, if no electrolyte is present, there will be no corrosion. Eliminating sump areas or providing drain holes can reduce corrosion problems, though it is difficult to eliminate moisture completely.*

Other aspects of proper design include avoiding crevices when possible, and avoiding design features that make it difficult for protective coatings to function. Crevices not only create corrosion cells, but also trap liquid corrosives. Sharp corners are difficult to coat evenly, and are therefore more vulnerable to corrosion than smooth, evenly coated surfaces.

Examples of proper design will be discussed further in subsequent parts of this report.

3.2.4 **Modification of the Environment** is not possible for parts of military vehicles and other equipment exposed to the elements. It is possible, however, to modify the environment in engine cooling, lubrication, and fuel systems. Good antifreezes contain corrosion

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* As far as the motor vehicle design engineer is concerned, 'electrolyte' and 'moisture' can be considered synonymous.

inhibitors, and lubricants can also be properly formulated for a given application. Fuels can be a problem, because of moisture, sulfur, and microorganisms. Additives are one way to address fuel system problems. Hydraulic and compressed air systems can suffer internal corrosion problems. Proper brake fluid specification (i.e., silicone fluids) is another example of corrosion prevention by modifying the environment.

3.3 Specific Design Approaches: Tailoring the Solution to Fit the Problem. If a design engineer knows what form of corrosion to expect with a given component, corrective measures can then be tailored to the problem. For example, pitting, intergranular corrosion, and stress-corrosion cracking (SCC) are known to be problems with stainless steels. Exfoliation and SCC are known to occur with aluminum alloys.

Methods of dealing with specific forms of corrosion are outlined below.

3.3.1 Pitting. This is normally a problem with "passive" alloys (i.e., stainless steels) in chloride-containing media. The designer can reduce pitting via these approaches:

o Suitable Alloying. Stainless steels modified with additions of molybdenum are less susceptible to pitting than non-molybdenum-bearing stainless steels. This is why type 316 stainless steel (18% chromium, 10% nickel, 2% molybdenum) is more resistant to pitting than type 304 (also 18% Chromium, 10% nickel, but no molybdenum.)

o Protective Coating. A suitable coating will isolate metal surfaces from pitting agents.

o Modification of the operating environment. In closed systems, inhibitors can reduce pitting by maintaining the passivity of a metal surface. Another modification that may be possible in closed systems is reducing the concentration of substances that promote pitting, i.e., the chloride ion.

3.3.2 Crevice and Poultice Corrosion. Crevices should be avoided when possible. Welded joints are preferable to bolted or riveted joints, and butt-type welds are preferable to overlapping welds if the latter are not necessary for structural strength. When crevices are unavoidable, metal surfaces in or near a crevice should be protected by organic coatings and suitable caulking compounds. Rustproofing compounds, with their ability to penetrate into crevices, are helpful. So are electrophoretic (E-Coat) primers, which can get into crevices better than conventional organic coatings.

Crevices can be created in welds with incomplete penetration (see Figure 11). Also, intermittent welds (see Figure 12) may conserve weld metal, but they also create sites for crevice attack. The design engineer should specify continuous weld seams so as to eliminate such sites.

When using bolts to fasten a bracket to a frame, the bracket and frame should each be cleaned, and subjected to the specified organic finishing scheme, prior to assembly. This way, unfinished (and unprotected!) metal

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will not be in a hard-to-reach crevice. In addition to the organic finishing scheme, the designer should also use a sealing compound between the surfaces being joined for additional protection.
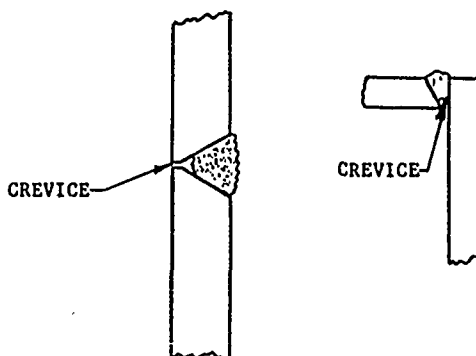
Fig. 11. CREVICES IN WELDS WITH INCOMPLETE PENETRATION
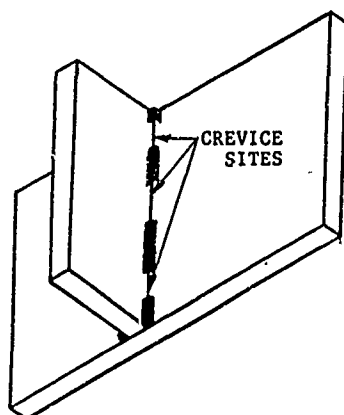
Fig. 12. CREVICE POSSIBILITY WITH INTERMITTENT WELDS

If a body or structure is to be welded, it is not possible to paint before assembly. Each piece should be cleaned in the area of the weld, and the designer should specify a continuous weld all around. After all welding is completed but before anything else is bolted on, the assembly should then be cleaned and painted.

Poultice corrosion can occur when absorbent materials that attract moisture are in contact with metals. Materials that may cause poultice corrosion include but are not necessarily limited to the following:

o   Wood
o   Cardboard
o   Open-cell foams
o   Sponge rubber

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The solution is to avoid placing materials such as these in contact with metals. Alternatively, one can employ protective coatings on the metal, and also specify suitable treatments for the offending non-metallic material.

Some varieties of wood are known to exude corrosive acids. The engineer should avoid placing them in contact, or even (in enclosed areas) in close proximity with metals, unless the metal is adequately protected and the wood properly treated.

Avoid, if at all possible, recessed areas that may collect dirt, mud, or debris. These deposits attract and retain moisture, causing poultice corrosion, particularly in salt-laden atmospheres.

3.3.3 <u>Galvanic Corrosion.</u> When dissimilar metals such as aluminum and steel are placed in contact with one another and subjected to an electrolyte, the potential difference may not be all that great--perhaps tenths of a volt. However, this unintentionally created 'battery' is subject to a virtually perfect short circuit'. Only the resistance of the electrolyte, or polarization effects limit current flow. Under these conditions, corrosion of metals such as aluminum or magnesium can be greatly accelerated. In dissimilar metal corrosion situations, the anode and cathode are distinct entities. The corrosion process can, therefore, be retarded by:

o coating the anode
o coating or, otherwise reducing the effect of, the cathode
o interrupting the electrical connection between anode and cathode
o eliminating the electrolyte

While the anode is the metal that corrodes, it should not be coated without coating the cathode as well. The engineer must be aware of the catchment area principle, whereby the anode current <u>intensity</u> (current, hence metal removal rate, <u>per unit area</u>) is inversely proportional to the anode/cathode area ratio.* If the anode is coated and subsequently placed in contact with an uncoated cathode, any discontinuity (holiday) in the coating will result in a large cathode/small anode situation. Intense corrosion of the anodic metal will occur at the discontinuity. If the cathode is coated while the anode is not, any discontinuity in the coating will result in a small cathode connected to a large anode. The ensuing increase in anode corrosion will be small, and furthermore will be distributed over a relatively large anode rather than concentrated in a small area.

When rivets are used to join sections of a given metal, they should be cathodic to the metal. Likewise, if sections of a given metal are to be welded by processes requiring filler metal, the engineer should select a

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* This principle assumes that corrosion rate is limited by the kinetics of oxygen reduction at the cathode.

filler that is somewhat (but not excessively) cathodic to the metal being welded. Utilization of cathodic rivets or cathodic weld filler metal reduces galvanic corrosion by minimizing cathode/anode area ratio.

Threaded connections between dissimilar metals are inadvisable due to the possibility of rapid corrosion of the anodic metal between the threads. Brazing is the preferred technique for joining tubing made from dissimilar metals. The brazing alloy should be cathodic to at least one of the metals.

When dissimilar metals are assembled with fasteners, a short-circuited electrochemical cell will not occur if one uses non-conducting fastener arrangements. Insulating washers, insulating bushings, and insulating sealing material between faying surfaces will accomplish this goal (see Figure 13). Tapes made from non-absorbent material will protect faying surfaces from corrosion. All surfaces should be coated before assembly to avoid exposing bare metal to galvanic and crevice effects. When using sealing tapes, the tape should extend an inch or two (or, a few centimeters) beyond the faying surfaces so as to lengthen the electrolyte path in atmospheric corrosion situations.

INSULATING BUSHING ⎯ INSULATING WASHER

SEALING MATERIAL OR TAPE

INSULATING WASHER

CLEAN/PRIME/COAT ALL SURFACES BEFORE ASSEMBLY
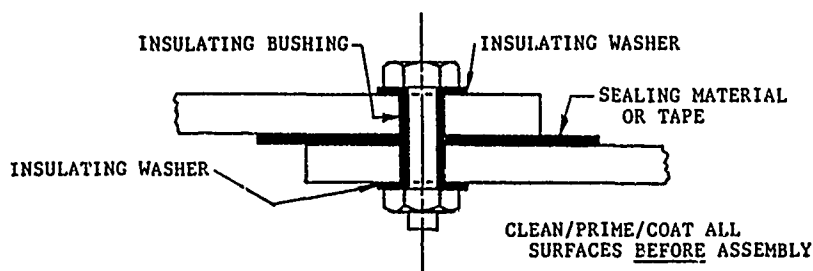
Fig. 13. PROPER DESIGN OF A DISSIMILAR METAL JOINT

Galvanic corrosion can be a problem even when similar metals are joined, because of electrochemical potential differences between the metal objects joined and the fastener. In atmospheric corrosion situations, the catchment area principle is not applicable because there is not enough electrolyte to "spread out" the cathodic effects of a fastener over a large anodic surface area. Accordingly, when joining metals such as aluminum or magnesium, the designer must use fasteners that are galvanically compatible with the parts being fastened. Cadmium-plated bolts, nuts and rivets are helpful in reducing aluminum corrosion. With magnesium, the only fasteners permissible are those made from certain aluminum alloys.

Galvanized Series and Metal Compatibility Considerations. The design engineer must consider not only the suitability of a given metal in the anticipated service environment, but also compatibility of metals with each other. Galvanic corrosion can be minimized by selecting dissimilar metals whose electrochemical potentials are close to one another, thus minimizing the "driving force" behind corrosion reactions.

When selecting metals and alloys for service in contact with one another, tables listing standard electromotive potentials should be used

with caution, because standard potentials do not represent the real world. Also, standard potentials are defined only for pure metals. A more realistic criterion is based on measurement of the electrical potential of a given metal in contact with an actual operating environment such as sea water.* The potentials of various metals and alloys determined in this manner constitute the basis for <u>galvanic series</u> charts, in which metals and alloys are listed in order of their measured electrical potentials in a specified environment. A galvanic series based on an NaCl solution would be most relevant to the design engineer, because common salt (NaCl) is a frequently encountered corrodent.

For military vehicles, a galvanic series based on sea water (see Table 2) is a reasonable criterion for material selection. Military vehicles such as main battle tanks have to withstand water (including sea water) as part of their assigned missions.

If two metals or alloys are widely separated on a galvanic series chart based on a given electrolyte, one can assume that the anodic material will have an increased tendency to corrode when the given metals are coupled in the presence of that electrolyte, vis-a-vis metals or alloys not as widely separated on said chart.

Finally, galvanic corrosion can be minimized by <u>eliminating the electrolyte</u>. This means following the same principles of 'designing out' corrosion-encouraging moisture traps that apply to single metal design.

3.3.4 <u>Stress Corrosion Cracking (S.C.C.)</u>, occurs when a vulnerable <u>material</u> is subjected to certain <u>corrosive</u> <u>media</u> while under applied or residual <u>tensile</u> <u>stress</u>.

Among aluminum alloys, some combinations of alloy composition and temper (metallurgical condition achieved through thermal and mechanical treatments) are susceptible to S.C.C. in aqueous media and in the presence of some non-aqueous substances. Copper alloys are subject to 'season cracking' caused by the presence of ammonia in the operating environment. Stainless steels are prone to S.C.C. in solutions containing certain ions, most notably the chloride ion.

Avoiding or eliminating S.C.C. essentially boils down to changing one (or more) of three essential elements: material, media, and tensile stress. Specific design practices include the following:

o Select the right material. For example, various high-strength aluminum alloy-temper combinations are known to be susceptible to SCC. Aluminum structures should therefore not utilize such combinations, particularly when residual tensile stresses are created during welding.

o Use stress-relieving heat treatment to eliminate residual tensile

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*   A standardized electrode, such as the saturated calomel half-cell, provides the required reference potential.

stress.* Another approach along these lines is to use shot
peening or surface rolling to induce residual compressive stresses
at the surface of a part.

o Specify a suitable coating or cladding. However, electroplating
high-strength steels can introduce hydrogen into the base metal and
thus cause embrittlement. Therefore, use coating processes that do
not introduce hydrogen, when treating high-strength steels.

o Avoid configurations that may result in thermal gradient induced
tensile stresses.

o Design parts and systems so as to avoid stress raisers; also, avoid
crevices where S.C.C.-promoting ions could concentrate.

o Modify the environment, if possible. In closed systems, one can
add a suitable inhibitor, adjust the Ph, or eliminate S.C.C.-
causing substances.

Metallic materials are not the only materials susceptible to
stress-corrosion cracking. Polycarbonates (i.e., "Lexan R ") are
susceptible to stress-cracking in the presence of oxygenated/chlorinated
degreasing solvents. Rubber suffers cracking due to ozone. The solution
to these problems is to to use antiozonants in rubber, and (as with metals
and alloys) avoid exposing susceptible materials to combinations of
tensile stress and specific chemicals known to cause cracking.

3.3.5 Intergranular Corrosion (preferential corrosive attack along grain
boundaries). This occurs in alloys that form precipitates at grain
boundaries during deliberate or unintended thermal or mechanical
treatments. Stainless steels and some aluminum alloys are most likely to
suffer this form of corrosion. Precipitation-hardenable aluminum alloys
based on the Al-Cu, Al-Mg (Mg content > 3% by weight) and Al-Zn-Mg systems
can become prone to intergranular corrosion as a result of precipitates
whose electrochemical potentials differ significantly from the potentials
of nearby grains. The precipitates and grain boundaries form galvanic
cells when subject to an electrolyte. As a result, either the precipitate
particles corrode, or they act as cathodes and stimulate attack on
adjacent grain boundaries.
    Austenitic stainless steels are prone to intergranular corrosion when
subjected to improper heat treatments. When these alloys are heated to
temperatures lying within the sensitization range for the right length of
time (see Figure 14), carbide precipitates form at the grain boundaries.
These carbides are chromium-rich. The required chromium comes from the

* Be aware, however, that such heat treatment may spoil the temper
or leave certain alloys (i.e., stainless steels) susceptible to
intergranular corrosion.

boundaries of adjacent grains; consequently the grain boundaries are deficient in chromium. This condition renders stainless steels susceptible to corrosive attack along these boundaries. Such sensitization can occur during welding. Narrow zones of metal on each side of a weld may be subjected to the right temperature range, for the right length of time, to cause carbide precipitation.
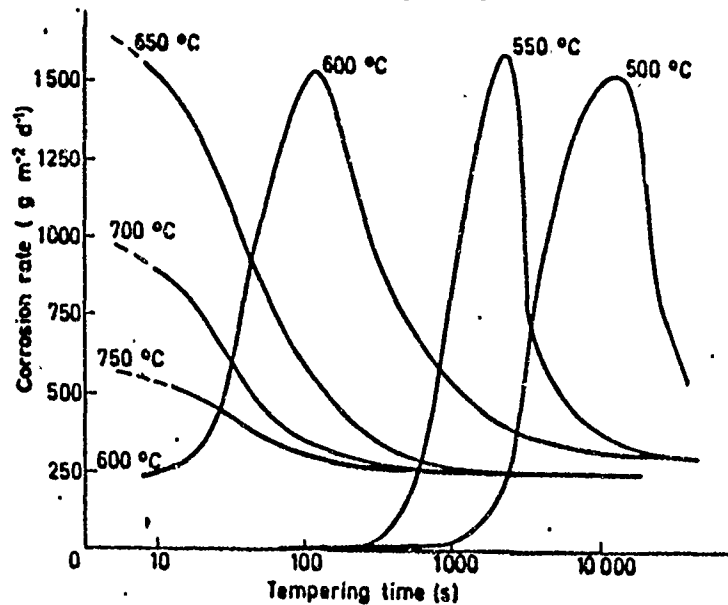
Effect of tempering treatment on corrosion resistance of 420 S45 (air cooled, 980 C)
Corrosion tests in 10% nitric acid solution at 20°C

Fig. 14a
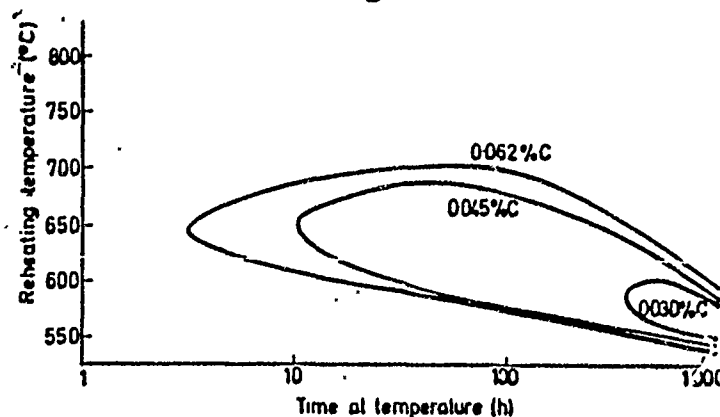
Temperature-time-sensitisation diagrams for three austenitic Cr-Ni steels solution treated at 1 050°C. The curves enclose the treatments causing susceptibility to intercrystalline corrosion in a boiling $CuSO_4 + H_2SO_4$ test reagent

Fig. 14b

Fig. 14.   SENSITIZATION OF STAINLESS STEELS TO
   INTERGRANULAR CORROSION BY TEMPERATURE-
   TIME EXPOSURE.

If intergranular corrosion is a problem, the design engineer can use these approaches:

o   Specify stainless steel (S.S.) with low carbon content. Low-carbon
    modifications of stainless steels such as AISI 316 (the low-carbon
    grade is known as type 316L) are available for applications
    involving welding.
o   Specify S.S. alloys which include columbium (also known as
    niobium), titanium, or tantalum in small amounts. These elements
    combine with carbon in preference to chromium, thus preventing
    depletion of chromium from grain boundaries.
o   Specify proper heat treatment before subjecting the part or
    assembly to the anticipated service environment. For example,
    heat treatment after welding is often necessary for stainless
    steels, to reverse grain boundary carbide precipitation caused by
    welding. This means heating to a temperature high enough to
    dissolve carbide precipitates. Subsequent quenching should be
    rapid enough to avoid subjecting the surface to temperatures in
    the sensitization range for periods of time sufficient to induce
    carbide precipitation. The temperature vs time curve of the
    quench operation should miss the "nose" of the time vs temperature
    curve representing carbide precipitation for the type of steel
    involved. (Refer to Figure 14*)

"Knife line" attack of stabilized S.S weldments can be prevented by heating the structure, after welding, to a temperature such as to cause columbium (or titanium) carbide to precipitate in preference to chromium carbide.

3.3.6   Exfoliation Corrosion. When using aluminum alloys in components or structures, exfoliation can be minimized by:

o   Utilizing alloy/temper combinations that do not suffer this
    form of corrosion.
o   Applying protective coatings, especially to faying surfaces and
    surfaces in contact with fasteners.
o   Avoiding exposure of the short transverse direction to the
    environment. (see Chapter 9, par. 9.1.3).

3.3.7   Dealloying (parting) corrosion. This is a problem mainly with grey cast iron or certain copper alloys. If it becomes a problem, the design engineer can:

o   Specify copper alloys whose zinc content is no greater than 15%.

*   Shrier, L.L., PhD., Corrosion, Vol. 1, page 3:46., Newnes-
    Butterworth, London, 1976.

o   Specify brasses inhibited with tin, antimony or arsenic. The
     latter is frequently used as an alloying addition to Cu alloys for
     inhibiting corrosion.
o   Avoid areas where stagnant solutions come into contact with
     susceptible Cu alloys, when designing closed systems. Such
     conditions, accompanied by surface deposits, encourage
     dezincification. Copper or brass radiators in automobiles and
     trucks can suffer external dezincification, due to exposure to
     road deicing salts. Arsenical cartridge brass, used in place of
     regular brass, solved this problem in northeastern Canada.*
o   Specify nodular, malleable, or white cast iron instead of grey
     iron, to avoid graphitization corrosion.

3.3.8   Fretting corrosion between moving parts in contact with each other
can be minimized by the following measures:

o   Increase surface hardness by shot-peening or cold working.
o   Use a sacrificial soft surface in contact with a hard surface.
     Example: tin-, lead-, or silver-coated metal in contact with
     steel.
o   Eliminate relative movement by roughening surfaces, or increase
     the load normal to the surfaces. Be aware, however, that if the
     load is not increased sufficiently, fretting corrosion can
     actually increase.
o   Specify proper lubricants and surface treatments, i.e., phosphate
     coatings and a low-viscosity, high-tenacity oil or grease.
o   When transporting wheeled vehicles, such as by railroad, one can
     prevent corrosion of wheel bearings by securing all axles. The
     idea is to prevent the slight back-and-forth movements that cause
     fretting.

3.3.9   Corrosion Fatigue. If premature fatigue failures in a given part
occur due to corrosive conditions acting in concert with repeated
stresses, corrective measures include:

o   Eliminating stress raisers (or reducing their effects).
o   Creating residual compressive stresses by shot peening or other
     means.
o   Specifying protective coatings.

3.3.10   Erosion Corrosion. This occurs mainly with marine systems or in
fluid handling systems such as heat exchangers. Some military vehicles,

*   Park, Kwang., Dezincification Corrosion and its Prevention for
     Copper/Brass Radiators. (SAE Paper #851829, From Proceedings of the
     2nd Automotive Corrosion Prevention Conference, SAE Publication
     P-136.

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such as the Light Armored Vehicle family, are expected to operate in water and are even provided with propellers for that purpose. The designer should therefore take a few precaution against erosion-corrosion as follows:

o   When using copper-nickel alloys, the alloy must have about 0.5% iron to resist erosion corrosion*

o   Propellers for watercraft must be designed so that the critical velocity for cavitation (a form of erosive attack) is not exceeded for the material used. Either limit the propeller diameter, or the RPM.

o   Wind, i.e., helicopter tail rotor slipstream, can erode protective coating. Consider hard chrome plate, or redesign the tail assembly to avoid direct impingement of slipstream.

*   La Que, F.L., Marine Corrosion, John Wiley and Sons, New York, 1975

Chapter IV
"Designing Out" Corrosion in Tactical and
Combat Vehicles

4.1 <u>Basic Principles</u>. Proper design of a vehicle body or structure can break the cycle of corrosion in a number of ways. Avoiding design features which trap debris or moisture will eliminate the sustained presence of electrolytes. One can reduce opportunities for corrosion sites to be activated by eliminating crevices where possible, or specifying sealing materials where crevices are unavoidable. Properly sized and located drain holes help reduce corrosion by allowing moisture to drain away from metal surfaces in "sump" areas, when such areas cannot be avoided. Prevention of sustained electrolyte contact is also accomplished via design features which prevent mud or other debris from accumulating on metal surfaces. Deposits of mud or other debris are undesirable because they tend to attract or retain moisture, causing localized corrosion by setting up differential aeration cells. In designing tactical vehicle body structures, it is preferable to avoid closed sections for the following reasons:

1) Moisture almost invariable enters and promotes internal corrosion.
2) It can be difficult to apply protective coatings on the interior surface.
3) These sections are frequently poorly ventilated, allowing humidity buildup.

For example, doors on commercial vehicles are vulnerable to corrosion because water can enter via the window slot and subsequently become trapped. Water accumulation in a door can cause waterline corrosion of the sheet metal panels. Also, inadequate air circulation causes humidity buildup, thus accelerating inside-out corrosion. A tactical vehicle's door design should aim at providing adequate drainage. The designer should also provide access for primers and (if necessary) supplementary corrosion-inhibiting agents.

When designing body structures, application of protective coating should be considered during the design stage. Properly sized and located access holes allow electrodeposited primers (to be discussed later) to reach all areas of metal where corrosion can start. Sharp corners on any metal part are undesirable because organic coatings tend to be thin on sharp convex (outside) corners. "Bridging" of coatings can occur on sharp concave (inside) corners. Smooth, rounded contours allow coatings to form a protective film of uniform thickness.

Joints involving sheet metal should be designed to minimize trapping of dirt or moisture in crevices formed by overlapping surfaces. Lap joints on the underbody of a vehicle should, if possible, be aligned so as to point the lap away from the direction of travel. On vertical sheet metal surfaces, lap welds should preferably be arranged so as to point the lap downward on exterior surfaces to allow drainage of rain and water thrown by wheels.

External metal surfaces of tactical and combat vehicle are subject to impact by stones, gravel, and other missiles generated by tires or tracks. These impacts can damage protective coatings, leaving underlying metal vulnerable to corrosion. For this reason, metal surfaces in the path of debris thrown by tires or tracks should, if possible, be arranged so that stones, gravel, and similar missiles will strike a glancing, angled blow rather than a direct blow. Areas subject to physical damage can be treated with undercoatings which do not completely harden and hence are 'self-healing'. Another solution is to use plastic coating materials such as PVC (or, flexible urethanes) to resist stone damage in vulnerable areas.

With riveted or bolted joints, be careful to prevent moisture from becoming trapped between faying surfaces. Pre-applied protective coatings will protect faying surfaces of joined metal. Caulking (sealing) compounds can be applied to keep moisture out. With welded lap joints, one can apply sealing compounds after welding to prevent moisture from seeping into edges at locations not already sealed by weld metal.

If structurally permissible, butt-type welds are preferable to lap welds in that there is no overlapping metal to form crevices.

Structural members should be designed to avoid pockets where debris might be trapped or where moisture could accumulate. An inverted U-channel will not trap moisture. When using concave-upward sections it is good practice to provide holes. Corners should be rounded rather than sharp, as sharp inside corners can trap debris while sharp outside edges are difficult to protect with coatings. Flanges should be designed so as to enable moisture to drain off of them.

Rusting of the interior side of floor pans of M151 and M880 vehicles has occurred due to trapped water. To avoid this problem, specify drain plugs to enable maintenance personnel to drain accumulated water from these areas. This idea is particularly applicable to open-body vehicles such as the M151. Closed-body vehicles should be constructed so as to exclude water from the interior as much as possible.

The following sections will elaborate on various aspects of corrosion engineering in tactical and combat vehicle design.

4.2 Welding and Joining. Whether the design engineer chooses welding or joining, care should be taken to avoid crevice formation. Consider Figure 15. In Fig. 15 (a), the crevice formed by the overlapping surfaces collects liquids and debris. Figure 15 (b) shows a fillet weld at the upward pointing lap, which eliminates the crevice there. However, the downward-pointing lap remains a possible corrosion site. Fig. 15 (c) shows an overlapping joint where the faying surfaces are isolated by soldering, walding, or caulking all around.

Figure 15 (d) is an overlapping joint with a continuous weld on both laps. Here, corrosives are isolated from the joint. This configuration is preferred from the viewpoint of mechanical strength.

Figure 15 (e) shows a combination of welding plus a protective after-coating. This configuration is, of course, necessary because in this day and age, unprotected metal is not in the best interest of the Army.

Figure 15 (f) shows a butt-type welded joint. If one can get by with this from the structural standpoint, it offers the advantage of no
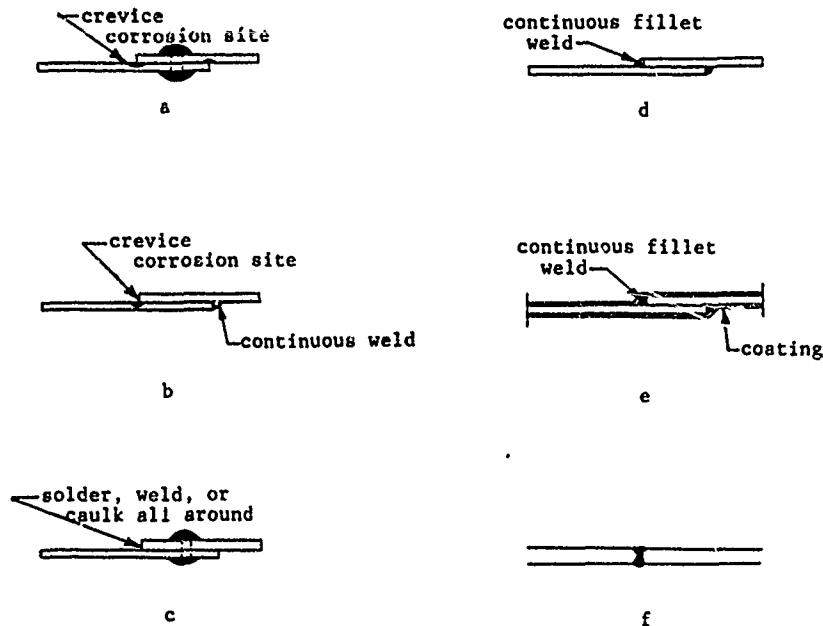
Fig. 15. DESIGN CONFIGURATIONS FOR OVERLAPPING
SHEET METAL JOINTS (Refer to text)

crevices. Good welding workmanship is necessary, for structural strength
and avoidance of crevices (see Figure 11). After welding, provide a
protective coating.

4.3 Integration of Metal Joining and Organic Finishing. Organic coatings
(to be covered in chapter 8) cannot be an afterthought, but must be
integrated into design and manufacturing. When assembling two components
by bolting, they should be painted before assembly. The flow chart in
Figure 16 illustrates the proper sequence of steps for assembling (for
example) a bracket to a frame.

When joining components by welding, different rules apply. Coatings
in a weld zone interfere with the welding process, or are destroyed. When
welding precoated* metals, the coating must be removed in the weld region,
and reapplied afterward. Figure 17 illustrates the flow chart for
assembly by welding.

*   All ferrous metals should have some form of protection at all times.
     Sheet metal and structural shapes should have a temporary coating, or
     a pre-applied primer, so they won't rust while waiting to be used.
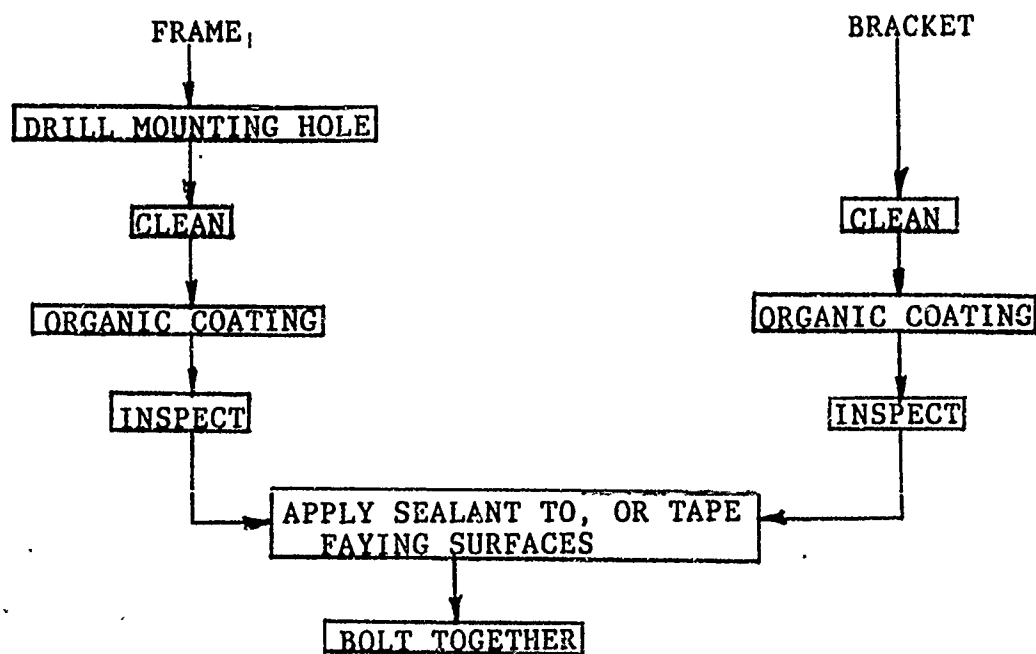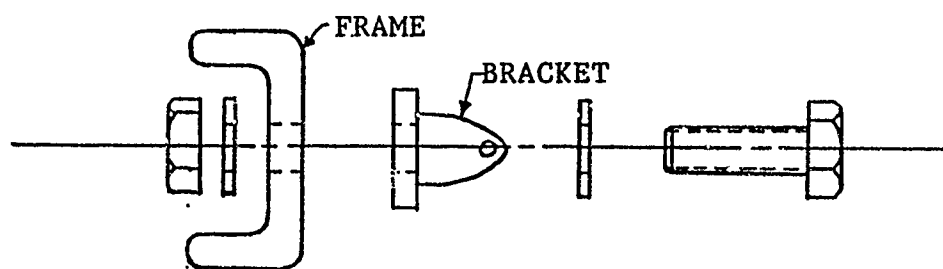
Fig. 16. SEQUENCE OF STEPS FOR ASSEMBLY BY BOLTING
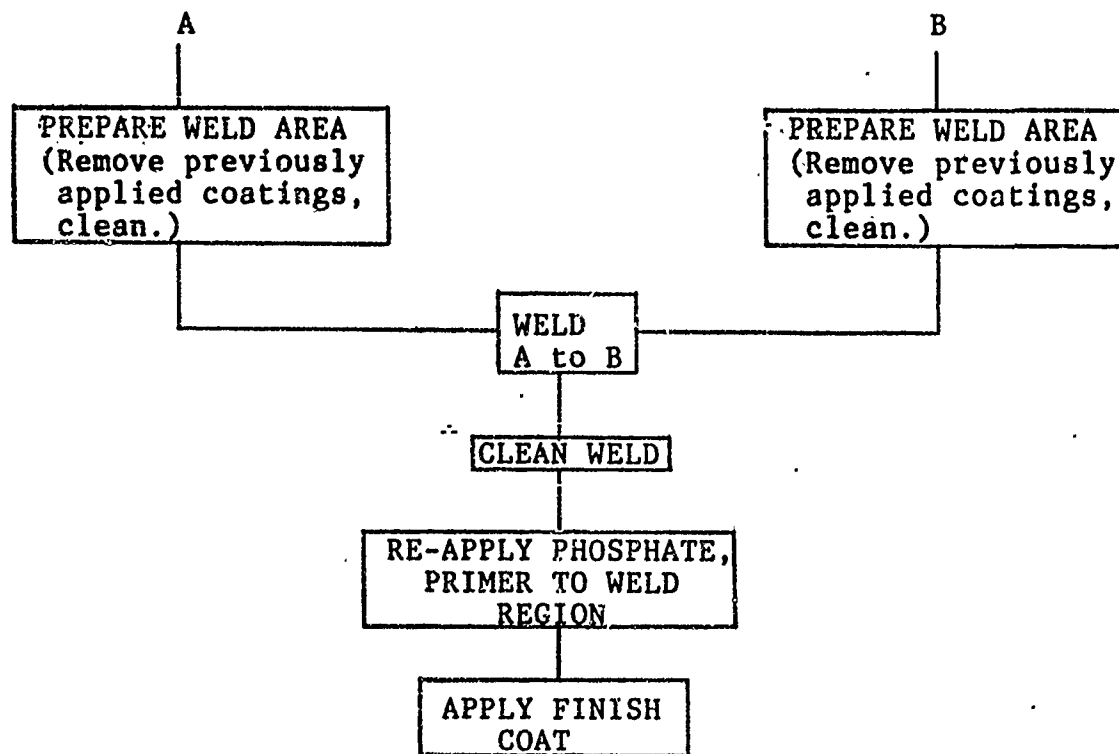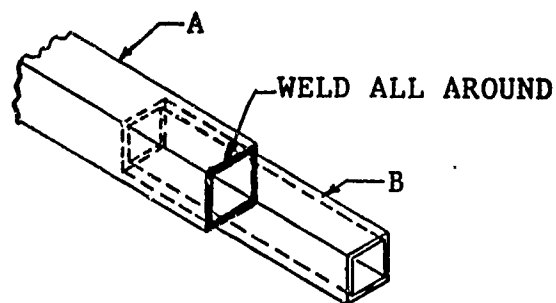
Fig. 17. SEQUENCE OF STEPS FOR ASSEMBLY BY WELDING
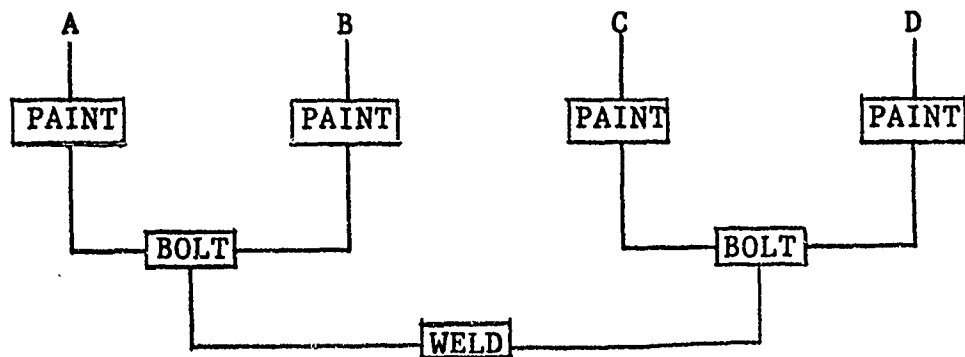
Fig. 18a
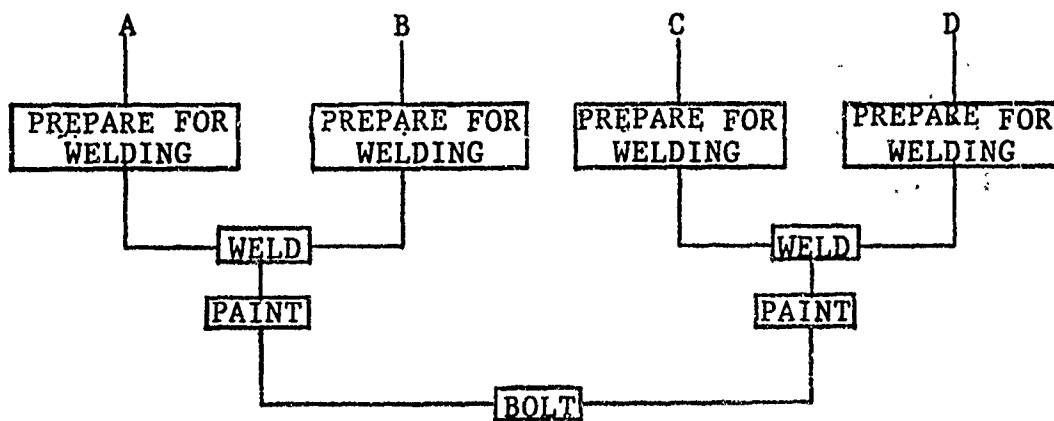
Fig. 18b

Fig. 18.   COMBINED WELDING AND BOLTING

With welded structures, do not apply the final coating until after the welding is done. The reason: Some coating materials, i.e., polyurethanes (CARC), may not apply too well over an existing, partially destroyed coating.

