# С

## **CADMIUM COATINGS**

These coatings are produced almost exclusively by electrodeposition. A cadmium coating on steel does not provide as much protection to the steel as does a zinc coating, since the potential between cadmium and iron is not as great as that between zinc and iron. Therefore, it becomes important to minimize defects in the cadmium coating.

Unlike zinc, a cadmium coating will retain a bright metallic appearance. It is more resistant to attack by salt spray and atmospheric condensation. In aqueous solutions cadmium will resist attack by strong alkalies but will be corroded by dilute acids and aqueous ammonia.

Since cadmium salts are toxic, these coatings should not be allowed to come into contact with food products. This coating is commonly used on nuts and bolts.

See Refs. 1 and 2.

## CAPPED STEEL

See "Killed Carbon Steel."

## CARBIDE PRECIPITATION

Carbon is added to stainless steels as an alloying ingredient to increase strength. During melting and high-temperature working operations, such as welding, the carbon content in stainless steel is generally in solid solution. As the steel cools from a temperature of approximately 1600°F (872°C) there is a preference for the formation of a chromium carbide compound, which precipitates preferentially at grain boundaries.

The chromium carbides in themselves do not suffer from poor corrosion resistance. The problem lies in the fact that in the formation of these chromium carbides the chromium has been depleted from the surrounding matrix. This depletion can be to such an extent that the chromium content locally can be below 11%, which is considered the minimum value for stainless steel, leaving this area open to corrosion.

The problem of carbide precipitation can be alleviated by the addition of titanium or niobium (columbium) as an alloying ingredient. These elements tie up the carbon, preventing the precipitation of chromium carbide. Another approach is to reduce the carbon content in the alloy from the usual 0.08% to below 0.035%. This prevents the precipitation of harmful levels of chromium carbide precipitate. The latter approach results in stainless steels known as low carbon, carrying the suffix L after the grade, e.g., 304L, 316L.

See Ref. 3.

## CARBON

Carbon has extremely good chemical resistance. It is produced from carbon particles bonded with materials that carbonize during subsequent heating. The operation is usually carried out below 2250°F (1230°C).

In an oxidizing atmosphere it may be used to 660°F (350°C), while in an inert or reducing environment it can be used to 5000°F (2760°C).

Table C.1 lists the compatibility of carbon in contact with selected corrodents. For a more complete listing see Ref. 4.

See also Ref. 5.

	Max.	Max. temp.	
Chemical	°F °C		
Acetaldehyde	340	171	
Acetamide	340	171	
Acetic acid 10%	340	171	
Acetic acid 50%	340	171	
Acetic acid 80%	340	171	
Acetic acid, glacial	340	171	
Acetic anhydride	340	171	
Acetone	340	171	
Acetyl chloride	340	171	
Acrylonitrile	340	171	
Adipic acid	340	171	
Allyl alcohol	340	171	
Allyl chloride	100	38	
Alum	340	171	
Aluminum chloride, aqueous	340	171	
Aluminum chloride, dry	340	171	
Aluminum fluoride	340	171	
Aluminum hydroxide	340	171	
Aluminum nitrate	340	171	
Ammonia gas	340	171	
Ammonium bifluoride	390	199	
Ammonium carbonate	340	171	
Ammonium chloride 10%	340	171	
Ammonium chloride 50%	340	171	
Ammonium chloride, sat.	340	171	
Ammonium fluoride 10%	330	166	
Ammonium fluoride 25%	340	171	
Ammonium hydroxide 25%	200	93	
Ammonium hydroxide, sat.	220	104	
Ammonium nitrate	340	171	
Ammonium persulfate	340	171	
Ammonium phosphate	340	171	
Ammonium sulfate 10–40%	340	171	
Ammonium sulfide	340	171	
Amyl acetate	340	171	
Amyl alcohol	200	93	

Table C.1	Compatibility of Carbon with
Selected Con	rrodents <sup>a</sup>

	Max.	Max. temp.		
Chemical	°F	°C		
Amyl chloride	210	99		
Aniline	340	171		
Barium carbonate	250	121		
Barium chloride	250	121		
Barium hydroxide	250	121		
Barium sulfate	250	121		
Barium sulfide	250	121		
Benzaldehyde	340	171		
Benzene	200	93		
Benzene sulfonic acid 10%	340	171		
Benzoic acid	350	177		
Borax	250	121		
Boric acid	210	99		
Bromine gas, dry	x	x		
Bromine gas, moist	x	x		
Bromine liquid	x	x		
Butadiene	340	171		
Butyl acetate	340	171		
Butyl alcohol	210	99		
<i>n</i> -Butylamine	100	38		
Butyl phthalate	90	32		
Butyric acid	340	171		
Calcium bisulfide	340	171		
Calcium bisulfite	340 340	171		
Calcium carbonate	340	171		
Calcium chlorate 10%	140	60		
Calcium chloride	340	171		
Calcium hydroxide 10%	200	93		
Calcium hydroxide, sat.	200 250	121		
	230 170	77		
Calcium hypochlorite	340			
Calcium nitrate	340 340	171		
Calcium oxide Calcium sulfate	340 340	171		
		171		
Caprylic acid	340 340	171		
Carbon bisulfide	•	171		
Carbon dioxide, dry	340	171		
Carbon dioxide, wet	340	171		
Carbon disulfide	340	171		
Carbon monoxide	340	171		
Carbon tetrachloride	250	121		
Carbonic acid	340	171		
Cellosolve	200	93		
Chloracetic acid, 50% water	340	171		
Chloracetic acid	340	171		
Chlorine gas, dry	180	82		
Chlorine gas, wet	80	27		
Chlorobenzene	340	171		
Chloroform	340	171		

 Table C.1
 Compatibility of Carbon with

 Selected Corrodents<sup>a</sup> (Continued)

	Max.	Max. temp.		
Chemical	°F	°Ċ		
Chlorosulfonic acid	340	171		
Chromic acid 10%	x	x		
Chromic acid 50%	х	x		
Citric acid 15%	340	171		
Citric acid, conc.	340	171		
Copper carbonate	340	171		
Copper chloride	340	171		
Copper cyanide	340	171		
Copper sulfate	340	171		
Cresol	400	238		
Cupric chloride 5%	340	171		
Cupric chloride 50%	340	171		
Cyclohexane	340	171		
Ethylene glycol	340	171		
Ferric chloride	340	171		
Ferric chloride 50% in water	340	171		
Ferric nitrate 10%–50%	340	171		
Ferrous chloride	340	171		
Ferrous nitrate	340	171		
Fluorine gas, dry	x	x		
Hydrobromic acid, dilute	340	171		
Hydrobromic acid 20%	340	171		
Hydrobromic acid 50%	340	171		
Hydrochloric acid 20%	340	171		
Hydrochloric acid 38%	340	171		
Hydrocyanic acid 10%	340	171		
Hydrofluoric acid 30%	340	171		
Hydrofluoric acid 70%	x	x		
Hydrofluoric acid 100%	x	x		
Hypochlorous acid	100	38		
Ketones, general	340	171		
Lactic acid 25%	340	171		
Lactic acid, concentrated	340	171		
Magnesium chloride	170	77		
Malic acid	100	38		
Manganese chloride	400	227		
Methyl chloride	340	171		
Methyl ethyl ketone	340	171		
Methyl isobutyl ketone	340	171		
Muriatic acid	340	171		
Nitric acid 5%	180	82		
Nitric acid 20%	140	60		
Nitric acid 70%	x	x		
Nitric acid, anhydrous	x	x		
Nitrous acid, concentrated	x	x		
Perchloric acid 10%	340	171		
Perchloric acid 70%	340 340	171		
Phenol	340 340	171		

Table C.1	Compatibility of Carbon with
Selected Cor	rodents <sup>a</sup> (Continued)

	Max. temp.		
Chemical	°F	°C	
Phosphoric acid 50–80%	200	93	
Picric acid	100	38	
Potassium bromide 30%	340	171	
Salicylic acid	340	171	
Sodium bromide	340	171	
Sodium carbonate	340	171	
Sodium chloride	340	171	
Sodium hydroxide 10%	240	116	
Sodium hydroxide 50%	270	132	
Sodium hydroxide, concentrated	260	127	
Sodium hypochlorite 20%	x	x	
Sodium hypochlorite, concentrated	х	х	
Sodium sulfide to 50%	120	49	
Stannic chloride	340	171	
Sulfuric acid 10%	340	171	
Sulfuric acid 50%	340	171	
Sulfuric acid 70%	340	171	
Sulfuric acid 90%	180	82	
Sulfuric acid 98%	х	х	
Sulfuric acid 100%	х	х	
Sulfurous acid	340	171	
Toluene	340	171	
Trichloroacetic acid	340	171	
White liquor	100	38	
Zinc chloride	340	171	

Table C.1	Compatibility of Carbon with
Selected Cor	rodents <sup>a</sup> (Continued)

<sup>a</sup>The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated. Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x.

Source: PA Schweitzer. Corrosion Resistance Tables. 4th ed. New York: Marcel Dekker, 1995.

## **CARBON FIBERS**

Carbon fibers are used to reinforce FRP laminates and to impart conductivity. See "Thermoset Reinforcing Materials."

## CARBON FIBER REINFORCED THERMOPLASTICS

See also "Zymaxx." There are many composite thermoplastic materials having carbon filler for reinforcement. Some typical examples of such thermoplastics are given in the table.

Nylon 6	Acetal
Nylon 6/6	PBT
Nylon 6/10	PPS
Nylon 6/12	PEEK
ABS	Polycarbonate
Polyetherimide	Polysulfone
PES	ETFE
FEP	PFA
PVDF	

These basic resins are available with various degrees of carbon reinforcement and may also contain a secondary reinforcing material or a lubricant additive. In all cases the mechanical properties of the base resin are improved by the addition of the reinforcement.

#### **CARBON/GRAPHITE YARNS**

For many years the predominant sealing material and mechanical material has been asbestos. However, the elimination of asbestos as an environmentally unsafe material has led to the acceptance of carbon/graphite as a reliable substitute. Carbon/graphite possesses the properties of strength, density, modulus, thermal conductivity, thermal stability, and corrosion resistance.

Its strong chemical resistance makes it ideally suited to the packing and sealing industries for use with acids, caustics, alkalies, and high-temperature applications. It is available in many styles and weights.

In general, it is inert to most chemicals in the pH range of 2–12. Typical examples are given in the table.

	Concentration	Temperature
Inorganic acids		
Hydrochloric acid	all	boiling point
Hydrofluoric acid	all	boiling point
Phosphoric acid	all	boiling point
Sulfuric acid	0-70%	boiling point
Chromic acid	0-10%	392°F (200°C)
Nitric acid	0-10%	185°F (85°C)
Nitric acid	0-20%	140°F (60°C)
Nitric acid	over 20%	104°F (40°C)
Organic acids		
Phenylsulfonic acid	60%	boiling point
Acetic acid	all	boiling point
Acetic anhydride	100%	boiling point
Chloracetic acid	all	boiling point
Amino acid	all	boiling point
Alkalies		
Caustic soda	all	boiling point
Sodium hydroxide	solid	melting point
Solvents		
Benzene	0-100%	boiling point
Ethers	0-100%	boiling point
Alcohols	0-100%	boiling point
Esters	0-100%	boiling point
Ketones	0-100%	boiling point
Halogenated hydrocarbons	0-100%	boiling point
Vinyl chloride	0-100%	boiling point
Mineral oils	0–100%	boiling point

See Ref. 4.