4.4 <u>Combined Welding and Bolting.</u> When a vehicle or trailer assembly is partly welded and partly bolted, manufacturing steps should be arranged so as to minimize disruption of protective coatings. In Figure 18 (a), parts A,B,C, and D are all painted first. Then, A is bolted to B, while C is bolted to D. Finally, A-B is welded to C-D. In Figure 18 (b), parts A,B,C, and D are first prepared for welding. A is welded to B, while C is welded to D. Next, A-B and C-D are pretreated, primed, and finish-coated. Finally, A-B and C-D are assembled by bolting.

The approach illustrated in Figure 18 (b) is superior for the following reasons: In Figure 18 (a), an organic coating is applied to A,B,C, and D only to be partially destroyed when A-B and C-D are welded. Either the coating is removed prior to welding, or it will be destroyed anyway by welding heat. The coating will then have to be reapplied to the weld region.

In Figure 18 (b), organic coatings are applied after A-B and C-D are welded, but before bolting. This has two advantages:

First, organic coatings are not exposed to welding heat. Second, faying surfaces are coated before bolting, so uncoated metal is not exposed to crevice corrosion.

In Figure 18 (a), one could coat the assembly after A-B is welded to C-D. However, this would cause difficulties, because the organic topcoat may not be able to penetrate into the crevice formed by bolting A to B, and C to D. Also, if insulating gaskets, washers, or sealing compounds are used, they will interfere with organic coating processes.

In reality, any tactical or combat vehicle is a hodgepodge of weldments, riveting, and bolting. Accordingly, the principles outlined above will have to be compromised at times. One of the advantages of electrophoretically applied primers is penetration into crevices formed by riveting and spot-welding. This process, especially with modern, high-build cathodic electrocoat materials, is highly recommended for tactical vehicles in today's Army.

A good compromise between rigid adherence to the above guidelines, and the realities of practical design and production, is as follows: When designing a system (be it a trailer, truck, or armored vehicle), brackets or fittings to be bolted should be pre-painted, as should the main chassis or frame. Coatings should be applied to bare metal surfaces created by the drilling of mounting holes, unless such holes are tapped. If something has to be welded after any coating was applied, the coating in the weld area will have to be thoroughly removed, and just as thoroughly reapplied after welding. The design engineer should try to minimize this through proper coordination of coating and manufacturing.

One rule must be regarded as ironclad: Supplementary corrosion-preventive agents (i.e., rustproofing greases or waxes), caulkings, and sealing compounds, must not be applied prior to organic coating.

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If a structure is to be bonded with adhesives, arrange for priming and topcoating after bonding.* Some adhesives cure when subjected to the temperatures necessary for paint drying and curing. If so, be wary about mishandling the assembly when the adhesive hasn't cured yet.

Adhesives have been developed for bonding electrodeposition-coated steel.** If using such adhesives, the metal surfaces should be E-coated, then bonded.

4.5 __Structural Member Design.__ Refer to Figure 19. In (a), all elements of bad design are present. Water will collect in the channel. The sharp edges are difficult to coat evenly. In (b), the sump area still exists, but a drain hole prevents moisture accumulation. In (c), the concave side faces downward, so that no sump area exists.***
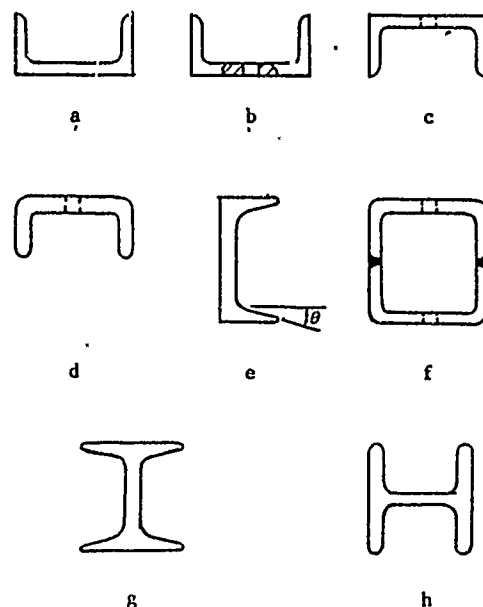
Fig. 19. STRUCTURAL MEMBER CROSS-SECTIONS
(Refer to Text)

Figure 19 (d) is the best configuration. Here, the concave side faces downward, as in 19 (c). In addition, all corners and edges are rounded, to prevent weak spots in protective coatings.

*   When bonding aluminum panels in the HMMWV, the panels are chemically treated with a conversion coating before bonding. Steel or zinc would probably be phosphated before bonding.
**   __Glue Bonds Auto Parts__, Automotive News, June 8, 1987, page 14.
***   Note that a drain hole is shown. This is so water will drain if the trailer or other structure is stored or shipped upside down.

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Figure 19 (e) is also acceptable. The angle (theta) allows moisture to drain.

The configuration shown in Figure 19 (f) is acceptable, if the design engineer specifies drain holes.* Note, also, that the welds are at the sides, rather than at the top and bottom. This is to avoid exposing a weld seam to moisture which might form a continuous film on a horizontal surface, in spite of drain holes.

The I-beam configuration shown in Figure 19 (g) is acceptable, but 19 (h) is not. The latter offers a sump area where moisture and dirt can accumulate. Drilling drain holes will weaken the web. Accordingly, use I-beams with the web in the vertical direction.

The structural detail shown in Figure 20 (a) is poor practice. Dirt, salt, and moisture can enter via the opening shown. Once such debris gets in, the entrapment area is difficult to clean. Figure 20 (b) or (c) is more acceptable. Here, moisture that gets in, can drain out again.* The inside surfaces of closed sections should be protected by coatings, as should the outside surfaces.
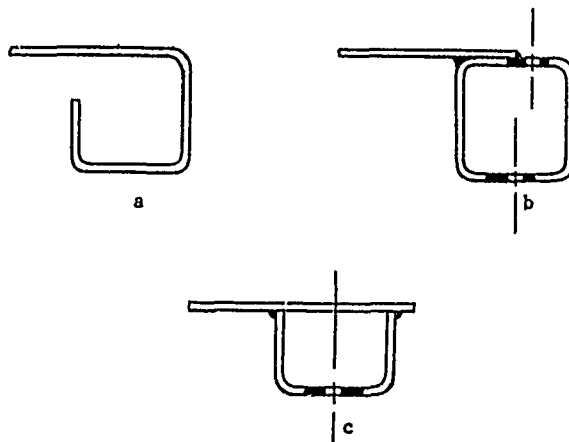
Fig. 20. REDESIGN OF STRUCTURAL DETAIL TO ELIMINATE
ENTRAPMENT OF DEBRIS (see text)

Frame rail design. Figure 21 illustrates frame rails for a typical tactical truck, the M939. These are straight rails, using a C-section, as in Figure 19 (e).

Figure 22 shows the frame rails used in the High Mobility Multipurpose Wheeled Vehicle. These rails are closed, as in Figure 19 (f). This is not good practice from a corrosion standpoint, because any moisture that gets in, cannot easily get out. There are no drain holes. The probable

* Locate drain holes in the lowest part of the beam, to avoid formation of sump areas. Beware, also, of shipment or storage in an unusual position, i.e., upside-down or sideways.

reason for this is that the beam is already structurally weakened by the numerous mounting holes. The inside of such a beam should be protected by coatings.

In Figures 21 and 22, there indeed are numerous holes for attaching cross-members and other components. These holes should be drilled before applying protective coatings.
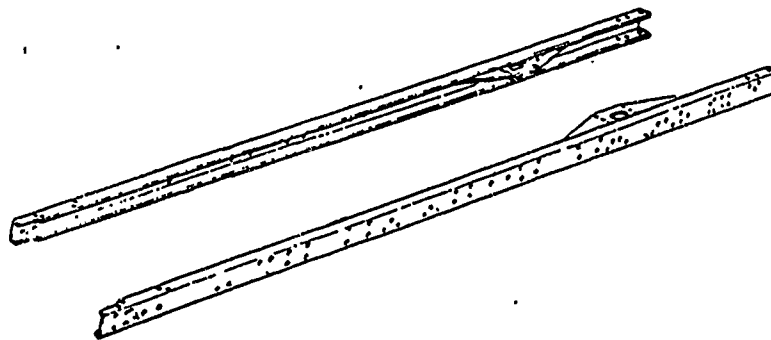
Fig. 21. M939 FRAME RAILS
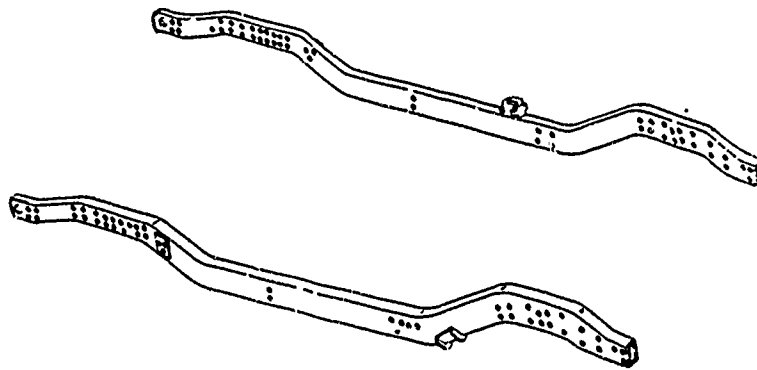
Fig. 22. HMMWV FRAME RAILS

4.6 **Miscellaneous Features to Use or Avoid.** Figure 23 illustrates cross-sectional forms which may occur in the design of bodies, frames, or suspension components. The features shown in Figure 23 (a) and (b) should, if possible, be shunned. The sharp corners trap moisture and debris. The features shown in Figures 23 (c) and (d) are good--the rounded surfaces are less prone to such effects.

Another particular design feature that deserves discussion is fasteners in thick steel sections. When a threaded fastener is used to join something to a thick section, use the configuration shown in Figure 24. A corrosion-preventive sealant is injected into the hole after drilling and tapping but before fastening. Excess sealant escapes through

a center hole in the fastener when the fastener is tightened. (In this case, drill and tap the hole in the thick section after applying protective coatings.)

Figure 25 illustrates how to avoid creating a difficult-to-protect crevice corrosion site in some fastened configurations. In (a), corrodents are difficult to exclude from the inner surfaces. In (b), it is easier to apply gaskets, or sealants to keep corrodents out of the joint.

a   b   c   d
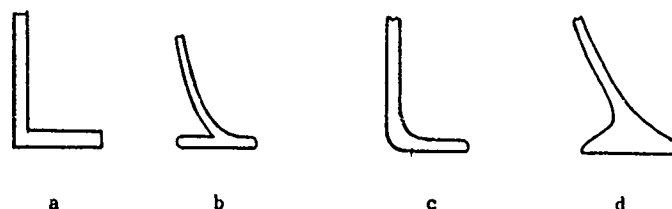
Fig. 23. REDESIGN OF STRUCTURAL DETAILS TO ELIMINATE SHARP EDGES AND CORNERS
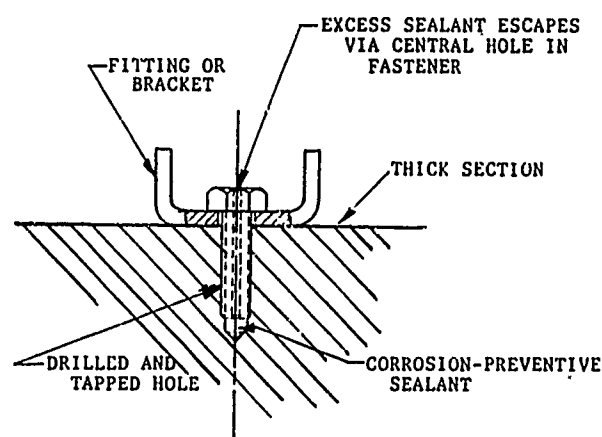
Fig. 24. DESIGN FOR CORROSION PREVENTION WHEN BOLTING A BRACKET TO A THICK SECTION
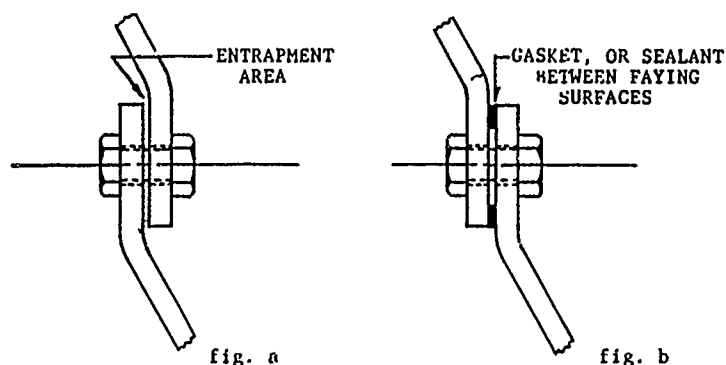
Fig. 25. REDESIGN OF STRUCTURAL DETAIL TO ELIMINATE CREVICE CORROSION SITE

Figure 26 illustrates structural design of a vertical reinforcing member. The left view (26a) is a closed-section reinforcing member with the bottom closed off. This configuration traps moisture and is therefore undesirable. Figure 26 (b) illustrates the same design, except for the open bottom. This allows moisture to drain away, and therefore 26 (b) is more desirable than 26 (a). Figure 26 (c), an H- or I- beam, is also acceptable. Use a continuous weld to avoid crevices.
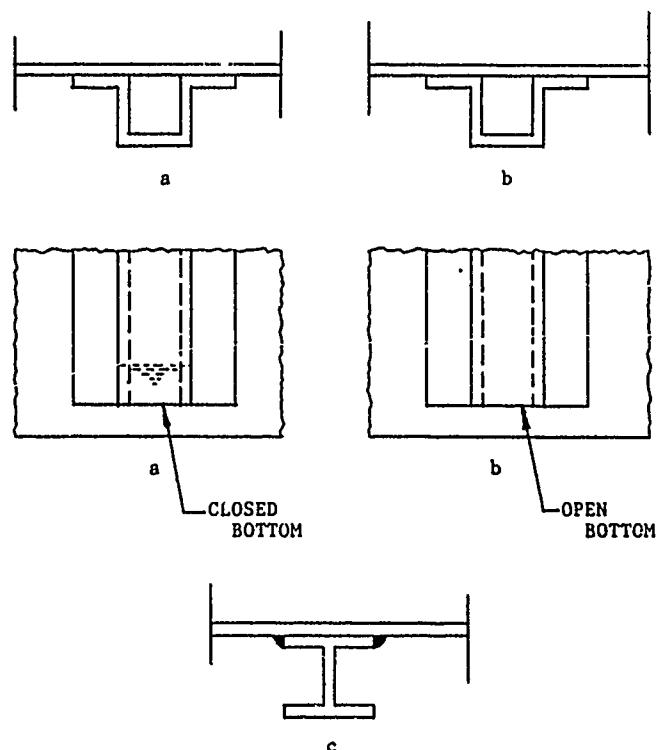
Fig. 26. PROPER DESIGN (b or c) OF REINFORCING BEAM (see text)

4.7 **Sheet Metal Design.** Figure 27 illustrates correct and incorrect fender designs. (A) allows moisture to drain away from the sheet metal. (B) is less preferable, because the shelf may hold moisture and debris. The designer should avoid the configurations shown in 27 (c) and (d), because of the pronounced sump areas.
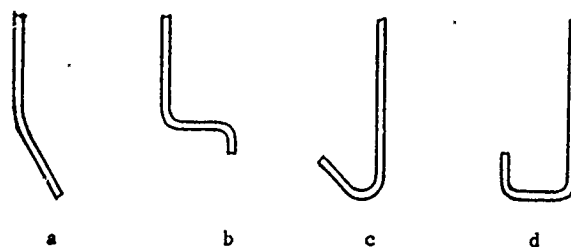
Fig. 27. SHEET METAL DESIGN--CORRECT(a & b)
INCORRECT(c & d)

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Figure 28 illustrates the principle of designing lap welds so as to point the exposed (exterior) lap away from the direction of travel if horizontal, or downward if vertical. The idea here is to prevent moisture from being driven into the crevice formed by overlapping metal, or to allow moisture to drain away from the weld.
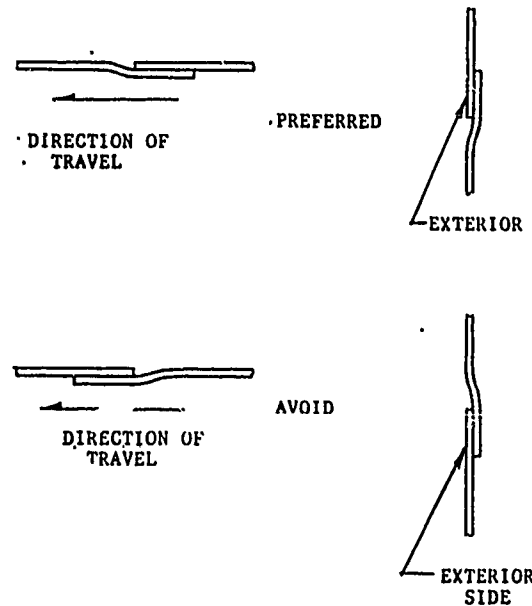
Fig. 28.   DIRECTION OF LAPS IN SHEET METAL JOINTS

Figure 29 illustrates principles to follow regarding sealants between riveted sheet metal surfaces. In Figure 29 (a), there is sufficient sealing compound to exclude moisture from the crevice. In Fig. 29 (b), there is a shallow crevice because of insufficient sealant. In Figure 29 (c), the joint is an unmitigated crevice corrosion site.
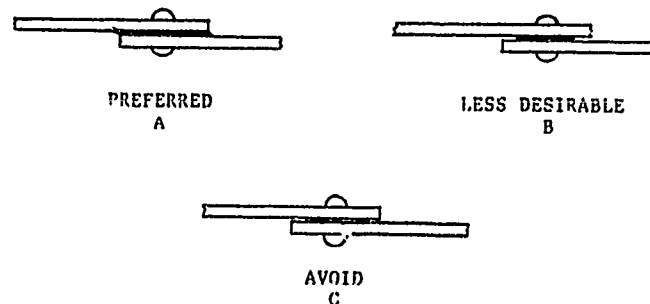
Fig. 29.   CORRECT AND INCORRECT USE OF SEALANTS IN
OVERLAPPING JOINTS

Sealants should be applied after phosphating, priming, painting and, if possible, before riveting. If using an electrophoretic primer, it can be applied after riveting. In that case, the manufacturing sequence may

be as follows: pretreat, rivet, electroprime, topcoat, and then use a
sealant suitable for injection into the edges of the resultant overlapping
joint. However, it is still preferable to precoat sheet metal parts
before riveting or other mechanical fastening.

In Figure 30 in the left view, the edge of a fender is arranged so as
to shield the edge of a sheet metal joint from tire-thrown spray. In the
right view, water can be thrown into the edge of a sheet metal joint.

Figure 31 illustrates how to join aluminum body panels to a steel
frame. Note that in the preferred arrangement, a sealer isolates the
dissimilar metals, and that a steel rivet is used to minimize the
cathode/anode area ratio. The right side illustrates the wrong
configuration--an aluminum rivet and no sealer between the aluminum and
steel surfaces.

Figure 32 illustrates 'open' and 'closed' design configurations. In
the closed design, inside-out corrosion is likely due to entrapped
moisture and humidity buildup.

The HMMWV doors are based on the 'open' configuration. The door latch
and window mechanisms are exposed on the inside, for easy maintenance.
Use of a single sheet metal panel, instead of inner and outer panels,
eliminates a notorious crevice corrosion site at the inside bottom where
the inner and outer panels meet. There is no sump area, so water cannot be
trapped.

Closed structural configurations. A variety of U.S. tactical
vehicles, including the M939 family, the 10-ton HEMMT, and the Commercial
Utility Cargo Vehicle (CUCV), use closed structural configurations for
their doors. Figure 33 illustrates the SAE recommended practice for door
design for commercial vehicles. The designer should provide drain holes,
adequately sized along the bottom so as to prevent moisture from
accumulating in the door assembly. Inner surfaces should slope toward
drain holes. The door assembly should be given a good protective coating
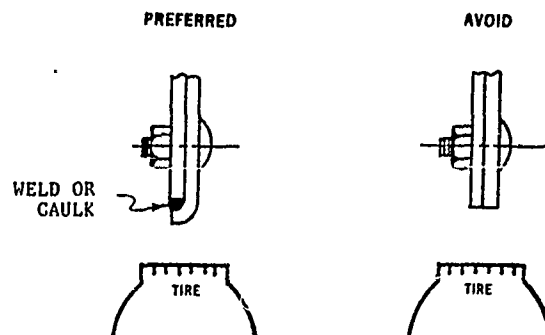
Fig. 30. DESIGN OF SHEET METAL JOINTS EXPOSED TO
TIRE-THROWN SPRAY

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PREFERRED   AVOID

ALUMINUM PANEL   ALUMINUM PANEL

STEEL FLOOR PLATE   STEEL FLOOR PLATE

SEALER   NO SEALER

ALUMINUM RIVET

STEEL RIVET

(LARGE ALUMINUM SURFACE AREA TO SMALL STEEL RIVET SURFACE AREA)

(SMALL ALUMINUM SURFACE AREA TO LARGE STEEL SURFACE AREA)
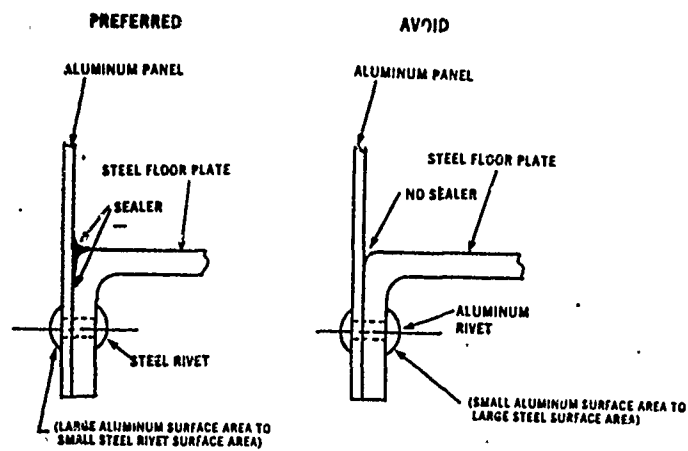
Fig. 31. CORRECT & INCORRECT JOINING OF ALUMINUM PANEL TO STEEL FRAME

PREFERRED

AVOID
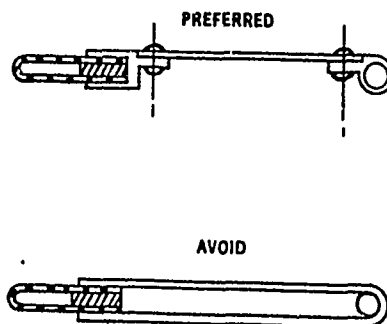
Fig. 32. OPEN AND CLOSED DOOR DESIGNS

PREFERRED   AVOID

DOOR OUTER PANEL

DOOR INNER PANEL

DOOR OUTER PANEL

DOOR INNER PANEL
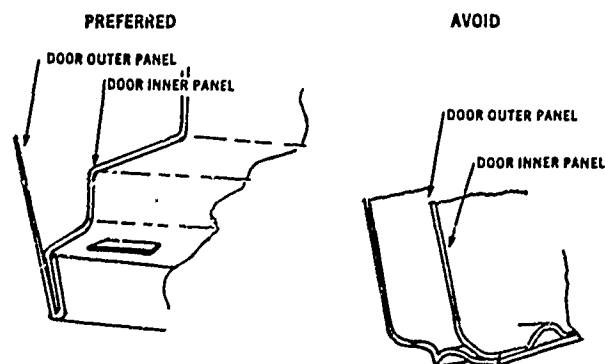
Fig. 33. SAE - RECOMMENDED CLOSED - SECTION DOOR DESIGN

treatment inside and out. Modern cathodic E-coat primers are highly recommended. If the design engineer is not at liberty to specify electrophoretic priming, supplemental corrosion protection may be had in the form of 'rustproofing' greases or waxes. These substances penetrate into seams and crevices, excluding moisture.

Another common corrosion site in commercial vehicles is front fenders and the rear quarter panel assembly. Inner and outer sheet metal panels should be designed for adequate drainage and coating material access. Drain holes should be provided at the lowest points of all sump areas. Horizontal seams formed by inner and outer panels should slope downward toward the drain openings to allow adequate drainage. Here too, application of E-coat primer is likewise very helpful. Supplementary rustproofing agents are helpful in this area, especially in vehicles not originally designed to resist corrosion.

Mud thrown by tires can form deposits on sheet metal, resulting in poultice corrosion. Accordingly, wheeled vehicles should have aprons or splash shields to prevent mud, stones, debris, and water from being thrown into sensitive areas.

Rocker Panels. This is the structure under the door of a vehicle. The designer should provide a drain hole arranged so that water and debris will not be driven into it during vehicle operations, yet large enough so it will not become clogged.

Hoods, rear hatches. Like any sheet metal structure, they are corrosion-prone if a sump is created by inner and outer panels joined so as to create a horizontal seam. They should therefore be designed with properly located holes for drainage and access by electrocoat primers. See Figures 34* and 35. Hoods should have drain holes on the lowest point forward of the radiator, so as not to drip water on engine components.
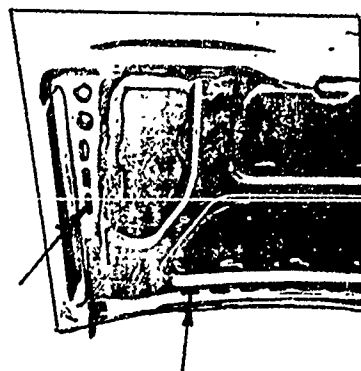
Fig. 34 TRUNK LID, ILLUSTRATING
HOLES FOR E-COAT PRIMER
ACCESS

*   Bryant, Arthur W., Designing Body Panels for Corrosion Prevention
    SAE paper 780916, in SAE Special Publication P-78.
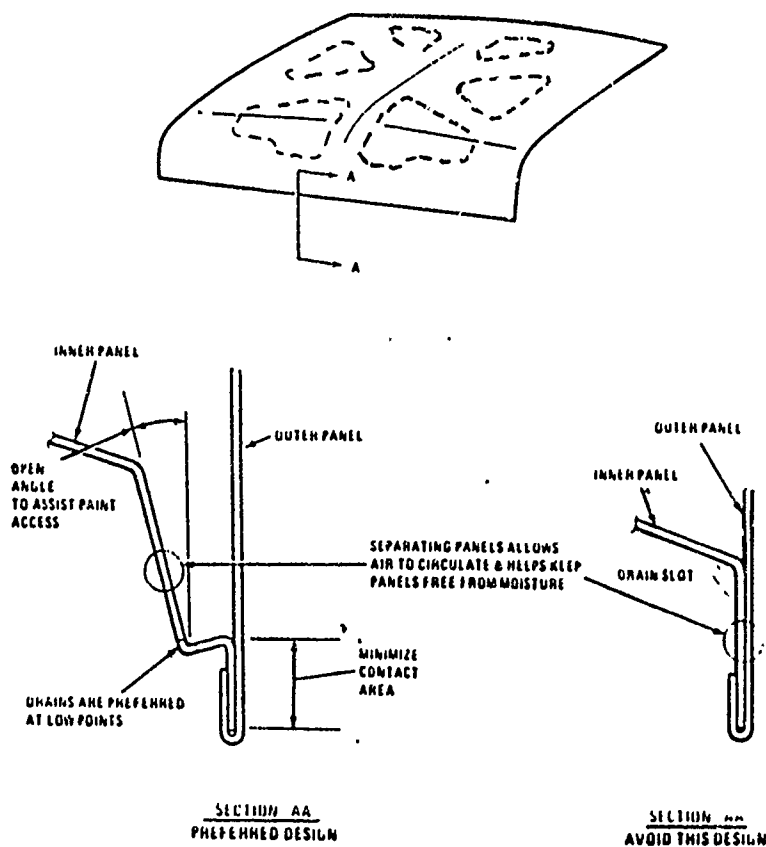
Fig. 35 DECK LID DESIGN as recommended by
Arthur W. Bryant in SAE Paper 780916,
_Designing Body Panels for Corrosion
Prevention._

Miscellaneous. The design features shown in Figures 36a and 36b
should be used with caution and avoided, respectively. In Figure 36a, the
caption 'avoid horizontal ledge' means just that. Such areas trap dirt
and debris. The configuration shown in Figure 36b is best avoided
altogether. If something like Figure 36b has to be used, the sump area
should be provided with drain holes, and adequately protected with
coatings.
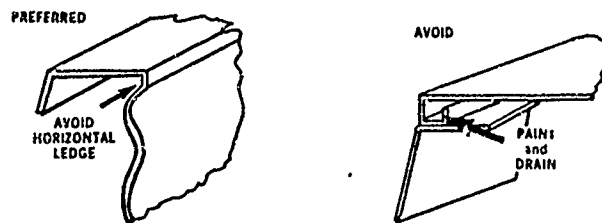
Fig. 36a. and 36b.   CORRECT & INCORRECT STRUCTURAL
DESIGN

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Stones, gravel, and other small missiles are a problem for vehicle
designers, especially off-road vehicles. Figure 37 illustrates the
principle of minimizing projected frontal area so as to minimize
stone/gravel damage to paint finishes on sheet metal.
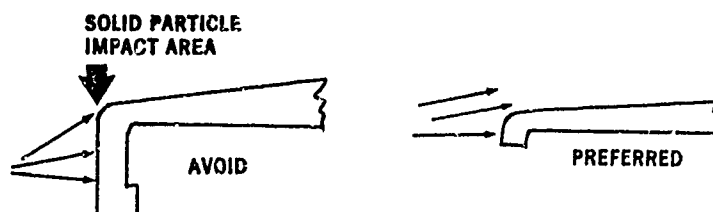
Fig. 37. DESIGN TO REDUCE MISSILE IMPACT DAMAGE TO COATINGS

The configuration shown in Figure 38 is a possible site for corrosion
initiation. Any joining of sheet metal where there are overlapping
(faying) surfaces is a potential crevice corrosion site. In addition,
paint coatings may 'bridge' the gap between the metal panels, resulting in
a site with little protection.
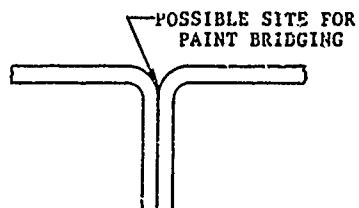
Fig. 38. INCORRECT SHEET METAL
JOINT DESIGN

Figure 39 illustrates what to avoid when designing exterior sheet
metal surfaces. Areas A,C,G, and H are susceptible to stone pecking.
Areas B,F, and I are sharp edges, which can be difficult to protect with
paint coatings. D is acceptable, if not too sharp. Area E, a sharp
corner (also, H) is liable to be 'bridged' by paints.
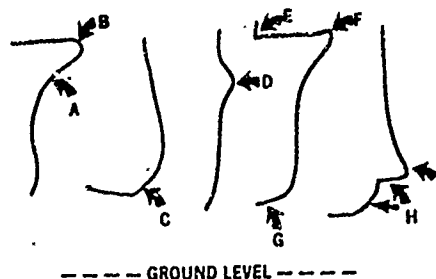
Fig. 39. SHEET METAL DESIGN DETAILS TO
AVOID

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4.8 Corrosion-Preventive Design Considerations for Armored Vehicles.

Armored combat vehicles, which may be propelled by rubber tires or tracklaying systems, are characterized by armor hulls, and sometimes also turrets. The hull serves two purposes: 1) protection from enemy ballistic, missile, and chemical threats and, 2) to enable the vehicle to swim. The armor hull of a main battle tank, personnel carrier, or fighting vehicle system presents these challenges to the corrosion engineer:

1) The corrosion engineer must see to it that drain cocks are located in the lowest portions of the hull, so the operator can drain accumulated moisture as part of daily checks and services.
2) The designer must locate equipment so it is clear of the bottom of the hull.
3) The inside, as well as the outside, of the hull must have an adequate protective coating system. The interior of the vehicle should be designed so that during overhauls, all areas of the inside surfaces (of both hull and turret) are accessible for inspection and maintenance of protective coatings.
4) The closed environment inside an armored vehicle becomes a humidity chamber when water gets in. Equipment in an armored vehicle must have adequate atmospheric corrosion protection.
5) Both tracklaying and rubber tire-based propulsion systems are efficient mud slingers. The underside of the hull must be designed so it is as simple and smooth as possible. Everything should be thoroughly "armored" against corrosion, with a good paint scheme. This includes components such as road wheel suspension arms.* Use rubber boots to protect components such as universal joints, and use seals to keep water and mud out of sensitive areas.

Where soldiers use high-pressure water hoses to clean armored vehicles, such areas must be designed to withstand this treatment.

During war or exercises in preparation for same, chemical decontaminating agents will be used to clean vehicles and equipment. These agents are known to degrade materials used in boots and seals. Answers to this problem do not come easily. The designer must seek, to the best of his ability and the extent of existing technology, to use coatings and elastomers resistant to agents and counter-agents used in chemical warfare.

4.9 Special Considerations--Fuel and Other Liquid Handling Systems.

Figure 40 illustrates the right and wrong ways to design tanks or other liquid reservoirs. Complete drainage (which occurs with the configuration

* Consider hot-dip galvanizing for such items, topped off with a good paint scheme.

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shown on the left) is necessary to prevent water or sediment from becoming
trapped, which may be the case with the configuration shown on the right.
Because water is a common fuel contaminant and because water settles to
the bottom of fuel reservoirs, the configuration on the right is the wrong
way to design a fuel tank.

RESERVOIR DRAIN

TRAPPED WATER

WELD &
DRESS

PREFERRED   AVOID
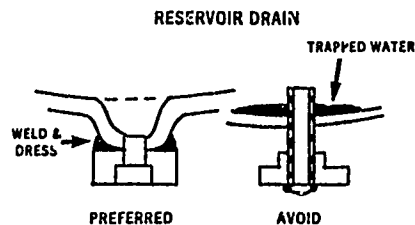
Fig. 40.   FUEL TANK DESIGN

Figure 41 illustrates how to design liquid passages in closed systems,
i.e., fuel, cooling, lubricant, or hydraulic systems.   The configuration
on the right provides a site for sediment to deposit.   This could lead to
corrosion problems, i.e., dezincification of copper-zinc alloy fittings.

LIQUID PASSAGES

ENTRAPMENT
AREA

PREFERRED   AVOID
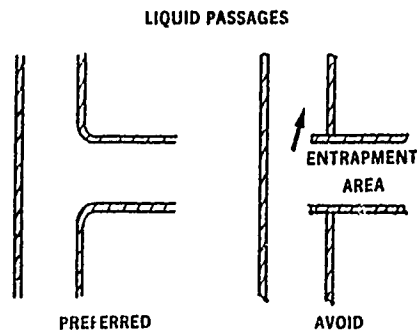
Fig. 41.   LIQUID HANDLING FLOW PATH
DESIGN

Impingement, or erosion-corrosion may occur in fluid handling systems
where high flow velocity encounters sharp bends.   Keep flow velocity down
by specifying adequate diameters for tubing, and avoid sharp bends by
specifying adequate radius for changes in flow direction.

Figure 42 illustrates proper design of a fuel tank to maximize
corrosion protection.   In the lefthand views, the design configurations do
not require solders, which contain fluxes that could be corrosive.   The
bottom righthand view illustrates a design mistake--a crevice area, where
deposits of sediment or entrapped moisture can set up a corrosion cell.

Compressed air systems must have drain cocks at the lowest points of
any sump areas.   Be aware, however, that soldiers under stress may not
have time to perform all the necessary maintenance procedures.   Some
components in compressed air or other fluid handling systems are
candidates for inherently corrosion-resisting materials, i.e., inhibited
brasses, stainless steels.

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PREFERRED   AVOID
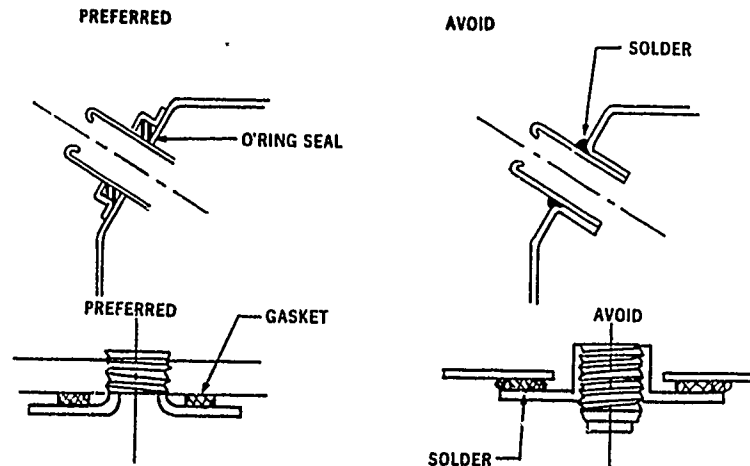
Fig. 42.   FUEL TANK DESIGN

4.10   Special Considerations for Electrical and Electronic Equipment.

Corrosion is a major cause of failure in electrical and electronic components in military weapon systems. According to the United States Air Force Materials Laboratory Electronic Failure Analysis Group at the Wright Aeronautical Laboratory, 20 percent of electronic component failures are corrosion related.* Corrosion of avionics systems is of special concern to the Navy, which operates aircraft in salt-laden atmospheres.

Designing electronic modules or 'black boxes' to reduce corrosion problems involves some of the same principles one would apply in designing other parts of a combat or tactical vehicle--or any piece of equipment.

The first step is to assume that unless a black box is hermetically sealed, moisture will invariably get inside. Once inside, moisture will invariably be present on uncoated metal surfaces, will pool in any sump area, is likely to be present at any bimetallic couple, and can propagate via wire bundles, or waveguides.

The designer must therefore reduce opportunities for moisture to corrode electrical and electronic components by eliminating sump areas where possible, or by providing drain holes. Printed circuit boards (PCB's) should be positioned vertically, never horizontally, so that moisture will run off the surface. PCB electrical connectors should be on a vertical edge of the board, never on the bottom edge. Printed circuit boards should have a clear conformal coating such as paraxylene.

Like any other system, an electronic assembly is vulnerable to galvanic corrosion whenever dissimilar metals are in contact. Use similar metals (i.e., as close together in the galvanic series as possible) for

*   Dobbs, B., G. Slenski, F.H. Meyer, Jr., Investigation of Corrosion Related Failures in Air Force Electronic Systems Failure Analysis Investigations. Paper presented at 1983 Tri-Service Corrosion Conference.

mating parts of electrical connectors. This is an important precaution, because the purpose of a connector is to conduct electricity, hence one cannot use electrical insulation between anode and cathode.

The designer should not only avoid highly dissimilar metals in contact,* but also avoid graphite contact with structural metals. Avoid graphite-containing lubricants, and be wary of joining an aluminum housing to graphite-reinforced composite structures.

Many corrosion failures involving electrical/electronic modules are caused by moisture intrusion. If total hermetic sealing is not possible, use seals, O-rings, and gaskets on access doors and penetrations (i.e., control shafts) into the enclosure. The Navy recommends 'shoe-box type' lids on the top of electronic modules for maintenance access. Otherwise, place access doors on the side of a box.

Cable connectors should be on the sides of a box, rather than on the top or bottom. The back of a connector, where a wire bundle enters, should be sealed with a suitable sealant such as non-acetic silicone RTV (more on this topic below). Use polysulfide sealants around the edges of screws on horizontal surfaces to prevent moisture from infiltrating the crevice.

A problem with closed boxes is accumulation of corrosive vapors. Polyvinyl chloride has been known to decompose, and the decomposition products include hydrogen chloride (hydrochloric acid when dissolved in water). Accordingly, the design engineer should avoid PVC insulation. Use non-PVC insulated wire meeting the requirements of MIL-STD-1568.

Corrosive vapors also arise from some RTV (room temperature vulcanizing) silicone sealing compounds. The type of RTV compound to avoid is that which contains acetic acid. Avoid using any silicone RTV compound with a vinegar-like odor.

Oil-containing paints, whether oleo-resinous or alkyd, give off corrosive vapors while drying. Avoid using such paints for the inside surfaces of electronic equipment housings,** unless thoroughly vented for at least two weeks after application of the paint. For electronics boxes not exposed to direct sunlight, epoxy primers and topcoats are satisfactory. Polyurethane (i.e., MIL-C-83286, MIL-C-46168) is a very satisfactory topcoat material. For best corrosion protection, drill all necessary holes, then pretreat, prime, and topcoat before installing anything in the box.

Specify gaskets made from non-hygroscopic materials, selected for resistance to heat, ozone, lubricants, hydraulic fluids, and moisture. The material should be of such a nature that when it does degrade, it will not form corrosive vapors.

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* MICOM policy is to avoid galvanic couples over 100 mV potential difference (Cobb, B.J., New Systems with CPC Flavor, presented at ADPA Corrosion Conference held on 29-30 April 1986.

** Or, for that matter, any closed container used for shipment and storage of corrosion-prone items.

While the designer should take precautions to prevent moisture intrusion, they are <u>not</u> a substitute for adequate drainage. Electronic equipment housings should have drain holes to allow moisture to get out. Arrange internal components so as to eliminate sump areas. Drain holes should be located at the lowest part of the box, and should bo large enough to allow moisture and debris. to drain freely. Incidently, the inside edge of the hole should be protected by the same coatings as other metal surfaces of the housing. The drain holes should be part of the housing design.

Dessicants should be used with caution. They may worsen corrosion problems by absorbing moisture at night when temperatures are low. As the sun rises and the inside of a vehicle heats up (particularly during operations), the dessicant may then give off moisture and turn an enclosure into a humidity chamber. Complex breathing apparatus are not suitable for tanks, personnel carriers, and so forth, but may be suitable for mobile communications posts or missile support trailers.

Some items of equipment use conductive or "EMI" (electromagnetic interference) gaskets on maintenance access doors, to prevent the passage of unwanted electromagnetic radiation into or out of an electronic system. Such gaskets contain conductive particles, to eliminate non-conductive gaps through which EMI could pass. These particles can cause galvanic corrosion of aluminum boxes. The solution is to apply water displacing corrosion preventive compound, MIL-C-81309 Type III, to the gasket before closing the door.

The same type of water displacing compound should be applied to the pins on the male portion of an electrical connector, before insertion into the socket. If the pins fit snugly into the socket, as they should, the coating will be wiped off the mating metal s' 'faces for good conductivity. The water displacing compound will, however, seal the mating surfaces against moisture intrusion.

To reduce water infiltration, reapply formed-in-place gaskets, and replace any deteriorated gaskets, when an item is opened for maintenance.

Gold plating on electrical contacts and connectors has advantages. It resists atmospheric corrosion and conducts electricity well. Use gold plating with caution: Gold should not be plated directly over copper. Plate copper with nickel first, then plate the nickel with gold.

Avoid silver-plated copper wire. Silver is cathodic to copper, and this results in a form of galvanic corrosion known as "red plague".

<u>Cables</u> should, if possible, lead upward toward a connector plugging into a module. This practice prevents moisture from draining into the connector. It is also good practice to provide for drainage at the low points of a cable, to prevent moisture from wicking into equipment. The designer should avoid tensile or side loadings on electrical connectors.

In armored vehicles, "black boxes", cables, and connectors should be located high enough above sump areas to avoid exposure to standing water. This is important because drain cocks must be closed during swimming or fording operations. If water builds up in the bilge, one does not want valuable electronic equipment to be exposed to it.

An abbreviated summary of do's and don'ts, taken from NAVMAT P-4855-2 (Design Guidelines for Prevention and Control of Avionic Corrosion), is listed here for the convenience of the reader:

DO:

o Design on the assumption that moisture will be present
o Seal all dissimilar metal couples
o Use conformal coatings (preferably, paraxylene) on printed circuit boards.
o Use adequate protective coating systems on aluminum and magnesium.
o Use a nickel sublayer under gold plating.
o Use solder with the lowest possible acid content.
o Use metals in low residual stress condition, and with high corrosion resistance heat treatment.
o Use fluorocarbon, or fluorosilicone materials for gaskets, O-rings, and seals.
o Seal conductive (EMI) gaskets against moisture infiltration.
o Locate drain holes at the lowest points of sump areas
o Mount parts and assemblies so they are clear of standing water levels.
o Use hermetically sealed components where possible
o Use sealants to prevent moisture/fluid intrusion
o Use 'shoebox'-type lids, if the top of a black box must be accessible for maintenance purposes.
o Mount printed circuit boards vertically.
o Mount PCB edge connectors and module connectors horizontally. The former should be on a vertical edge or on the back of a PCB.
o If using forced-air cooling, use a filter and dessicant arrangement to remove moisture and particulates.
o Use 'O' rings to seal shafts that penetrate an enclosure.

DON'T:

o Use dissimilar metals in contact, if it can be avoided
o Use an RTV sealant that employs acetic acid as a curing agent.
o Place graphite (in lubricants or in fiber-reinforced composites) in contact with structural metals.
o Plate gold directly over silver or copper
o Plate silver over copper
o Use organic materials that support fungi, emit corrosive vapors, absorb moisture, or are degraded by fluids encountered in the operating environment.
o Use rubber susceptible to ozone
o Locate edge connectors on the bottom of a printed circuit board.
o Use direct air cooling on electronic components.
o Permit undrained sump areas.
o Use nickel-plated connectors (Do use nickel/chromium, or cadmium)

Automotive Components. __Headlamps__ are vulnerable to moisture entry. The
Society of Automotive Engineers recommends using a mastic-type sealant and
a rubber boot (See Figure 43) to prevent moisture intrusion.

Figure 44 shows how an electrical connector can be designed to
minimize infiltration of corrosives into the metal-to-metal contact
areas. Because electrical conductivity is the connector's purpose, the
designer cannot protect the metal with non-conductive coatings.

RUBBER BOOT AT REAR OF SOCKET

APPLY MASTIC SEALER

SEALING ON LAMPS TO PREVENT CORROSION
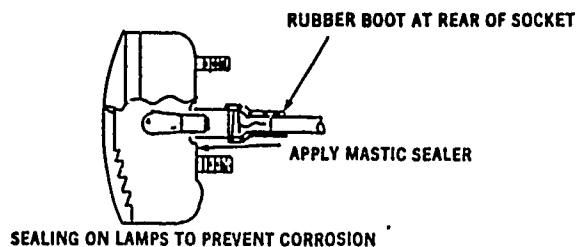
Fig. 43.   HEADLIGHT DESIGN

ELECTRICAL CONNECTOR
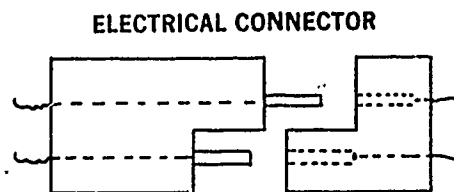
Fig. 44

Chapter 5
Protective Coatings--Basics

In tactical and combat vehicle design, the operating environment cannot be changed. The vehicle has to be designed for its environment, not vice-versa. Also, it is frequently not economical to utilize materials whose inherent corrosion resistance is adequate, as these materials may be too costly. Corrosion can be reduced by applying good design principles. However, to achieve maximum life and minimum corrosion-related maintenance costs during the expected lifetime, the design engineer has to know how to specify corrosion-protective coatings and treatments.

Coatings and treatments for metals can be grouped into three categories:

1) <u>Metallic</u>, (see Chapter 6) i.e., one metal or alloy applied to the surface of another metal. Metal coatings can be applied by electrolytic deposition (electroplating), immersion in a bath of molten metal, metallic bonding (cladding), chemical deposition, or vapor deposition. Zinc on steel (galvanizing) is the most important example of metallic coatings for design engineers dealing with motor vehicle body corrosion. Chromium, nickel, terne (lead-tin alloy) and cadmium are commonly plated onto steel for protection against wear or corrosion. Metallic coatings are also used for decorative purposes.

2) <u>Conversion coatings</u>. Processes such as anodizing (electrolytic oxidation), chromate treatments, and phosphate treatments fall into this category. Conversion coatings are actually controlled corrosion in that the metal reacts with process chemicals to form a layer on the surface. Phosphate coatings are often applied to metal surfaces to improve the adhesion of subsequently applied organic coatings.

3) <u>Organic coatings</u>. This classification applies to all paints, lacquers, enamels, varnishes, primers, plus temporary and semi-permanent corrosion-inhibiting greases, waxes, and oils.

Chapter 6
Protective Coatings--Metallic

6.1 General

6.1.1 Electroplating.

Electroplating of steel with nickel, chromium, or combined layers of these metals is used for decorative purposes, and for protection against wear or corrosion. Nickel and chromium are not good choices for protecting structural steel or sheet metalwork, because 1) These metals are costly and 2) they do not offer protection at pores and discontinuities. (Zinc coatings do offer this protection.) Nickel/chromium electroplating offers an attractive finish as well as corrosion protection for automotive bumpers, door handles, and trim items.

Fasteners are plated with tin, zinc, or cadmium to reduce their own corrosion, and to reduce galvanic corrosion of other metals, notably aluminum and magnesium alloys. One problem that arises when high-strength steel parts are electroplated is hydrogen-induced embrittlement. Because of this phenomenon, non-electrolytic means of plating are advantageous. Such methods include 'peen' plating, electroplating of aluminum onto another metal using non-aqueous solutions, and coatings such as SermaGuard.*

Parts of electrical and electronic apparatus are often plated with zinc, tin cadmium, or noble metals to reduce corrosion or enhance solderability. (Note: Cadmium must be employed and handled with great caution because of its extreme toxicity.)

6.1.2 Cladding (also known as roll-bonding).

Storage tanks and pressure vessels in many cases have to be constructed with heavy steel sections to provide the necessary strength. Also, when handling various chemicals, the structural material may need to resist corrosion both to maintain structural integrity and to avoid contaminating the chemicals with corrosion product. Fabricating a thick-walled vessel out of a corrosion-resisting alloy such as type 316 stainless steel may be possible, but such a practice would be wasteful when corrosion resistance is needed only at the inner surface.

A corrosion-resisting but costly metal or alloy can be clad by roll-bonding (or explosive bonding) onto a less expensive substrate alloy. The latter provides the required structural strength while the former provides the necessary degree of corrosion resistance in the operating environment.

One automotive application of cladding is aluminum alloy 5052 clad with AISI type 301 stainless steel, used for the bumpers on fire-fighting vehicles manufactured by American LaFrance. The S.S.-clad aluminum alloy bumper is just as attractive, costs 20% less, and weighs 48% less than the S.S. bumper it replaces.

*   Trademark of SermaTech International, Inc.

A common application of cladding is unalloyed or selected low-allc aluminum on high-strength aluminum alloys. High-strength Al alloys dc ... resist corrosion as well as unalloyed aluminum, hence the former are offered in sheet, tube, or wire form as 'Alclad', i.e., clad with a corrosion-protective aluminum layer.

6.1.3 Hot-dip coatings. Aluminum and zinc coatings can be applied to steel substrates by dipping an article in molten aluminum or zinc. Sheet steel in coil form is hot-dip galvanized by running it through molten zinc on a continuous production line. Aluminum (or Al alloyed with approximately 8 percent silicon) coatings are applied to steel to protect the latter from atmospheric corrosion, attack by salt spray, and high-temperature oxidation that are the bane of steels used in exhaust systems. Hot dip aluminizing can protect automotive frame members from corrosion.

6.1.4 Miscellaneous Methods of Applying Metallic Coatings. It is possible to apply metals such as gold, zinc, chromium, and aluminum by cathode sputtering, mechanical plating, vacuum evaporation, chemical reduction (i.e., 'electroless' nickel), laser surface alloying, and metal spraying. All of these methods have a place in military weapon systems.

Consider the problem of fasteners and small components. They may not be amenable to hot dipping because of difficulties in obtaining uniform coating thickness, parts sticking together, or interference with threads. Electroplating can cause hydrogen embrittlement of high-strength steels. Processes such as mechanical plating, vacuum evaporation, and cathode sputtering therefore offer valuable alternatives to the design engineer.

Mechanical or 'peen' plating is a process in which parts to be plated are placed in a barrel along with glass beads, a liquid media, and fine particles of the plating metal (or metals, or alloy). The glass beads peen the particles against the substrate, forming a bond. Zinc, tin, cadmium, or combinations thereof, can be applied to small parts by this process.

Vacuum evaporation and cathode sputtering are useful for applying thin layers of a coating material, such as aluminum or gold, to an item in a vacuum or low-pressure chamber. These techniques are useful for small items such as electrical/electronic components.

Laser surface alloying may find applications in military vehicle systems design. This technique uses a laser beam to heat the surface of a metal substrate, along with powders of the cladding metals. The powders are melted into the surface so as to form an alloyed surface layer.

Metal spraying is a process whereby a metal or alloy is melted by an electric arc or oxygen-fuel gas flame, atomized by a blast of air, and propelled toward the surface to be coated (see Figure 45*). Upon impact, the molten particles coalesce, solidify, and form the coating layer. The

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* From 1983 Tri Service Corrosion Conference (Shaw, Barbara, and Richard Parks, Thermal Spray Aluminum for Corrosion Control.

coating metal may be fed into the spraying apparatus as powder, wire, or rod, but if the coating metal can be drawn into wire, that would be the most convenient form to use.

HOW THERMAL SPRAY COATINGS ARE FORMED

FEEDSTOCK
(SOLID OR
POWDER)   HEAT SOURCE
(ELECTRIC OR
GAS)   MOLTEN
PARTICLE
ACCELERATION   SUBSTRATE
IMPACT   COATING
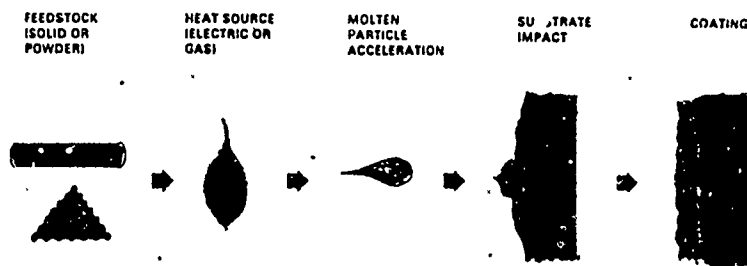
Fig. 45. SCHEMATIC REPRESENTATION OF THERMAL SPRAY COATING PROCESS

A typical wire spraying apparatus resembles a large pistol (see Figure 46*) and contains a spool for the feed wire, and provisions for continuously feeding the wire into a hot zone created by oxygen-fuel gas combustion. A compressed air source is then required for subsequent atomization and spraying of the molten feed metal. (see Figure 47*).

Wire sprayed aluminum (WSA) is used to protect corrosion-prone parts and equipment on U.S. Navy ships.** Aluminum, zinc, or combinations thereof, applied by wire-spraying, may be a good coating technique for combat vehicles. The atmosphere inside an armored vehicle hull tends to be corrosive because of humidity buildup. Hulls, turrets, and various items within the armor envelope are good candidates for protection by metal spraying.

One can apply virtually any coating material, even high-melting-point ceramics, by plasma spraying. The coating material is fed as a powder into a high temperature zone generated by electrical discharge. The molten particles of ceramic, or refractory metal, are then propelled toward the surface to be coated, as with metal spraying.

6.2 Zinc, Galvanizing, and Precoated Steel--The Leading Edge in the War on Automotive Corrosion.

*   Burns, R.M. and W.W. Bradley, Protective Coatings for Metals, 3rd ed., Reinhold Publishing Cc., New York, 1967.
**   National Materials Advisory Board, Metallized Coatings for Corrosion Control of Naval Ship Structures and Components. National Academy Press, Washington, D.C., 1983.
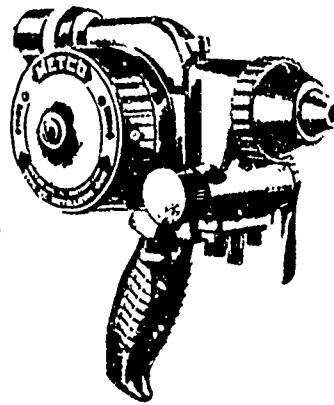
Fig. 46. A TYPICAL WIRE-SPRAY
METALLIZING GUN
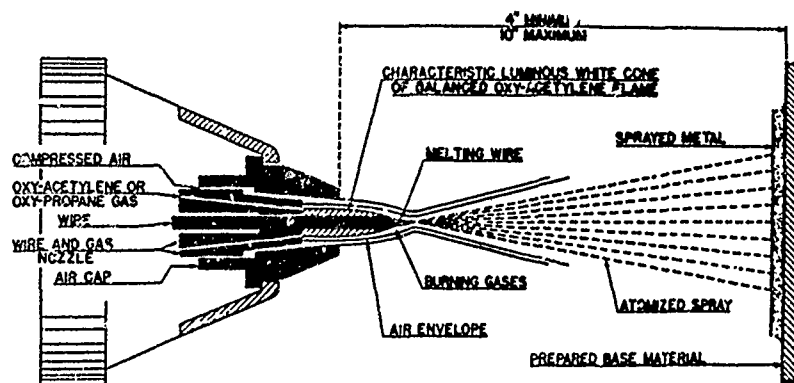
Fig. 47. CROSS-SECTIONAL VIEW OF WIRE SPRAYING
APPARATUS

6.2.1 **Advantages of Zinc Coatings.** Zinc is the most common metal for protecting ferrous metals against corrosion in a variety of vehicular and stationary applications. The reasons for the widespread use of zinc include but are not necessarily limited to the following:

1) Zinc, unlike nickel or chromium, is not a scarce or expensive metal.

2) Zinc is reasonably resistant to corrosion in many environments, due to the adherent and insoluble nature of its corrosion products in aqueous media.

3) Zinc tends to be anodic to ferrous metals. If discontinuities occur in a zinc coating, an electrochemical cell forms, with the steel substrate acting as the cathode. The zinc then corrodes sacrificially, offering protection to ferrous metals exposed by the discontinuity.

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4) The melting point of zinc is high enough to render it suitable as a coating material for a number of applications, yet low enough for it to be applied by hot dipping.

5) Zinc coatings can be applied by hot dipping, electrolytic deposition (electrogalvanizing), metal spraying, or in the form of fine particles suspended in a film-forming carrier (zinc-rich primer).

6) While zinc fumes are hazardous and while it is not advisable to ingest compounds of the metal, zinc is not a terribly toxic substance. It is, in fact, a necessary mineral in our bodies (but not in excessive quantities!). Zinc is far less dangerous than cadmium, which is also used as a protective coating on ferrous metals.

6.2.2 Galvanized steel sheets. The most common anticorrosion application of zinc in automotive engineering is the familiar 'galvanizing' applied to sheet steel prior to shipment to stamping plants, where it is formed into body panels. Engineers designing military vehicle systems have a variety of commercially available zinc-coated sheet steels to choose from. These products include:

o Hot-dip galvanized steel, with the zinc coating applied to one or both sides.

o Steel strip with electrodeposited zinc applied to one side only, or with a heavy zinc coating on one side and a thin coating on the other side.

o Steels with a zinc-iron alloy layer.

In addition to steel strip with metallic zinc coatings, a major product innovation is a precoating system marketed under the Zincrometal trade name. This process coats steel strip with a zinc-based primer system. However, Zincrometal is being replaced by better corrosion resistant coatings, such as two-side galvanizing combined with cathodic electrodeposited primers.

Galvanized steel can be obtained with various coating weights and with a variety of base materials. If formability is not required, the designer may specify commercial quality (CQ) steel. For applications where forming qualities are important, drawing quality (DQ), drawing quality-special killed (DQSK), and DQSK steels with low carbon contents, or with carbon stabilizers (niobium, titanium) are available. The latest steelmaking technology, combined with proper metallurgy and heat treatment, makes it possible to produce deep drawing quality-special killed (DDQSK) galvanized steels to meet the demands of difficult forming operations.

At one time, galvanized sheet steel was specified according to the ASTM A525 coating weight designation system, where G90 (the typical commercial coating weight), for example, meant a total of 0.90 ounces of zinc per square foot, both sides combined (0.45 ounces of zinc per square foot on each side). Products with zinc-iron alloy surface coating were designated by A rather than G, thus A60 is zinc-iron alloy coated sheet with 0.60 ounces per square foot, both sides combined.

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Presently, galvanized sheet steel products are specified with metric units. A designation of 130/130 means 130 grams of zinc per square meter of surface on each side, while 100/25 is a differentially coated product with 100 grams of zinc per square meter on one side and 25 gm/sq meter on the other side.

6.2.3 <u>Painting, forming, and welding galvanized steels.</u> Galvanized steels were used in the 1960's for rocker panels of motor vehicles, which were prone to severe corrosion due to increased use of road salt during the 1950's. As utilization of galvanized steel increased, manufacturers encountered the following problems:

1) Zinc coatings applied by hot-dipping do not lend themselves to attractive paint finishes. The 'spangle' associated with galvanized surfaces tends to be visible through paint coatings. In addition, paint coatings do not adhere well to galvanized surfaces unless special precautions are taken.

2) Electrical resistance (spot) welding is widely used to join sheet metal surfaces in assembling automotive bodies. This is a process whereby a very high electric current at low voltage is applied to localized areas of faying surfaces of sheet metal being welded. The high temperature produced where the electrodes press against the metal causes localized melting and coalescence between the adjoining metal surfaces. This process works well with uncoated steels, but galvanized steels introduce difficulties. The presence of zinc on the sides opposite the faying surfaces causes contamination of spot welding electrodes. These electrodes are made from copper, which alloys with zinc to form a brass. This alloy has a higher electrical resistance than copper, hence the electrode face temperature increases. Electrode tip life is therefore shortened.

In addition to electrode contamination, another problem arises due to zinc on the faying surfaces. The zinc coating lowers contact resistance; and furthermore forms a ring of molten zinc around the weld which shunts current away from the weld region. Hence increased amperage is required to generate the required heat.

Due to the aforementioned difficulties, it is necessary to use increased amperage, higher contact pressure, and longer weld time when spot-welding galvanized steel. The electrode tips will have to be 'dressed' more frequently. When spot-welding bare steel, electrode tips require dressing after approximately 10,000 welds. When spot-welding galvanized steel, the electrodes will have to be dressed after 2000 to 2500 welds.

3) When sheet steel is run through molten zinc, the high temperature (approximately 900F or 482C) affects the properties of the substrate. Accordingly, galvanized steels have tended to be less formable than ungalvanized cold-rolled steels.

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6.2.4 Solutions to Galvanized Steel Problems. Automobile manufacturers have adopted various strategies to get around these problems. These include:

1) One-side galvanizing. Steel galvanized on one side has been used for external body panels. The galvanized surface faces inward and offers resistance to 'inside out' corrosion. Assembly plants can paint the outer surface with the usual organic coating systems. A significant disadvantage of one-side galvanized steel is the possibility of corrosion on the ungalvanized side if a discontinuity occurs in the paint coating applied to that side.

2) Zinc-iron alloy coatings. Steel producers have developed sheet steels with a paintable zinc-iron alloy layer on one or both sides. This is accomplished by annealing a conventional galvanized steel, causing the zinc to diffuse into, and alloy with, the steel substrate. Zn-Fe coated steel can also be produced by wiping the free zinc off a regular galvanized steel as it emerges from the galvanizing bath.*

Steels lightly coated with zinc-iron layers are amenable to attractive paint finishes. However, there is a sacrifice in corrosion resistance. One automotive manufacturer has made extensive use of '1 1/2 side' galvanized steel, whereby one side is coated with free zinc, while the other side has a light Zn-Fe alloy layer. The galvanized side faces inward for inside-out corrosion protection, while the Zn-Fe coated surface is painted. The Zn-Fe layer protects against cosmetic corrosion if the paint is damaged.

3) Electrogalvanizing offers the advantages of accurate coating weight control, smooth appearance (no spangles), improved paintability, and improved formability. The lattermost advantage is because the process occurs at temperatures no higher than 140F (60C), which is too low to affect base metal properties.

Generally, electrogalvanized steels have thinner zinc layers than hot dip galvanized steel. A typical hot dip galvanized steel, G90, has 275 grams of zinc per square meter (137 grams on each side), while a typical Automotive industry specification for electrogalvanized steel is 70 grams per square meter on one side, and 90 gm. per sq. m. on the other side. Lighter coatings have been specified for some applications.

Electrogalvanizing is a versatile process. Not only can coating weight on each side be tailored for a given application, but also, the process can apply alloy layers such as zinc-iron or zinc-nickel. One Japanese steel manufacturer has developed an electroplated sheet steel product with a lower layer of zinc-10% nickel and an outer layer of zinc-80% iron.

4) Improvements in hot-dip galvanizing. Steel manufacturers have developed innovative variations of traditional hot dip galvanizing. One manufacturer has developed a process whereby steel strip is run through

* All hot-dipped galvanized steels have a Zn-Fe alloy layer, topped off by a free zinc layer.

molten zinc in a surrounding environment of pure nitrogen.* As the steel
emerges from the bath, nitrogen jets accurately regulate coating weight
(see Figure 48*). By excluding oxygen and using these nitrogen jets, one
obtains a smooth coating, free of dross and ripples. Both one- and two-
side galvanized products can be made by this process.
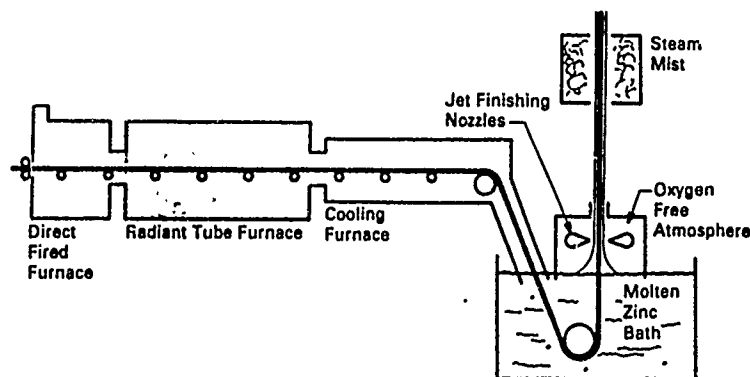
Fig. 48. PROCESS FOR APPLYING SMOOTH ZINC COATING ON SHEET STEEL

Processes have been devised for minimizing or eliminating the
'spangle' one normally sees on galvanized steels. For example, there is
the Heurtey process, whereby zinc dust is blown onto a freshly galvanized
surface, just before it solidifies. Another way to reduce spangles is to
maintain the lead content in the zinc bath at a very low level. Steam
mists are yet another post-bath treatment to minimize spangling.