## **CARBON AND LOW-ALLOY STEELS**

Carbon and low-alloy steels are affected primarily by general corrosion. The corrosion of steel is the most common form of corrosion the average person sees. The steels tend to

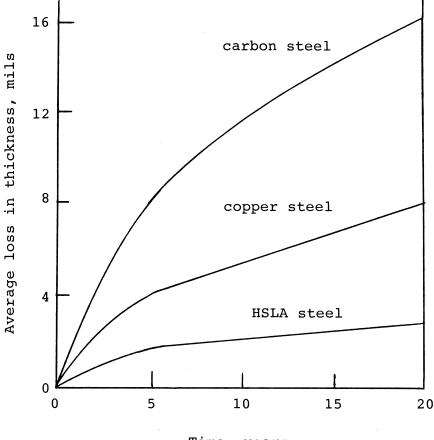
return to their oxide form by a process we call rusting. The most common corrosive solvent is water, in everything from dilute solutions to concentrated acids and salt solutions, but organic systems are capable of causing serious corrosion as well.

The carbon steels are subject to localized corrosion such as pitting, stress corrosion cracking, hydrogen embrittlement, and corrosion fatigue, as well as uniform corrosion.

Atmospheric corrosion of alloy steels is a prime factor in most applications. Fig. C.1 compares test results in a semi-industrial or industrial environment, of plain carbon steel with structural copper steel and high-strength–low-alloy (HSLA) steels. It is evident that the alloy steels are more resistant than the plain carbon steel. Table C.2 lists the average reduction in thickness for various steels in several environments.

The susceptibility of a low-alloy steel to stress corrosion cracking (SCC) depends on the strength level. The higher the tensile strength, the greater the susceptibility. General guidelines for steels such as AISI 4130 and AISI 4340 are as follows:

- 1. High SCC resistance: tensile strength below 180,000 psi
- 2. Moderate SCC resistance: tensile strength 180,000–200,000 psi
- 3. Low SCC resistance: tensile strength over 200,000 psi



Time, years

Figure C.1 Atmospheric corrosion in a semi-industrial or industrial atmosphere.

Environment	Average reduction in thickness (mils)				
	Exposure time (yr)	Carbon steel	A242(K11510) Cu-P steel	A588(K11430) Cr-V-Cu steel	
Urban industrial	3.5	3.3	1.3	1.8	
	4.5	4.1	1.5	2.1	
Rural	3.5	2.0	1.1	1.4	
	7.5	3.0	1.3	1.5	
Severe marine	0.5	7.2	2.2	3.8	
(80 ft from ocean)	2.0	36.0	3.3	12.2	
	3.5	57.0	_	28.7	
	5.0	D	19.4	38.8	
Chloralkali plant	0.5	4.1	2.4	2.7	
-	2.0	18.8	5.7	7.4	
Sulfur plant	0.5	15.5	7.4	9.4	
•	2.0	43.3	20.4	32.4	
Chlorinated	0.5	5.4	1.8	1.8	
hydrocarbon plant	2.0	44.1	4.1	4.6	
Hydrochloric	0.5	12.3	5.8	7.1	
acid plant	2.0	49.8	25.2	31.6	

 Table C.2
 Corrosion of Various Steels in Various Environments

D = Destroyed

Stress corrosion cracking can be induced in carbon or low-alloy steels, even at low concentrations, by the following chemical species:

Hydroxides, gaseous hydrogen Gaseous chlorine, HCl, and HBr Hydrogen sulfide gas, MnS and MnSe inclusions in alloy Aqueous nitrate solution As, Sb, and Bi ions in aqueous solutions Carbon monoxide–carbon dioxide–water mixtures Anhydrous ammonia

Carbon and low-alloy steels are also affected by pitting. One environment that pits steel is soil, which becomes a factor for buried pipelines. Other chemicals that cause pitting in steels include

Antimony trichloride Carbonic acid–carbon dioxide Epichlorohydrin Methylamine Nickel nitrate

Buried pipelines can best be protected with the application of protective coatings or by applying cathodic protection.

The diffusion of hydrogen through steel to affect mechanical properties involves nascent or atomic hydrogen since molecular hydrogen cannot diffuse through metals.

Corrosion sources of atomic hydrogen include corrosion; misapplied cathodic protection; high-temperature, moist atmospheres; electroplating; and welding. Hydrogen blistering and hydrogen embrittlement are two forms of hydrogen damage.

During some acid services, such as acid pickling of steels, hydrogen atoms may enter the crystal lattice and collect in fissures or cavities in the steel. These atoms then combine into hydrogen gas molecules, eventually reaching pressures of several hundred thousand atmospheres and forming blisters on the steel surface.

Hydrogen embrittlement is another harmful effect of hydrogen penetration. This is a more complicated metallurgical effect, possibly involving the interaction of hydrogen atoms with the tip of an advancing crack. For the low-alloy steels the alloys are most susceptible in their highest strength levels. Alloys containing nickel or molybdenum are less susceptible.

If hydrogen is initially present in the steel—for example, from electroplating—the hydrogen can be baked out. This embrittlement decreases with increasing service temperature, especially above 150°F (65°C). Generally, hydrogen embrittlement is not a problem in steels having yield strengths below about 150,000 psi, but if hydrofluoric acid or hydrogen sulfide is present the yield strength must be below 80,000 psi. Welding conditions should be dry and low-hydrogen filler metal should be used to minimize hydrogen embrittlement.

High-temperature hydrogen attack is the result of a reaction between hydrogen and a component of the alloy. For example, in steels hydrogen reacts with iron carbide at high temperatures to form methane gas. Because methane cannot diffuse out of the steel, it accumulates and causes fissuring and blistering, which reduces alloy strength and ductility. Alloy steels containing chromium and molybdenum are helpful since the carbides formed by these alloying elements are more stable than iron carbide and therefore resist hydrogen attack.

Organic compounds can also be corrosive to steels, specifically those in the following categories:

- **1.** Organic acids such as acetic and formic.
- 2. Compounds that hydrolyze to produce acids. These include chlorinated hydrocarbons such as carbon tetrachloride or trichloroethane, which react with water to produce hydrochloric acid. Other compounds are ethyl acetate, which hydrolyzes to produce acetic acid, and dimethyl sulfate, which hydrolyzes to produce sulfuric acid.
- 3. Chelating agents which take up or combine with transition elements.
- **4.** Inorganic corrosives dissolved and dissociated in organic solvents. This may include hydrochloric acid dissolved in dimethylformamide. Other possibilities include chlorine, bromine, or iodine dissolved in methanol.

Reference 4 provides an extensive listing of the compatibility of carbon steel with selected corrodents.

# CARBURIZATION

Carburization is the absorption of carbon atoms into a metal surface at high temperature, which reduces the effectiveness of a prior oxide film by the formation of chromium carbides. This depletes the matrix of chromium.

Series	Alloy system		
1XX.X	99.9% minimum aluminum		
2XX.X	Aluminum plus copper		
3XX.X	Aluminum plus silicon plus magnesium		
	Aluminum plus silicon plus copper		
	Aluminum plus silicon plus copper plus magnesium		
4XX.X	Aluminum plus silicon		
5XX.X	Aluminum plus magnesium		
6XX.X	Currently unused		
7XX.X	Aluminum plus zinc		
8XX.X	Aluminum plus tin		
9XX.X	Currently unused		

 Table C.3
 Designation of Aluminum Castings

#### **CAST ALUMINUM**

There is no single commercial designation system for aluminum castings. The most widely used system is that of the Aluminum Association. It consists of a four-digit numbering system incorporating a decimal point to separate the third and fourth digits. The first digit identifies the alloy group, as listed in Table C.3.

Aluminum castings are of two types: heat treatable, corresponding to the same type of wrought alloys where strengthening is produced by dissolution of soluble alloying elements and their subsequent precipitation, and non-heat treatable, in which strengthening is produced primarily by constituents of insoluble or undissolved alloying elements. Tempers of heat-treatable casting alloys are designated by an F. Alloys of the heat-treatable type are usually thermally treated subsequent to their casting, but for a few in which a considerable amount of alloying elements are retained in solution during casting, they may not be thermally treated after casting; thus they may be used in both the F and fully strengthened T tempers.

The 1XX.X series is assigned to pure aluminum. Besides ingot, the only major commercial use of pure aluminum castings is electrical conductor parts such as collector rings and bus bars. Because of their low strength these alloys are usually cast with integral steel stiffeners.

The 2XX.X series of the aluminum + copper alloys were the first type of casting alloys used commercially and are still used. They provide medium to high strength but are difficult to cast. These alloys are the least corrosion resistant and can be susceptible to SCC in the maximum strength of T6 temper.

The 3XX.X alloys provide the best combination of strength and corrosion resistance. They are produced in both as-cast (F) tempers and heat-treated tempers T5 through T7.

The 4XX.X castings are the most prevalent because of their superior casting characteristics. They provide reasonably good corrosion resistance but low to medium strength.

The 5XX.X castings provide the highest resistance to corrosion and good machinability and weldability. However, they have low to medium strength and are difficult to cast, being limited to sand castings or simple permanent mold shapes.

The 7XX.X castings find limited applications. They are difficult to cast and are limited to simple shapes. They have medium to good resistance to corrosion and high melting points.

Alloy	Alloying elements (%)				
	Si	Cu	Mg	Ni	Zn
Alloys not normally heat treated					
360.0	9.5		0.5		
380.0	8.5	3.5			
443.0	5.3				
514.0			4.0		
710.0		0.5	0.7		6.5
Alloys normally heat treated					
295.0	0.8	4.5			
336.0	12.0	1.0	1.0	2.5	
355.0	5.0	1.3	0.5		
356.0	7.0		0.3		
357.0	7.0		0.5		

Table C.4Nominal Chemical Compositions ofRepresentative Aluminum Casting Alloys

The 8XX.X castings were designed for bearings and bushings in internal combustion engines. Required properties are the ability to carry high compressive loads and good fatigue resistance.

Nominal chemical compositions of representative aluminum alloys are shown in Table C.4.

In general, the corrosion resistance of a cast aluminum alloy is equivalent to that of the comparable wrought aluminum alloy.

## CAST COPPER ALLOYS

The UNS designations for cast copper alloys consist of numbers C80000 through C99999. As with other metals, the composition of the cast copper alloys varies from that of the wrought alloys. Copper castings possess some advantages over wrought copper, in that the casting process permits greater latitude in alloying because hot- and cold-working properties are not important. This is particularly true relative to the use of lead as an alloying ingredient. The chemical compositions of the more common copper alloys are given in Table C.5. Commercially pure copper alloys are not normally cast.

Copper alloys are normally selected not because of their corrosion resistance alone, but rather for that characteristic plus one or more other properties. In many applications conductivity may be the deciding factor.

The brasses are the most useful of the copper alloys. They find application in seawater, with the higher-strength, higher-hardness materials used under high-velocity and turbulent conditions. In general, brass has less corrosion resistance in aqueous solution than the other copper alloys, although red brass is superior to copper for handling hard water. The addition of zinc does improve the resistance to sulfur compounds, but decreases the resistance to season cracking in ammonia. Refer to the section on dezincification under wrought copper alloys (see page 172). The brasses also find application in boric acid, neutral salts (such as magnesium chloride and barium chloride), organics (such as ethylene glycol and formaldehyde), and organic acids.

UNS	ASTM	C	7	Sn	ы	M	A 1	Б	с.	NI.	CI
no.	spec.	Cu	Zn	Sn	Pb	Mn	Al	Fe	Si	Ni	Cb
C83600	B584	85	5	5	5	_	_	_	_		_
C85200	B584	72	24	1	3	_	_	_		_	
C85800	B176	61	36	1	1	_	_	_		_	
C86200	B584	63	27	_		3	4	3		_	_
C86300	B584	61	21	_		3	6	3		_	_
C87200	B584	89	5	1		1.5	1.5	2.5	3	_	_
C87300	B584	95		_		1	_	_	3		_
C87800	B176	87	14	_		_	_	_	4	_	_
C90300	B584	88	4	8		_	_	_		_	_
C90500	B584	88	2	10			_	_			_
C92200	B61	85	4	6	1.5		_	_		_	_
C92300	B584	83	3	7	7		_	_			_
C95200	B184	88		_		_	9	3		_	_
C95400	B148	85		_		_	11	4		_	_
C95500	B148	81		_		_	11	4		4	_
C95800	B148	81	_	_	_		9	4	_	4	
C96200	B369	87.5		_		0.9	_	1.5	0.1	10	
C96400	B369	68	—	_	—	—	—	1	—	30	1

 Table C.5
 Chemical Composition of Cast Copper Alloys (wt%)

The next major group of copper alloys are the bronzes, which from a corrosion standpoint are very similar to the brasses. Copper-aluminum (aluminum bronze), copper-silicon (silicon bronze), and copper-tin (tin bronze) are the main cast bronze alloys. The addition of aluminum to the bronzes improves resistance to high-temperature oxidation, increases the tensile strength properties, and provides excellent resistance to impingement corrosion. They are resistant to many nonoxidizing acids. Oxidizing acids and metallic salts will cause attack. Alloys having more than 8% aluminum should be heat treated since it improves corrosion resistance and toughness. Aluminum bronzes are susceptible to stress corrosion cracking in moist ammonia.

Silicon bronze has approximately the same corrosion resistance as copper but better mechanical properties and superior weldability. The corrosion rates are affected less by oxygen and carbon dioxide content than is the case with other copper alloys. Silicon bronzes can handle cold dilute hydrochloric acid, cold and hot dilute sulfuric acid, and cold concentrated sulfuric acid. They have better resistance to stress corrosion cracking than the common brasses. In the presence of high-pressure steam, silicon bronze is susceptible to embrittlement.

Tin bronze is less susceptible to stress corrosion cracking than brass, but has less resistance to corrosion by sulfur compounds. The addition of 8–10% tin provides good resistance to impingement attack. Tin bronze has good resistance to flowing seawater and some nonoxidizing acids (except hydrochloric acid).

The final group of copper alloys are the copper-nickel (cupronickels) alloys. They exhibit the best resistance to corrosion, impingement, and stress corrosion cracking of all the copper alloys. They are among the best alloys for seawater service and are immune to season cracking. Dilute hydrochloric, phosphoric, and sulfuric acids can be handled. They are almost as resistant as Monel to caustic soda.

## CAST IRONS

The term cast iron is inclusive of a number of alloys of iron, carbon, and silicon. Typically these alloys have a carbon content of approximately 1.8% to 4.0% and a silicon content of 0.5% to 3.0%. This composition range describes all grades of cast irons from highly wear-resistant hard materials to ductile energy-absorbing alloys suitable for applications involving high stress and shock loads. The carbon content of the alloy can be in several forms: graphite flakes, irregular graphite modules, graphite spheres, iron carbides or cementite, or a combination of these. The basic types of cast irons are gray iron, ductile (nodular) iron, compacted graphite iron, white iron, malleable iron, and high-alloy cast irons.

## Gray Iron

This is the most common cast iron. When the material fractures it has a gray appearance—thus the name gray iron. Gray iron contains 1.7%–4.5% carbon and 1%–3% silicon. It is the least expensive of all the cast metals, and because of its properties it has become the most widely used cast material on a weight basis.

In gray iron the carbon is in the form of graphite flakes. Silicon additions assist in making the Fe<sub>3</sub>C unstable. As the metal slowly cools in the mold, the Fe<sub>3</sub>C decomposes to graphite. Gray iron has relatively poor toughness because of the stress concentration effect of the graphite flake tips. The mechanical properties vary with the cooling rate and are measured from separately cast bars poured from the same metal as the casting.

In general, gray iron castings are not recommended for applications where impact strength is required. Gray iron castings are normally used in neutral or compressive applications because the graphite flake form acts as an internal stress raiser. The graphite flake form provides advantages in machining, sound damping, and heat transfer applications.

Graphite is essentially an inert material and is cathodic to iron; consequently, the iron will suffer rapid attack in even mildly corrosive atmospheres. Gray iron is subject to a form of corrosion known as graphitization, which involves the selective leaching of the iron matrix, leaving only a graphite network. Even though no apparent dimensional change has taken place, there can be sufficient loss of section and strength to lead to failure. In general, gray iron is used in the same environments as carbon steel and low-alloy steels, although the corrosion resistance of gray iron is somewhat better than that of carbon steel. Corrosion rates in rural, industrial, and seacoast environments are generally acceptable. The advantage of gray iron over carbon steel in certain environments is due to a porous graphite-iron corrosion product film that forms on the surface. This film provides a particular advantage under velocity conditions, such as in pipelines. This is the reason for the widespread use of gray iron in underground water pipes.

Gray iron is not resistant to corrosion in acid except for concentrated acids, where a protective film is formed. It is not suitable for use with oleum. It has been known to rupture in this service with explosive violence.

Gray iron exhibits good resistance to alkaline solutions such as sodium hydroxide and molten caustic soda. Likewise, it exhibits good resistance to alkaline salt solutions such as cyanides, silicates, carbonates, and sulfides. Acids and oxidizing salts rapidly attack gray iron. Gray iron will contain sulfur at temperatures of 350–400°F (177–205°C). Molten sulfur must be air free and solid sulfur must be water free.

Gray iron finds application in flue gas handling such as in wood- and coal-fired furnaces and heat exchangers. Large quantities are also used to produce piping which is buried. Normally, gray iron pipe will outlast carbon steel pipe depending on soil type, drainage, and other factors.

#### Ductile (Nodular) Iron

Ductile iron has basically the same chemical composition as gray iron with a small chemical modification. Just prior to pouring the molten iron, an appropriate inoculant such as magnesium is added. This alters the structure of iron to produce a microstructure in which the graphite form produced during the solidification process is spheroidal instead of flake form. The flake form has better machinability, but the spheroidal form yields much higher strength and ductility. The matrix can be ferritic, pearlitic, or martensitic depending on the heat treatment process. Graphite nodules surrounded by white ferrite, all in a pearlitic matrix, the most common form. Other elements can be used to produce the nodular graphite form, including yttrium, calcium, and cerium.

The corrosion resistance of ductile iron is comparable to that of gray iron, with one exception. Under velocity conditions the resistance of ductile iron may be slightly less than that of gray iron since it does not form the same type of film that is present on gray iron.

#### Austenitic Gray Cast Iron

Austenitic cast iron is also referred to as an Ni-resist alloy. This group consists of highnickel austenitic cast irons used primarily for their corrosion resistance. These alloys have improved toughness over unalloyed gray iron but relatively low tensile strengths, ranging from 20,000 to 30,000 psi.

The corrosion resistance lies between that of gray iron and the 300 series stainless steels. It finds wide application in hydrogen sulfide–containing oil field applications. Excessive attack is prevented by the formation of a protective film. It is superior to gray iron under exposure to atmospheric conditions, seawater, caustic soda, or sodium hydroxide, and dilute and concentrated (unaerated) sulfuric acid.

## Austenitic Ductile Cast Irons

These alloys are commonly called ductile Ni-resist. They are similar to the austenitic gray irons except that magnesium is added just prior to pouring to produce a nodular graphite structure. As a result of the nodular structure, higher strength and greater ductility are produced compared with the flake graphite structure. Although several grades are produced, type 2D is the most commonly used grade.

The corrosion resistance is similar to that of austenitic gray iron, although alloys containing 2% or more chromium are superior. The compatibility of Ni-resist with selected corrodents is shown in the following table:

#### CAST IRONS

9

## Compatability of Ni-Resist Alloy with Selected Corrodents

	Maxi	mum		Maximum	
	temp.			temp.	
Chemical	°F	°C	Chemical	°F	°C
Acetic anhydride	х	x	Ethanol amine	200	93
Acetone	140	60	Ethyl acetate	90	32
Acetylene	90	32	Ethyl chloride, dry	90	32
Alum	100	38	Ehtylene glycol	460	238
Aluminum hydroxide, 10%	470	243	Ethylene oxide	х	2
Aluminum potassium sulfate	100	38	Ferric sulfate	460	238
Ammonia, anhydrous	460	238	Ferrous sulfate	х	x
Ammonium carbonate, 1%	90	32	Fuel oil	х	x
Ammonium chloride	210	99	Fufural, 25%	210	99
Ammonium hydroxide	90	32	Gallic acid	90	32
Ammonium nitrate, 60%	120	49	Gas, natural	90	32
Ammonium persulfate, 60%	120	49	Gasoline, leaded	400	204
Ammonium phosphate	х	x	Gasoline, unleaded	400	204
Ammonium sulfate	130	54	Glycerine	320	160
Amyl acetate	300	149	Hydrochloric acid	х	x
Aniline	100	38	Hydrogen chlorine gas, dry	х	x
Arsenic acid	х	x	Hydrogen sulfide, dry	460	238
Barium carbonate	х	х	Hydrogen sulfide, wet	460	238
Barium chloride	х	x	Isooctane	90	32
Barium hydroxide	х	x	Magnesium hydroxide	х	x
Barium sulfate	х	x	Magnesium sulfate	150	66
Barium sulfide	х	x	Methyl alcohol	160	71
Benzene	400	204	Methyl chloride	х	x
Black liquor	90	32	Phosphoric acid	х	x
Boric acid	х	x	Sodium borate	90	32
Bromine gas	х	x	Sodium hydroxide, to 70%	170	77
Butyl acetate	х	x	Sodium nitrate	90	32
Calcium carbonate	460	238	Sodium nitrite	90	32
Calcium hydroxide	90	32	Sodium peroxide, 10%	90	32
Calcium nitrate	210	99	Sodium silicate	90	32
Calcium sulfate	440	227	Sodium sulfate	х	x
Carbon dioxide, dry	300	149	Sodium sulfide	х	x
Carbon dioxide, wet	х	x	Steam, low pressure	350	177
Carbon monoxide	300	149	Sulfate liquors	100	38
Carbon tetrachloride	170	77	Sulfur	100	38
Carbonic acid	460	238	Sulfur dioxide, dry	90	32
Chlorine gas, dry	90	32	Tartaric acid	100	38
Chromic acid	x	x	Tomato juice	120	49
Cyclohexane	90	32	Vinegar	230	110
Diethelylene glycol	300	149	Water, acid mine	210	99
Diphenyl	210	99	White liquor	90	32

*Note:* The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated.

Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x. When compatible, corrosion rate is less than 20 mpy.

Source: Ref. 4.

#### White Iron

This alloy is also referred to as Ni-hard. The carbon in these alloys is essentially all in solution and the fracture surface appears white. These alloys contain nickel in the range of 4-5% and chromium in the range of 1.5-3.5%.

White iron solidifies with a "chilled" structure. Instead of forming free graphite, the carbon forms abrasion-resistant iron-chromium carbides. These alloys are used primarily for abrasive applications. After machining, the material is generally heat treated to form a martensitic matrix for maximum hardness and wear resistance.

#### Malleable Iron

Malleable iron and ductile iron are very similar, but malleable iron is declining in use because of economic reasons. Malleable iron contains a carbon form referred to as "temper carbon" graphite. This carbon form is generated by a heat treatment of the as-cast product after solidification. It is the cost of this heat treatment operation that is the reason for the decline in usage.

In general, there is little difference in corrosion resistance between gray iron and malleable iron. Malleable iron may be inferior to gray iron in flowing conditions since there are no graphite flakes to hold the corrosion products in place; therefore the attack continues at a constant rate rather than declining with time.

## CAST NICKEL AND NICKEL BASE ALLOYS

The nickel base alloys are more difficult to cast than the austenitics. A wrought trade name should never be used when purchasing a nickel alloy casting.

Because of the high cost of these alloys, they are generally used only in specialty areas and very severe service. As with the stainless steels, ACI designations have been adopted for these alloys since their compositions and properties in many cases vary significantly from the wrought equivalents. ASTM standard A-94 covers cast nickel base alloys. The chemical compositions of the nickel base alloys can be found in Table C.6.

CZ-100 is the cast equivalent of wrought nickel 200. In order to ensure adequate castability, the carbon and silicon levels are higher in the cast grade than in the wrought grade. In the molten state the alloy is treated with magnesium, which causes the carbon to nodularize, leading to an increase in the mechanical properties, much as with ductile iron.

This alloy is used for dry halogen gases and liquids and ambient-temperature hydrofluoric acid, but its widest use is in alkaline services. It has excellent resistance to all bases except ammonium hydroxide, which will cause rapid attack at any concentration above 1%. CZ-100 is resistant to all concentrations and temperatures of sodium and potassium hydroxide. If chlorates or oxidizable sulfur compounds are present in caustic, the corrosion rate will be accelerated. CZ-100 also finds application in food processing where product purity is important.

M-35-1, M-35-2, M-30-G, and M-25-S cast alloys are the equivalent of wrought Monel 400. The most common cast grade is M-35-1. The lower level of silicon makes alloy M-35-1 suitable for the handling of air-free hydrofluoric acid. Since this alloy exhibits good resistance to fluorides, it finds application in uranium enrichment. The highersilicon-grade alloy, M-30-H, is used for rotating parts and wear rings since it combines corrosion resistance with high strength. and wear resistance.

Specification and grade	Wrought equivalent	C max.	Cr	Ni	Fe	Мо	Others
ASTM A494 Grade CZ100	Nickel 200	1	_	95 <sup>a</sup>	3 <sup>a</sup>	_	_
ASTM A494 Grade M35-1	Monel 400	0.35	_	Balance	3.5 <sup>a</sup>	_	Si 1.25 <sup>a</sup>
ASTM A494 Grade M35-2	Monel 400	0.35	_	Balance	3.5 <sup>a</sup>	_	Si 2 <sup>a</sup>
ASTM A494 Grade M30C	Monel 400	0.3	_	Balance	3.5 <sup>a</sup>	_	Si 1–2, Cb 1–3
ASTM A494 Grade M25S	S-Monel	0.25	_	Balance	3.5 <sup>a</sup>	_	Si 3.5–4.5
ASTM A494 Grade CY40	Inconel 600	0.4	14–17	Balance	11 <sup>a</sup>	_	_
ASTM A494 Grade CW6MC	Inconel 625	0.06	20-23	Balance	5 <sup>a</sup>	8–10	Cb 3.15–4.5
ASTM A494 Grade CW2M	Hastelloy C	0.02	15–17.5	Balance	2 <sup>a</sup>	15–17.5	_
ASTM A494 Grade CX2MW	Hastelloy C22	0.02	20-22.5	Balance	2–6	12.5–14.5	W 2.5–3.6
ASTM A494 Grade CW6M	Chlorimet 3	0.07	17–20	Balance	3 <sup>a</sup>	17–20	_
ASTM A494 Grade N7M	Hastelloy B2	0.07	1 <sup>a</sup>	Balance	3 <sup>a</sup>	30–33	—
ASTM A494 Grade CY5SnBiM	Waukesha 88	0.05	11–14	Balance	2 <sup>a</sup>	2–3.5	Bi 3–5, Sn 3–5

 Table C.6
 Cast Nickel Base Alloys

<sup>a</sup>Maximum content.

In general, the cast Monel alloys exhibit excellent resistance to mineral acids, organic acids, and salt solutions. These alloys are also used in sulfuric acid services where reducing conditions are present and in chlorinated solvents. Oxidizing conditions accelerate the corrosion rate in all services

CY-40 is the cast equivalent of wrought Inconel alloy 600. It is a nickel-chromium alloy without the molybdenum content of most nickel-chromium alloys. In order to provide castability, the carbon and silicon content are higher than in the wrought alloy. In order to maximize corrosion resistance, this alloy is solution annealed.

Applications for this alloy are found where oxidation resistance and strength retention at high temperatures are required. This alloy resists stress corrosion cracking in chloride environments and at times is substituted for CZ-l00 in caustic soda containing halogens. CY-40 is widely used in nuclear reactor service because of its resistance to chloride stress corrosion cracking and corrosion by high-purity water. It also finds application in steam, boiler feedwater, and alkaline solutions including ammonium hydroxide.

CW-12MW is the original cast equivalent of alloy 276. Because of segregation problems with the alloy, the corrosion resistance is inferior to wrought C-276.

CW-2M is essentially a low-carbon version of CW-12MW, having improved ductility and high-temperature service, and is the presently used cast version of wrought alloy 276. This alloy may be used in corrosive environments in the welded condition without postweld heat treatment since it resists the formation of grain boundary precipitation. It has excellent corrosion resistance in hydrochloric and sulfuric acids at temperatures below 129°F (52°C), with a much higher temperature range at low concentrations. Excellent resistance is also exhibited in organic acids. Contamination by strong oxidizing species such as cupric and ferric ions will not cause accelerated attack of CW-2M as is experienced with other alloys. It is also resistant to most sources of stress corrosion cracking, including chloride, caustic, and hydrogen sulfide.

CW-6M is the cast version of Chlorimet 3 (Duriron Co.) and is intended primarily for corrosive services. The tungsten and vanadium have been removed and the chromium, molybdenum, and nickel levels raised. These modifications in the composition result in improved corrosion resistance.

CW-6MC is the cast equivalent of wrought Inconel 625. In order to maximize corrosion resistance, the alloy is solution annealed. The alloy is used primarily for oxidation resistance at high temperatures. Alloy CW-6MC has superior corrosion resistance compared with alloy CY-40.

CX-2MW is the cast version of alloy C-22 of Waukesha Foundry and is known as Waukesha 88. This alloy is not as corrosion resistant as other nickel base alloys but performs well in the food industry.

N-7M is the cast equivalent of alloy B-2 and is a nickel-molybdenum alloy. To ensure maximum corrosion resistance, solution annealing, heat treatment, and alloy purity are essential to produce a suitable microstructure.

This alloy is particularly recommended for handling hydrochloric acid at all concentrations and temperatures, including boiling. Oxidizing contaminants or conditions can lead to rapid failure. Accelerated corrosion will result when cupric or ferric chloride, hypochlorites, nitric acid, or even aeration are present. In 100% hydrochloric acid the maximum allowable ferric ion concentration is 5000 ppm at 78°F (26°C), while the maximum allowable concentration at 150°F (66°C) is less than 1000 ppm and at boiling less than 75 ppm. This alloy is also resistant to hot sulfuric acid as long as no oxidizing contaminants are present. Phosphoric acid in all concentrations up to 300°F (149°C) can be handled.

N-12MV is also a nickel-molybdenum alloy. This alloy is similar to N-7M but with less ductility. Its corrosion resistance is basically the same as that of N-7M.

#### CAST STAINLESS STEELS

Iron-based alloys containing at least 11.5% chromium are referred to as stainless steels. This level of chromium is necessary to produce passivity. Cast stainless steels may be found in all grades comparable with the wrought grades plus many additional grades for special end-use applications. Cast alloys can be produced with improvement in specific properties, but the composition cannot be produced in the wrought form. Some alloys have high silicon and/or carbon content for superior corrosion abrasion resistance, but the low ductility and high strength may make rolling or forging impossible.

#### Martensitic Alloys

The chemical composition of typical cast martensitic stainless steel alloys is found in Table C.7. Alloy CA-15 contains the minimum amount of chromium required to make it a rust-proof alloy. It exhibits good resistance to atmospheric corrosion and finds applications in

			Alloy (wt%	)	
Chemical	CA-6NM	CA-15	CA-15M	CA-28MWV	CA-40
Carbon	0.06	0.05	0.15	0.2-0.28	0.20-0.40
Manganese	1.00	1.00	1.00	_	1.00
Silicon	1.00	1.50	0.65	_	1.50
Phosphorus	0.04	0.04	0.04	_	0.04
Sulfur	0.03	0.04	0.04	_	0.04
Chromium	11.5-14.0	11.5–14.0	11.5-14.0	11.0-1 2.5	11.5-14.0
Nickel	3.5-4.5	1.00 <sup>a</sup>	1.00 <sup>a</sup>	_	1.0
Molybdenum	0.40-1.0	0.50	0.15-1.0	0.9-1.25	0.5
Tungsten		_	_	0.9-1.25	_
Vanadium	_	_	_	0.2-0.3	_
Iron	Balance	Balance	Balance	Balance	Balance

 Table C.7
 Chemical Composition of Cast Martensitic Stainless Alloys

<sup>a</sup>Maximum unless otherwise indicated.

mildly corrosive organic services. Because the alloy is martensitic, it is used in some abrasive applications. Specific areas of application include alkaline liquids, ammonia water, boiler feedwater, pulp, steam, and food products.

Alloy CA-40 is a higher-carbon version of CA-15. The higher carbon content permits heat treatment to higher strength and hardness levels. The addition of molybdenum forms alloy CA-15M, which has improved elevated-temperature resistance over alloy CA-15. Alloys CA-40 and CA-15M each have a corrosion resistance comparable to that of alloy CA-15.

CA-6NM is an iron-chromium-nickel-molybdenum alloy that is hardenable by heat treatment. Its corrosion resistance is comparable to that of alloy CA-15 with improved corrosion resistance in seawater as a result of the molybdenum content. Typical applications include seawater, boiler feedwater, and other waters up to a temperature of 400°F (204°C).

Alloy CA-28MWV is a modified version of wrought alloy type 410 with improved high-temperature strength.

The martensitic grades are resistant to corrosion in mild atmospheres, water, steam, and other nonsevere environments. They will rust quickly in marine and humid industrial atmospheres and are attacked by most inorgnic acids. When used at high hardness levels, they are susceptible to several forms of stress corrosion cracking. Hardened martensitic grades have poor resistance to sour environments and may crack in humid industrial atmospheres. Resistance is greatly improved in the quenched and fully tempered condition (generally below Rockwell C-25), especially for CA-6NM. In general, the martensitic grades are less corrosion resistant than the austenitic grades.