As mentioned earlier, careful control of steel chemistry can reduce
formability problems.

6.2.5 Field Tests of Galvanized vs Non-Galvanized Steels. According to
tests performed by Dofasco, Inc., in 1981,** heavy hot-dip zinc coatings
provide superior corrosion protection vis-a-vis lighter, electrodeposited
zinc alloy coatings. These tests were conducted with specimens of
cold-rolled steel, steels coated by hot-dipping with zinc, zinc-aluminum,
and zinc-iron (galvannealed), and specimens electroplated with zinc and
zinc-nickel alloys. Some specimens were exposed with no coating except
the aforementioned metallic layers, while others combined the zinc-based
layers with phosphating and ELPO (cathodic electrophoretic) primer
protection. All specimens were mounted on the underside of commercial

* Obrzut, J.J., New Galvanized Product Assumes Dual Roles, in Iron
  Age, 6 April 1981, page 71.
** Neville, R.J. and K.M. De Sauza, Undervehicle Testing of Zinc and
  Zinc Alloy Coated Steels, J. of Materials for Energy Systems, Vol.
  8, #3.

trucks operating in the heavily corrosive salt belt area of southern Ontario. The generally superior performance of the hot-dipped specimens may be because they had thicker coatings than the electrogalvanized specimens. In any event, galvanized steels outperformed bare cold rolled steel. Tests by AM General show that, if steel is to be used at all, galvanized steel is the way to go.

Based on the Dofasco tests and improvements in hot-dip galvanizing, 2-side hot-dip, galvanized steel is the sheet steel of choice for military applications. For steel panels that are to be painted, some reduction in zinc coating thickness is justifiable on the painted side. This would reduce welding problems. However, even painted surfaces should have some zinc, to reduce corrosion in the vicinity of paint film discontinuities.

6.2.6 <u>Galvanizing of Material other than sheet steel</u>. Normally, when one thinks about galvanizing in connection with automotive engineering, he or she thinks of pregalvanized steel sheet. . However, steel components can be galvanized after fabrication. Hot-dip galvanizing shops can treat previously fabricated floorpans, suspension components, space frames, and chassis assemblies. Post-assembly galvanizing offers the advantage of using existing metal forming and assembly techniques without having to worry about damaging a previously applied coating. If a welded assembly is to be zinc-coated, the zinc should be applied afterward, because zinc fumes are not healthy to breathe. In some applications, steel components are aluminum,- rather than zinc-coated because of this problem.

Remember that any protective coating is useless if vaporized or otherwise destroyed during welding. Coatings in such areas must be applied, or re-applied, after welding if that happens.

6.2.7 <u>Zinc-Aluminum Combinations.</u> It has long been known that aluminum coatings are superior to zinc in offering <u>barrier</u> protection to steel, while zinc offers better sacrificial protection. Steel manufacturers have therefore sought to develop zinc-aluminum alloy coatings, so as to offer both the barrier protection of aluminum and the sacrificial protection offered by zinc at edges, scratches, or defects in the coating.

<u>Galvalume (R)</u>. Bethlehem Steel Corporation, after years of research and field testing, introduced a 44 % zinc, 55% aluminum, 1% silicon alloy coating for steel, in 1976. This coating is marketed as Galvalume, and is claimed to possess superior corrosion resistance vis-a-vis conventional galvanizing. Galvalume-coated steels reflect infrared radiation better than type 1 aluminum-coated steel,* and can be used at temperatures up to 600F (316C). This is not as high a temperature as that which exhaust systems can generate. Yet Galvalume-coated steels, given their corrosion resistance and thermal reflectivity, may be a good choice of material for some applications. Possible applications include engine or engine compartment components not subjected to temperatures such that stainless steels would be more suitable.

* Hart, R.G. and H.E. Townsend, <u>Galvalume Excels as Heat Reflector</u>, in Nov. 1983., <u>Metal Progress</u>, Page 29.

This main disadvantage of Galvalume-coated steels is limited
formability, between CQ (commercial quality) and DQ (drawing quality).

Galfan*. In 1979, the International Lead and Zinc Research
Organization (ILZRO) undertook research on the zinc-aluminum eutectic (see
Figure 49) that occurs at approximately 95% Zinc, 5% aluminum. The actual
work was performed by the Centre de Recherches Metallurgiques (CRM) in
Leige, Belgium. The purpose of this research was to find a way to protect
the market for zinc, which would be threatened if Galvalume became
popular. Also, ILZRO wanted a zinc-aluminum combination that would be
usable on existing hot-dip galvanizing lines.
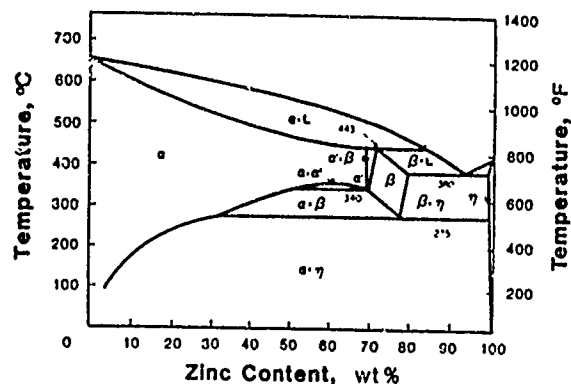
Fig. 49. PHASE DIAGRAM, ZINC-ALUMINUM SYSTEM

Inland Steel Corporation had previously carried out research on the
Zinc-5% aluminum eutectic, and their researchers were issued three United
States patents. Unfortunately, Inland Steel did not solve the technical
problems that arose in producing a high quality commercial sheet steel
coating. Researchers at CRM studied various additives, hoping to find an
alloying ingredient or combination which, when added in small quantities
to Zinc-5% aluminum, would result in a coating with the desired surface
smoothness, corrosion resistance, and formability.

Fortunately, nature sees fit that such a combination should exist.
Cerium and Lanthanum, present in small concentrations, achieves the
desired results. A naturally occurring mixture of cerium and lanthanum,
known as mischmetal, is satisfactory. Tramp elements (lead, cadmium, tin,
etc.) must be held to low levels (0.005% for lead and cadmium, 0.04% for
total tramp element content).

The resulting system--zinc, with about 5% aluminum and up to a tenth
of a percent mischmetal, was subjected to extensive testing to verify its
producibility and corrosion resistance. In 1981, full scale trials were
carried out by a consortium of steel producers at a facility in France.
It was at this time that the Zn-5% Al mischmetal, hot-dip applied coating
was given the name by which it is now known--Galvanizing Fantastique, or
Galfan. Galfan-coated sheet, wire, and tubing has been produced for
various engineering applications.

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* Guttman, H. and S. Belisle, Galfan--A New Coating for Automotive
Tubing., SAE paper 860274, in SAE special publication SP-649.

Galfan may best be described as a high performance galvanizing with a small amount of aluminum, rather than a zinc-aluminum combination. With a 95% zinc content, Galfan offers the unparalled sacrificial protection of zinc at edges and scratches. It has proven its mettle in actual field tests, such as the one conducted in Southern Ontario. Galfan coated specimens proved superior to others in corrosion resistance, whether painted or unpainted. It has proven to be at least a good as Galvalume under various tests. Figure 50* shows how Galfan compares to conventional galvanizing in salt spray tests.
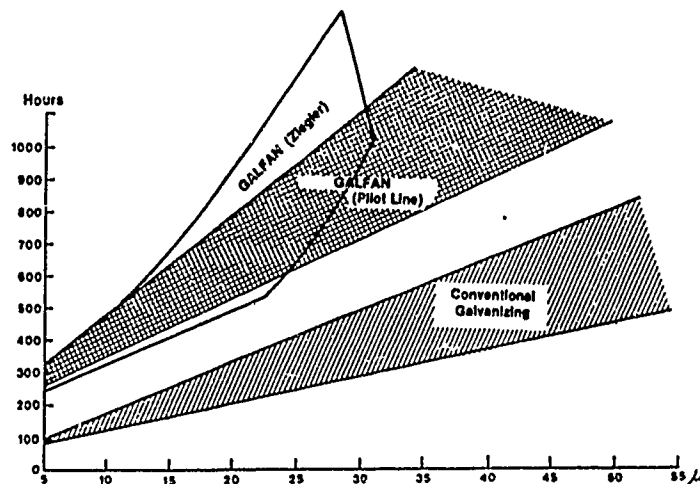
Fig. 50. CORROSION PREVENTION PERFORMANCE OF CONVENTIONAL GALVANIZING AND GALFAN

Galfan-coated sheet steel has proven superior to conventional galvanized steel in formability.** This makes Galfan suitable for applications involving deep drawing, such as oil filter cans and brake housings. Compared with conventional galvanizing, Galfan has little tendency to flake off during drawing or forming.

Galfan possesses the same problems as conventional hot-dip galvanizing with regard to spot-welding. Electrode tip life tends to be short. One automobile manufacturer has achieved 2000 welds between changing of machine settings, by using a harder copper or a specially contoured tip in the electrodes.**

Finally Galfan-coated steels can be phosphated and painted as readily as conventional galvanized steel. Specimens painted by E-coat primers (such as PPG epoxy) have demonstrated fine corrosion resistance when scribed and subjected to 1000 hours of salt spray.**

*   Herrschaft, D.C., et. al., Galfan: A New Zinc-Alloy Coated Steel for Automotive Body Use., SAE paper 830517, in SP-538.
**   Lynch, R.F., Galfan Coated Steel for Vehicle Applications Requiring Superior Formability and Corrosion Resistance. Paper presented at ADPA meeting, 29 Apr. 1986, Williamsburg, Virginia.

Final notes: All hot-dip galvanizing uses aluminum, in small amounts, to regulate the coating-substrate alloying that is essential to hot dip applied metallic coatings. Also, one steel manufacturer has improved the performance of zinc coatings by adding a small amount of magnesium to the molten zinc. In any event, improvements in galvanizing assure that zinc coatings will remain the cutting edge in the war on corrosion.

CHAPTER 7
CONVERSION COATINGS

Three types of conversion coatings are applied to metals for improving wear or corrosion resistance, or to improve the adhesion of subsequently applied organic coatings. These coatings are as follows:

1) Phosphate coatings, consisting of crystalline phosphates of iron, zinc, or manganese integrated into the metal surface.
2) Chromate coatings. Chemicals containing chromium in the trivalent and hexavalent states are commonly used as corrosion inhibitors. Zinc, cadmium, aluminum, and magnesium are amenable to chromate treatments.
3) Anodic oxide coatings (anodizing), applicable mainly to aluminum and magnesium.

7.1 <u>Phosphate Conversion Coatings</u>. Phosphate conversion coatings are applicable to steel, zinc (as on galvanized steel), aluminum, and cadmium. Their most important application is as preparation for organic coatings on steel. The crystalline nature of iron and zinc phosphates serves well as a transition layer between a metallic surface and an organic coating. Phosphate layers greatly improve paint adhesion and reduce the propagation of corrosion that otherwise rapidly occurs at scratches or other defects. Historically, phosphating was developed to improve corrosion protection by painting for iron and steel. Today, with galvanized steels and modern electrophoretic primers, phosphate treatments are still an essential part of product finishing technology.

Phosphate coatings also serve to retain lubricants and metalworking compounds. They have been widely used to aid forming operations, and to reduce wear when steel surfaces are in sliding contact with one another.

As mentioned before, phosphate coatings can be iron, zinc, or manganese. Iron phosphate is a satisfactory paint base for applications where corrosion protection is less important than appearance and cost. Zinc phosphate provides excellent preparation for organic coatings. It offers better corrosion protection than iron phosphate, and is applicable to cold-rolled steel, zinc-coated, or zinc-iron coated surfaces.

The only application for manganese phosphate is to provide wear resistance for bearing surfaces. Even here, the recent trend is heavy zinc, rather than manganese phosphate.

A phosphating solution is almost always aqueous*, and consists of the desired metal phosphate, and a sufficient concentration of phosphoric acid to keep the metal phosphate in solution. Commercial phosphating solutions

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* Phosphating solutions based on chlorinated organic solvents have been devised.

also have _accelerators_ to speed up the coating process. The accelerator is an oxidizing agent. Nitrites, nitrates, peroxides, and chlorates have been used. Nitrite accelerators yield the best results.

When a phosphate solution is applied to a ferrous surface, the iron reacts with the free phosphoric acid. This causes the Ph of the solution to rise in the vicinity of the surface. The metal phosphate is now less soluble as a result, and precipitates on the surface, forming the coating. The acid dissolves iron in anodic regions, which shift from time to time as the reaction progresses. The process is controlled corrosion; and like any corrosion reaction involving an acid, hydrogen forms on cathodic regions. The purpose of the accelerator is to depolarize the cathodes by combining with the hydrogen, thus speeding up the reaction.

The ratio of free phosphoric acid to total phosphate is critical to the phosphating process. Excess acid merely pickles the surface, while too little free acid results in sludge formation and poor results.

Phosphate coatings on steel formed by a zinc phosphate solution consist mainly of hopeite (hydrated zinc phosphate, $Zn_3(PO_4)_2-4H_2O$, with phosphophyllite (hydrated zinc-iron phosphate, $Zn_2Fe(PO_4)_2-4H_2O$ also present.

When phosphating zinc surfaces, such as galvanized steel, the solution likewise consists of free phosphoric acid and zinc phosphate in carefully balanced proportions. (It is possible to treat both steel and zinc with one solution). Again, the idea is to maintain a pH low enough to react with the surface, yet not so low (or, not so highly acidic) as to prevent a phosphate coating from forming.

Phosphating is a process requiring a high degree of quality control. There must be careful control of solution temperatures, concentration, and impurity levels. Surfaces to be treated must be absolutely free of grease, oils, drawing compounds, and dirt. Treatment sequences include multiple cleaning, rinsing, conditioning, phosphating, and post-phosphating rinsing. A typical zinc phosphating sequence for automobile bodies is:

1. A prewash, to remove heavy dirt, solder grind dust, etc.
2. Medium duty alkaline cleaner
3. Hot water rinse
4. Secondary cleaning
5. Conditioning rinse. This step applies a conditioning agent((i.e., sodium phosphate with a small concentration of titanium phosphate) to provide nucleation sites on the surface.
6. Treatment with the phosphating solution.
7. Cold water rinsing
8. Chromic acid rinse. Traditionally, chromic acid rinses have been applied after phosphating to improve paint bonding and corrosion resistance. Metal product finishers have sought in recent years to eliminate chromium ion-containing rinses, because of health and environmental considerations.
9. A final deionized water rinse. This step is mandatory when phosphating is performed prior to electrophoretic priming, as residual chemical contamination is harmful to that process.

The various cleaners and solutions can be applied by spray or immersion. Immersion is the preferred method for steps 2, 3, 5, 6, and 7, while spraying is preferred for the last step.

The goal is to form a coating with a uniform, dense, fine-grained crystal structure. Some phosphating solutions use calcium phosphate as a grain refining agent. Phosphate coatings applied for reasons other than subsequent organic coating do not require as fine a crystal structure.

A properly applied phosphate coating consists of an interlocking network of crystals integrated into the metal surface. This results in a network of capillaries which absorb and retain organic coatings. Also, the nature of the metal surface is altered. Bare metal surface tend to be alkaline, which inherently causes failure of many paint binders. The electrical conductivity of metals, combined with surface non-uniformities, causes electrochemical cells to form underneath paint coatings. This results in underfilm corrosion upon exposure to water or high humidity. Phosphate coatings are non-conductive, thus electrically as well as physically isolating the metal surface. These are the reasons why motor vehicle bodies and other ferrous items, are phosphated before painting. Zinc is by nature a poor paint base, so phosphating is as important as ever when painting galvanized bodies.

Phosphate layers also retain lubricants, and are therefore applied to aid forming operations and to improve wear resistance of metal parts in sliding contact with one another. Yet another application is to retain rust-preventive agents on ferrous items during storage or while under transport.

7.1.1 <u>Coating weights.</u> Iron phosphate layers range from 20 to 100 mg./ft.^{2} (0.22 to 1.1 gr./m^2). Light zinc phosphate coatings, applied as paint bases, range from 120 to 300 mg./ft.^{2} (1.29 to 3.24 mg./m.^{2}). Heavy zinc phosphate coatings, applied as bases for forming operations or to retain rust-preventive agents, range from 800 to 3000 mg./ft.^{2} (8.7 to 32.4 mg./m.^{2}). Manganese phosphate is applied to produce heavy coatings, up to 4000 mg./ft.^{2} (43.2 gr./m.^{2}).

7.1.2 <u>Phosphate coatings for aluminum.</u> Crystalline phosphate coatings are adaptable to aluminum surfaces. The solution must be properly formulated with zinc or manganese phosphate, an oxidizer such as the nitrate NO^{-3} ion, and a fluoride, to serve as an activating agent. A typical solution contains 0.7% zinc ion, 1% phosphate ion, 2% nitrate ion, and 1% fluoborate BF^{-4} ion. The fluorine-containing ion is necessary because aluminum's natural oxide layer would otherwise interfere with the film-forming process. The resulting film ranges from 100 to 500 milligrams per square foot (1.076 to 5.382 gr./m.^{2}), and can be a base for organic coatings. Phosphate layers on aluminum are also an aid to forming operations.

Crystalline phosphate conversic coatings for aluminum were developed during the 1940's. This process was later superceded by amorphous phosphates and chromates. The crystalline phosphate process offers the advantage of being usable on assemblies of steel and aluminum.

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7.2 **Chromate Conversion Coatings.** Chromates have been versatile workhorses in the metal finishing industry. Conversion coatings based on trivalent and hexavalent chromium have been widely used on zinc, cadmium, aluminum, magnesium, and other metals. At one time, phosphated steel surfaces were treated with a chromic acid rinse to augment corrosion protection. Chromate-containing pigments have long been used in anticorrosion primers. Non-chromium containing pigments and metal treatments are replacing chromates in some applications, because of health and environmental problems. Non-chromate conversion coatings have been used in the container industry. However, no completely satisfactory substitute for chromates as pretreatments for aluminum or magnesium, have been found.

Chromate conversion coatings serve as bases for organic coatings on aluminum and magnesium, just as phosphates do for ferrous and zinc surfaces.

All chromate treatment solutions contain hexavalent chromium ions. Other chemicals are needed to adjust the pH and accelerate the reactions. When chromating a metal surface, some of the base metal dissolves. This causes hexavalent chromium to be reduced to the trivalent state. The metal surface is converted to a superficial layer containing trivalent and hexavalent chromium. The metal finishing industry has developed a variety of solutions and processes using chromium compounds.

7.2 1 **Chromate treatments for aluminum.** Three chromate-type treatments for aluminum will be discussed here. They are 1) alkaline oxide, 2) chromium phosphate, and 3) chromium chromate.

Alkaline oxide coatings are typified by the modified Bauer-Vogel (MBV) process, which is applied to aluminum surfaces with a solution containing sodium carbonate, sodium chromate, plus additions such as silicates or fluorides. Sodium carbonate is an alkali-like salt, and serves as the active agent. The chromate regulates the reaction. The deposited film consists of aluminum oxide, with chromic oxide formed by reduction of the sodium chromate.

Alkaline oxide coatings are not commonly used nowadays, because anodic oxide coatings (anodizing) are superior when oxide coatings are wanted. Also, for non-electrolytic treatment of aluminum, chromium phosphate and chromium chromate are superior.

Chromium phosphate conversion coatings are applied to aluminum surfaces by using solutions containing phosphate, chromate, and fluoride with the pH on the acid side. The proportions of phosphate as H_3PO_4, fluoride, and chromium ion (as CrO_3) must be within the boundaries illustrated in Figure 51). The fluoride acts as an activator, breaking down the natural oxide layer, while the phosphoric acid provide the necessary acidity. Some of the aluminum dissolves at anodic sites, forming aluminum phosphate. At cathodic sites, hexavalent chromium acts as a depolarizer, and is reduced to trivalent chromium, which is incorporated into the film. This treatment produces a conversion coating consisting of chromium and aluminum phosphates, with a small quantity of fluoride. The coating is green in color due to the presence of reduced chromium.

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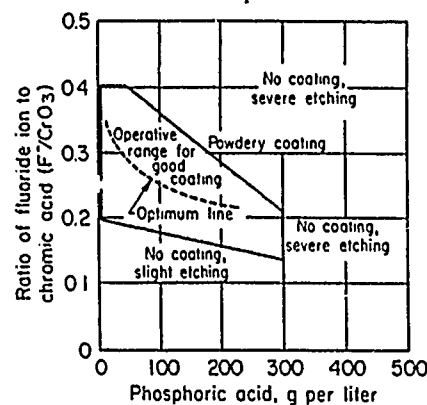
Fig. 51. OPERATING RANGE CHART FOR
CHROMATE-PHOSPHATE CONVERSION COATINGS
FOR ALUMINUM.

Another coating process applies a coating consisting of trivalent and hexavalent chromium, in the form of hydrated chromium chromate, Cr_2O_3-CrO_3-xH_2O. The solutions used to apply these coatings are proprietary; a typical formulation consists of sodium dichromate, potassium ferricyanide, sodium fluoride, and nitric acid. The first component provides hexavalent chromium. The nitric acid provides acidity, and the fluoride is the attacking agent, dissolving the oxide film. The ferricyanide acts as an accelerator.

Chromium chromate and chromium phosphate films are amorphous, as opposed to the crystalline structure characteristic of phosphate coatings on steel surfaces. Accordingly, organic coatings used on aluminum surfaces with these pretreatments must have good adhesive properties, because the conversion coating does not provide a network of crystals to mechanically hold such coatings. Properly applied chromate coatings will, however, retard underfilm corrosion and paint adhesion failure on aluminum surfaces.

Chromate conversion coatings offer some degree of corrosion protection by themselves. An interesting feature of these coatings is low electrical resistance, which makes them suitable for treating electrical and electronic components.

7.2.2 Chromate Coatings on Zinc. Chromate treatments applied to zinc surfaces, such as galvanized steel, inhibit the 'wet storage stain' characteristic of galvanized articles stored under wet or humid conditions. Chromate passivation is also applicable to cadmium-plated components. Items being packaged for storage or shipment can benefit from chromate passivation, because vapors from wood or paints can be corrosive to unprotected zinc or cadmium surfaces.

A typical chromate treatment for zinc uses sodium dichromate and sulfuric acid. The coating formed is primarily chromium chromate.

Finally, magnesium surfaces can be chromate-treated, either as a base for subsequent organic coatings or, in environments not too corrosive, as

a protective coating in itself. In civilian automotive applications, for example, a magnesium alternator frame may require no protective coatings other than a good chromate passivation treatment. In military applications, any magnesium components would have to protected by a good organic coating system.

7.3 <u>Anodic Oxide Coatings.</u> Anodizing is defined as any process which develops an oxide coating on a metal surface by making it the anode in an electrochemical cell. Aluminum and magnesium, and their alloys, are the most familiar metals regularly anodized. Aluminum alloys are anodized to improve corrosion resistance, for decorative purposes, or to protect the surface against abrasion. Magnesium alloys are anodized to improve corrosion resistance and to serve as a paint base.

Anodizing will be discussed further in the sections of this report dealing with aluminum alloys.

CHAPTER 8
ORGANIC COATINGS

The category of coatings labeled 'organic' includes paints, varnishes, lacquers, and enamels. One may also include temporary and semipermanent rust-preventive greases, oils, and waxes under the 'organic' classification.

The world of organic coatings has changed. Laws designed to protect our atmosphere are restricting what was formerly the unrestrained use of organic solvents. Accordingly, powder coatings and water-borne coatings are playing a more prominent role than formerly. One also hears a lot about high solids coatings employing little, or even no solvents. Electrophoretic (a.k.a. E-coat, ELPO) primers are now the standard method of applying primer coatings to motor vehicle bodies. Nonetheless, to understand organic coatings, the engineer must start by studying classical coating systems.

Classical paints, enamels, varnishes, and lacquers consist of three major components: film-former, pigment, and solvent. The film-former or binder may be a drying oil, or it may be a resin which is fluid only when dissolved in a solvent, or it may be a polymerizable material. Pigments are very finely divided materials for imparting color, inhibiting corrosion, or adding strength to a coating layer. The solvent, or thinner, lowers the viscosity to a desired level for easier application.

A complete coating system for a metal surface begins with cleaning to remove mill-scale, dirt, grease, and all other surface contamination. This is very important: It has been said that a mediocre paint applied to a well prepared surface is better than an excellent coating material applied to a poorly prepared surface. The quality of the base material is also important. Sheet steel with heavy surface contamination (i.e., carbon particles), can be difficult to clean and phosphate, and subsequently applied organic coatings will not adhere well.

The next step is a phosphate or other suitable conditioning treatment, to improve coating adhesion and retard the spread of corrosion beneath coatings. An alternative to phosphate treatments for large structures is to employ a 'wash primer', which is a brushed or sprayed-on phosphate treatment employing an organic binder and pigments.

After cleaning and phosphating (or otherwise conditioning) a metal surface, a primer coating is the initial organic coating layer. Subsequent coating layers following the primer include surfacers and topcoats. The surfacer, as its name implies, levels out unevenesses. The topcoat protects the underlying layers from the elements, and contains pigments which impart the desired color for decorative, or camouflage, purposes. (The primer contains the corrosion-inhibiting pigments).

8.1 Film-Forming Mechanisms and Materials. The classical film-former in house paints is a drying oil, such as linseed. The oil, along with pigment particles, is diluted with a solvent for ease of application. When the painter applies the paint to a surface, the solvent evaporates quickly. The drying oil combines with oxygen in the air and, in so doing,

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the molecules link up with one another to form a solid film. This film holds the pigment particles in place.

The mechanism drying oils use to form a solid film is known as oxidative polymerization. Oil-based paints using red lead as the pigment were widely used as primers for steel structures, before being supplanted by better materials. Today, drying oils are still used in paints, enamels, and varnishes,* but are modified by various processes. Resins (solid materials) can be mixed with oils to improve film properties.

Another way to apply an organic coating film is to use a resin which is fluid when dissolved in a suitable solvent, but which forms a solid film as soon as the solvent evaporates. These coatings are known as lacquers (or lacquer enamels, if pigmented). Film formation is solely by solvent evaporation, with no need for cross-linking or polymerization. This is known as lacquer drying.

Nitrocellulose lacquers were introduced in the 1920's. These consist of nitrocellulose dissolved in solvent, with pigment particles added to impart color. The resulting lacquer is applied by spraying. When the solvent evaporates, the nitrocellulose stays behind, on the surface, as a film.

The fast drying of nitrocellulose lacquers made possible the rapid finishing of automobile bodies on production lines, with attractive and durable finishes in colors other than black. Because nitrocellulose is brittle, plasticizers are added to impart flexibility to the film. Manufacturers have also used various resins, such as alkyds, acrylics, and natural resins to further improve film properties. The trend in lacquer formulation over the years has been toward lower viscosity nitrocellulose and increased proportions of other resins, resulting in lower solvent (and higher solids) content. This means lower material and applications costs.

Eventually, nitrocellulose lacquers were superceded by thermoplastic acrylic lacquers for automotive finishing. Thermosetting acrylics were later adopted as baking enamels.

So far, two mechanisms of paint drying have been discussed: oxidative polymerization and lacquer drying. A third drying mechanism consists of polymerization reactions between ingredients in a coating formulation without the aid of atmospheric oxygen. This is how epoxy and polyurethane resins 'cure' when ingredients of two-package formulations are mixed. Other synthetic resins that harden by polymerization include urea-formaldehyde, melamine-formaldehyde, and acrylics.

Modern finishes for buildings, consumer items, military equipment, and industrial applications are made from a variety of natural and synthetic materials. Coating manufacturers combine drying oils with other materials to make alkyds. The variety of resins available to coating manufacturers enables them to produce paints, varnishes, and enamels with a variety of properties. To fully describe all of the materials used in protective coatings would require a very voluminous report. Accordingly, only a

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* Paint is a general term for organic coatings using a pigment and binder. An enamel is a paint that forms a smooth surface finish. Varnish refers to a coating without pigment particles.

limited number of coating materials will be described here, to provide the engineer with a basic background in organic coatings for military equipment.

8.2   Alkyd Resin - Based Coatings.   Primers and topcoats based on alkyd resins are the classic military coatings.   They have served the Army for decades, until recent needs for chemical agent resistant coatings resulted in their replacement by more modern coating materials, notably, polyurethanes.

An alkyd (a̲l̲cohol + ac̲i̲d) is a polymer resin based on chemical reaction between polybasic acids and polyhydric alcohols.   The former are organic acids or acid anhydrides with two or more -COOH groups characteristic of organic acid molecules.   The latter are alcohols with two or more -OH groups.   One possible alkyd combination is phthalic anhydride, a bifunctional organic acid substance, and ethylene glycol, a bifunctional alcohol.   The functionality groups cause formation of a polymer (See Figure 52).
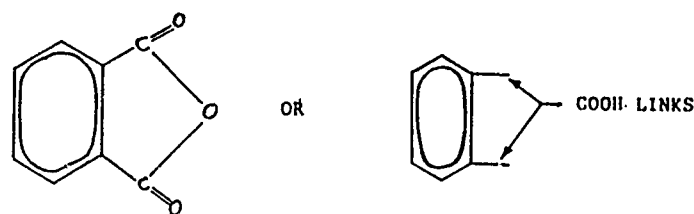
Fig. 52a   PHTHALIC ANHYDRIDE
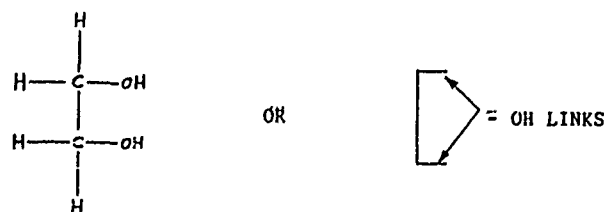
Fig. 52b.   ETHYLENE GLYCOL
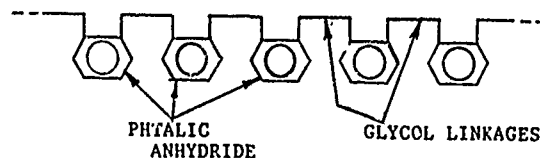
Fig. 52c.   A SIMPLE ALKYD, FORMED BY PHTHALIC ANHYDRIDE
AND ETHYLENE GLYCOL.

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Now, suppose one were to formulate an alkyd with phthalic anhydride as the polyfunctional acid but with glycerol as the polyfunctional alcohol. Glycerol has three -OH groups. Hence one of these groups can react with a monofunctional acid (i.e., an acid with only one -COOH group), leaving the remaining -OH groups free to react with the phthalic anhydride. Accordingly, fatty acids characteristic of drying oils can chemically combine with phthalic/glycerol alkyds to form a resin combining the favorable characteristics of glycerol phthalate and drying oil. Pure glycerol phthalate is brittle because of extensive cross-linking between the linear chains. Adding drying oil makes the film more flexible.

Drying oils are naturally occurring triglycerides of unsaturated fatty acids (see Figure 53). In classical linseed oil-based paint, multiple double bonds in the fatty acid chains (resulting from non-saturation) provide sites for the oxidative cross-linking described earlier. If a drying oil is mixed with glycerol in the right proportions and heated in a kettle, an interchange reaction (see Figure 54) occurs. The objective is to form glycerol molecules with one, or at most two, fatty acid chains, rather than three.

Fig. 53a GLYCEROL

or : $R \cdot COOH$
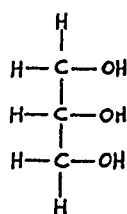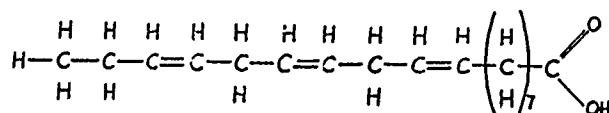
Fig. 53b. LINOLENIC ACIC, A TYPICAL DRYING OIL FATTY ACID
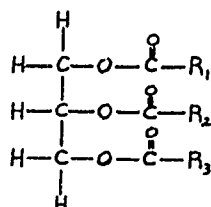
Fig. 53c. DRYING OIL MOLECULE. R_1, R_2, R_3
ARE FATTY ACID RADICALS SUCH AS Fig. 53b ABOVE.

77
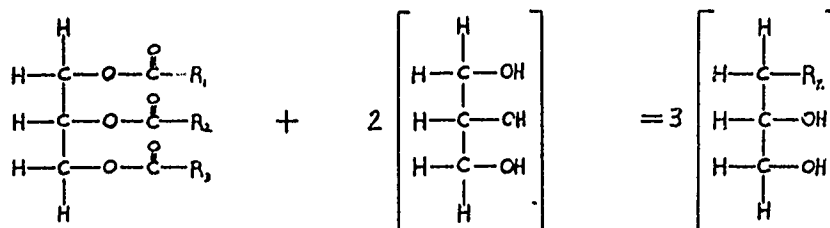
Fig. 54   FORMATION OF FATTY ACID MONOGLYCERIDE

The resulting fatty acid monoglyceride has two -OH groups that can form linear chains with bifunctional acids such as phthalic anhydride. If glycerol is reacted with drying oil to yield fatty acid monoglyceride and subsequently combined with phthalic anhydride, the result is an alkyd consisting of random couplings of glycerol, phthalic anhydride, and fatty acid (see Figure 55). This is the alkyd system used for years in military coatings.

GLYCEROL/PHTHALIC ANHYDRIDE/DRYING OIL ALKYD RESIN
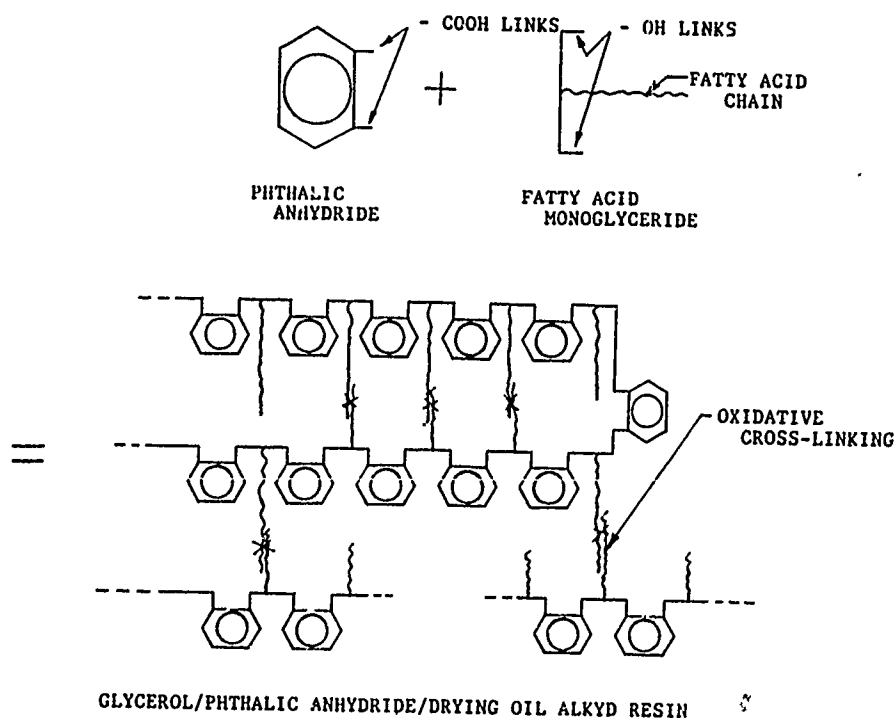
Fig. 55.