## **Ferritic Alloys**

The ferritic stainless castings have properties much different from those of the austenitic stainless castings, some of which can be very advantageous in certain applications. The two most common cast ferritic stainless steels are CB-30 and CC-50. Their chemical compositions are found in Table C.8.

CB-30 is essentially all ferritic and therefore is nonhardenable. The chromium content of CB-30 is sufficient to give this alloy much better corrosion resistance in oxidizing environments. This alloy has found application in food products, nitric acid, steam, sulfur

	Alloy	7 (wt%)
Chemical	CB-30	CC-50
Carbon	0.3	0.5
Manganese	1.00	1.00
Silicon	1.50	1.50
Phosphorus	0.04	0.04
Sulfur	0.04	0.04
Chromium	18.0-21.0	26.0-30.0
Nickel	2.00	4.00
Iron	Balance	Balance

Table C.8	Chemical Composition	of
Cast Ferritic	Stainless Steels	

Maximum unless otherwise noted.

atmospheres, and other oxidizing atmospheres at temperatures up to 400°F (204°C). It is also resistant to alkaline solutions and many inorganic chemicals.

CC-50 has a higher chromium content than CB-30, which gives it improved corrosion resistance in oxidizing media. In addition, at least 2% nickel and 0.15% nitrogen are usually added to CC-50, giving it improved toughness. Applications for CC-50 include acid mine waters, sulfuric and nitric acid mixtures, alkaline liquors, and sulfurous liquors.

Because of the low nickel content, these alloys have better resistance to stress corrosion cracking than the austenitic alloys.

#### Austenitic Alloys

The austenitic cast alloys represent the largest group of cast stainless steels in terms of both the number of compositions and the quantity of material produced. This group of alloys illustrates the differences that can exist between the so-called cast and wrought grades.

The austenitic cast alloys are the equivalents of the wrought 300 series stainless steels. Wrought 300 series stainless steels are fully austenitic. This structure is necessary to permit the hot and cold forming operations used to produce the various wrought shapes. Since castings are produced essentially to the finished shape, it is not necessary for the cast alloys to be fully austenitic. Even though these alloys are referred to as cast austenitic alloys, the cast compositions can be balanced such that the microstructure contains from 5% to 40% ferrite. Using Fig. C.2 as a guide, the amount of ferrite present can be estimated from the composition. The cast equivalents of the 300 series alloys can display a magnetic response from none to quite strong. The wrought 300 series contain no ferrite and in the annealed condition are nonmagnetic.

The presence of ferrite increases the resistance of the cast alloys to stress corrosion cracking compared with the fully austenitic wrought equivalents. It is possible to specify castings with specific ferrite levels.

The high-temperature service of these alloys is limited because of the presence of a continuous phase of ferrite. Above 600°F (315°C) chromium precipitates in the ferrite phase, which embrittles the ferrite. A noncontinuous ferrite phase can be provided as long as the ferrite number is maintained below 10%.

Table C.9 provides the chemical composition of the cast austenitic stainless steels. The CF series of cast alloys makes up the majority of the corrosion-resistant casting

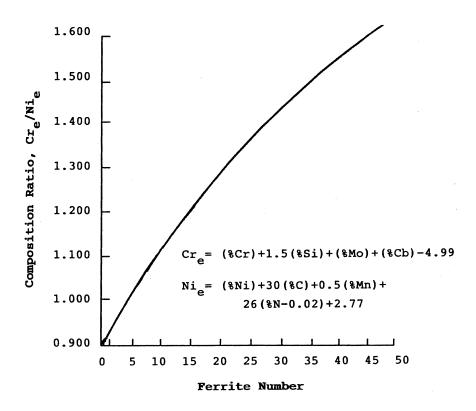


Figure C.2 Diagram for estimating ferrite content in cast stainless steel.

alloys. These are 19% chromium/9% nickel materials. The alloys are generally ferrite in austenite, with the composition balanced to provide 5% to 25% ferrite. Fully austenitic castings can be provided. However, because of the many benefits derived from the presence of ferrite in the structure, it is usually present in the alloy.

These alloys are furnished in the fully solution-annealed condition in order to provide the maximum corrosion resistance, which is at least equal to that of its wrought equivalent.

CF-8 is the base composition for the CF alloy group, and its wrought equivalent is type 304. Like wrought 304 alloy, CF-8 is resistant to strongly oxidizing media, such as boiling nitric acid. Other typical applications include adipic acid, copper sulfate, fatty acids, organic acid and liquids, sewage, sodium sulfite, sodium carbonate, vinegars, and white liquor.

CF-3 is a low-carbon version of CF-8 and is equivalent to wrought 304L. For the optimum corrosion resistance the casting should be solution annealed. The overall corrosion resistance of CF-3 is somewhat better than that of CF-8, but in general they are used in the same applications.

CF-8C is the stabilized grade of CF-8 and is equivalent to wrought 347. Carbon in the alloy is tied up to prevent the formation of chromium carbides by the addition of niobium or niobium plus tantalum. This alloy finds application in the same areas as alloy CF-3 and has the equivalent corrosion resistance of CF-8.

CF-8A and CF-3A are controlled ferrite grades. By controlling the composition and thus the percentage of ferrite present, an increase in resistance to stress corrosion

			-			Characterit	(+0/ )		
						Chemical (			
Alloy	С	Mn	Si	Р	S	Cr	Ni	Mo	Other
CE-30	0.30	1.50	2.00	0.04	0.04	26.0-30.0	8.0-11.0	_	_
CF-3	0.03	1.50	2.00	0.04	0.04	12.0-21.0	8.0-12.0	0.5	_
CF-3A	0.03	1.50	2.00	0.04	0.04	17.0-21.0	8.0-12.0	0.5	_
CF-3M	0.03	1.50	1.50	0.04	0.04	17.0-21.0	9.0-13.0	2.0-3.0	
CF-8	0.08	1.50	2.00	0.04	0.04	18.0-21.0	8.0-11.0	0.5	_
CF-8A	0.08	1.50	2.00	0.04	0.04	18.0-21.0	8.0-11.0	0.5	—
CF-20	0.20	1.50	2.00	0.04	0.04	18.0-21.0	8.0-11.0		—
CF-3MA	0.03	1.50	1.50	0.04	0.04	12.0-21.0	9.0-13.0	2.0 - 3.0	—
CF-8M	0.08	1.50	2.00	0.04	0.04	18.0-21.0	9.0-12.0	2.0-3.0	—
CF-8C	0.08	1.50	2.00	0.04	0.04	18.0-21.0	9.0-12.0	0.5	$8 \times C Cb$ ,
									1.0 Cb
CF-10MC	0.10	1.50	1.50	0.04	0.04	15.0–18.0	13.0–16.0	1.75–2.25	$10 \times C Cb$ ,
									1.2 Cb
CF-10SMMN	0.1	7–9	3.5–4.5	—	—	16.0–18.0	8.0-9.0		0.08–0.18 N
CF-16F	0.16	1.50	2.00	0.17	0.04	18.0-21.0	9.0-12.0	1.50	0.20–0.35 Se
CG-6MMN	0.06	4–6	—	—	—	20.5-23.5	11.5–13.5	1.5–3	0.1–0.3 Cb,
									0.1–0.3 V,
									0.2–0.4 N
CG-8M	0.08	1.50	1.50	0.04	0.04	18.0-21.0	9.0-13.0	3.0-4.0	
CG-12	0.12	1.50	2.00	0.04	0.04	20.0-23.0	10.0-13.0		
CH-20	0.20	1.50	2.00	0.04	0.04	22.0-26.0	12.0-15.0	0.05	
CK-20	0.20	2.00	2.00	0.04	0.04	23.0-27.0	19.0–22.0	0.05	—

Table C.9 Chemical Composition of Cast Austenitic Stainless Steels

Maximum unless otherwise specified; iron balance in all cases.

cracking is achieved without any loss in corrosion resistance. Mechanical properties are also improved. CF-3A finds application in nuclear power plant construction.

CF-20 is a high-carbon version of CF-8 and is equivlent to wrought type 302. This alloy is resistant to moderately oxidizing environments. The alloy is fully austenitic and is nonmagnetic. Applications include caustic salts, food products, sulfite liquors, and sulfurous acid.

CF-8 is the cast equivalent of wrought type 316. It contains slightly more nickel than CF-8 to offset the ferritizing influence of the molybdenum and thus maintain a comparable ferrite level in the microstructure. This alloy can be made fully austenitic and nonmagnetic. Addition of the molybdenum improves the general corrosion resistance, provides greater elevated-temperature strength, and particularly improves pitting resistance in chloride environments. By adding the molybdenum, some resistance to strongly oxidizing environments is sacrificed, such as in boiling nitric acid. However, passivity is increased in weakly oxidizing conditions compared with CF-8. This alloy has good resistance in the presence of reducing media. Overall corrosion resistance is equal to or better than that of wrought 316. Typical services include acetic acid, acetone, black liquor, chloride solution, hot dyes, fatty acids, phosphoric acid, sulfurous acid, and vinyl alcohol. The alloy is supplied in the solution-annealed condition.

CF-8M has excellent corrosion resistance in normal atmospheric conditions, including seacoast exposure. It also resists hot water and brines at ambient temperature.

С

115

Under low flow or at stagnant conditions, or at elevated temperatures, seawater may cause pitting. One application of CF-8M is the handling of 80–100% sulfuric acid at ambient temperature. Good resistance is also exhibited to phosphoric acid at all concentrations up to 170°F (77°C). It is also used for nitric acid up to boiling at all concentrations to 65%. Although CF-8M is not attacked by organic solvents, chlorinated organics may attack CF-8M, particularly under condensing conditions such as when water may be present.

CF-8M resists many alkaline solutions and alkaline salts, ammonium hydroxide at all concentrations to boiling, and sodium hydroxide at all concentrations to 150°F (65°C), above which stress corrosion cracking may occur.

Metallic chloride salts, such as ferric chloride and cupric chloride, can be very corrosive to CF-8M. Chloride can cause stress corrosion cracking above 160°F (71°C). The combination of chlorides, oxygen, water, and surface tensile stress can result in cracking at stresses far below the tensile stress of all austenitic stainless steels. Whenever chlorides are present at a few hundred ppm and the temperature exceeds 160°F (71°C), there is the possibile development of stress corrosion cracking.

CF-3M is the cast equivalent of 316L and is intended for use where postweld heat treatment is not possible. The areas of application for CF-3M are essentially the same as for CF-8M.

CF-3MA is a controlled ferrite grade with improved yield and tensile strengths.

CF-1OMC is the stabilized grade of CF-8M for field welding applications.

CF-16F is the cast equivalent of wrought type 303. It is a free-machining stainless steel. This alloy and CF-20 are used in similar applications, although the corrosion resistance of CF-16F is inferior to that of CF-20.

CG-8M is the cast version of wrought type 317. This alloy is resistant to reducing media and is resistant to sulfuric and sulfurous acids. It also resists the pitting of halogen compounds. Strongly oxidizing environments will attack CG-8M. As a result of the high ferrite content, this alloy exhibits very good stress corrosion cracking resistance but also has an upper temperature limit of 800°F (425°C). Applications are found in the pulp and paper industry, where it resists attack from pulping liquors and bleach-containing water.

CE-30 is a high-carbon cast stainless steel. The alloy has a microstructure of ferrite in austenite with carbide precipitates present in the as-cast condition. Resistance to intergranular corrosion is not seriously impaired since there is sufficient chromium present. Since the alloy does retain good corrosion resistance as cast, it is useful where heat treatment is not possible or where heat treatment following welding cannot be performed. By solution annealing of the casting, corrosion resistance and ductility can be greatly improved.

This alloy is resistant to sulfurous acid, sulfites, mixtures of sulfurous and sulfuric acids, and sulfuric and nitric acids.

CF-30A, which is a controlled ferrite grade, is resistant to stress corrosion cracking in polythionic acid and chlorides. Other applications are found in pulp and paper manufacture, caustic soda, organic acids, and acid mine water.

CH-20 is similar to CE-30 but has a composition containing a greater amount of nickel and a lesser amount of chromium. This alloy is considerably more corrosion resistant than CF-8 and less susceptible to intergranular corrosion than CF-8 after exposure to sensitizing temperatures. The alloy must be solution annealed to achieve the maximum corrosion resistance.

CK-20 is used in the same applications as CH-20 but at higher temperatures.

CG-6MMN is the cast equivalent of nitronic 50 (Armco Inc.). This alloy is used in place of CF-8M when higher strength and/or better corrosion resistance is required.

CF-1OSMMN is the cast equivalent of nitronic 60 (Armco Inc.). The corrosion resistance is similar to CF-8 but not as good in hot nitric acid. This alloy does have the advantage of better galling resistance than the other CF grades.

## **Duplex Alloys**

Stainless steels with approximately 50% ferrite and 50% austenite are known as duplex stainless steels. These alloys have superior corrosion resistance and higher yield strength than the austenitics with lower alloy content. Refer to Table C.10 for the chemical composition of the cast duplex stainless steels.

These alloys are limited to a maximum operating temperature of 500°F (260°C) as a result of the formation of a sigma phase at elevated temperatures. Both toughness and corrosion resistance are adversely affected by the formation of a sigma phase. Welding of duplex alloys is somewhat difficult because of the potential of the formation of a sigma phase.

The duplex alloys exhibit improved resistance to erosion and velocity conditions as a result of increased hardness. They also exhibit exceptional resistance to chloride stress cracking.

The duplex alloys are completely resistant to corrosion from atmospheric and marine environments, fresh water, brine, boiler feedwater, and steam. They are especially suitable for high-temperature chloride-containing environments where stress corrosion cracking and pitting are common causes of failure of other stainless steels. The two phases of the duplex alloys result in inherently better stress corrosion cracking resistance compared with single-phase alloys. Usually at least one of the phases is resistant to cracking in a given environment. These alloys are highly resistant to acetic, formic, and other organic acids and compounds.

CD-4MCu is the cast equivalent of Ferralium 255. Its high chromium level makes it particularly useful in oxidizing media such as nitric acid. This alloy can also be used in

		1	Alloy (wt%)	
Chemical	CD-4MCu	CD-3MN	CD-3MWN	Z6CNDU 20.08M
Carbon	0.04	0.03	0.03	0.08
Manganese	1.00	_	_	_
Silicon	1.00	_	_	_
Phosphorus	0.04	_	_	_
Sulfur	0.04	_	_	_
Chromium	24.5-26.5	21-23.5	24–26	19–23
Nickel	4.75-6.00	4.5-6.5	6.5-8.5	7–9
Molybdenum	1.75-2.25	2.5-3.5	3-4	2.3
Copper	2.75-3.25	_	0.0-1	1.2
Nitrogen	_	0.1-0.3	0.2-0.3	_
Tungsten	_		0.5–1	_
Iron	Balance	Balance	Balance	Balance

 Table C.10
 Chemical Composition of Cast Duplex Stainless Steel

Maximum unless otherwise noted.

С

CD-3MN is the cast version of wrought UNS 31803 or 2205. Compared with the other duplex grades it has a lower alloy content. Consequently, its cost is lower, but some corrosion resistance is sacrificed.

CD-3MWN is the cast version of wrought zeron 100. It has a corrosion resistance nearly as good as that of the superaustenitic alloys.

Z6CNDU 20.08M is the cast version of Uranus 50M. In terms of corrosion resistance it is slightly better than CF-8M but inferior to the other duplex stainless steels.

## Superaustenitic Alloys

Superaustenitic alloys are those austenitic stainless steels having alloying elements, particularly nickel and/or molybdenum, in higher percentages than the conventional 300 series stainless steels. Table C.11 lists the chemical compositions of these cast alloys. In some instances these alloys have been classified as nickel alloys. As can be seen in Table C.11 these alloys contain 16–25% chromium, 30–35% nickel, molybdenum, and nitrogen, and some also contain copper. No single element exceeds 50%.

Added resistance to reducing environments is provided by the additional nickel, while the extra molybdenum, copper, and nitrogen increase the resistance to pitting in chlorides. These alloys are fully austenitic, which makes them more difficult to cast than the ferrite-containing grades.

Superaustenitics are used for high-temperature chloride-containing environments where pitting and stress corrosion cracking are common causes of failure of other stainless steels. These alloys resist chloride stress corrosion cracking above 250°F (121°C). They also exhibit excellent resistance to sulfide stress cracking.

			Alloy (wt%)		
Chemical	CD-7M	CN-7MS	CK-3MCuN	CE-3MN	CU-MCuC
Carbon	0.07	0.07	0.025	0.03	0.05
Manganese	1.50	_	_	_	_
Silicon	1.50	_	_	_	_
Phosphorus	0.04	_	_	_	_
Sulfur	0.04	_	_	_	_
Chromium	19.0-22.0	18.0-20.0	19.5-20.5	20.0-22.0	19.5-23.5
Nickel	27.5-30.5	22.0-25.0	17.5–19.5	23.5-25.5	38.0-46.0
Molybdenum	2.0-3.0	2.5-3.0	6.0-7.0	6.0-7.0	2.50-3.50
Copper	3.0-4.0	1.5-2.0	0.5-1.0	_	1.50-3.50
Nitrogen	_	_	0.18-0.24	0.18-0.26	_
Columbium	_	_	_	_	0.6-1.2
Iron	Balance	Balance	Balance	—	—

 Table C.11
 Chemical Composition of Cast Superaustenitic Stainless Steel

Maximum unless otherwise noted.

CN-7M is the cast equivalent of wrought alloy 20Cb3. This alloy resists sulfuric acid in all concentrations at temperatures up to 150°F (65°C) and higher for most concentrations. The high nickel content of CN-7M imparts excellent resistance to alkaline environments, such as sodium hydroxide, where it can be used up to 73% and at temperatures to 300°F (149°C). The chromium content of this alloy makes it superior to the CF grades in nitric acid—even better than CF-3, which is generally considered the best alloy for this service. Hydrochloric acid, certain chlorides, and strong reducing agents such as hydrogen sulfide, carbon disulfide, and sulfur dioxide will accelerate corrosion. Applications for CN-7M have also included hot acetic acid, dilute hydrofluoric and hydrofluosilicic acids, nitric-hydrofluoric pickling solutions, phosphoric acid, and plating solutions.

Alloy CN-7MS is a modified version of alloy CN-7M.

Alloys CK-3MCuN and CE-3MN are superior for chloride environments and are the cast equivalents of wrought alloys 254SM0 and A16XN, respectively.

CU-5MCuC is the cast version of wrought alloy 825, although niobium is substituted for titanium. Titanium will oxidize rapidly during air melting, while niobium will not. This alloy is similar in corrosion resistance to CN-7M. See Refs. 6 and 7.

#### Precipitation Hardening Alloys

Table C.12 lists the cast precipitation-hardening stainless steels and gives their chemical compositions.

CB-7Cu is the cast equivalent of wrought alloy 326. The alloy is martensitic with minor amounts of retained austenite present in the microstructure. In the age-hardened condition this alloy exhibits corrosion resistance superior to the straight martensitic and ferritic grades. This alloy is used where moderate corrosion resistance and high strength are required. Typical applications include aircraft parts, pump shafting, and food processing equipment.

CB-7Cu-1 and CB-7Cu-2 are cast versions of wrought alloys 17-4PH and 15-5PH. CB-7Cu-1 is more commonly cast than CB-7Cu-2.

These alloys are similar in corrosion resistance to alloys CF-8 and wrought type 304, and better than the 400 series of stainless steels. They will resist atmospheric attack in all but the most severe environments. When in contact with seawater the alloys will pit, but they are resistant to natural water. Applications include uses in steam, boiler feedwater, condensate, and dry gases.

		Alloy (wt%)					
Chemical	CB-7Cu	CB-7Cu-1	CB-7Cu-2				
Carbon	0.07	0.07	0.07				
Manganese	1.00	_	_				
Silicon	1.00	_	_				
Phosphorus	0.04	_	_				
Sulfur	0.04	_	_				
Chromium	15.5-17.0	15.5-17.7	14.0-15.5				
Nickel	3.6-4.6	3.6-4.6	4.5-5.5				
Copper	2.3-3.3	2.5-3.2	2.5-3.2				
Columbium	_	0.15-0.35	0.15-0.35				
Iron	Balance	Balance	Balance				

Table C.12Chemical Composition of CastPrecipitation-Hardening Stainless Steels

Maximum unless otherwise noted.

## CATHODE

A cathode is a negatively charged electrode where reduction is the principal reaction.

## **CATHODIC CORROSION**

Cathodic corrosion is an unusual condition in which metal loss is accelerated at the cathode as a result of the alkaline condition there being corrosive to certain amphoteric metals, primarily aluminum, zinc, and lead.

## CATHODIC DELAMINATION

Cathodic delamination is the loss of adhesion of a paint film adjacent to defects, when cathodic protection is applied to a coated metal.

## **CATHODIC PROTECTION**

When dissimilar metals are in physical or electrical contact (the latter via a conductive electrolyte), such as a process fluid or soil, galvanic corrosion can take place. The galvanic corrosion process is similar to the action of a simple DC cell in which the more active metal becomes an anode, and corrodes, while the less active metal becomes a cathode, and is protected. It is possible to predict which metals will corrode when in contact with others based on the galvanic series shown in the table.

Galvanic Series	
Anodic end	
Magnesium	Hastelloy C (active)
Magnesium alloys	Brasses
Zinc	Copper
Aluminum 5052	Bronzes
Aluminum 6061	Cupronickel alloys
Cadmium	Monel
Aluminum AA2017	Silver solder
Iron and carbon steel	Nickel (passive)
Copper steel	Inconel (passive)
4–6% chromium steel	Ferritic stainless (passive)
Ferritic stainless (active) 400 series	Austenitic stainless (passive)
Austenitic stainless (active) 18-8 series	Titanium
Lead-tin solder	Hastelloy C (passive)
Lead	Silver
Tin	Graphite
Nickel (active)	Gold
Iconel (active)	Platinum
	Cathodic end

All metals and alloys have certain inherent properties that cause them to react as anodes or cathodes when in contact with dissimilar metals or alloys. Whether a particular material will react as a cathode or an anode can be determined from its relative position in

Copyright © 2004 by Marcel Dekker, Inc.

the galvanic series. The further apart two materials are from each other in the galvanic series, all other factors being equal, the greater the rate of corrosion. The material closest to the anodic end will be the one to corrode. For example, if tin and zinc were in contact, the zinc would corrode, whereas if tin and copper were in contact, the tin would corrode.