A ypical alkyd primer is based on standard TT-P-664. The film-former is an alkyd resin formed by esterification of glycerine, phthalic anhydride, and fatty acids obtained from linseed, soya, safflower, and sunflower oils. The specification calls for a minimum of 38 percent (by weight) phthalic anhydride, and 32 percent oil acids, expressed as percentage of vehicle solids.

The pigment is a mixture of zinc chromate, iron oxides, and siliceous extenders. The purpose of this pigment mixture is rust inhibition rather than any specific color requirement.

The solvent meets one of two specifications: Compositon G, for general use, consists of volatile aromatic solvents. Compositon L is for use in areas where air quality standards restrict solvent emissions into the atmosphere. Under the composition L standard, certain photo-chemically reactive solvents are restricted or eliminated. Both G and L standards forbid highly toxic solvents such as benzene and chlorinated hydrocarbons.

A typical alkyd topcoat enamel is specified under MIL-E-52798A (Enamel, Alkyd, Camouflage). The film former is a glycerol/phthalic anhydride/oil alkyd. The oil acids constitute 45 to 55 percent, by weight, of the resin solids. Phthalic anhydride occupies 30 percent of the resin weight.

The pigment must meet color and infrared spectral characteristics. The following colors are covered under the standard:

o	Light green	o	Earth yellow
o	Forest green	o	Earth red
o	Dark green	o	Desert sand
o	Olive drab	o	Black
o	Field drab		

All pigment formulations must meet requirements for chemical composition, visual-spectral, and infrared-spectral characteristics for camouflage purposes. A typical camouflage pigment mixture is forest green, with visual and infrared characteristics adjusted so as to duplicate the characteristics of naturally occurring chlorophyll, as in tree leaves and other vegetation.

A typical earlier paint system before CARC was mandated, applied to M60 series main battle tanks, consists of TT-C-490 phosphate treatment, TT-P-664C primer, and MIL-E-52798 enamel.

In recent years years, military surface coatings have been reformulated to eliminate lead- and chromate- containing pigments. For example, TT-P-664C has been replaced by MIL-P-52995, which calls for a corrosion inhibiting, lacquer-resistant, lead and chromate free primer. The pigment consists of iron oxide, zinc phosphate, a proprietary material, and siliceous extenders. The pigment must not have hexavalent chromium. The binder is a resin-modified, drying oil-phthalic alkyd resin.

Drying oil modified, glycerol phthalate alkyd resins have attained an important place in coating technology since their introduction in 1930, because their durability is much better than the oleoresinous materials they replaced. This is why alkyd primers and topcoats have been

standardized by the military for protective coating of vehicles and other items. The coatings chemist can obtain a range of properties by using different oils, and by varying the proportion of oil fatty acids in the alkyd formulation.* While glycerol is the most commonly employed polyfunctional alcohol, others have been used. Coatings chemist have also used acids other than phthalic anhydride.

Finally, alkyds can be modified with styrene, silicones, acrylics, and other materials. The main disadvantage of oil-containing alkyds is that they are vulnerable to attack by alkalies and other chemicals. Accordingly, coatings chemists have, over the years, sought more durable, and more chemical-resistant paint binders.

8.3 Epoxy resins. Epoxies are synthetic resins which harden by cross-linking. These resins have a number of applications, including surface coatings, adhesives, and fiber-reinforced composites. The most common epoxy resins are formed by the reaction of epichlorohydrin and bisphenol A, resulting in the molecular structure shown in Figure 56. The epoxide groups (from which the familiar term 'epoxy' is derived) at the ends of the molecule can react with a variety of curing agents. The epoxy molecule can also combine with other materials via the -OH groups.
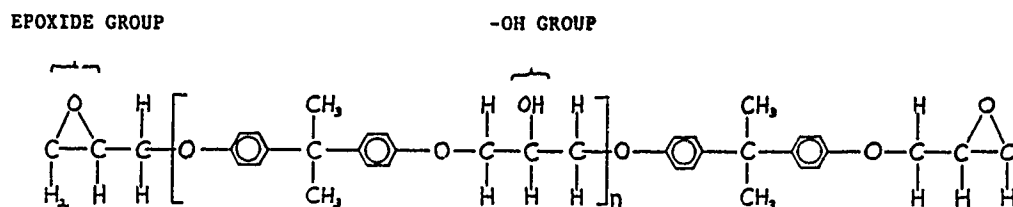
Fig. 56.   THE MOLECULAR STRUCTURE OF A COMMON EPOXY RESIN, FORMED BY POLYMERIZATION OF EPICHLOROCHYDRIN AND BISPHENOL A.

Epoxy-based film formers for surface coatings can be made by reacting the basic epoxy molecule with drying oil fatty acids, or by cross-linking epoxy with amines, amides, phenols, amino resins, or other materials whose molecular structures have reactive hydrogen. Commercial epoxy packages consist of a basic epoxy resin, typically epichlorohydrin/bisphenol A, plus a cross-linker. Some formulations use a catalylst to accelerate the reaction.

Curing agents such as amines react with epoxy so quickly that the two must be kept in separate containers, and mixed shortly before utilization

*   People in the coatings field use the term oil length to describe the proportion of oil acids in alkyd resins.

as a coating, adhesive, etc.* The maximum time an epoxy mixture can be allowed to sit, before excessive cross-linking renders it unfit for application, is called pot life.

In surface coatings for military applications, epoxy resins are mainly used as primers. A classical epoxy primer used by the Army is MIL-P-23377D, a two-component, epoxy-polyamide, chemical and solvent resistant primer coating, compatible with aliphatic polyurethane (CARC) topcoats. One component consists of epoxy resin, along with pigment and solvent. The other component consists of a polyamide resin, plus solvent. The user mixes the two components in equal proportions, by volume, to obtain a product meeting the specification. The mixture may be thinned with solvents meeting MIL-T-81772, for ease of application.

The pigment is primarily strontium chromate. Type I pigment is 52% of the above, with 10% titanium dioxide and up to 38% by weight siliceous extenders and antisettling agents. Type II pigment consists of 42% (minimum) strontium chromate, up to 32% extender, and up to 26% coloring pigments.

When applied to pretreated aluminum test panels, the primer must resist 5% salt spray for 1000 hours.

Two-component epoxy systems, once mixed, do not have infinite pot life. MIL-P-23377D requires, however, that when initially mixed and thinned to 20 seconds (viscosity, measured in accordance with a specified procedure), the primer shall have a viscosity of no more than 25 seconds when stored in a closed container for 8 hours at 23C (73F), or three days at 4.4C (40F).

Another epoxy primer, specification MIL-P-53022A, covers a corrosion-inhibiting, lead- and chromate-free primer, formulated so as to meet air pollution requirements regarding solvent emissions. The film former is bisphenol A-type epoxy, cross-linked with an aliphatic amine-epoxy adduct. Like all such systems, the resins and cross-linking compound are stored separately and mixed prior to application.

The pigment cannot contain the familiar chromate compounds traditionally used for corrosion inhibition. It consists o titanium dioxide (50% by weight), zinc phosphate (9 to 11%), and siliceous extenders. The pigment must test negative for hexavalent chromium. About 1% of the pigment is a proprietary substance.

MIL-P-53030 is a specification for a water-reducible, corrosion inhibiting, epoxy primer. This primer contains no more than 340 grams per liter (2.8 Lb. per gallon) of volatile organic compounds.

In industry, epoxies offer the advantages of good adhesion, and resistance to abrasion and chemical attack. Because epoxy resins harden by cross-linking, they can be applied at low molecular weights, thus permitting reduction, even elimination, of solvents. Epoxies are also applicable by electrophoretic processes. Combinations of epoxy resin and coal tar have been used in heavy-duty corrosion protection applications.

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* Some epoxy systems react so slowly at room temperatures that they can be issued in a single package. The coating must then be heated to activate cross-linking.

Epoxy coatings are not employed as external topcoats, as they do not offer the durability characteristics of alternative topcoats under sunlight (UV radiation). They make good primers for ferrous and non-ferrous metals, and are the standard primer for CARC systems using polyurethane topcoats.

8.4 Polyurethane resins. Polyurethanes are based on chemicals such as toluene di-isocyanate, which contain two or more -NCO groups. Like the epoxide functionality, -NCO will link up with virtually anything that has reactive hydrogen. Polyurethane resins have applications in foams, elastomers, adhesives, and coatings. With regard to coatings, a number of systems have been devised. Some are one package formulations, while others have to be issued in two containers. Figure 57 illustrates some polyurethane systems.

By strict definition, a polyurethane resin is a polymer formed by reaction between the isocyanate (-NCO) and hydroxyl (-OH) groups in polyfunctional isocyanates and polyhydroxyl (or polyol) compounds. The polyurethane coatings we use today are based on technology developed in Germany during the 1930's and -40's. This technology owes much to the pioneering work of Dr. Otto Bayer, who discovered the diisocyanate polymerization reaction in 1937. By the 1950's, the Bayer chemical firm had standardized polyurethane products on the market. The 'Desmodurs' were polyisocyanate compounds, while 'Desmophens were polyesters with multiple -OH groups. A polyurethane forms when a Desmophen is mixed with a Desmodur.

In 1954, Bayer in Germany and Monsanto in the United States established the Mobay Chemical Corporation (Mobay = Monsanto + Bayer) to bring polyurethane technology to the United States.

In recent years, increased attention has been given to the possibility of NBC warfare. What military vehicles (and other equipment) need, is a topcoat material that does not absorb chemical agents, and can be easily decontaminated after such exposure. Coatings based on Desmodur-Desmophen technology meet this need.

Chemical agent resistant polyurethane coatings (CARC) are specified under MIL-C-46168. This specification calls for an aliphatic* system whose components must be kept separated until shortly before application. Component A is a prepolymer consisting of phthalic anhydride combined with trimethylol propane dissolved in a solvent. This component also carries the pigment called out in the specification. The second component (B) is an aliphatic polyisocyanate, dissolved in a solvent. Components A and B are mixed in a 4:1 ratio to yield a product meeting the specification.

MIL-C-46168 polyurethane coating can be applied by spraying apparatus which mixes the components, in the required proportions, in the nozzle head. The surface being coated must be thoroughly cleaned and

* Military polyurethane coatings are based on aliphatic polyisocyanates. This results in improved properties compared to the aromatic polyurethanes that were the basis of a lot of the early work on polyurethane coatings.

TOLUENE DIISOCYANATE,
(AN AROMATIC ISOCYANATE)

HEXAMETHYLENE DI ISOCYATE
(AN ALIPHATIC ISOCYANATE)
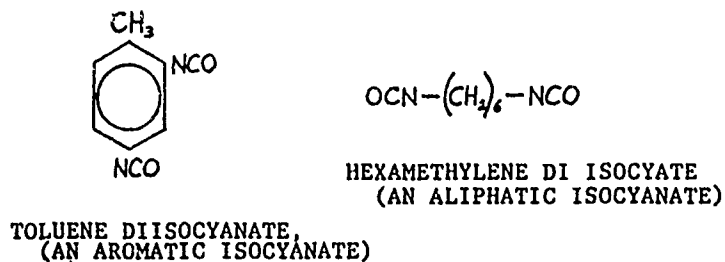
Fig. 57a. TYPICAL DI ISOCYANATES
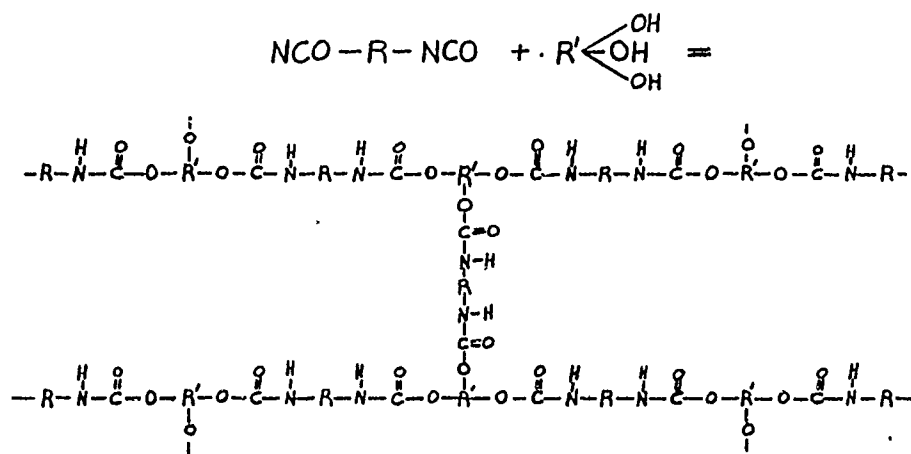
Fig. 57b. FORMATION OF POLYURETHANE RESIN FROM DI ISOCYANATE AND
A TRIOL

$$R' \cdot NCO + H \cdot OH = R' \cdot NH_2 + CO_2$$

ISOCYANATE   WATER   AMINE
(from humidity)

$$R \cdot NCO + R' \cdot NH_2 = R - \overset{H}{\underset{}{N}} - \overset{O}{\underset{}{C}} - \overset{H}{\underset{}{N}} - R'$$

ISOCYANATE   AMINE   SUBSTITUTED UREA
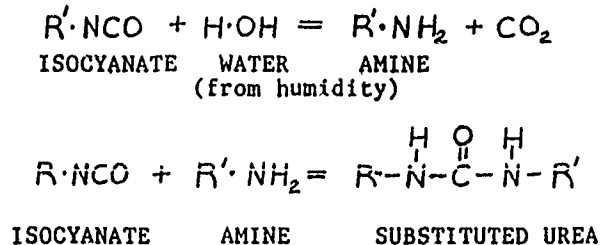
Fig. 57c. MOISTURE-CURING POLYURETHANE REACTIONS

pretreated. The standard polyurethane coating system consists of an epoxy
primer, followed by the polyurethane topcoat. It is not necessary to use
elevated temperature baking to cure either the epoxy primer or the
topcoat, because they cross-link at normal temperatures. This means,
however, that neither of these coatings may be allowed to sit very long
after mixing the components.

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MIL-C-461680 calls out 25 colors. Some colors are camouflage type. The pigments may meet one of two standards: Type I calls for standard formulation for all colors. Types II and III call for lead- and chromate-free pigments. Type III is a specification for reduced volatile organic component solvent formulation.

The driving force behind development of polyurethane coatings for military applications is resistance to chemical agents. Alkyd topcoats readily absorb toxic agents, and decontaminating solutions (i.e., DS-2) will strip the coating off the surface. Polyurethane topcoats are not given to absorbing toxic agents. Also, one can decontaminate a polyurethane-coated surface with standard decontaminating agents. The aliphatic polyurethanes also offer excellent durability in other areas. Disadvantages include the following:

o   Sensitivity to surface preparation -- stringent quality control required
o   Need to mix two components
o   Toxicity of di-isocyanate compounds
o   Difficulty of application in the field (Repairing a damaged coating could be difficult)

These disadvantages can be overcome with experience, and the advantages of not being 'stripped' during NBC training (or actual warfare!) makes polyurethane coatings worth their added expense and difficulty.

8.4.1   One - Component Polyurethane Coatings. There are techniques by which polyurethane coatings can be offered in one package instead of two. Moisture curing formulations consist of a polyhydroxyl material reacted with excess polyisocyanate to form a prepolymer with excess -NCO groups. This prepolymer must be protected from moisture at all times, until it is applied to the surface being coated. Then, moisture normally in the atmosphere reacts with free -NCO groups to form amine groups. These then react with other free -NCO's to cross-link the prepolymer into a resin with the desired properties (see Fig. 53C).

Blocked, or 'disguised' polyisocyanate systems, use a temporary blocking agent, notably phenol, to react with free -NCO groups of an isocyanate adduct or prepolymer. This is mixed with -OH bearing components and pigments, solvents, and catalysts to make a one-component coating. Because the -NCO groups are blocked, no reaction occurs in the container. When applied to the surface being coated, the coating must be heated to a temperature high enough to break the blocking agent away from the -NCO bearing component. The blocking agent evaporates. Isocyanate groups, now free, form urethane linkages in a manner similar to two-part systems. 'Blocked' polyurethanes suffer the disadvantages of requiring high temperature (150C for phenol-blocked systems) baking, and the need to dispose of the vaporized blocking agent.

In addition to the above, polyfunctional isocyanates can be used in conjunction with drying oil derivatives to yield urethane oils, or 'uralkyds'. These have been used in varnishes and enamels.

There is a military specification for a one-component, aliphatic polyurethane, chemical agent resistant coating. MIL-C-53039 (ME) is a lead-and chromate-free, low VOC solvent coating based on aliphatic polyisocyanate reacted with an -OH terminated prepolymer. The resulting material is such that when applied to a surface, moisture from the atmosphere completes the film-forming process. Moisture-curing, one-component polyurethanes tend to have limited shelf life.

One coatings manufacturer has attempted to sell the Army on the merits of a low VOC, blocked isocyanate one-package coating. This material uses 3.5 lb./gallon of volatile organic solvents at an application viscosity of 25 seconds (Zahn #3). It must be baked for 20 minutes at 325F.

Polyurethanes have an assured future in the Army, because they are the only topcoating materials which have proven ability to meet CARC requirements. CARC coatings have been mandatory since Oct. 1985 for all combat zone equipment. As far as the author knows, 2-component polyurethane (MIL-C-46168) and moisture-curing one-component urethane (MIL-C-53039) are the only exterior topcoat materials which meet CARC requirements and, at the same time, do not require high temperature baking.

Polyurethane enamels have long been used on aircraft, which require smooth coatings for good aerodynamic efficiency. Aircraft coatings must also resist abrasion. On both points, the urethanes outperform other coatings. The automotive industry has also taken notice of the possibilities offered by these coatings.*

In terms of resistance to chemicals, sunlight, and abrasion, polyurethanes may well be called the king of topcoating materials.

8.5 Other Resins.

8.5.1 Urea- and Melamine - Formaldehydes. Urea and melamine (see Fig. 58) are amino compounds used for various purposes in the polymer industry. In surface coatings, urea-formaldehyde and melamine-formaldehyde resins have been used in baking enamels. Generally, melamine-formaldehyde is a higher performance material than urea-formaldehyde.

A once-popular baking enamel for consumer goods consists of specially formulated alkyd resin fortified with 20 to 35 percent melamine-formaldehyde resin. Such enamels had found wide acceptance for finishing appliances where detergents (washing machines) or food chemicals (refrigerators) will attack cheaply made coating materials. A number of federal alkyd enamel specifications call for 20% melamine-formaldehyde as a fortifier. Such enamels are baked after application. The melamine allows it and performance demands it.

* Polyurethane Coatings Help Solve U.S. Automotive Paint Challenges, page 36, Modern Paint and Coatings, July 1987.
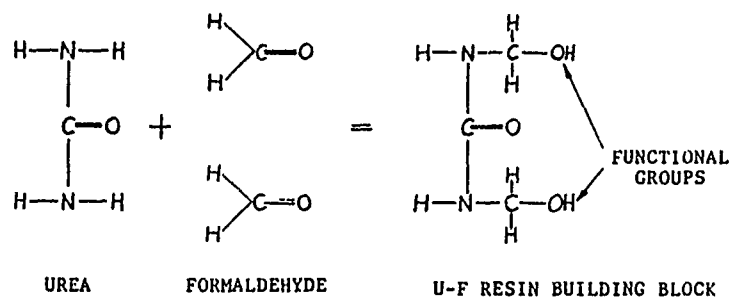
Fig. 58a. UREA-FORMALDEHYDE
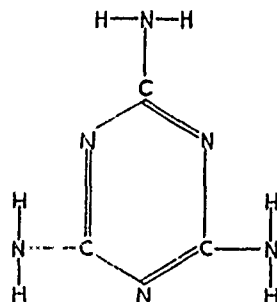
Fig. 58b. MELAMINE. Used as the basis for
many cross-linkers for epoxies,
alkyds, acrylics, etc.

At one time, melamine-fortified alkyd baking enamels were used as automotive topcoats. Melamine-formaldehyde and melamine-alkyds have also been used in nitrocellulose finishes. Urea and melamine can cross-link epoxy resins, and melamine can combine with acrylic polymers to make acrylic baking enamels.

MIL-E-52835A (Enamel, Modified Alkyd, Camouflage, Lusterless) covers a forest green camouflage enamel consisting of phthalic anhydride/drying oil alkyd resin modified with 20 percent, by weight, of butylated melamine-formaldehyde resin. The latter is a cross-linking resin which polymerizes only under baking heat. Typical baking parameters: 30 minutes at 300F (149C).

8.5.2 <u>Phenols.</u> Phenol C₆H₅OH and its derivatives
(i.e.,paraphenylphenol) can combine with formaldehyde and polymerize.
Phenol-formaldehyde resin, introduced in 1909 by Leo Baekeland, was our
first truly synthetic material.

Oleoresinous film-formers, using substituted phenols to form the resin
and tung oil as the oil component, are classics in the history of
varnishes. Phenolic-tung oil coatings can withstand salt water spray, and
therefore make good marine spar varnishes.

The surface coating industry has utilized phenol-based resins in a
number of forms. Thermoplastic phenolic resins are used with oils to make
air drying varnishes. Low molecular weight thermosetting phenols are
blended with oils and solvents to make baking varnishes and enamels.
Oil-free phenol-formaldehyde resin can cross-link epoxy molecules.

Highly polymerized phenolic resins can be modified with natural resins
to make them oil-soluble. Resin-modified phenolic resin, blended with
drying oil, was the basis for the 'four hour' enamels commonly used in the
1920's and early 1930's, before alkyds were adopted.

Phenolic coating materials have proven their ability to protect brake
assemblies from salt water corrosion. (Flandermeyer, <u>Test of Methods for</u>
<u>Protection of Brake Assemblies from Salt Water Corrosion</u>, Ft. Belvoir,
1968.)

8.5.3 <u>Vinyl Resins.</u> The term 'vinyl' refers to any monomer with the
molecular structure shown in Figure 59. Like ethylene, the vinyls (which
are simply substituted ethylenes) form polymers under the right
conditions.

ARBITRARY RADICAL (May be
chloride, acetate, etc.)
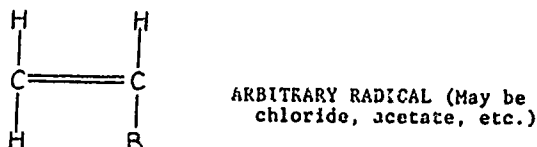
Fig. 59. GENERAL STRUCTURE OF VINYL RESIN

Polyvinyl Chloride (PVC) is a widely used plastic. Highly polymerized
PVC is tough, hard, and resists moisture and many chemicals. However,
coatings chemists do not use PVC by itself because it does not dissolve in
commonly used solvents, and is brittle. Also, PVC tends to decompose when
subjected to heat.

Particles of PVC, suspended in a plasticizer along with stabilizers,
is the basis for 'plastisol' coatings. This system was investigated,

along with other coatings, for protecting high-strength steel torsion bars.* Plastisol coatings proved more cost-effective than a 2-component polyurethane elastomer coating, and exhibited the necessary flexibility, adhesion, abrasion and impact resistance, and resistance to diesel fuel. PVC-plastisols for metal coating are specified under MIL-P-20689C. They must be applied to properly primed surfaces, and baked at 325F (163C) for 15 minutes.

A common commercial automotive application for PVC - plastisol is to protect vulnerable areas of motor vehicles from stone and gravel damage.

Because PVC by itself is brittle and difficult to solvate (dissolve), coatings chemists copolymerize vinyl chloride with other vinyls, notably vinyl acetate and vinyl alcohol. Solution - type vinyl resins are mostly vinyl chloride, with other monomers added so the resin will dissolve in carrier solvents. These resins have been used in anticorrosion primers and antifouling topcoats for ships. They can be used by themselves, or in combination with alkyds.

Other vinyls include vinylbenzene (styrene), polyvinlformal, and polyvinyl butyral. The last is the film-former in 'wash' primers, and also serves as the flexible layer in safety glass.

8.5.4 Acrylics are a subcategory of the vinyls. They are derivatives of acrylic acid or methacrylic acid (see figures 60a and 60b). Polymethyl methacrylate (figure 60c) serves the plastics industry as a transparent polymer. Acrylic compounds also serve as adhesives.

Acrylics are versatile workhorses in the surface coatings industry. They have been used in lacquers, enamels, high-solids enamels, waterborne latex paints, electrophoretic primers, and powder coatings. In the automotive industry, acrylic enamels have replaced every other basic resin type for topcoating purposes. Only polyurethane enamels and polyester-based powder coatings threaten their supremacy.

Lacquers based on thermoplastic acrylic resins were, at one time, widely used as automotive finishing topcoats. Eventually, lacquers were superceded because their high solvent content created air quality compliance problems.

Thermosetting acrylics are used in baking enamels. The practice here is to form a linear copolymer with two or three monomers, one of which is an acrylic capable of engaging in cross-linking reactions. Melamine or urethane crosslinkers can be used to form a polymer network.

Non aqueous dispersion (NAD) acrylic enamels use resin dispersed, rather than dissolved, in an organic carrier. This allows higher solids for a given application viscosity than solution-type coatings.

Finally, acrylics can be adapted to waterborne baking enamels.

A typical high-performance finishing system for commercial automobiles starts with phosphate treatment, and is followed by cathodic electrophoretic primer. The primer is then baked. The topcoat consists

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* Austin, Avery J., N.F. Hayes, and K. Navasaitis, Improved Coating System For High Strength Steel Torsion Bars, U.S. Army TACOM R & D Center, April 1981.

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
| & & | \\
\text{C} & = & \text{C} \\
| & & | \\
\text{H} & & \text{COOH}
\end{array}
$$

Fig. 60a. ACRYLIC ACID

$$
\begin{array}{ccc}
\text{H} & & \text{CH}_3 \\
| & & | \\
\text{C} & = & \text{C} \\
| & & | \\
\text{H} & & \text{COOH}
\end{array}
$$
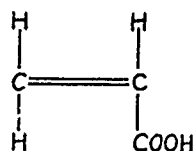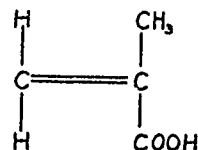
Fig. 60b. METHACRYLIC ACID

$$
\begin{array}{cccccccccccc}
& \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 \\
& | & & | & & | & & | & & | & & | \\
-\!\!\!&\text{C}&\!\!\!-\!\!\!&\text{C}&\!\!\!-\!\!\!&\text{C}&\!\!\!-\!\!\!&\text{C}&\!\!\!-\!\!\!&\text{C}&\!\!\!-\!\!\!&\text{C}&\!\!\!- \\
& | & & | & & | & & | & & | & & | \\
& \text{H} & & \text{COOCH}_3 & & \text{H} & & \text{COOCH}_3 & & \text{H} & & \text{COOCH}_3
\end{array}
$$
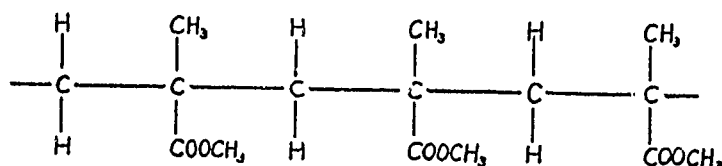
Fig. 60c. POLYMETHYL METHACRYLATE

of two layers: A pigmented acrylic/urethane enamel color coat, and an unpigmented acrylic enamel clear coat. The clear coat protects the underlying pigments from sunlight and environmental chemicals.

8.5.5   Polyesters. A polyester is any polymer formed by condensation polymerization of polyfunctional acids and alcohols. Insofar as alkyd resins consist of bifunctional acids and polyfunctional alcohols, they are polyesters in the strict technical sense.

Polymer chemists use the term 'polyester' to describe oil-free systems in which the alcohol components, or acid components, or both, have unsaturation points so that linear chains can be cross-linked to form resin systems. The cross-linker may be a vinyl substance (i.e., styrene), an isocyanate (urethane - polyester), melamine, or a low molecular weight epoxy.

Polyester resins serve the plastics industry as a matrix material in fiberglass reinforced composites. For surface coatings, polyesters can be effectively used as powders.

8.5.0 **Silicones** are based on the molecular structure shown in Figure 61. Silicone polymers can be cold-blended or chemically combined with other resins to make coatings with special properties. Combinations of silicone resin and baking-type alkyd are suitable binders for white enamels for surfaces subjected to temperatures up to 500F (260C). Silicone intermediates can chemically combine with alkyd and other resins to improve their properties, particularly for high-temperature applications. Aluminum-pigmented, silicone-modified enamels could be used to advantage in parts of military vehicles exposed to high temperatures, i.e., gas turbine-powered main battle tank exhaust grilles. Silicone-alkyd enamels have been used with success for finishing the topsides of ships, an application requiring resistance to ultraviolet radiation, salt spray, and temperatures fluctuation.*
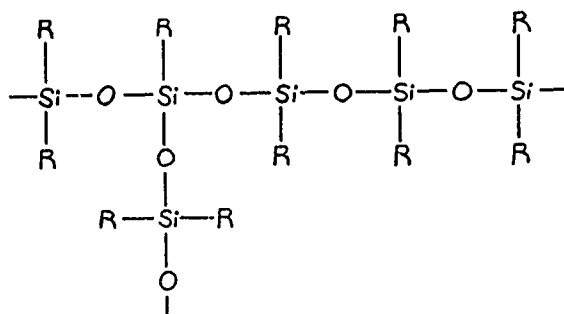
Fig. 61 SILICONE STRUCTURE

Straight silicone resins are used mainly in special high temperature applications. Such resins, when aluminum pigmented, have been used on surfaces exposed to temperatures on the order of 1000F (538C).

Silicone compounds, added to paints in small amounts, improve flow properties during application.

Binders, like structural and adhesive polymers, have been made in endless variety. There is much a chemist can do to 'play around' with various systems. Accordingly, only a general outline can be given here. The various coating resins discussed in the preceding paragraphs hopefully will provide the engineer with an appreciation of the variety of organic coatings at his or her disposal to protect metals from corrosion.

8.6 **Non - Traditional Coating Systems**. Organic coating systems using a binder dissolved in an organic solvent, to which pigments, driers, and other ingredients are added, are traditional coating systems. The problem with traditional coatings is that they assume the user is at liberty to use the atmosphere as a dumping ground for organic solvents which, once

* A Guide to Silicone Coatings for Metal Products, Metal Finishing, June 1982, Page 49.

evaporated, serve no further purpose. Today, there are laws in every state restricting volatile organic component (VOC) emissions resulting from surface coating operations.

Non - traditional coating systems are those that seek to eliminate (or greatly reduce) organic solvents, to comply with air pollution regulations. These systems include:

1.   High Solids coatings
2.   Waterborne coatings (including electrophoretic systems)
3.   Powder coatings.

8.6.1 High Solids Coatings seek to meet VOC regulations by using no more organic solvents than are allowed for a given type of coating.

Meeting VOC regulations via solvent level reduction is difficult. If the legal limit on VOC's is 2.8 Lb per gallon, the coating must contain 62% solids. A 3.5 Lb/gallon VOC limit means approximately 50% solids. By comparison, traditional coatings contain 25 - 30% solids.

Binders used in coatings are viscous, if not outright solid. The need to reduce viscosity so the user can apply a high quality coating, is the reason solvents were used at traditional levels in the first place. Referring to Figure 62*, the viscosity of a polymer solution increases with the percentage of solids and the molecular weight of the dissolved solid polymer. Note that viscosity greatly increases when going from 25 to 60% solids.

Generally, high solids content may be attained by using a low molecular weight binder material, or by heating the coating material before application to reduce viscosity. The former approach means enhanced dependence on post-application polymerization to develop desired film properties. The automotive industry uses in-line paint heaters to heat high solids acrylic enamels to 100 - 120F (38 - 49C) to lower the viscosity before spraying. This approach may not be a good idea for two-component coatings, which may prematurely react in the spraying apparatus if heated.

In spite of the technical difficulties involved, coatings manufacturers now formulate coatings with up to 60% solids. The military specification for 2-part polyurethane coatings has been rewritten to specify reduced VOC formulations. MIL-C-46168D, types III and IV, restrict VOC's to 3.5 lbs. per gallon (420 gram/liter).

Some coating manufacturers and users have attempted to meet federal and state air quality requirements by using non-photochemically reactive solvents. An example of such a solvent is 1,1,1 Trichloroethane. This solvent, however, is expensive, and it is possible that chlorinated solvents may not be permitted in the future because of other ecological effects. MIL-C-46168D, type III, allows chlorinated 'compliance' solvent. Type IV does not allow these solvents.

*   Paul, Swaraj, Surface Coating: Science and Technology, Wiley-Interscience, New York, 1985, page 704.

VISCOSITY vs SOLIDS
(Theory vs Experiment)
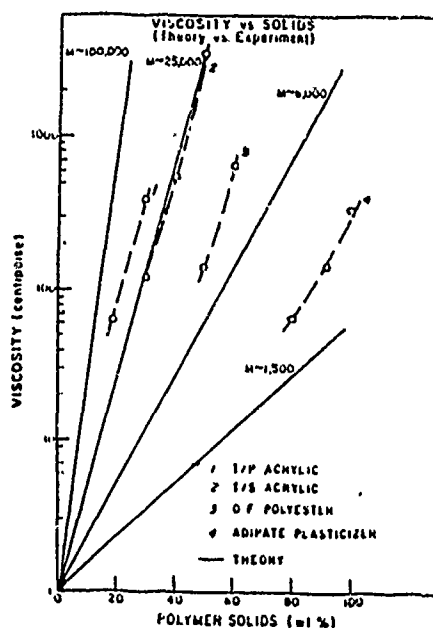
Fig. 62. INCREASE IN VISCOSITY OF
A POLYMER SOLUITON WITH INCREASE
IN MOLECULAR WEIGHT AND PERCENTAGE
OF SOLIDS.

A subcategory of the high-solids approach is <u>radiation cured coatings</u>.
The idea here is to use low molecular weight monomers or oligomers (low
mol. wt. polymer) that are liquid at normal temperatures, and are not too
viscous. This eliminates the need for solvents during application. The
coating material is applied to the surface being coated, and irradiated
with ultraviolet radiaticn. The molecules then link together and form a
cured coating film. Radiation curing suffers the disadvantage of
requiring ultraviolet access to all areas of the part being coated. Also,
tne radiation has to penetrate the entire thickness of the coating.
Nonetheless, radiation curing may well offer advantages as VOC regulations
are progressively tightened.