The rate of attack is also affected by the relative size of the material and the specific electrolyte present. A small anode area in contact with a large cathode area will result in a rapid severe attack. Conversely, a large anode area in contact with a small cathode area will lessen the rate of galvanic attack since the same total emf driving force of corrosion will be spread out over a larger area. Also, the higher the degree of ionization of the electrolyte, the greater the rate of attack.

Galvanic corrosion can also take place when metals having the same analysis have different surface conditions and an electrolyte is present. In general, the formation of a corrosion cell is induced by the nonuniformity of the surface condition, such as with defects in the surface oxide film, localized distribution of elements, and difference in crystal face or phase. These nonuniformities of surface cause potential difference between portions of the surface and thereby promote the formation of a corrosion cell.

Galvanic corrosion can be stopped by means of cathodic protection, which is an electrochemical technique. It can be applied to metals immersed in water, buried in soil, or in contact with electrolytes in a process application. Cathodic protection consists of a cathodic current flowing through the metal electrolyte interface, favoring the reduction reaction over the anodic metal dissolution. The entire structure works as a cathode.

This electrochemical technique was developed by Sir Humphrey Davy in 1824. The British Admiralty had blocks of iron attached to the hulls of copper-sheathed vessels to provide cathodic protection. Unfortunately, cathodically protected copper is subject to fouling by marine life, which reduced the speed of vessels under sail and forced the Admiralty to discontinue the practice. Unprotected copper provides a sufficient number of copper ions to poison fouling organisms. However, the corrosion rate of the copper had been appreciably reduced.

In 1829 Edmund Davy was successful in protecting the iron portions of buoys by using zinc blocks, and in 1840 Robert Mallet produced a zinc alloy that was particularly suited as a sacrificial anode. As steel hulls replaced wooden hulls, the fitting of zinc slabs to the steel hulls, to provide cathodic protection, became standard practice.

In 1950 the Canadian Navy determined that the proper use of antifouling paints in conjunction with corrosion-resisting paints made cathodic protection of ships feasible and could reduce maintenance costs.

Cathodic protection is achieved by applying electrochemical principles to metallic components buried in soil or immersed in water. It is accomplished by flowing a cathodic current through a metal-electrolyte interface, favoring the reduction reaction over the anodic metal dissolution. This enables the entire structure to work as a cathode.

The basis of cathodic protection is shown in the polarization diagram for a copperzinc cell in Fig. C.3. If polarization of the cathode is continued by use of an external current beyond the corrosion potential to the open-circuit potential of the anode, both electrodes reach the same potential and no corrosion of the zinc can take place.

Cathodic protection is accomplished by supplying an external current to the corroding metal on the surface of which local action cells operate, as shown in Fig. C.4. Current flows from the auxiliary anode and enters the anodic and cathodic areas of the corrosion cells, returning to the source of the DC current (B). Local action current will

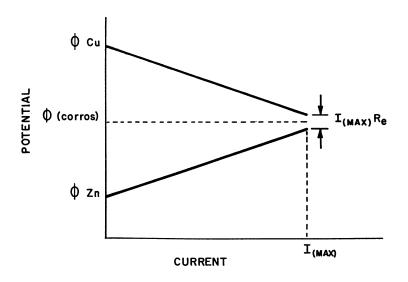


Figure C.3 Polarization of copper-zinc cell.

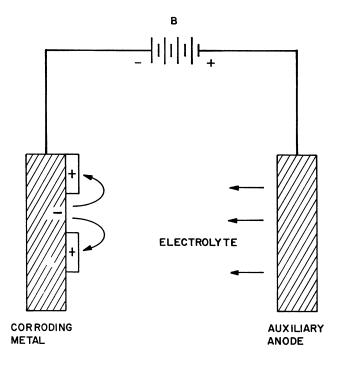


Figure C.4 Cathodic protection using impressed current on local action cell.

cease to flow when all the metal surface is at the same potential as a result of the cathodic areas being polarized by an external current to the open-circuit potential of the anodes. As long as this external current is maintained, the metal cannot corrode.

There are two methods by which cathodic protection can be accomplished. One is by coupling the structure with a more active metal, such as zinc or magnesium. This produces a galvanic cell in which the active metal works as an anode and provides a flux of electrons to the structure. The structure then becomes the cathode and is protected, while the anode is destroyed progressively and is called a sacrificial anode.

The second method is to impress a direct current between an inert anode and the structure. The structure receives the excess of electrons, which protects it. About 1910–1912 the first application of cathodic protection by means of an impressed electric current was undertaken in England and the United States. Since that time the general use of cathodic protection has been widespread. There are thousands of miles of buried pipelines and cables that are protected in this manner. This form of protection is also used for water tanks, submarines, canal gates, marine piping, condensers, and chemical equipment.

## Sacrificial Anodes

In cathodic protection, the structure to be protected must receive a cathodic current flow so that it operates as a cathode. The need for an external DC current to accomplish this can be eliminated by selecting an anode constructed of a metal that is more active in the galvanic series than the metal to be protected. A galvanic cell will be established with the current direction as required. These sacrificial anodes are usually composed of magnesium or magnesium-based alloys. On occasion zinc or aluminum have been used.

Magnesium is more active than steel, it has a greater tendency to ionize, and its potential is more active than iron. The open-circuit potential difference between magnesium and steel is about 1 volt. This means that one anode can protect only a limited length of pipeline. This low voltage can have an advantage over higher impressed voltages in that the danger of overprotection to some portions of the structure is less and because the total current per anode is limited; the danger of stray-current damage to adjoining metal structures is reduced.

Magnesium rods have also been placed in steel hot water tanks to increase their life. The greatest degree of protection is afforded in hard waters, since the degree of conductivity is greater than in soft waters.

#### Sacrificial Anode Requirements

To provide cathodic protection, a current density of a few milliamps (mA) is required. In order to determine the anodic requirement, it is necessary to know the energy content of the anode and its efficiency. With this information it is possible to determine the size of the anode required, its expected life, and the number of anodes required.

The three most common metals used as sacrificial anodes are magnesium, zinc, and aluminum. The energy content and efficiency of these metals are shown in the table.

Metal	Theoretical energy content (A h/lb)	Anodic efficiency %	Practical energy content (A h/lb) (PE)
Magnesium	1000	50	500
Zinc	370	90	333
Aluminum	1345	60	810

Zinc is more economical to use than magnesium, but because of the relatively small cell voltage it produces, it is primarily useful under special circumstances, such as to protect ships in seawater or to prevent corrosion of systems with low current requirements.

Although magnesium is more expensive than zinc, and although it is consumed faster than zinc or aluminum, it does provide the largest cell voltage and the largest current. Care must be taken not to use aluminum in environments having a pH of 8 or greater, since alkaline conditions will produce a rapid self-corrosion of aluminum.

In determining anodic requirements to provide cathodic protection, several calculations are required. The number of pounds of metal required to provide a current of 1 A for one year is calculated as

lb metal/A-yr = 
$$\frac{8760 \text{ h/yr}}{\text{PE}}$$

For magnesium this would be

lb Mg/A-yr = 
$$\frac{8760}{500}$$
 = 17.52

The number of years (YN) for which 1 lb of metal can produce a current of 1 mA is determined from

$$YN = \frac{PE}{10^{-3}A 8760 \text{ hr/yr}}$$

For magnesium this would be

$$YN = \frac{500}{10^{-3}(8760)} = 60 \text{ yr}$$

The current density requirements for cathodic protection is on the order of a few milliamps. The life expectancy (L) of an anode of W lb delivering a current of 1 mA is calculated as

$$L = \frac{\mathrm{YN}(W)}{i}$$

For magnesium this would be

$$L = \frac{60W}{i}$$

which is based on 50% anodic efficiency. Since actual efficiencies tend to be somewhat less, it is advisable to apply a safety factor and multiply the result by 0.75.

The current required to secure protection of a structure and the available cell voltage between the metal structure and the sacrificial anode determine the number of anodes required. This can be illustrated by the following example.

Assume that an underground pipeline has an external area of 200 sq ft and a soil resistivity of 600 ohm cm. Field tests indicate that 6 mA/sq ft is required for protection. To provide protection for the entire pipeline,

$$(6 \text{ mA/ft}^2)(200 \text{ ft}^2) = 1200 \text{ mA}$$

is required. Magnesium anodes used in this particular soil have a voltage of –1.65 V or a galvanic cell voltage of

$$E_{\text{calc}} = E_c - E_a$$
  
= -0.85 - (-1.65)  
= + 0.8V

Therefore, the resistance is

$$R = \frac{V}{I} = \frac{0.8}{1.2} = 0.67$$
 ohm

As the number of anodes is increased, the total resistance of the system decreases. Each anode that is added provides a new path for current flow, parallel to the existing system. The relationship between the resistance of the system and the number of anodes is shown in the Sunde equation:

$$R = \frac{0.00521P}{NL} \left( 2.3 \log \frac{8L}{d-1} + \frac{2L}{S} \ 2.3 \log 0.656N \right)$$

where

R = resistance (ohms) P = soil resistivity (ohm-cm) N = number of anodes L = anode length (ft) d = diameter of anode (ft)S = distance between anodes (ft)

Fig. C.5 shows the typical plotting of the results of this equation. Different anodic shapes will have different curves.

## Impressed Current Systems

For these systems the source of electricity is external. A rectifier converts high voltage to a low-voltage DC current. This direct current is impressed between buried anodes and the structure to be protected.

It is preferable to use inert anodes, which will last for the longest possible time. Typical materials used for these anodes are graphite, silicon, titanium, and niobium plated with platinum.

For a given applied voltage, the current is limited by electrolyte resistivity and by the anodic and cathodic polarization. With the impressed current system it is possible to impose whatever potential is necessary to obtain the current density required by means of the rectifier.

Electric current flows in the soil from the buried anode to the underground structure to be protected. Therefore, the anode must be connected to the positive pole of the rectifier and the structure to the negative pole. All cables from the rectifier to the anode and to the structure must be electrically insulated. If not, those from the rectifier to the anode will act as an anode and deteriorate rapidly, while those from the rectifier to the structure may pick up some of the electric current, which would then be lost for protection.

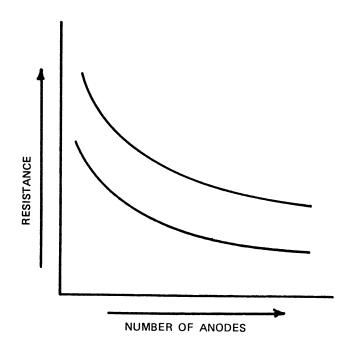


Figure C.5 Plot of Sunde equation.

## **Current Requirements**

The specific metal and the environment will determine the current density required for complete protection. The applied current density must always exceed the current density equivalent to the measured corrosion rate under the same conditions. Therefore, as the corrosion rate increases, the impressed current density must be increased to provide protection.