8.6.2 <u>Waterborne Coatings</u> use water as the sole thinner, or the major
component of an overall thinning system containing some organic solvent.
Waterborne systems eliminate, or greatly reduce, VOC emissions. The result
is freedom from air quality compliance hassles, and reduced fire hazards.

   There are two ways a pigment/binder system can be thinned by water:
as a <u>dispersion</u> or as a <u>solution</u>. A dispersion-type waterborne coating
system consists of very small particles of resin and pigment dispersed in
water. The "latex" family of architectural paints are dispersions. Early
latex paints were dispersions of styrene-butadiene polymer formed by
in-situ polymerization of the monomers in water. Pigments were then
added, along with surfactants, thickeners, protective colloids, and
preservatives. When applied to a surface, the water evaporates. The

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styrene-butadiene particles then coalesce, along with the pigment particles, to form the paint film.

Today, latex paints use other resins, notably vinyl acetate-based polymers, and acrylic resins. The latter are used in the best latex paints. Latex systems offer advantages for architectural painting. They do not emit noxious vapors, nor create fire hazards. Water cleans up accidental spills. An important advantage of dispersions is that viscosity is independent of the molecular weight of the dispersed resin particles. A disadvantage of dispersion-type waterborne coatings is lack of inherent freeze-thaw stability.

Solution-type waterborne coatings use resins modified to make them water soluble. The classical technique is to adduct a resin with an acidic molecule, or formulate a resin with acid groups (-COOH) in its structure. The resin is subsequently reacted with ammonia or an amine to form a water-soluble salt. The ammonia or amine evaporates when the paint dries. The deposited resin may be a cross-linking type which is baked to develop the desired film properties. Many systems of this type use water-miscible organic liquids to act as co-solvents to reduce application viscosity. A coating system of this type is actually a high-solids organic-solvent coating formulated so as to be water-reducible. The percentage of solids without the water determines whether the material complies with applicable state and federal VOC regulations. A number of resins can be made water-soluble, including alkyds, acrylics, polyesters, and epoxies.

Early generation waterborne industrial coatings suffered a number of disadvantages, such as flash rusting of steel surfaces, limited storage life, and reduced performance compared with traditional coating materials. These problems have been reduced with third-and later-generation waterborne coatings.

For military purposes, perhaps the biggest problem is that water reacts with free -NCO groups. This means that polyurethane CARC coatings cannot be waterborne, unless they are the 'blocked' type. The latter have to be baked, and this is not convenient for armored vehicles with their large thermal inertia. There are waterborne epoxy primers (i.e., MIL-P-53030) which, though requiring organic co-solvent, meet VOC regulations not more stringent than 2.8 lbs. VOC per gallon.

A word is in order about VOC limits. An air-drying coating is legally defined as requiring temperatures no higher than 194F (90C) to develop the desired film properties. Coatings requiring higher temperatures are legally defined as baking enamels. The latter have lower legal VOC limits than the former. In California, the legal VOC limits are 2.8 lb/gal (336 gram/liter) for air-drying coatings, and only 2.3 lb/gal (276 gram/liter) for baking enamels. The latter means 69% solids. Meeting this stringent a VOC limit is problematical, unless water or some acceptable non-photochemically reactive solvent can be used to thin the material to a reasonable application viscosity.

8.6.3 Powder Coatings are 100% solid. These coatings have found an increasing number of applications in recent years because of federal and state VOC regulations. Powder coatings have other advantages besides VOC compliance. Their non-use of solvents means one does not have to allow

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for solvent vapors when baking article to cure the coating. Powders, unlike solvent-borne coatings, do not generate messy sludges to cause waste-disposal problems. Powder transfer efficiency (percentage of material that ends up on the article being coated) is as high as 95%. Powder that fails to reach its target is often reusable. A variety of items have been successfully powder coated, including the following:

o   Consumer goods (i.e., refrigerators, air conditioners, etc.)
o   Aluminum architectural items
o   Metal furniture

In the automotive industry, powder coatings can protect the following:

o   Coil springs
o   Wheels
o   Underhood components   .
o   Chassis components; i.e., axle casings

Powder coatings have been used as intermediate or 'primer-surfacer' coats for small trucks and recreational vehicles.* The powder is applied over a cathodic E-coat primer. This provides a smooth surface for the final topcoat, which is a high-solids acrylic enamel.

Clear and pigmented powder coatings can protect aluminum wheels. The user may color-match pigmented powders to the vehicle they are installed on.

If powder coatings are to be used for topcoating military vehicles, they will have to meet CARC requirements. If such a powder is possible, it could be used to advantage on a number of vehicle components. Factories applying powder coatings would be free from solvent problems, and also would not have to worry about the viscosity problems of high-solids solvent-borne coatings. A powerful advantage is that powder coatings, in many cases, do not require a primer.

Disadvantages of powder coatings are as follows: First, they have to be baked at temperatures ranging from 250 to 350F** (121 to 177C). This would be a problem for armored vehicles, or for materials not able to withstand the temperature. Second, if powder is applied by electrostatic spray, there may be a problem with sharp internal corners because of 'Faraday cage' shielding effects.

Powder coating materials are thermoplastic or thermosetting. The former include plastic materials such as polyethylene, polypropylene, nylon, and polyvinylchloride. Thermoplastic powder coatings do not compete with liquid coatings. They are used in applications requiring a thick layer, i.e., 5 to 40 mils. (0.127 to 1.016 mm).

*   Metal Finishing, February 1987.
**   The coatings application engineer may use higher temperatures to shorten baking time.

Thermosetting powders are the materials used in applications such as those described above. The following resins are used in thermosetting powders:

o   Epoxy
o   Thermosetting polyesters:
        -urethane - polyester
        -triglycidyl isocyanurate (TGIC) - polyester
        -epoxy - polyester hybrid
o   Acrylic
        -usually urethane-linked.

Epoxy powders are the workhorse of the powder coating industry. They offer good adhesion and corrosion protection. Unfortunately epoxy powder coatings, like other epoxy materials, cannot withstand ultraviolet radiation. Therefore, they are not recommended for exterior topcoatings.

Thermosetting acrylic powders have been used in applications that previously used liquid acrylics. Acrylic powders have been used as automotive topcoats in Japan.

One can use thermosetting polyester powders to powder-coat aluminum wheels.* The most successful polyester for this purpose is cured with a cyclicized isocyanate called triglycidyl isocyanurate, or TGIC. TGIC-polyester is also the powder material of choice for architectural purposes, as it can withstand external exposure very well.

Fluidized beds and electrostatic spray guns are the most common methods of applying powder coatings. The former lends itself to automated production-line coating (see Figure 63**), while the latter approach is best for large items.

8.7 Electrodeposited Polymer Coatings. If 2-component, aliphatic polyurethanes are the king of topcoat materials, then modern electrodeposited (a.k.a. electrophoretic, E-coat, Elpo) coatings can lay claim to the same status among primers. The E-coat process can apply 1-coat finishes which are sufficient for some applications, but is most famous as a method for applying primer coatings to motor vehicle bodies.

Electrodeposition is a dip, or immersion process, whereby the object being coated is immersed in a liquid medium. The process resembles electroplating, in that a current of electricity deposits coating material from the medium onto the surface of the object. The surface need not necessarily be metal, but it must conduct electricity for the process to work.

Unlike nickel, chromium, and other metals, electrodeposited polymers do not conduct electricity. Accordingly, E-coat is a self-limiting

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*   Wesson, J., Colorful Future For Aluminum Wheels, page 54, Products Finishing, December 1986.
** User's Guide to Powder Coating, Association for Finishing Processes of the Society of Manufacturing Engineers, Dearborn, MI, 1985, page 971.
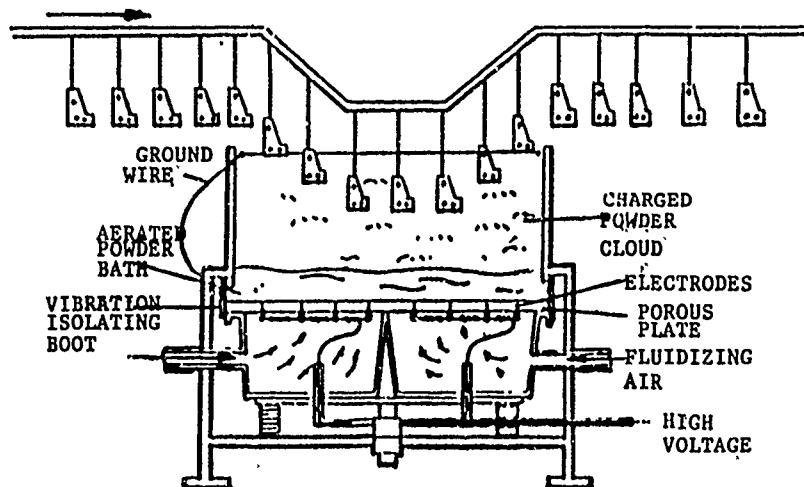
Fig. 63. A FLUIDIZED BED, ELECTROSTATIC POWDER
COATING SYSTEM FOR PRODUCTION LINES.

process. Once a film forms to a certain thickness, its insulating nature
curtails further growth. As a result, E-coat primers seek out all areas
of an item, including nooks, crevices, and boxed-in areas that spray-type
primers often miss.

E-coat materials are solution-type waterborne polymers, using some
organic solvent. They comply with all VOC regulations, and do not create
fire hazards. Other advantages include:

o   Efficient utilization of materials
o   Applicability to automated production lines
o   Rapid deposition of material, simultaneously over the entire
        surface being coated. Films deposited in 1 to 2 minutes.
o   Uniform build, with no runs, sags, or beads.
o   Any conductive object that will fit into a given tank can be
        coated.

The first electrodeposited polymers were anodic, whereby an automobile
body or other item was made the anode in an electrochemical cell
consisting of it, a cathode, and the coating medium (see Fig. 64a).
Today, the automotive industry uses cathodic E-coat primers, which deposit
on the cathode (see fig. 64b). Cathodic materials have proven superior to
anodic materials in corrosion protection. The reason anodic E-coat
primers were used in the first place was because they are a logical
extension of classical water-soluble resin technology.

Recall that if a polymer has organic acid (COOH) groups hanging onto
its structure, these groups will combine with ammonia or amines to form a
water-soluble salt. When a polymeric substance of the type R-COOH is

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RESIN MACRO-ION
NEGATIVELY CHARGED

COO⁻

NH⁺

COO⁻

NH⁺

CATHODE

OBJECT BEING
E-COATED

POSITIVELY CHARGED
SOLUBILIZER ION
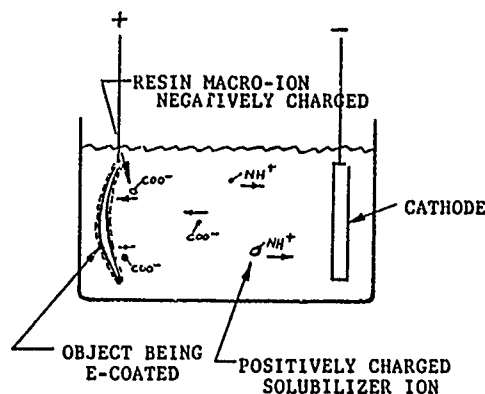
Fig. 64a. ANODIC ELECTRODEPOSITION

RESIN MACRO-ION
POSITIVELY CHARGED

NH⁺

ANODE

X⁻

NH⁺

X⁻

OBJECT BEING
E-COATED

NEGATIVELY CHARGED
SOLUBILIZER IONS
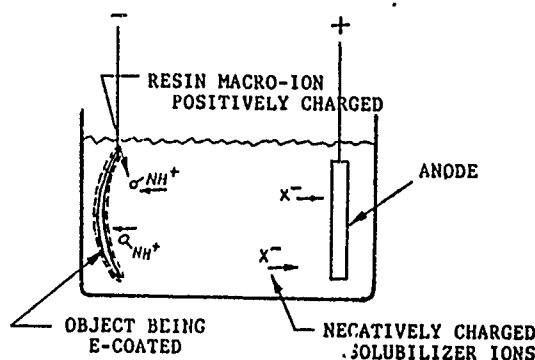
Fig. 64b. CATHODIC E-COAT

dispersed in water made alkaline with ammonia (NH_3) or an amine
($NR'H_2$), this is what happens:

$$R\text{-}COOH + NH_3,\ NR'H_2\ (aq) \longrightarrow RCOO^- + NH_4^+,\ NR'H_3^+\ (aq).$$
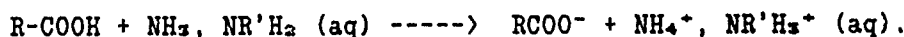
The polymeric macro-ions, RCOO-, behave like any other negatively charged
ion or particle, migrating toward the anode in an electrochemical cell.
When they reach the anode, the $RCOO^-$ ions participate in these reactions:

$$H_2O \longrightarrow 1/2 O_2 + 2H^+ + 2e^-$$

$$RCOO^- + H^+ \longrightarrow R\text{-}COOH$$
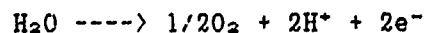
The macroions, thus neutralized, coagulate and form the coating. This is
the process first used in the early 1960's by the Ford Motor Company when
they pioneered electrophoretic primer deposition for motor vehicle bodies.
Other manufacturers also adopted this process.

Early anodic E-coat materials demonstrated the ability of electrophoresis to drive the polymer into cracks and crevices. Unfortunately, the early materials were not all that good. What was accomplished was superior application and utilization of mediocre materials. Chemists later developed better materials, and electrodeposition of polymers found increased application and sales volume during the 1960's. Later-generation anodic E-coats were better than the first such materials.

Unfortunately, all anodic E-coat materials suffer from basic limitations. Anytime one makes a metal object the anode in an electrochemical cell, some metal is going to be dissolved. The metal ions are then incorporated into the coating film as oxides, or as compounds with the polymer. Also, the polymer R-COOH tends to be acidic, and this is not good for corrosion resistance.

Accordingly, R & D organizations sought methods of modifying polymers to form positive macroions in aqueous solution, so the item being coated could be made the cathode instead of the anode. The classical technique for accomplishing this is to graft an amine-type molecule onto the polymer structure, forming a macro-amine with the general formula $R_1R_2R_3N$ (see fig. 65). When dispersed in water whose Ph is adjusted to the acid side (less than 7), the polymer forms positive macroions:

$$R_1R_2R_3N + HX \text{ (aq.)} \longrightarrow R_1R_2R_3NH^+ + X^-,$$
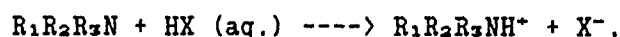
where HX is an organic acid, i.e., acetic (see Fig. 66).

When the object to be coated is immersed in the medium and made the cathode, the polymer ions drift toward it, are neutralized, and form the film.

In cathodic E-coat systems, the item being coated is not attacked by the solution because it is held at a negative potential -- it is cathodically protected. Advantages of cathodic E-coating over corresponding anodic processes are as follows:

o   No bare metal attack
o   Phosphate coatings not dissolved
o   No metallic salts in deposited films
o   Improved corrosion protection.

The last advantage is because the polymer itself is alkaline rather than acid, and therefore serves as a corrosion inhibitor.

Development of polymers suitable for cathodic electrodeposition was difficult. Early materials had poor throwing power. These problems were solved, and today's cathodic E-coat technology offers the aforementioned advantages over anodic electrodeposition plus the advantages of E-coat in general. All automotive manufacturers now use cathodic E-coat for applying primer coatings to motor vehicle bodies.

At present, two resins have been developed for cathodic E-coat systems: epoxies, and acrylics. The former are superior as primers, offering better corrosion protection than acrylics. The latter have

EPOXY RESIN MACRO-MOLECULE

+   PRIMARY OR SECONDARY AMINE

AMINE FUNCTIONAL EPOXY
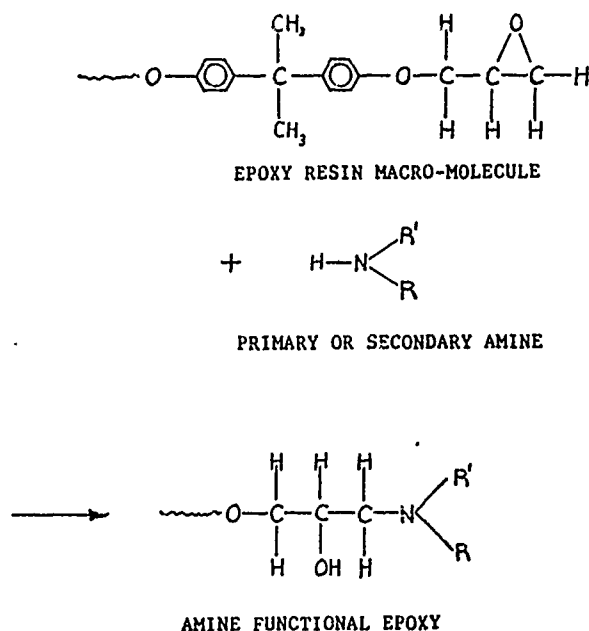
Fig. 65.   FORMATION OF RESIN (Epoxy, in this example)
WITH AMINE FUNCTIONAL GROUP

AMINE FUNCTIONAL EPOXY   AQEOUS ACID SOLUTION

POSITIVELY CHARGED   NEGATIVELY CHARGED
RESIN MACRO-ION   ACID RADICAL
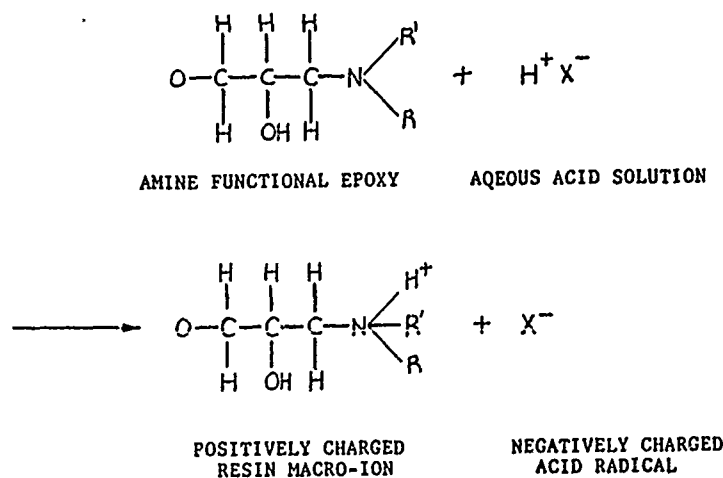
Fig. 66.   FORMATION OF POSITIVELY CHARGED RESIN MACRO-ION IN
A CATHODIC E-COAT SOLUTION

superior ultraviolet and weathering resistance, and are therefore used as
topcoats.

The latest development is 'high build' cathodic E-coat formulations.
These develop coating films approximately 30 microns (1.2 mils.) thick,

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rather than the 15 microns (0.6 mils.) characteristic of the first cathodic E-coat materials.*

Electrodeposited polymers have to be baked, because they rely on cross-linking to develop their properties. Anodic resins employ melamine-based cross-linkers, while cathodic resins use a blocked isocyanate (urethane) cross-linking mechanism. When baked, the isocyanate unblocks, cross-linking the resin to form a network polymer.

E-coat materials can be pigmented. Epoxy materials are usually black, gray, or brown. Acrylics can be pigmented so as to provide a variety of colors.

To provide the reader with a feel for the characteristics of a typical cathodic E-coat epoxy primer, data sheets from one of the leading suppliers are provided in Figures 67 through 69.

Disadvantages of E-Coat Systems. While cathodic electrodeposition has much to offer, it also has disadvantages, which may be summarized as follows:

- o   High capital cost
- o   Limited film thickness
- o   Limited to conductive objects
- o   Not easy to change colors
- o   VOC not zero
- c   Deposited films require baking

The high capital cost arises from the large tanks and complicated systems required. Cathodic E-coating requires careful control of bath chemistry, and sophisticated ultrafiltration systems to achieve the high materials utilization efficiency theoretically possible with this system. Accordingly, E-coat systems are economically justified only where there is a large number of items to be coated. In compensation, E-coat systems are not sensitive to changes in item shape or configuration. Provided the tank is big enough, one can use the system for "jeeps" or 5 ton trucks.

Limited film thickness arises from the self-limiting nature of polymer electrodeposition. Today's high-build E-coat primers deposit 1.2 mils. (30 microns). This enables automotive manufacturers to eliminate the surfacer coat from body finishing operations.

Nonetheless, electrodeposition is pretty much limited to about 1.5 mils. This is one reason why spraying is employed for the basecoat and clearcoat layers of high-performance finishing systems, after electrodeposition has applied the primer.

The requirement for electrical conductivity means non-metallic (i.e., plastics, fiber-reinforced composites) items cannot be painted by electrodeposition, unless the surface is made conductive.

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*   Loop, Federich M., <u>High Film Build Cathodic Electrodeposition Provides Improved Corrosion Protection</u>.   SAE paper 831313, in SAE Special Publication P-136, page 35.

APPLICATION DATA

MATERIAL NAME:	POWERCRON© 600
SUPPLY CODE:	P600-611
DESCRIPTION:	Gray Cationic Epoxy Electrocoat
SUBSTRATES:	Properly Cleaned and Treated Cold Rolled, and Hot Rolled and Stainless Steel; Galvanized and Zinc-alloy Coated Steel; Aluminum, Magnesium, and Zinc Die-casting.
PRETREATMENT:	Various
COLOR:	Light Gray
GLOSS:	Medium
FILM THICKNESS:	0.5 - 1.5 Mil
HARDNESS:	2H Minimum
COATING VOLTAGE:	150 - 400 Volts
ELECTRICAL EFFICIENCY:	2.0 - 2.5 AMPS Per Ft.^{2} Per Minute Per Mil
BAKE CYCLE:	20 Minutes at 350° F Metal Temperature
VOC:	1.1 Pounds Per Gallon Minus Water (131 Grams Per Liter)
COVERAGE:	529 Ft.^{2} Per Gallon of Feed
HEAVY METAL CONTENT:	None

Fig. 67. A TYPICAL CATHODIC E-COAT MATERIAL

OPERATING PARAMETERS

GRAY POWERCRON® 600 P600-611

SOLIDS:	$10.0 - 20.0 \pm 1\%$ (105° c)
P/B RATIO:	0.30 ± 0.05 (Correction Factor = 1.00)
pH:	6.15 ± 0.15
CONDUCTIVITY	$1000 - 1600 \pm 100$ Microhos
SOLVENT: TOTAL:	$1.0 - 3.0\%$
BUTYL CELLOSOLVE:	$0.8 - 2.0\%$
DOWANOL PPH:	$0.2 - 1.0\%$
BATH TEMPERATURE:	$70 - 100°$ F $\pm 2°$ F
ANOLYTE CONDUCTIVITY:	$300 - 2000 \pm 100$ Micromhos
DEIONIZED WATER CONDUCTIVITY:	10 Micromhos Maximum
PRE-RINSE CONDUCTIVITY:	50 Micromhos Maximum

Note: Bath Solids, Conductivity, Solvent and Temperature
       Parameters are Set According to Film Thickness and
       Throwpower Requirements.

Fig. 68. A Typical Cathodic E-Coat Material

CHEMICAL ANALYSIS

GRAY POWERCRON® 600

P600-611

	PAINT	PERMEATE	ANOLYTE
pH	6.0 – 6.3	5.5 – 6.0	2.5 – 3/5
CONDUCTIVITY	1000-1600 umhos	800-1200 umhos	300-200 umhos
SOLIDS	10 – 20 %	0.2 – 0.4 %	300 – 1000 PPM
RESIN [1]	8 – 15 %	0.2 – 0.4 %	250 – 750 PPM
PIGMENT [2]	2 – 5 %	50 – 100 PPM	10 – 20 PPM
SOLVENT [3]	1.5 – 2.5 %	0.5 – 1.5 %	0.05 – 0.1 %
SOLUBILIZER [4]	0.2 – 0.5 %	0.1 –0.2 %	0.2 – 0.5 %
WATER	80 – 85 %	98 – 99 %	99.0 – 99.5 %
CHROME	None	None	None
LEAD	None	None	None
PHENOL	5.0 – 10.0 PPM	1.0 – 5.0 PPM	0.10 – 1.0 PPM
BOD/COD	300,000-500,000 PPM	10,000-50,000 PPM	5,000-10,000 PPM

1   Modified Epoxy/Polyurethane
2   Aluminum Silicate, Carbon Black, Titanium Dioxide
3   Glycol Ethers
4   Lactic Acid

Figure 69   A Typical Cathodic E-Coat Material

When using E-coat for the final finish, it is not easy to change colors because of the large inventory of material in the tank and associated piping.

VOC emissions are low. However they are not zero, because E-coat formulations use some organic components (about 1.2 lb/gallon, or 144 gram/liter) as cosolvents.

The need for baking is partly compensated by the fact that electrodeposited films have low moisture levels due to a phenomenon called electro-osmosis. This means that one does not expend much energy vaporizing water and cosolvent. Nonetheless, items with large thermal inertia (i.e., a main battle tank) will require a lot of energy to heat to baking temperature, which is 350F (177C) for a typical cathodic epoxy electrocoat primer.

As with any coating process, the engineer can help electrophoretic priming to do its job better by designing structures so as to accommodate the process. Access holes will allow the primer to find its way into boxed-in areas. Because the part or structure is immersed into a bath, care should be taken to prevent entrapped air bubbles from interfering with the deposition process.

Cathodic E-coat as a Final Finishing Process.* If the finishing requirement for an item can be satisfied by an organic film whose total thickness is 1.4 mils. (35 microns), the engineer might want to consider cathodic acrylic E-coat. An example is truck refrigeration units (Products Finishing, November 1986, page 54). The units receive a zinc phosphate pretreatment, followed by 1.3 mils. of white acrylic E-coat enamel. The enamel is baked for 30 minutes at 360F. The result is a high quality finish whose ultraviolet resistance is excellent, and whose salt spray resistance is adequate for that application. It is doubtful such a procedure would be adequate for military vehicles, which operate in harsher environments and are required to have a topcoat meeting CARC standards.

8.8 Autophoretic Deposition--The Next Wave?** Just as there is 'electroless' nickel, there is likewise an 'electroless' polymer deposition process. Like anodic and cathodic E-coat, autodeposition is a waterborne, dip-type process. At the time this was written, autophoretic deposition works only with ferrous metals.

The chemistry of autodeposition (AD) represents a fusion of phosphating/chromating, and latex paint technology. In fact, the corporation that commercialized this process, Amchem Products, Inc., is a leading manufacturer of metal pretreatment systems. The polymer material is disposed as a latex-type dispersion, along with pigments, in water containing hydrofluoric acid and hydrogen peroxide. The acid and oxidizer

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*   Jozwaik, E.L., Cationic Acrylics: Electrodeposition's Topcoats., SAE paper 862019, in SAE page 188.

**   Holyk, Nestor M. and Thomas C. Jones, Autodeposition of Organic Films--Some Unique Applications., SAE paper 862020, in SAE Special Publication P-188.

etch the surface in a manner similar to what happens in a phosphate or chromate pretreatment. Because autodeposition depends on this etching action, items to be coated are not phosphated beforehand, as they are with other organic coatings (including electrodeposition).

The ferric ions formed by this controlled attack, react with the nearby latex particles and cause the latter to deposit on the surface. The film forms in 1 to 2 minutes, and is from 0.3 to 1.0 mils. thick. 'Autodeposition was introduced in 1975, and has progressed to Generations II and III. These generations are, respectively, acrylic resin and polyvinylidene chloride. The latter has excellent resistance to moisture permeation; latex paint formulators have been 'rediscovering' this polymer for use in high performance systems. A disadvantage of polyvinylidene chloride is limited high temperature tolerance.

As of this writing, black is the only color available in AD systems.

Autodeposition offers a number of advantages:

o   No electric power required
o   High throwing power
o   No VOC

The most significant advantage of AD is its superior throwing power. Electrodeposition offers good, but not unlimited, throwing power, because of Faraday cage effects. AD has shown its ability to coat the insides of closed structural sections, and to deposit uniform films on complex and intricate parts.

AD does not use organic co-solvents, because it is based on latex technology, rather than water-soluble resins. This eliminates VOC emission problems that, in the future, could arise with water-reducible coatings that use organic solvents to aid polymer solvation.

The films deposited by AD offer 168 to 336 hours salt spray resistance. The coating systems engineer may specify a topcoat for additional protection.

Applications. Autodeposition has been used to coat automotive components, such as suspension arms based on hollow sections, jack assemblies, and belt pulleys. One manufacturer has used AD to treat compact car frames.*

8.9   Special Coating for Fasteners.

Why special fastener coating are necessary. A threaded fastener cannot be protected by a coating system such as G-90 thickness galvanizing, followed by 0.8 - 1.3 mils. of cathodic E-coat, followed by another 1.8 mils. of CARC. Such a thick coating system would interfere with threads.

*   Metal Finishing, October 1983, page 77.

Accordingly, fasteners in corrosive environments require high-performance coatings capable of providing adequate protection with no more than 0.8 to 1.3 mils. total thickness.

8.9.1 Cadmium Coatings. Fasteners have traditionally been electroplated with cadmium for corrosion protection. Cadmium offers the following advantages over zinc for fasteners:

o   Its corrosion products are less voluminous than those of zinc
o   Cadmium has a low coefficient of friction, which is desirable in a threaded fastener coating.
o   Cadmium offers superior corrosion resistance in humid and marine environments (zinc, however, is superior in industrial environments).

Electrodeposited cadmium is specified under QQ-P-416E, which calls out thickness, supplementary chromate and phosphate conversion coatings, and post-plating baking to relieve hydrogen embrittlement. QQ-P-416, type II, class 3 calls out 0.0002 inches (minimum) thickness, with supplementary chromate treatment. This coating specification has been used for small fasteners.

High strength steels suffer hydrogen embrittlement when electroplated. QQ-P-416 calls for 375+/-25 degrees F post-plating baking to relieve hydrogen embrittlement, for parts whose hardness exceeds Rc-40. The baking must be done as soon as possible after plating, and should last long enough (at least several hours) to assure that the hydrogen will be redistributed* to the extent needed to reduce embrittlement. For very high strength fasteners or others parts, it is best to use non-electrolytic processes such as peen-plating, or vacuum-deposited cadmium.

Cadmium has several disadvantages as a protective coating for fasteners. It is more expensive than zinc, melts at a relatively low temperature (320.9C -vs- 419.5C for zinc), and is prone to attack by organic vapors. The solutions used in cadmium electroplating create toxic waste disposal problems. One must not employ cadmium on components exposed to vacuum or high temperatures. Cadmium must not be applied to any titanium component, nor on any component that comes into contact with titanium.

For small fasteners cadmium plating, with good quality control (particularly regarding adequate minimum thickness), is advantageous. Cadmium plating on rivets has proven its ability to reduce galvanic

* H_2 does not readily diffuse out of a part, because the cadmium acts as a barrier.

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corrosion of aluminum sheet, which otherwise occurs with uncoated steel
fasteners.*

8.9.2   Ceramic-Metallic Coatings.   This family of coating systems is
commercially available.   One corporation markets these products under the
trade names Sermaguard and Sermatel.(R)**   Ceramic-metallic coatings
consist of aluminum particles, plus phosphates and chromates in a
water-based slurry.   When the slurry is applied to a surface and baked,
the cured coating film consists of aluminum pigment in a ceramic matrix.
The aluminum particles add strength to the film, and also offer
sacrificial protection to steel articles.
      Ceramic-metallic fastener coatings are applied to fasteners by
dip-spinning.   This process can treat large numbers of fasteners
simultaneously, thus reducing applications costs relative to coating each
part separately.   The coating must be cured at approximately 300C (572F).
The cured coating does not conduct electricity, despite the aluminum
pigmentation, unless burnished (lightly abraded) with alumina grit.   The
dip-spin/cure cycle, repeated twice, produces coatings up to 20 microns,
or 0.8 mils., thick.   A fastener coated with 0.8 mils. of ceramic-metallic
coating can withstand 400 hours of salt spray per ASTM B117.   The coating
possesses a torque coefficient of 0.45 - .55.   A wax coating applied after
curing and burnishing will reduce the torque coefficient to 0.12 -
0.15.***
      The design engineer must remember that ceramic-metallic fastener
coatings are not identical to the ceramic-metallic coatings applied to gas
turbine blades.

8.9.3   Fluorocarbon Coatings.****   'Fastener - Class' fluorocarbon
coatings offer several advantages.   They offer good lubricity, enabling
the fastener engineer to easily calculate the torque necessary for a given
bolt tension.   Unlike electroplated cadmium, fluorocarbon coatings applied
by the dip-spin process do not create environmental problems, nor do they
cause hydrogen embrittlement of high strength bolts.   Fluorocarbon-type
coatings can be applied over a zinc phosphate base, or over
ceramic-metallic coatings, or over a zinc-rich primer.
      A high-performance Sermaguard-type coating system for fasteners
consists of a two coat ceramic/metallic base, and a fluorocarbon -

*   Howard, R.M., and S.P. Sunday, The Corrosion Performance of Steel
          Self-Piercing Rivets When Used With Aluminum Components. SAE
          Report #831816, in SAE Special Publication P-136.
**   Registered Tradenames of products marketed by Sermatech
          International,Inc.
***   Mosser, Mark F. and B.G. McMordie, Evaluation of Aluminum/Ceramic
          Coatings on Fasteners to Eliminate Galvanic Corrosion.   SAE Paper
          #860112, in SAE Special Publication SP-649.
****   Willis, David P., Jr., Engineered Coatings for Fasteners, Page 42,
          May 1987, Products Finishing.

modified silicone topcoat. This system, with a total thickness of 1.3 mils., provides approximately 1000 hours salt spray resistance. This means adequate protection from atmospheric corrosion for the fastener. In addition, the parts being joined, if made from aluminum, are insulated from the galvanic corrosive influence of the fastener material.

Ceramic-metallic base fastener systems, topped off by the fluorocarbon-modified silicone topcoat, meet the requirements of General Motors specification GM 6164 M, Chrysler specification PS - 8059, and Ford specification EST - M21P9.

8.9.4 <u>Phosphate/Oil Coatings</u>.* Zinc phosphate may serve as a base for fastener-class fluorocarbon coatings. In this case, the phosphate is of the microcrystalline type, with a coating weight of 200-300 mg. per square foot.

Phosphate/oil coating systems consist of a heavy zinc phosphate layer impregnated with a polymeric oil emulsion. The oil emulsion contains a proprietary polymer which fills the network created by the phosphate coating. This process provides at least 168 hours of salt spray resistance, as required by General Motors Specification GM 6035 M. In one test of a phosphate/oil system, a number of parts showed 0.1 percent rust after 400 hours salt spray.

For military vehicles, it is doubtful that phosphate/oil coatings would be adequate for fasteners exposed to severely corrosive conditions. Since the Environmental Protection Agency (EPA) frowns on cadmium, the best bet for structural fasteners exposed to severe conditions is ceramic-metallic coating with fluorocarbon/silicone topcoat. If a fastener is not exposed to highly corrosive conditions, a good phosphate/polymeric oil system may be acceptable.

Other fastener coatings include nickel plating (for brass fasteners) and ion vapor deposited aluminum. Electrophoretic epoxy coatings are another coating option for fasteners, if the process does not introduce hydrogen embrittlement. High-strength fasteners may be electroplated with a low embrittlement, cadmium-titanium process in accordance with MIL-STD-1500.

8.10 <u>Temporary and Supplementary Corrosion - Preventive Agents</u>. A number of oils, greases, solvent-thinned compounds, and petrolatum-type materials have been devised as temporary corrosion-preventive coatings or preservatives.

The Department of Defense and its varied branches have issued numerous specifications to govern procurement of corrosion-preventive agents for aircraft engines, food handling equipment, machine components, small arms, artillery, ordnance items (i.e., mechanical time fuses), and so forth.

*   Willis, David P. Jr.. Op Cit. See also Roberts, J., <u>Meeting GM6035M</u>, Products Finishing, May 1987., and Smith, Noel A., <u>Advancements in Phosphate and Oil Coatings</u>, SAE Paper 831836, in SAE SP-136.

Many of these are identical to lubricating oils and greases, except for addition of corrosion inhibitors. Some are film-formers, leaving behind films of a specified hardness and thickness which act as barriers against corrosive environments. Film-forming agents include petrolatum, waxes, and asphaltic solids. These materials may be cutback (thinned) with solvents for ease of application.

Films formed by temporary protective agents typically are softer than the organic coatings that have been discussed up to this point. The idea is to form a flexible barrier that will not flake off, and will protect metal surfaces from corrosion for a reasonable time. One can remove these coatings by solvents or steam cleaning, when an item is to be put to use.

Temporary coatings based on plastics or rubber are designed so that, when they are no longer needed, the user can peel them off.

Oils may contain water displacing or fingerprint removing compounds. These oils are intended to protect items from corrosives characteristic of fingerprint oils, and otherwise to protect metal surfaces for limited periods of time.

Some of the many military specifications for temporary and supplementary corrosion-preventive agents are given below.

8.10.1 MIL-C-11796C (Corrosion-Preventive Compounds, Petrolatum, Hot Application) calls out a group of materials meeting the requirements of MIL-P-116H (Preservation, Methods of). There are four materials called out under MIL-C-11796: Classes 1, 1A, 2, and 3. Classes 1 and 1A are regular and non-slick (i.e., will not leave an oil slick on salt water), hard-film materials intended for protection of gun tubes and similar items stored outdoors. Classes 1 and 1A withstand outdoor exposure, and are also useful for protecting items with highly finished surfaces when stored indoors. Class 2 is a medium-hardness material for preservation of items stored outdoors in moderate climates (temperature at metal surface not to exceed 145F). It is also intended for packaging of automotive parts under conditions when the Class 3 material is too soft. Class 3 is intended for preservation of bearings and other items requiring ease of application and removal at normal temperatures.

All materials under MIL-C-11796C are applied by dipping or spraying. Class 3 is brushable at room temperatures. Application temperatures for spray or dip range from 150F for class 3 to 220F for class 1.

8.10.2 MIL-C-40084B calls for a water-emulsifiable, oil-type corrosion preventive compound. It consists of mineral oil with corrosion inhibitors. This material eliminates fire hazards associated with solvent-thinned corrosion-preventive agents. It forms a soft, thin film, offering best results when applied to zinc-phosphated surfaces. The user may apply this material by dipping, spraying, or brushing.

8.10.3 MIL-C-15074D calls for a corrosion-preventive fingerprint remover consisting of solvents and inhibitors. It is intended for removing fingerprint residues and suppression of corrosion caused by same.

8.10.4 <u>VV-L-800C</u> calls for a general purpose, water displacing, preservative lubricating oil. This material is intended for lubrication and protection against corrosion of small arms, automatic weapons, and other items that require a general-purpose, water displacing, low temperature preservative oil.

8.10.5 <u>MIL-C-16173D</u> calls out a group of five cold-application, solvent cutback corrosion preventive compounds, Grades 1 through 5. Grade 1 is a hard film (175F minimum flow point) material, Grade 2 is a soft film material, Grade 3 is a soft film, water-displacing compound, Grade 4 produces a transparent, non-tacky film and Grade 5 specifies a material so formulated as to be removable with low pressure steam. Application is by brushing, dipping, or spraying at normal room temperatures. The use of organic solvent for thinning is disadvantageous from the standpoint of air quality and fire hazards.

8.10.6 <u>MIL-L-21260C</u> is a preservative and break-in oil for internal combustion engines, available as SAE 10W, 30W, and 50W (NATO codes C-640, C-642, C-644). Use of this preservative oil is called for in various procedures (i.e., MIL-C-10062E) for preparing engines for storage and shipment to prevent internal corrosion.

8.10.7 <u>MIL-P-46002B</u> is a preservative oil formulated with a volatile corrosion inhibitor, intended for protection of closed systems.

8.10.8 <u>MIL-G-10924D</u> (Grease, Automotive and Artillery) is a long-standing military specification for a multipurpose grease, intended for lubrication and surface corrosion protection of automotive and artillery equipment. It corresponds to National Lubricating Grease Institute No. 2 consistency, and is usable in applications requiring a grease of that consistency with rust-preventive properties.

8.11 <u>Automotive Rustproofing Agents</u>. Automotive rustproofing agents are applied to sheet metal and structural members of already-assembled vehicles for supplementary corrosion protection. They are related to petrolatums and solvent-cutback corrosion preventive compounds such as those described above.

A corrosion-inhibiting material intended for post-assembly application should be formulated so as to be applicable by spraying. It should penetrate into crevices where corrosion often starts, provide uniform coverage, and develop a film which remains slightly "tacky", so as not to flake away from the surface being protected. The protective film should remain flexible, neither becoming brittle nor excessively soft, over the range of temperatures anticipated with reasonable certainty for the vehicle to be protected. A properly formulated rustproofing material adheres to metals and displaces moisture from the surface.

The current military specification for automotive rustproofing compounds is MIL-C-62218A, which calls out two solvent-dispersed, corrosion-preventive compounds. Type I is for new motor vehicles and trailers, while type II is for fielded equipment

MIL-C-62218A does not specify an exact material, saying only that it shall be a nonvolatile base material dispersed in a petroleum solvent. The latter must be free of benzene and halogenated hydrocarbons.

When sprayed on a vertical surface, Type I must form a dry film not less than 6 mils., and must not sag when wet. Type II must form a film 8+/-2 mils. thick, and, like Type I, must not sag. When tested in accordance with specified procedures, both types must exhibit 0.25 inches (6.35 mm) or more of creep. Type II must be able to creep when tested on mildly corroded test panels.

The compound, whether type I or II, must not be corrosive to copper. Also, while charring is acceptable, it must be self-extinguishing 15 seconds after removal from a flame source.

The material must be applicable by spraying at temperatures between 40 and 100F (5 to 37C). When dry, the coating film must be flexible down to -20F (-28.9C), and must not sag when exposed to temperatures up to 300F (149C). The coating must inhibit corrosion of test panels subjected to salt fog atmospheres. Type II must inhibit further corrosion when applied to pre-corroded test panels. Types I and II must also inhibit corrosion of panels immersed in salt water, and when test panels are exposed to cyclic environmental conditions.

Ingredients in commercial rustproofing agents vary, and tend to be proprietary. A typical rustproofing agent consists of mineral oil, petrolatum, alkyl stearate, aluminum stearate, and fatty material cut back with a mineral solvent. Commercial rustproofers apply this material by spraying, using licensed application tools and methods.

For military vehicles, MIL-R-46164C calls out application tools and procedures for applying rustproofing materials.

Temporary and supplementary corrosion-preventive agents are not a replacement for good design practices, galvanizing, and well-engineered organic protection systems. They do have their place in management of Army materiel. Solvent-removable, corrosion-inhibiting materials can prevent deterioration of otherwise vulnerable items stored in warehouses or outdoors, or during transportation. A field or depot commander might want to use rustproofing services to halt corrosion in vehicles already fielded, for supplementary corrosion protection in severe environments, or to protect equipment not originally designed with corrosion prevention in mind.

In 1981, the U.S. Army Tank-Automotive Command announced a new policy with regard to procurement of future tactical vehicles. The policy stated, in effect, that such vehicles were to be inherently rust free for total service life ranging from 15 to 25 years. The specific requirement is that such vehicles, by a combination of design techniques, materials selection, and manufacturing procedures shall prevent or minimize corrosion so that perforation of metallic areas requiring replacement of parts shall not occur.

The primary reason for this new policy is related to the difficulties encountered in achieving a satisfactory long-term result from commercial or mil-spec rustproofing. Such rustproofing requires the drilling of

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holes in body/cab/frame areas, a water wash to remove loose rust and dirt, a thorough drying of the vehicle, spraying a qualified rust-proofing compound through the holes provided, and then a final cleanup. It is almost impossible to obtain consistent high-quality workmanship on a mass production scale. The process also involves health, safety, and fire hazards. Finally, rustproofing requires periodic inspection, maintenance, and touch-up.

Studies conducted by the U.S. Army Tank-Automotive Command show that the life cycle costs of rustproofing, rust damage, and repair are greater than the potential costs of designing a vehicle to avoid corrosion without supplementary rustproofing agents.

8.12 Dry Film Lubricants and Corrosion.

When using a dry-film lubricant, remember this commandment: NO GRAPHITE.

Graphite is cathodic to all metals, exept gold and platinum. In the past, graphite has been used in solid-film lubricants such as MIL-L-8937.

MIL-L-46010B calls out graphite-free, corrosion-inhibiting, bonded solid film lubricants. Type I is cured at 150C (302F), while Type II requires 204C (about 400F) for curing. Both types, when applied to properly prepared surfaces and subjected to their respective curing temperatures, form films within 60 minutes.

Solid film lubricants meeting this specification, when applied to phosphated steel at 0.0005 inch (0.013mm) thickness, protect against corrosion for up to two years in outdoor storage, or four years in indoor storage. A 1-mil coating provides up to 4 years corrosion protection in outdoor storage.

Applications include lubrication under conditions where oils and greases are difficult to apply or retain, mechanisms operated infrequently or 'lubricated for life', or bearings involving sliding motion. MIL-L-46010B solid lubricants are not recommended when the material cannot tolerate the required curing cycle, nor for rolling element bearings, nor for equipment handling oxygen (especially liquid oxygen).

MIL-L-46010B solid film lubricants must be used within 1 year after the date of manufacture. They are suitable for aluminum, copper, magnesium, steels, titanium, stainless steels, and alloy systems based on the aforementioned metals. The appendix to MIL-L-46010B provides inrtructions for applying these lubricants to various materials.

8.13 Rust Converters and Rusted Surface Coating.

Rust Converters (also known as rust transformers) are surface pretreating agents (or pretreatment/primers) intended for application to rusted surfaces. The basic claim made for these preparations is that they transform rust to a form that can serve as a base for subsequent organic coating.

The most promising type of rust transformer is based on tannic acid, a complex organic acid derived from various forms of vegetation. A typical rust converter consists of tannic acid, hypophosphorous acid, and

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isopropyl alcohol.* When this preparation acts on a rusted ferrous surface, the rust is converted to a ferric salt, which in turn reacts with the tannic acid to form an organometallic iron tannate. This is a more satisfactory paint base than ordinary rust.

A number of tannic acid-based rust converters have been sold under such tradenames as Cortex 420, Neutra Rust, Extend, RCP, and Chesterton Rust Transformer. Some of these products combine the tannic acid rust converter with a latex-type primer. When one applies this combination to a rusted ferrous surface, the result will be a primed surface that can be topcoated after the rust converter/primer has reacted and dried.

Other commercial rust converters consist of the tannic acid system alone, without a built-in primer. This type of material is intended for application to a rusted surface as a pretreatment. The preparation is given time to react and dry, after which the surface is ready for priming and topcoating.

A number of commercial rust converters were tested in Puerto Rico under the direction of the Army Material Command.** Based on the results of 1 year of testing, the team conducting the test judged only two preparations to be worth further study. Generally, painting over rusted surfaces is not recommended. If rust transformers are to be used, they should be the type with out a built-in latex primer. The technician should brush away loose rust, clean and dry the surface, and then apply the rust converter.

After the rust converter reacts and dries, the converted surface should then be primed with a properly formulated primer. The primer should be based on a low viscosity binder such as fish-oil alkyd.*** The solvents should be slow-evaporating, so the viscosity of the whole primer will remain low until it penetrates through the neutralized rust layer. One of the advantages of fish-oil for this purpose is that its own viscosity is low; furthermore, it is slow drying, therefore a slow-evaporating solvent can be used with it.**** Water-based latex primers are not good for painting rusted surfaces, because the latex particles may be filtered out by the rust layer, allowing only water to get through the rust to the substrate.

After the rust layer has been neutralized and primed, one may then apply a supplementary primer and topcoat.

8.14 Water-Displacing Touch-Up Paint. The U.S. Navy has developed a water-displacing, touchup paint that can be applied to bare metal

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*   Information provided by Mr. J. Menke, AMCCOM, Rock Island.
**   Warshawsky, I., memorandum to Director, TATD (AMSTA-R), 21 Feb. 1986, on trip to Puerto Rico National Guard, 10 - 13 Feb. 1986.
***   A rusty metal primer commonly sold in hardware stores uses a fish-oil alkyd binder. This is claimed to penetrate through a rust layer, surrounding rust particles, to reach the substrate.
****   Wicks, Z.W., Jr., Principles of Formulating Corrosion Protective Coatings, p.29, in Corrosion Control by Coatings, H. Leidheiser, Jr., editor. Science Press, Princeton, 1979.

surfaces for temporary protection against corrosion. The original purpose
of this coating material is prevention of corrosion of carrier-based
aircraft in areas where their regular organic coatings are chipped or
cracked. This product was developed at the U.S. Navy Aeronautical
Material Laboratory (AML) and has been distributed via Department of
Defense channels under the same 'Amlguard'.

Material called out under MIL-C-85054A (AS) (Corrosion Preventive
Compound, Water Displacing, Clear (Amlguard)) displaces moisture or salt
water, and leaves a clear, corrosion-preventive film. It is intended for
use on all metals, and its applicability from pressurized spray cans makes
it particularly suited for service use.

Amlguard, as specified under MIL-C-85054A, consists of barium
petroleum sulfonate, alkyl ammonium organic phosphate, silicone and
silicone/alkyd resins, and non-photochemically reactive solvents.

Water-displacing, touch up paint does not conform to CARC standards,
therefore, one should not specify it as an original equipment
manufacturer's finish. It could come in handy, however, for the
maintenance-conscious field commander who wants to limit corrosion on the
surfaces of combat and tactical vehicles (or other items) in locations
where the authorized paint finish has been violated by various accidental
impacts or abrasions. The user cleans off the surface, and sprays on two
uniform coats, waiting a half-hour between the first and second coats.

CHAPTER 9
ALUMINUM

Aluminum and its alloys are generally less susceptible to corrosion than mild steel. There are many circumstances where one can expose aluminum to the elements without the extensive corrosion (rusting) that ferrous metals suffer under the same conditions. Aluminum is not corrosion-free, however. The engineer/designer must know the corrosion characteristics of aluminum and its alloys, and of aluminum surface treatments and coatings. Only then can one realize the benefits of aluminum in engineering design.

The corrosion of aluminum and its alloys is governed by two basic phenomena:

1) Aluminum is more active (less noble) than most other metals. This means that when in contact with ferrous metals (or, worse yet, copper and its alloys), aluminum and its alloys corrode sacrificially when an electrolyte is present.

2) Aluminum forms an adherent oxide layer when exposed to air. This layer, like the passive oxide layer on stainless steels, greatly reduces uniform corrosion, characteristic of the kind one encounters with mild steel. Like stainless steels, aluminum and its alloys are prone to localized corrosion including pitting, stress-corrosion cracking, and intergranular corrosion. The surface oxide layer on aluminum is vulnerable to aggressive ions such as chloride.

9.1 Specific Corrosion Problems.

9.1.1 Galvanic and crevice corrosion. When using aluminum alloys in structures where steel is also present, one must be aware of galvanic corrosion. If there are no dissimilar metals, aluminum can still suffer crevice corrosion. The designer must use proper joint design techniques, as discussed in Chapter 4. Use a sealant, such as polysulfide, between faying surfaces and around fastener's holes. Aluminum components should be drilled, milled, or otherwise machined, before applying protective coating systems. Then, apply sealing compound and fasten. For joints requiring disassembly at some later time, use a temporary corrosion preventive compound compatible with aluminum and the metal to which it is fastened.

Welded construction must be treated differently, because welding heat would burn off previously applied coatings.

Figure 70 illustrates the consequences of corrosion in an improperly constructed aluminum joint.* On the left side, corrosion between the

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* Aluminum, Vol. 1, Chapter 7 (Resistance to Corrosion and Stress Corrosion). American Society for Metals, 1967. page 218
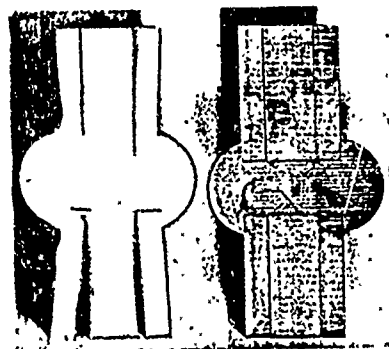
Fig. 70. CONSEQUENCES OF IMPROPER ALUMINUM
JOINT DESIGN (left), ALUMINUM JOINT
PROPERLY PROTECTED (Right).

faying surfaces generated enough pressure to push the plates apart. The
joint on the right was prepared by applying one coat of aluminum paint to
the surfaces before fastening. All surfaces should be coated, and this
definitely includes steel surfaces in contact with aluminum.* Fasteners
should be properly treated, i.e., with cadmium, or other metal plate
galvanically compatible with aluminum. Alternatively, one can use
coatings such as ceramic-metallic. The designer should remember that
exfoliation (see below) has been known to start in the vicinity of
fasteners, due to crevice and galvanic effects.

Aluminum hinges on electronic equipment shelters have been known to
seize due to galvanic corrosion caused by a stainless steel pin**. Here
is another lesson in the importance of providing a suitable coating of
some form on cathodic metals in contact with aluminum. For hinges, a
corrosion-inhibiting lubricant, compatible with both aluminum and the pin,
is also desirable. The pin should not fit in the hinge too tightly, lest
corrosion products cause jamming.

Graphite should not come into contact with aluminum. If an aluminum
component is to be joined to a graphite fiber-reinforced composite
structure, they must be electrically isolated from one another. (For that

*   Painting only aluminum, when in contact with a cathodic metal, will
        cause a large cathode/small anode situation at paint coating
        defects.
**   Unruh, Kenneth S., Corrosion of Aluminum Hinges on the Electronics
        Shop, Shelter Mounted, Avionics, AN/ASM-147B During Sea Transport.
        USA AMSAA, Aberdeen Proving Grounds, Maryland, March 1986.

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matter, be wary of possible galvanic corrosion whenever any structural metal is joined to graphite fiber composite material.)*

Finally, one must not mark on an aluminum surface with a graphite pencil. Use only those marking instruments specifically authorized for aluminum surfaces.

9.1.2 Intergranular attack, Stress-Corrosion Cracking, Exfoliation.
Aluminum alloys are susceptible, in varying degrees, to intergranular attack, stress-corrosion cracking, and exfoliation. These phenomena are particularly troublesome in high-strength aluminum alloys whose metallurgical structures contain dispersed phases.

An example is the Al-Cu system, i.e., the 2000-series alloys. Solution heat treatment followed by artificial aging results in $CuAl_2$ precipitates at grain boundaries. These precipitates are good for mechanical strength, but they also cause unwanted galvanic effects.

Recall that with stainless steels, improper heat treatment causes depletion of chromium from grain boundaries, because of CrC precipitate formation. In copper-containing aluminum alloys, the heat treatments needed for maximum strength cause depletion of copper from grain boundaries adjacent to $CuAl_2$ precipitates. This sensitizes the alloy to stress-corrosion cracking and exfoliation, because a copper-depleted grain boundary is anodic to the microstructure as a whole.

In 5000-series aluminum alloys, magnesium is the most important alloying constituent. Magnesium forms a solid solution in aluminum up to a limit of approximately 3 weight percent. If the percentage of magnesium in an aluminum alloy exceeds the solubility limit, Al_3Mg_2 forms as a second phase. This precipitated phase is anodic to adjacent grains, and will corrode preferentially when exposed to an electrolyte. If certain Al-Mg alloys are heat-treated, intentionally or not, so as to cause a continuous network of Al_3Mg_2 at grain boundaries, an item made from such an alloy will be susceptible to preferential grain boundary attack. This may lead to stress-corrosion cracking or exfoliation.

9.1.3 Stress-Corrosion Cracking (S.C.C.) has long been an important
consideration in the design of aircraft. In the Army, one is concerned about S.C.C. in helicopters and in armored vehicles using aluminum alloy armor. In some cases, strength has had to be sacrificed to attain the desired resistance to S.C.C..

The aluminum alloy systems prone to S.C.C. include Al-Cu (the 2000 series), Al-Zn-Mg and Al-Zn-Mg-Cu (the 7000 series), Al-Mg (5000 series), and Al-Mg-Si (6000 series). The latter two alloy systems may suffer S.C.C. when the magnesium content is above 3%, or when high silicon contents are present in the Al-Mg-Si system. The Al-Mn alloys (3000

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* Danford, M.D., and A.H. Higgins. Galvanic Coupling Between D6AC Steel, 6061-T6 Aluminum, Inconel 718, and Graphite-Epoxy Composite Material: Corrosion Occurrence and Prevention. NASA Technical Paper #2236, December 1983.

series), Al-Si (4000 series), and Al-Mg (Mg content < 3%) do not
experience stress-corrosion cracking.

Metallurgical condition brought about by heat treatment and cold work
has a significant bearing on whether or not S.C.C. will occur. For
example, alloy 7075 (a high-strength alloy used in aerospace applications)
is susceptible to S.C.C. when used in thick sections in the T6 (solution
heat treated and artificially aged) temper. The same alloy in the T73
temper (solution heat treated, followed by overaging) exhibits improved
resistance to S.C.C. relative to the T6 temper, with an accompanying
sacrifice in strength.

Susceptibility of aluminum alloys to S.C.C. also varies with grain
orientation relative to the direction of applied tensile stress. Refer to
Figure 71. If tensile test specimens are machined from a thick slab of
rolled high strength alloy such as 7075-T6 or 2024-T4, specimens in which
tensile stress is applied in the short transverse direction will be most
susceptible to S.C.C. Specimens machined so that the tensile stress is
along the long traverse axis are less susceptible to S.C.C.. Longitudinal
test specimens are most resistant to stress corrosion cracking. Referring
to Figure 72*, one can see that for typical high strength alloy-temper
combinations, stress-corrosion cracking occurs at a much lower stress
level when applied in the short transverse direction than in either of the
two other major directions. When using rolled aluminum alloys, avoid
exposing the short transverse direction to combinations of tensile stress
and corrosive influences.
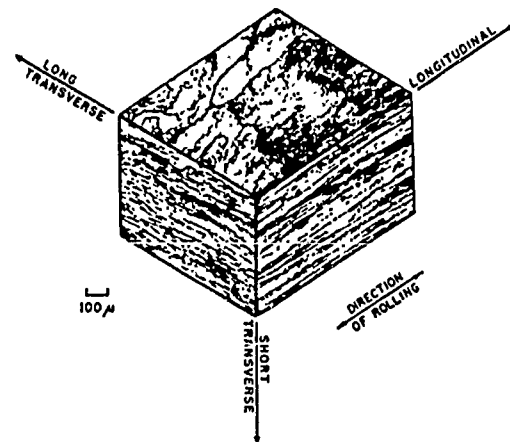
Fig. 71. ROLLED ALUMINUM PLATE GRAIN STRUCTURE

Thin sheet does not exhibit directionality in susceptibility to
S.C.C.. Castings are supposed to be isotropic, yet the parting plane or
seam may expose a highly S.C.C.-susceptible transverse grain structure.

*   Lifka, B.W., et al, Exfoliation and Stress-Corrosion Characteristics
     of High Strength Heat Treatable Aluminum Alloy Plate.

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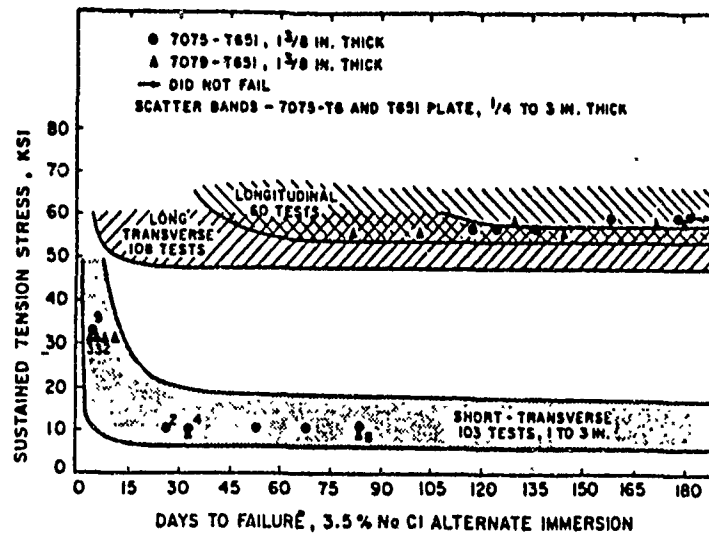
Fig. 72. SENSITIVITY TO SCC AS A FUNCTION OF
GRAIN DIRECTION

A number of publications list corrosion and stress-corrosion
susceptibility of various aluminum alloy-temper combinations. The
engineer-designer should refer to such publications as ATSM G64-85
(Standard Classification of the Resistance to Stress-Corrosion Cracking of
High Strength Aluminum Alloys), Metals Handbook (Corrosion Resistance of
Aluminum and Aluminum Alloys, Vol. 2, 9th ed., pages 204-235), the SAE
Handbook (published annually), and MIL-STD-1568 (Materials and Processes
for Corrosion Prevention and Control in Aerospace Weapons Systems). See
also MIL-HDBK-5E, Metallic Materials and Elements for Aerospace Vehicle
Structures: This handbook presents tables showing maximum stresses at
which test specimens will not fail when subjected to the ASTM G47
alternate immersion stress-corrosion test. Such stress values are not to
be used for design calculations, but are a useful comparison of S.C.C.
resistance among various aluminum alloys. Published stress-corrosion
resistance ratings are based on a combination of standardized tests and
service experience. In the SAE Handbook, a rating of A means no known
instance of failure in service or in laboratory tests. A "B" rating is as
above, except that laboratory tests have revealed some instances of
failure in short transverse specimens.

Specific material choice recommendations are as follows:

o   Aluminum-magnesium alloys with more than 3% mg. should not be used
    under high constant applied stress at temperatures in excess of
    150F, because of the possibility of Al-Mg precipitates forming a
    network at grain boundaries. Alloys such as 5083, 5086, and 5456
    should not be used in the H30 series tempers because they can
    become vulnerable to S.C.C. (par. 3.1.2.3.1, MIL-HDBK-5E).

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o The U.S. Army Missile Command (MICOM)* does not allow 2024-T3 or
   T4, or 7075-T6 in new systems under its jurisdiction, recommending
   instead 2024 in the T8 series tempers (i.e., T851), 7075-T73, the
   5000 or 6000 series, or 7050 series. The U.S. Air Force does not
   allow 7075-T6 in forgings and milled products.
o A few high strength aluminum alloys have shown excellent resistance
   to stress-corrosion cracking, even in the vulnerable short
   transverse direction. These are 2020-T651, 2024-T851, 2219-T851,
   7075-T7351**, and 5454-H34 (N. Kackley, MTL).

   Prevention of S.C.C. via design. Aside from proper material
selection, one can avoid stress-corrosion cracking by reducing (or
eliminating) tensile stresses, or by isolating vulnerable areas from the
environment. MIL-HDBK-5 recommends against practices such as press or
shrink fits, taper pins, clevis joints in which tightening of the bolt
imposes a bending load on the female lugs, and assembly operations which
impose sustained surface tensile stresses (especially if in the short
transverse direction) when using materials 2014-T451, -T4, -T6, -T651,
T652; 2024-T3, -T351, -T4, and 7075-T6, -T651, -T652.
   Shot peening is required by MIL-STD-1568A, par. 5.4.3.1.4, on critical
surfaces of forgings, machined plate, and extrusions, after final
machining and heat treatment. This places surface layers in a residual
compression state, which eliminates one leg of the S.C.C. triangle
(tensile stress).
   In parts not stress-relieved, MIL-STD-1568A forbids machining away
more than 0.150 inches per side, because doing so may expose vulnerable
(short transverse) grain structure in a tensile residual stress condition.
   The above two requirements are waived if the material demonstrates a
stress-corrosion resistance not less than 25 ksi (173 megapascals) in the
short transverse direction when tested in accordance with a defined test
procedure.
   Coating a vulnerable area can be effective in preventing S.C.C by
isolating the short transverse grain structure from corrosive agents.
High-strength aluminum alloy 7039, once widely used as an armor material,
had experienced S.C.C. in the vicinity of welds due to residual tensile
stresses acting on regions of short transverse grain structure exposed at
the edges of rolled alloy armor slabs. An effective, though expensive,
solution was to 'butter' the edges with 5356 alloy. This procedure
created compressive stresses at the edges, and also sealed the

*   Cobb, B.J., New Systems with CPC Flavor. Proceedings of Conference
    on Corrosion Prevention and Control, Williamsburg, VA, 29-30 April
    1986.
** Lifka, B.J., et al, Exfoliation and Stress-Corrosion of High
    Strength, Heat Treatable Aluminum Alloy Plate. (Reprinted with
    permission from Corrosion, November 1967, in Prevention of Material
    Deterioration: Corrosion Control Course. Published by Logistics
    Engineering Directorate, U.S. Army Armament Material Readiness
    Command, Rock Island.

alloy 7039 surface with a more stress-corrosion-resistant material*.
Attempts were made to use sprayed metal coatings to protect the edges;
however, shot or brush peening proved more effective.

Aluminum armored vehicles are currently being constructed using
aluminum alloy 5083, which is less prone to S.C.C. than 7039. The
designer should be aware however, that shot peening (or, brush peening)
is available as a means of relieving residual tensile stresses at
vulnerable short transverse surfaces. Also, weld buttering, though time
consuming and costly, is nonetheless also available as an option.

In recent years, new aluminum alloys have been developed as options
for armored vehicle design. A cast alloy, A206-T4, meets S.C.C.
requirements when tested in accordance with prescribed test procedures**.
This particular cast alloy-temper combination, is not as good as
high-strength rolled aluminum alloy from a ballistics standpoint. It is,
however, less disadvantageous than other aluminum cast alloys that were
studied.

Aluminum alloy 2519-T87 was recently developed as an alternative to
5083-H131 and 7039-T64. This alloy offers tensile and ballistic
properties equivalent to 7039, without the latter's susceptibility to
stress-corrosion cracking. Alloy 2519-T87 needs additional developmental
work, however, becaus experimental weldments do not withstand as high a
ballistic shock as is required by MIL-STD-1946 (Welding of Aluminum Alloy
Armor).***

If the engineer must use alloys such as 2024-T4 or 7075-T6, rapid
quench rates are desirable, as both yield strength and corrosion
resistance increase with the rate of quenching from solution heat
treatment temperature. Unfortunately, high quench rates are not possible
for thick sections. This is why 2000 series alloys are usually overaged
to the T8 series tempers (i.e., 2219-T851), and why 7000 series alloys are
used in T7 series tempers, i.e., 7075-T73.

9.1.4 Exfoliation. This occurs in aluminum alloys with an elongated
grain structure. The alloys most susceptible to exfoliation are those
based on the Al-Cu, Al-Zn-Mg-Cu, and Al-Mg systems. Metallurgical
condition also influences the degree of exfoliation susceptibility.

Exfoliation has occurred in aircraft structures in the vicinity of
fasteners. Corrosive agents enter the crevice between fastener and
surrounding aluminum, and attack the latter along elongated grain
boundaries. This results in delamination, caused by pressure exerted by
corrosion products beneath the surface.

*   Gilliland, H. Manufacturing Methods and Technology: Metal Arc Spray
        Processing. USATACOM R.D. & E. Center, Warren, MI, February 1986.
**   Hare, R.B., and R.L. Malik., Cast Aluminum Components: Phase 1,
        Volume 1. USATACOM R.D. & E. Center, Warren, MI, February 1933.
***   Wolfe, Thomas D. and Steven A. Gedeon. Weldability of 2219-T851 and
        2519-T87 Aluminum Armor Alloys for use in Army Vehicle Systems.
        Army Materials Technology Laboratory Repcrt #MTL TR 87-28,
        MA, June 1987.

As with stress-corrosion cracking, high strength alloy-temper combinations such as 7075-T6 are particularly vulnerable to exfoliation. Accordingly, the designer must prescribe overageing-type heat treatments when using high strength aluminum alloys under conditions where exfoliation is likely. If this form of corrosion is more of a problem than S.C.C. in a particular application, the designer might want to use 7000-series alloys in the T76 temper, which is stronger than the T73 temper while possessing elevated resistance to exfoliation.

The 5000-series alloys are susceptible to exfoliation (and S.C.C.) when a continuous network of Al_3Mg_2 precipitates forms at grain boundaries. Accordingly, corrosion resistance of this alloy series can be improved by thermal-mechanical treatments which cause precipitates to form within the grains, rather than at grain boundaries exclusively. The H116 and H117 tempers have been developed for exfoliation resistance in 5000-series alloys (N. Kackley, MTL).

If exfoliation occurs in threaded or riveted joints, plated fasteners can help allieviate the problem. Sealers such as elastomeric polysulfide compounds (per MIL-S-81733C) have been used successfully in aircraft structures. Metallic coatings, such as sprayed aluminum or zinc, on affected areas (edges of plates, insides of fastener holes) are also helpful. Fastener holes should be primed with epoxy primer (i.e., MIL-P-23377) if the fastener must be removable.

9.2   Coating Systems for Aluminum.

9.2.1   Conversion Coatings. Aluminum surfaces must have some kind of pretreatment for organic coatings to adhere successfully. The classical prepaint treatments for aluminum include amorphous chromate, amorphous phosphate (chromium phosphate), zinc phosphate, and alkaline oxides.

Chromium chromate (amorphous chromate) produces excellent results as a paint base. Even when used alone, amorphous chromate provides excellent resistance to salt spray. Furthermore, this type of conversion coating is electrically conductive, making it useful for electronic equipment chassis. It is also good for applications where electrical conductivity between aluminum surfaces is desired for EMI shielding.

Chromium phosphate and chromium chromate meet the requirements of MIL-C-5541C (Chemical Conversion Coatings on Aluminum and Aluminum Alloys), which calls for 168 hours salt spray resistance. The former meets the requirements of MIL-C-5541C , class 1A, while the latter, because of its electrical conductivity, meets the requirements of MIL-C-5541C, Class 3.

While chromate conversion coatings are excellent paint bases for aluminum, they unfortunately create hazardous waste disposal problems. Accordingly, efforts have been made to find non-toxic, non-environmentally hazardous substitutes.

The FMC Corporation has investigated a number of aluminum alloy pretreatment systems, in their quest for a system that would greatly reduce waste treatment costs, and prove equivalent, when used with a

primer coating, to chromate pretreatments.*

A good finishing system for aluminum must begin with cleaning and deoxidizing the surface. No paint will adhere well to non-deoxidized aluminum, no matter how well it is cleaned. The reason is that the oxide coating naturally occurring on an aluminum surface interferes with adhesion. One might reasonably ask: If an aluminum surface is thoroughly cleaned and deoxidized, will a primer coating adhere without a conversion coating?

The FMC program showed that if water-reducible epoxy primer, MIL-P-53030, is applied to aluminum surfaces immediately following cleaning and deoxidizing, it will adhere well without a conversion coating.

Another alternative to MIL-C-5541C chromate conversion coatings is the wash primer (DOD-P-15328D) pretreatment system. This is a two part system which, when mixed, consists of phosphoric acid, polyvinyl butyral, zinc tetroxychromate pigment, and solvents (isopropanol, butanol, water). The phosphoric acid serves as an etching agent to assure adhesion of the polyvinyl butyral binder. The pigment is similar to the classical zinc chromate pigment traditionally used in primers for aluminum.

Wash primers work well. Tests conducted by FMC demonstrated that when organic coatings are applied over wash primer per DOD-P-15328, they adhere just as well as when applied over a MIL-C-5541C, class IA conversion coating such as Alodine 1200s (R)** Unfortunately, the wash primer system has disadvantages. It uses large amounts of solvents, creating an air quality compliance problem. Film thickness is critical, because excess primer may leave unreacted phosphoric acid in the coating. Finally, the wash primer system uses chromate pigments. Though W.P. does not generate large volumes of liquid waste, the chromate pigment is still a health hazard to workers. If applied by spraying, any overspray would have to be treated as hazardous waste, as would unused material (Wash primer, once mixed, has limited pot life).

'Dry in place' or 'no-rinse' chromate conversion coatings have been devised in an attempt to deal with the hazardous waste disposal problem of traditional chromate treatments. They do indeed produce less waste effluent, and eliminate final rinse steps. Such systems lend themselves well to coil-coating or for treating simple shapes. However, they are not so good when it comes to complex items such as aluminum armored vehicle hulls. No-rinse chromate systems are a viable option for parts which drain easily.

Modified zinc phosphate treatments, described earlier, will form a phosphate coating on aluminum. Unfortunately, they do not offer the performance one can expect from anodizing, or from amorphous chromates per MIL-C-5541C. Furthermore, the waste effluent from modified zinc phosphate baths are not free of waste disposal problems. Unless one is treating a

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*   Thompson, Sharon, <u>Prepaint Cleaning</u>. USATACOM R.D. & E. Center, Warren, MI, October 1985.
** Trademark of Amchem Products, Inc.

Mixed assembly of steel and aluminum, it is best to use zinc phosphate for pretreatment of steel, and chromates (or something equivalent) for aluminum.

Another possible conversion coating for aluminum is aluminum hydroxyoxide, a variation of the old 'boehmite' oxide coatings. The process consists of exposing an aluminum surface, coated first with a chemical reagent, to an oxidizing environment containing steam. The reagent provides nucleation sites for growth of aluminum hydroxyoxide crystals. This process is used commercially and results in a good paint base.

Disadvantages are as follows: If the surface is damaged, the oxide layer offers no sacrificial protection. A chromate-pigment containing primer has to be used for best results. Finally, the FMC study did not find it adaptable for production.

Finally, there are immersion-type, non-chromate conversion coating systems for aluminum. U.S. Patent 3,964,936 (Das, N.) describes a treatment bath consisting of boric acid, a source of fluoride, a source of zirconium, and nitric acid for Ph adjustment. This system forms a fluorooxy-zirconium complex on an aluminum surface. It has met the requirements of the aluminum container industry. However, it does not meet the requirements of MIL-C-5541.

According to FMC, one non-chromate system works satisfactorily on aluminum alloy 5083. This system is as follows:

1. Parco No. 2351 alkaline cleaner
2. Hot water rinse
3. Parco No. 2356 deoxidizer
4. Hot water rinse
5. Parker TD1325 non-chromate conversion coating, consisting of compounds of titanium, fluoride, zirconium, nitric acid, and phosphate.
6. Cold rinse
7. Polymeric sealer
8. Cold rinse
9. prime and paint

This treatment, excluding primer (i.e. up to and including the eighth step), meets the 168 hour salt spray requirement when applied to alloy 5083. Both this treatment and Alodine 1200s, when applied to 5083/7039 welded panels, suffer corrosion near the weld after 168 hours salt spray.

While Alodine 1200s passes the 168 hour salt spray test when applied to aluminum alloys 2024, 6061, and 7075, the aforementioned non-chromate treatment does not.

When aluminum panels were treated with the non-chromate conversion coating described above and then primed with MIL-P-53030 epoxy primer, the following results were noted:

1000 Hour Salt Spray:

5083 alloy:	passed
5083/7039 Welded panels:	small amount of corrosion on weld spatter
2024:	passed
6061:	passed
7075:	failed
dry & wet adhesion:	passed
120 lb. reverse impact:	passed

In contrast, the Alodine 1200s process, when similarly followed by the primer, passed all tests, with all alloys.

One can see that there is the technical possibility of achieving reasonable results with a non-chromate conversion coating if the aluminum surface is thoroughly cleaned and deoxidized, and if the conversion coating is followed by a good primer. However, it doesn't work on some alloys (High-strength, copper-bearing alloys are known to be more difficult to finish than other aluminum alloys), and its performance in the field has not been demonstrated. Ultimate protection of aluminum in tactical and combat vehicles still requires chromates, in the conversion coating if not also the primer pigment as well.

It should be noted that the current chromate conversion coatings, i.e., Alodine, also require thorough metal cleaning and deoxidizing for best results.

9.2.2 <u>Anodizing</u>. Oxide films on aluminum and its alloys are formed by natural processes. These films do not flake and crumble like ferrous oxide films, and hence offer protection to underlying metal. Normally, the naturally occurring oxide film on an aluminum surface is approximately 100 angstroms (.00010 mm.) thick.

Because Al_2O_3 is a wear-and corrosion-resisting substance, the deliberate formation of this oxide in films of greater than the naturally occurring thickness, is desired in some applications. Various processes do in fact accomplish this. All of them use an electrolyte and an electrical potential to form an artificial aluminum oxide coating. Because the article to be treated is made the anode in an electrochemical cell, these processes are known as anodizing.

Aluminum items are anodized to improve corrosion resistance, provide a colored film for decorative purposes, or to develop a hard surface for wear resistance. Oxide films developed by anodizing do not conduct electricity.

Early anodizing processes used chromic acid solutions as electrolytes. Subsequently, sulfuric and oxalic acid electrolytes were introduced. Boric and phosphoric acids are also usable as anodizing electrolytes. The chromic acid process uses 40 grams CrO_3 per liter of solution, with a 35C (95F) bath temperature. The item to be treated is

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made the anode and subjected to 40 volts for approximately 30 minutes. The resulting oxide film is 0.0025 to 0.0050 mm. thick.

An oxalic acid solution at 2 to 6% concentration, at a temperature of 15 to 30C is the basis for the "Eloxal" process. Oxide layers formed on aluminum by this process are up to 0.006 mm. thick, and are golden yellow in color.

The most common media for anodizing is sulfuric acid. H_2SO_4 is very corrosive, unlike chromic acid which in fact is an inhibitor. This means that care should be taken not to allow sulfuric acid solutions to become trapped in crevices of parts being anodized. However, the "Alumilite (R)" process has the advantage of lower cost, higher speed, and the possibility of a range of properties, with a variety of aluminum alloys. Typically, sulfuric acid anodizing is carried out at low temperatures (20 - 25C or approximately "room" temperature). H_2SO_4 anodizing has another advantage: There are no chromium ions to cause water pollution.

"Hard" anodizing refers to processes whereby the oxide film is thicker than usual. Such films range from 0.001 inch (0.025 mm.) upwards.

Hard anodic coatings form in sulfuric acid anodizing cells with some of the parameters modified. The current density (amperes per square foot of surface area anodized) is higher than in conventional anodizing. The bath temperature is lowered from 70F used in conventional anodizing to 50F. The Alumilite hard-coating solution uses 12% (by weight) H_2SO_4, along with one weight percent oxalic acid. The Martin Hard Coat (MHC) process uses 15% H_2SO_4 saturated with carbon dioxide.

Oxide films developed by hard anodizing processes are not actually harder, but are thicker and denser than conventional anodic coatings. They exhibit good corrosion and wear resistance. Unsealed coatings hold lubricants well.

Anodic coatings must be sealed for maximum resistance to corrosion, or when it is necessary to have resistance to staining. Hard anodic coatings, when used for abrasion resistance, are not sealed. One may seal anodic coatings by immersing an anodized coating in boiling water for 10 to 30 minutes. Dichromate sealing solutions produce the best corrosion resistance.

Anodizing is applicable to a variety of wrought and cast aluminum alloys. Pure aluminum is the easiest to anodize. With copper-bearing alloys such as 2024 (4.5% Cu) or 7075 (1.6% Cu), it is more difficult to form a thick anodic coating, and the film will offer less resistance to corrosion.

A potential disadvantage of anodizing is reduced fatigue strength.

Recently, Lockheed developed a process whereby anodized aluminum is sealed with polyurethane resin.* This process may be applicable to aluminum components of tactical and combat vehicles. The seal-priming process may be augmented by topcoating.

* Aviation Week & Space Technology, pg. 71, May 11, 1987.

9.2.3 Alcladding and Aluminum Spraying. Pure aluminum possesses excellent atmospheric corrosion resistance, while various aluminum alloys (particularly high strength, copper-bearing alloys) tend to suffer in this respect. Accordingly, high-strength alloys should be used in 'alclad' form. Alclad aluminum alloys, available in sheet, plate, and tubular forms, consist of a high-strength aluminum alloy core clad with unalloyed aluminum, or selected aluminum alloy such as Al - 1% Zn. The idea is to provide a corrosion-sensitive, high-strength aluminum alloy with a coating of Al or Al alloy which resists atmospheric corrosion, yet is anodic to the base material. This system affords sacrificial protection to the base material, and is similar in this regard to zinc coatings on ferrous metals.

Alclad plate should be considered for armored vehicles. An advantage of alclad products is, they are easier to conversion-coat than bare, Al-Cu or other high-strength alloys. This is very important if chromate systems cannot be used.

Aluminum armored vehicle hulls can be coated with pure aluminum, zinc, or Zn-Al alloys, by wire spraying. This is another option for aluminum hulls, turrets, and other components.

9.2.4 Organic Coatings. Traditionally, aluminum surfaces have been primed with zinc or strontium chromate pigmented primers. Red lead is not a corrosion-inhibiting pigment for aluminum, and is therefore not to be used for this purpose.

A classic primer specification for aluminum is TT-P-1757. This specification calls for a zinc chromate pigmented, oil-modified phenol/formaldehyde-alkyd primer coating.

Later, epoxy primers were developed. Typical epoxy primers were discussed in section 8.3.

Today, primer specifications have changed, because of VOC and chromate problems. A water-reducible, lead and chromate-free epoxy primer for aluminum is called out under MIL-P-53030. This is a two-component system which meets VOC (water not yet added) limits not more stringent than 2.8 lb. per gallon, or 340 gram/liter. Storage stability is 1 year for both components, and pot life, once mixed, is no less than 6 hours at 73F.

If the elimination of chromates from both conversion coatings and primers is stringently enforced, adequate protection of aluminum could prove difficult. Enforcement of quality controls will be more important than ever. Hopefully, adequate coating systems will be developed that will meet the needs of protecting our environment. Hopefully, too, methods of safely handling chromates will be developed so this most effective method of protecting aluminum from corrosion can still be used where required.

Many topcoating materials used for protecting steel can also be applied to aluminum. These materials include:

o   Alkyds
o   Acrylics
o   Vinyls
o   Epoxies
o   Urethanes

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A good system for aluminum is epoxy primer, followed by polyurethane topcoat.

. Electrophoretic coatings are applicable to aluminum, as are powder coatings. Be aware, however, that these materials require elevated temperature baking. Make sure that the alloy-temper system in question can take the baking temperature.

References: 1. Binger, W.W., et al. <u>Resistance to Corrosion and Stress Corrosion</u> (<u>Aluminum</u>, Volume I, Chapter 7, edited by Kent R. Van Horn. American Society for Metals, Metals Park, Ohio, 1967.

2. Burns, R.M. and Bradley, W.W., <u>Protective Coatings for Metals</u>, 3rd edition, pages 588-604. Reinhold Publishing Corp., New York, 1967.

3. Cochran, W.C., <u>Anodizing</u> (<u>Aluminum</u>, Volume III, Chapter 19).

4. George, D.J. et al. <u>Chemical Pretreating and Finishing</u>. (Aluminum, Volume III, Chapter 17).

5. LaQue, F.L., <u>Corrosion Resistance of Metals and Alloys</u>, 2nd edition, pages 184-194. Reinhold Publishing Corporation, New York, 1963.

6. Lifka, B.W. et al. <u>Exfoliation and Stress Corrosion of High Strength, Heat Treatable Aluminum Alloy Plate</u>. (Reprinted with permission from <u>Corrosion</u> , Nov 67, in <u>Prevention of Material Deterioration</u>: Corrosion Control Course. Published by Logistics Engineering Directorate, US Army Armament Materiel Readiness Command, Rock Island).

CHAPTER 10
LESSONS LEARNED IN CORROSION PREVENTION AND CONTROL

This document concludes with a chapter on lessons learned from actual field experience with corrosion in Army weapon systems. Regardless of how much theoretical knowledge the engineer may have regarding corrosion, it is better yet for he or she to have studied actual case histories. In so doing, we can all learn what to do and what not to do in designing hardware for today's military.

10.1   Case History #1. The Corrosion Digest, Number 6, 10/86, page 1.
Letterkenny Arsenal reported leakage of IBCC shop shelters, caused by corrosion between aluminum panels and foam insulation.

Cause: This is an example of poultice corrosion. Aluminum and its alloys depend on a natural oxide layer for protection against corrosion. When a poultice such as foam insulation is in contact with aluminum, retained moisture (possibly containing corrosives leached from the foam) can initiate corrosion at weak points in the protective film. The film is, at this point, not self-healing.
Although the aluminum was protected by chemical pretreatment and painting, the coating system was not adequate for the conditions encountered.

Solution: Remove all aluminum skins and replace with aluminum epoxy-bonded to the foam. It was further recommended that new shelters be fabricated with insulation that would be less likely to cause corrosion of the aluminum skin.

Lesson to be learned: Beware of poultice-type corrosion when insulating foams are in contact with metals. Use an adequate protective coating to protect the metal surface. Such coating should be able to withstand prolonged moisture exposure without blistering. Also, select insulation materials that will not leach corrosive salts.

10.2   Case History #2. Floor pans of M939 (5-ton) trucks were rusting out, because of moisture retained in place by floor covering.
This is another case of poultice corrosion. It is not possible to eliminate the floor covering, because its soundproofing function is considered essential.

Solution: The only coating on the steel surface was TT-C-490 phosphate treatment. Obviously, this is not adequate. TACOM considered elimination of adhesive from the bottom of floor mats so they could be removed at the end of a day's operations. This would allow air to circulate and dry out the floor area.

Lessons to be learned. Here, again, the engineer must be aware of poultice effects when items such as floor mats come into contact with metals. Also, whenever there is a sump area, prolonged electrolyte contact is likely to be a problem. The author recommends the following measures:

1. Use adequate coatings on all metal surfaces. Both outside and inside surfaces of floor pans should be galvanized. Here is a possible application for high performance coatings such as Galvalume or Galfan.* The inside surface, because of contact with the floor covering, should also have a good organic coating scheme. Use a good phosphate treatment so as to retard underfilm corrosion at paint coating defects.
2. Drain all sump areas, using either drain holes at the low points of such areas, or (for vehicles required to ford or swim deep streams) removable drain cocks.
3. Specify removable floor mats. When the truck is not in use, the mats should be removed and stored where they will dry out. The floor mat should be of closed-cell, rather than open-cell, type.

If the design engineer specifies removable drain plugs, the truck should be stored with the plugs removed. Before beginning a day's operations, the responsible maintenance person must re-install the drain plugs to prevent flooding of the vehicle interior while fording or swimming.

10.3 <u>Case History #3</u> (The MADPAC Digest, Number 2.3, 1/85, page 11.)
Hardware in S-280 and S-250 shelters was found to be corroded, producing a white, powdery corrosion product.

The cause: An RTV silicone sealant was giving off corrosive acetic acid vapor.

Solution: Change to non-acetic acid type sealant.

Lesson: Beware of vapor corrosion in enclosed areas. Avoid RTV compounds that use acetic acid. This was pointed out in part 4.10 (special considerations for electrical and electronic equipment).

10.4 <u>Case History #4</u> (The MADPAC Digest, Number 2.3, 1/85, page 47.)
In another case of vapor corrosion, MICOM reported severe corrosion of cadmium plated parts in TOW missile guidance sets.

* The superior barrier (as opposed to sacrificial) protection of aluminum coatings might be the solution to floor-pan corrosion, if nothing else works.

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Cause: The items were stored in a metal container that was recently painted with alkyd enamel. The alkyd gave off formic acid vapor, which is very corrosive to zinc and cadmium.

Solution: Corroded items were cleaned and treated with varnish. MICOM issued instructions to allow at least two weeks air dry for metal containers painted with alkyd enamel, and to use CARC in the future.

Lesson: Alkyd paints preferably should not be used for painting insides of storage containers. Use either the CARC system (epoxy primer/polyurethane topcoat) or, for surfaces not exposed to sunlight, MIL-C-22750 epoxy enamel applied over MIL-P-23377 (NAVMAT P 4855-2, Design Guidelines for Prevention and Control of Avionic Corrosion).

10.5   Case History #5   (MADPAC Disgest, Number 2.3, 1/85, page 50. See also PS magazine, November 1983, page 14). ·
Hollow dock bumpers on M871 semitrailers were rusting out due to water accumulation.

Solution: Drill three drain holes, 1/4 inch (6.35mm) diameter, in the underside of the bumper, 6 inches from each side of the trailer and 45 inches from the left side. M871's built after the defect was ascertained, had this modification incorporated at the factory.

Lesson: This is a classic case of inside-out corrosion caused by moisture entrapment in a sump area. Beware of sump areas in hollow structural sections. (See figures 19 and 20, and the accompanying text).

10.6   Case History #6 (Op cit., page 54) Magnesium castings used in the Blackhawk helicopter auxiliary power unit gearbox suffered corrosion.

Cause: Some of the protective coating (Dow #17) had been machined off, leaving exposed metal.

Solution: Seal the bolted joints after assembly with a sealant. Touch up machined areas with chromic acid brush-on per Dow #19. Seal coatings with MIL-S-8784 sealant.

Lesson: When a protective coating is destroyed by machining or welding, it must be re-applied.
This case history is an example of why metal finishing must be integrated into the overall assembly procedure, rather that being an afterthought.

10.7   Case History #7 (The Corrosion Digest, Number 8, 4/87, page 32).
Letterkenny Arsenal reported severe corrosion on crossmembers of M105A2 trailers brought in for maintenance.

Cause: The trailers were stored outdoors. Water penetrated into weld seams and frame sections.

    Solutions:
1. Provide covered storage, if possible.
2. Provide drain holes at the lowest points (sump areas) of frame sections.*
3. Use continuous welds to eliminate crevices.
4. Apply rust preventive coatings on insides of hollow sections.

    Lessons to be learned: Several examples of poor practice regarding CPC are evident in the initial M105A2 design. First, non-continuous welds conserve weld metal, but they also set up crevices which invite corrosion. Second, when using hollow frame sections, sump areas invite internal corrosion. Finally, the inside surfaces of frame members have to be protected, just as the outside surfaces must be, with protective coatings.

10.8   Case History #8 (Op Cit, page 43)
    MICOM reported the breakage of a high-strength maraging steel clevis bolt used in the patriot antenna mast.

    Cause: The bolt was cadmium plated per QQ-P-416, type II, class 3, and stress relieved for 24 hours at 500 degrees F.
    In spite of the post-plating baking, the bolt suffered hydrogen embrittlement.

    Solution: The cadmium requirement was deleted. MICOM substituted a dry film lubricant coating, per MIL-L-46010.

    Lesson: High-strength steels are very sensitive to hydrogen embrittlement. Do not electroplate such materials. Use surface treatments that are proven not to cause hydrogen embrittlement.

10.9   Case History #9 (Op Cit, page 47). MICOM reported corrosion of cadmium-plated mild steel latches on Hellfire containers.

    Cause: The containers, apparently aluminum alloy, were treated with chromate conversion coating per MIL-C-5541. This treatment degraded the cadmium plating on the latch, and interfered with paint adhesion on that component.

* Beware that trailers are sometimes stored upside-down to save space. Provide drain holes that will be at the lowest points for storage/shipment positions, in addition to drain holes for the normal position.

Solution: MICOM specified wash primer treatment, per DOD-P-15328, on containers in place of MIL-C-5541. In addition, use of stainless steel latches was investigated.

Lesson: When specifying a dip-type treatment for an item, consider all materials which may be exposed to the chemicals involved. MIL-C-5541 chromate treatments are intended for aluminum but not for cadmium surfaces.

10.10   Case History #10 (MADPAC Digest, Number 1, 6/84, page 12).
TACOM reported failure of electric starter in M113A2 armored personnel carrier.

Cause: Internal corrosion due to water entry.

Solution: A gasket was added to the technical data package to prevent water entry.

Lesson: With some components, it is vital to use seals and gaskets to keep moisture out.

10.11   Case History #11 (MADPAC Digest, Number 1, 6/84, page 17).
TACOM reported paint failures on aluminum fenders on M1 tanks.

Cause: The contractor wasn't following the specification (MIL-C-5541) for pretreating the surface prior to painting. This resulted in poor paint adhesion.

Solution: Proper pretreatment in accordance with specification, plus tightened inspection procedures prior to acceptance.

Lesson to be learned: Proper quality assurance is vital to corrosion prevention and control. The best standards are useless if not enforced.

10.12   Case History #12 (The Corrosion Digest, Number 8, 10/86 page 2).
Sharpe reported pitting and exfoliation of an aluminum alloy 2024 side rail.

Solution: Replace with type 6061-T6 aluminum alloy.

Lesson: Though 2000- and 7000- series aluminum alloys are strong, they are also vulnerable to corrosion, especially in higher strength tempers.

10.13   Case History #13 (Op Cit, page 7). MICOM reported corrosion of rotary coupler in chaparral radar set.

Cause: Moisture ingress

Solution: Install rubber seal with packing material over the top of the rotary coupler.

Lesson: Use seals, gaskets, packing in places where moisture may enter. (Seals on top, drain holes on bottom).

10.14 Case History #14 (Op Cit, page 10)
Anniston Depot reported corrosion of approximately 200 self-locking steel head bolts on the M1 tank's X-1100-3B transmission. Corrosion also occurred on the aluminum alloy 355-T71 transmission housing cover where the bolts are fastened.

Causes: Although the bolts were supposed to have been cadmium-plated, the plating was omitted. This resulted in the bolts suffering corrosion themselves, and also caused the bolts to act as cathodes with respect to the aluminum housing.

Solution: Here is another instance of lapse in quality control. With the present arrangement, make sure the plating on the bolts is per drawing specification.
For the future, use a more compatible fastening system. Here is a good application for fasteners coated with a good protective finish, i.e., ceramic-metallic.
The transmission housing should be treated with protective finish after drilling holes and after all machining operations. To prevent a large cathode/small anode situation at possible defects in the coating applied to the aluminum, use properly treated bolts. Such bolts will be less likely to act as cathodes, and less likely to corrode themselves. (See figures 13, 16, and 24.)

10.15 Case History #15 (Op Cit, page 17)
MICOM reported corrosion of various parts inside multiple launch rocket system (MLRS) electronic box.

Cause: Moisture intrusion.

Solution: Engineering change proposal included design changes to eliminate moisture leakage paths into the units.

10.16 Case History #16 (Op Cit, page 18) In another example of electronic component failure reported by MICOM, a conformal coating, per MIL-I-46058, type AR, proved inadequate during humidity testing of Hellfire autopilot circuit card assemblies.

Solution: Coating composition and application method were modified. Circuit cards are now screened for adequate performance with water mist tests.

10.17   **Case History #17** (Op Cit, page 18) TACOM reported corrosion of a ferrous metal gage rod cover assembly around the area where it was welded to the gage rod.

Cause: Plating too thin, also, plating not reapplied after welding.

Solution: Drawing was changed to specify application of coating after welding.

Lessons: 1.   Adequate QA should be enforced regarding coating thickness.
           2.   Anytime something is assembled by welding, protective coatings should be applied (or, reapplied) afterwards.
           3.   Beware, also, that forming operations may rub off cadmium or other protective coatings. Apply such coatings after any such operations.

10.18   **Case History #18** (Op Cit, page 20) The Corpus Christi Depot reported corrosion on the inside surface of magnesium alloy AZ91 tail rotor gearboxes on UH-1 helicopters.

Causes: 1.   The gearbox housings had Dow 7 dichromate/MIL-P-23377 epoxy primer on the outside surfaces, but the inside surfaces were unprotected.
          2.   Moisture intrusion.

Solution: Provide a corrosion resistant coating on the inside surfaces.

Lessons: With magnesium housings (i.e., if such are used for ground vehicle transfer cases), the designer should use high purity magnesium alloy (as free as possible from copper, nickel, iron), adequately protected on all surfaces. And, use seals and gaskets to keep environmental moisture out of the unit.

10.19   **Case History** #19 (Op Cit, page 23) Corpus Christi Depot reported corrosion of lids on storage/shipping containers for aircraft components.

Cause: Though painted, the container lids were designed (albeit unintentionally) such that water was trapped.

Solution: Re-design container and lid so that water will run off it.

Lesson learned: Any undrained sump area is a potential corrosion site.
The "tuition" for this lesson was very high. Expensive aviation components were ruined by water intrusion into the containers, because of the lid corrosion.

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For expensive items in storage, consider temporary corrosion preventive
agents (i.e., temporary coatings and/or vapor-phase corrosion inhibitors),
and other measures specified in MIL-P-116H (Preservation, methods of).

10.20   Case History #20 (Op Cit, page 28)
MICOM reported that MIL-P-52192 primer and MIL-C-52929 topcoat failed
wet tape adhesion test.

Cause: Paint was applied, and curing attempted, at temperatures
below 50F, which is too low.

Solution: Avoid painting when ambient temperature is too low for
proper curing.

10.21   Case History #21 (Op Cit, page 56) Anniston Depot reported
receiving M48 and M60 tank final drive units, from various places, with
rust on machined areas.

Cause: Units not properly prepared for shipment.

Solutions: Apply P-19 preservative to threads and machined areas
prior to shipment.

Lesson: Iron, as in mild or cast steel, wants to be an oxide. All
surfaces should be protected during storage and shipment. This is where
temporary corrosion-preventive compounds are useful.

10.22   Case History #22 (Op Cit, page 59) MICOM reported corrosion of
cadmium-plated steel rivets during salt, fog, humidity, and rain
environmental portions of first article testing of light weight missile
launcher.

Solution: Additional tests demostrated that nickel-plated brass
rivets would be satisfactory. The necessary design change was made before
the item was put into full scale production.

Lesson: This case history demonstrates the value of first-article
testing.

10.23   Case History #23 (MADPAC Digest, Number 1, 6/84 page 16, also
MADPAC, Number 213, 1/85, page 25.
Welded stainless steel water tanks (M149A2) suffered corrosion in the
weld areas.
The cause was found to be free iron present in weld slag, or
introduced by improper grinding and wire brushing.

Solution: New cleaning procedures, including non-chlorinated
scouring powder, non-metallic brushing, and flushing with clean water.

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Lesson: This case shows the importance of proper welding procedures when welding certain materials. The author reminds readers that, when welding austenitic stainless steels, be wary of intergranular corrosion (See par. 3.3.5).

10.24   Case History #24   (Corrosion Digest, Number 6, 10/86, page 64). TACOM reported superficial rusting of GLCM transporters.

Cause: The paint system (CARC) was inadequately applied. The paint thickness was less than what was specified.

Solution: Legal action was taken to reclaim the cost from the contractor.

Lessons: Even the best paint system is worthless without adequate QA. All layers, from pretreatment to final topcoat, must be applied according to specifications and must be within specified thickness allowances. Use thickness gaging to inspect the contractor's work, and also use tests such as adhesive tape to check paint adhesion.
However, don't be too quick to blame the contractor when paint quality lapses occur. The design engineer should remember that some design features (sharp corners, deep recesses) are difficult to coat evenly.

10.25   Case History #25 (Op Cit, page 66) Anniston Depot reported severe corrosion of rear drain valve control rod assembly on M60 tanks. They suggested using stainless steel, or an effective corrosion-resistant coating.

Lesson: Components that must be located near the bottom of an armored vehicle hull have to be able to withstand water immersion.
Consider using powder-coated steel parts, using a coating material that can withstand continuous water immersion.
If using stainless steel, remember that s.s. materials suffer pitting in chloride-containing media. Type 316 s.s. is more resistant to pitting than type 304. However, the designer should specify the least expensive material that can satisfy performance requirements.

10.26   Case History #26   (Op Cit, page 72) MICOM reported failure of MLRS azimuth resolve and switch assemblies.

Cause: Moisture intrusion during vehicle cleaning with high pressure water. Access doors were inadequately secured against water streams.

Solution: Engineering change proposal was issued to stiffen the access doors, improve the fastening arrangement, and change from cork to rubber gaskets.

Lesson: Armored vehicles should be designed to be cleaned with high pressure water streams. This is how soldiers clean off deposits of mud that are likely to build up on such vehicles during field exercizes.

10.27   High Mobility Multipurpose Wheeled Vehicle Corrosion Problems.
   The following corrosion problems encountered with the HMMWV, and their resolutions, were contributed by I. Carl Handsy of the TACOM Corrosion and Materials Group.

HMMWV problem #1:   Mirror bracket assemblies.
Mirror assemblies experienced rust, due to poor finish.

Possible solutions: 1.   Improve Q.C. inspection.
                      2.   Stainless steel construction.
                      3.   Galvanizing.
                      4.   Use reinforced polymer ('Composite') material.

Recommendations: Use galvanized steel, followed by zinc phosphate pretreament, epoxy primer, and polyurethane (CARC) topcoat.

Author's comment: The zinc layer (galvanizing) doesn't have to be as thick as would be needed if it were the sole protective layer. A thin zinc layer, with Zn phosphate pretreatment, helps retard paint peeling at local paint defects (holidays). These may occur due to quality lapses, or damage to the paint coating by stones or other missiles.

HMMWV problem #2:   Strike, catch, cargo shell door.

Said components rusted, because of poor quality control of protective plating and painting.

Possible solutions: 1.   Improve Q.C. of plating.
                      2.   Improve Q.C. of painting.

Recommendations: Both of the above.

For small components, fluidized bed powder coatings are a possible option, if a material can be found that meets CARC requirements. TGIC-cured polyester is a possibility.

HMMWV problem #3:   Body mounting bolts.

Bolts were rusting.

Possible solutions: 1.   Seal bolts after assembly with dry film coating.
                      2.   Use ceramic-metallic coating (see par.8.9.2)
                      3.   Stainless steel bolts
                      4.   Composite bolts

Recommendations: Ceramic-metallic coatings, or stainless steel.

Author's comment: Try the former. Stainless steels are known to suffer stress-corrosion cracking in some environments. Polymer composites are _not_ fastener materials.

HMMWV problem #4: Latch assembly, hood release.

Problem: Rust

Possible solutions: 1.   Hot dip galvanize.
                       2.   Composite material.
                       3.   Stainless steel.

Recommendation: Hot dip galvanize.

HMMWV problem #5: Floor mats.

Moisture, retained by floor mats, causes corrosion of floor pan.

Possible solutions: Use closed cell foam contruction, or encapsulated foam material, depending on cost.
See case history #2 (M939 trucks). It cannot be emphasized enough that a floor pan must be protected on the crew compartment side with a coating system that can withstand continuous exposure to dampness. The HMMWV floor pan is aluminum, not steel as with the M939. Accordingly, a different coating system is required. Consider using anodizing sealed with polyurethane, followed with a CARC topcoat (see par 9.2.2). Another possibility is a powder coating system.
Otherwise, the floor pan corrosion problem in the HMMWV should be addressed in the same manner as the corresponding problem with the M939.

HMMWV problem #6: Frame rails.

Problem: Rust on inside of frame rail.

Cause: Insufficient cleaning and inadequate E-coat primer application.

Possible solutions: Improved immersion cleaning and 0.5 mil of E-coat primer.

Recommendations: Both of the above

This problem was resolved between TACOM and the HMMWV prime contractor, AM general. All future frame rails will be thoroughly cleaned, and a minimum of 0.5 Mil E-coat primer is required on all surfaces. (Author's comment: Drill all necessary holes _before applying surface treatments)_

HMMWV problem #7: Roll bar, B pillar.

Problem: Rust caused by poor paint finish and abrasion of door panel against the pillar.

Solutions: 1. Galvanize steel parts.
2. Apply self-sticking tape to faying surfaces of door frame and pillar.
3. Improve paint application quality.

Lesson: Beware of abrasion between mating parts that would remove protective coatings.

HMMWV problem #8: Steel troop seats.

Problem: Corrosion of assembly due to dissimilar metal effects (the HMMWV has an aluminum body) and poor quality of protective coatings.

Solutions: 1) Isolate dissimilar metals.
2) Galvanize steel parts.
3) E-coat primer/CARC topcoat.
4) Zinc phosphate pretreatment,
5) Use aluminum, rather than steel seats.

The recommendation was to use solutions 1 thru 4.

Comment: Dissimilar metal joints should be as shown in Figure 13. Assembly procedure should be as in Figure 16. Separately treat the seat assembly and aluminum body with their respective coating systems, then assemble, using joint design techniques that electrically isolate the steel and aluminum.

Finally, use fasteners treated to resist corrosion.

HMMWV problem #9: Roof panel assembly, basic armor.

Problem: Rust, due to poor quality of paint finish.
Solutions: Galvanize the steel panels and tighten quality controls regarding painting.

AM General now uses E-coat primer for roof panels. Good QA is a challenge, because the E-coat process is performed by a subcontractor.

HMMWV problem #10: Drain holes.

Problem: Poor drainage.
Solution: Relocate drain holes to lowest points on the floor.
Action taken: AM General has redesigned the drainage hole system to enlarge drain holes, and to add more where needed.