Factors that affect current requirements are

- **1.** The nature of the electrolyte
- 2. The soil resistivity
- 3. The degree of aeration

The more acid the electrolyte, the greater will be the potential for corrosion and the greater will be the current requirement. Soils that exhibit a high resistance require a lower cathodic current to provide protection. In the area of violent agitation or high aeration, an increase in current will be required. The required current to provide cathodic protection can vary from 0.5 to 20 mA/sq ft of bare surface.

Field testing may be required to determine the necessary current density to provide cathodic protection in a specific area. These testing techniques will only provide an approximation. After completion of the installation, it will be necessary to conduct a potential survey and make the necessary adjustments to provide the desired degree of protection.

# Anode Materials and Backfill

Although it is generally preferred to use inert anodes, it is possible to use scrap iron. Scrap iron is consumed at a considerably faster rate than graphite or other inert anode materials.

CATHODIC PROTECTION

The advantage of scrap iron is its lower initial cost and lower operating cost, since its power requirements are less. In areas where replacement poses a problem, the cost of the use of the more inert anodes outweighs the reduced cost of the scrap iron.

Platinum clad or 2% silver-lead electrodes have been used for protection of structures in seawater and are estimated to last 10 years, whereas sacrificial magnesium anodes have a life of 2 years.

Since the effective resistivity of soil surrounding an anode is limited to the immediate area of the electrode, this local resistance is usually reduced by using backfill. The anode is usually surrounded by a thick bed of coke mixed with 3 or 4 parts of gypsum to one part of sodium chloride. The consumption of the anode itself is reduced somewhat, since the coke backfill carries a part of the current. Backfill is not required when the anode is immersed in a river bed, lake, or ocean.

#### Testing for Completeness of Protection

Once the system has been installed, it must be tested for completeness of protection. The preferred method is to take potential measurements. By measuring the potential of the protected structure, the degree of protection including overprotection can be determined. The basis for this determination is the fundamental concept that cathodic protection is complete when the protected structure is polarized to the open-circuit anodic potential of the local action cells.

The reference electrode is placed as closely as possible to the protected structure to avoid and to minimize an error caused by internal resistance (IR) drop through the soil. For buried pipelines a compromise location is directly over the buried pipe at the soil surface because cathodic protection currents flow mostly to the lower surface and are minimum at the upper surface of the pipe buried a few feet below the surface.

The potential for steel is equal to -0.85 V versus the copper-saturated copper sulfate half-cell, or 0.53 V on the standard hydrogen scale. The theoretical open-circuit anodic potential for other metals may be calculated using the Nernst equation. Several typical calculated values are shown in the table.

Metal	E° (V)	Solubility product M(OH) <sub>2</sub>	OH <sub>2</sub> scale (V)	O vs. Cu–CuSO <sub>4</sub> reference (V)
Iron	0.440	$\begin{array}{c} 1.8 \times 10^{-15} \\ 1.6 \times 10^{-19} \\ 4.5 \times 10^{-17} \\ 4.2 \times 10^{-15} \end{array}$	-0.59	-0.91
Copper	-0.337		0.16	-0.16
Zinc	0.763		-0.93	-1.25
Lead	0.126		-0.27	-0.59

Overprotection of steel structures, to a moderate degree, does not cause any problems. The primary disadvantages are waste of electric power and increased consumption of auxiliary anodes. When overprotection is excessive, hydrogen can be generated at the protected structure in sufficient quantities to cause blistering of organic coatings, hydrogen embrittlement of the steel, or hydrogen cracking.

Overprotection of systems with amphoteric metals (e.g., aluminum, zinc, lead, tin) will damage the metal by causing increased attack instead of reduction of corrosion. This stresses the need for making potential measurements of protected structures.

#### Use with Coatings

It is advantageous to use insulating coatings with sacrificial anodes or impressed current systems when supplying cathodic protection. These coatings need not be pore free, because the protective current flows preferentially to the exposed metal areas, which require the protection. Coatings are useful in distributing the protective current, in reducing total current requirements, and in extending the life of the anode. Compared to a bare pipeline, the current distribution in a coated pipeline is greatly improved, the total number of anodes required is reduced, and the total current required is less. In addition, one anode can protect a much longer section of pipeline. For example, one magnesium anode is capable of protecting approximately 100 feet (30 m) of a bare pipeline, whereas the same anode can provide protection for approximately 5 miles of a coated pipeline.

In a hot water tank coated with glass or an organic coating, the life of the magnesium anode is increased and more uniform protection is supplied to the tank. Without the coating the tendency is for excess current to flow to the side, and insufficient current flows to the top and bottom.

Because of these factors cathodic protection is usually provided with coated surfaces.

#### Economics

The installation of cathodic protection systems has made it economically feasible to transport oil and high-pressure natural gas across the American continent by

- 1. Guaranteeing there will be no corrosion on the soil side of the pipe
- 2. Permitting the use of thinner-walled pipe
- 3. Eliminating the need for an external corrosion allowance
- 4. Reducing maintenance costs
- **5.** Permitting longer operating periods between routine inspections and maintenance periods

The cost of the cathodic protection system is more than recovered as a result of the above savings. Similar savings and advantages have been realized on other types of installations where cathodic protection systems have been installed.

See Refs. 1, 8–10.

## CAUSTIC EMBRITTLEMENT

Caustic embrittlement is a form of stress corrosion cracking occurring in metals in contact with caustic under certain conditions. The developing cracks result from the combined actions of tensile stress and corrosion. The cracking can he intergranular or transgranular.

See "Stress Corrosion Cracking."

#### **CAVITATION CORROSION**

This form of corrosion is similar to erosion corrosion. It is caused by the formation and collapse of tiny vapor bubbles near a metallic surface in the presence of a corrodent. The protective film is damaged by the high pressure caused by the collapse of the bubbles. This form of corrosion is found quite frequently on pump impellers and condensers.

## **CELL POTENTIALS**

A reaction will occur only if there is a negative free energy change ( $\Delta G$ ). For electrochemical reactions the free energy change is calculated by

$$\Delta G = -nFE$$

where *n* is the number of electrons, *F* is Faraday's constant, and *E* is the cell potential.

For a given reaction to take place the cell potential must be positive. The cell potential is the difference between the two half-cell reactions, the one at the cathode minus the one at the anode.

The cell potential for iron corroding freely in acid is calculated to be

$$E = \text{ cathode half-cell} - \text{ anode half-cell}$$
$$E = E(H^{1}/H_{2}) - E(Fe/Fe^{21})$$
$$E = (0) - (-0.440) = + 0.44$$

The reaction can take place because the cell potential is positive. The larger the potential difference, the greater the driving force for the reaction. In order for corrosion to occur, there must be a current flow and a completed circuit, which is then governed by Ohm's law:

$$I = \frac{E}{R}$$

The cell potential calculated here represents the peak value for the case of the two independent reactions. If the resistance were infinite, the cell potential would remain as calculated, but there would be no corrosion at all. If the resistance of the circuit were zero, the potentials of each half-cell would approach the other while the rate of corrosion would be infinite.

See Refs. 10, 11.

#### **CERAMIC MATERIALS**

Ceramic materials are various hard, brittle, heat-resistant, and corrosion-resistant materials produced by firing (heat treating) clay, other minerals, or synthetic inorganic compositions. They usually consist of one or more metals in combination with a nonmetal, usually oxygen.

Ceramics are subject to many of the forms of corrosion that metals are subject to, including uniform corrosion, crevice corrosion, pitting, cavitation corrosion, erosion corrosion, galvanic corrosion, intergranular corrosion, and corrosion-assisted cracking.

Corrosion data reported on ceramic materials presents two problems: the wide variety of units used and the use of units that make it difficult to compare results from different investigators. From an engineering and practical aspect, for ceramics the two main criteria for corrosion performance are loss of physical dimension and loss of mechanical properties.

The preferred units for measuring loss of physical dimension are penetration rates, such as mils per year (mpy). This is comparable to the measurement used for metallic corrosion.

erosion.

Corrosion of ceramic materials is a complicated process. It can take place by C any one or a combination of mechanisms. In general, the environment will attack the ceramic, forming a reaction product that may be a gas, a liquid, a solid, or a combination. When the reaction product formed is a solid, it may form a protective layer preventing further corrosion. If the reaction product formed is a combination

Some of the fundamental concepts of chemistry will help to permit understanding of the corrosion of a ceramic section. A ceramic with acidic character tends to be attacked by an environment with a basic character, and vice versa; ionic materials tend to be soluble in polar solvents while covalent materials tend to be soluble in nonpolar solvents; the solubility of solids in liquids generally increases with increasing temperatures.

of a solid and a liquid, the protective layer formed may be removed by the process of

# **Crystalline Materials**

Polycrystalline materials are made up of several components. Corrosive attack on these materials starts with the least corrosion-resistant component, which normally is the ingredient used for bonding, or more generally the minor component of the material.

The corrosion of a solid crystalline material by a liquid can result from either indirect dissolution or direct dissolution. In the former, an interface or reaction product is formed between the solid crystalline material and the solvent. This reaction product, being less soluble than the bulk solid, may or may not form an attached surface layer. In direct dissolution the solid crystalline material dissolves directly into the solvent.

When a silicate is leached by an aqueous solution, an ion is removed from a site within the crystal structure and is placed into the aqueous phase. Whether or not leaching occurs will depend upon the ease with which the ions can be removed from the crystal structure.

The corrosion of polycrystalline ceramic by a vapor can be more serious than attack by either liquids or solids. Porosity or permeability of the ceramic is one of the most important properties related to its corrosion by a vapor or gas. If the vapor can penetrate the material, the surface area exposed to attack is greatly increased and corrosion proceeds rapidly. A combined attack of vapor may also take place. In this situation the vapor may penetrate the material under a thermal gradient to a lower temperature, condense, and then dissolve material by liquid solution. The liquid solution can then penetrate further along temperature gradients until it freezes. If the thermal gradient is changed, it is possible for the solid reaction products to melt, causing excessive corrosion and spalling at the point of melting.

If two dissimilar solid materials react when in contact with each other, corrosion can take place. Common types of reactions involve the formation of a solid, a liquid, or a gas. Solid-solid reactions are predominantly reactions involving diffusion.

Porosity plays an important role in the corrosion resistance of ceramics. The greater the porosity, the greater will be the corrosion. The fact that one material may yield a better corrosion resistance than another does not necessarily make it a better material, if the two materials have different porosities.

Ceramics that have an acid or base characteristic similar to the corrodent will tend to resist corrosion the best. In some cases the minor components of a ceramic, such as the bonding agent, may have a different acid/base character than the major component. In this instance the acid/base character of the corrodent will determine which phase corrodes first.

In the area of corrosion resistance of ceramics we will be dealing with the so-called traditional ceramics, which include brick-type products.

Common bricks, though hard to the touch, have a high water adsorption (anywhere from 8% to 15%) and are leached or destroyed by exposure to strong acid or alkali. Acid bricks, whether of shale or fireclay body, are made from selected clays containing few acid-soluble components. These bricks are fired for a longer period of time at higher temperatures than the same clay when used to make common brick. This firing eliminates any organics that may be present and produces a brick with a much lower absorption rate, under 1% for best-quality red shale and under 5% for high-quality fireclay. See "Acid Brick."

Zirconia-containing materials will be attacked by alkali solutions containing lithium, potassium, or sodium hydroxide, and potassium carbonate.

The transition metal carbides and nitrides are chemically stable at room temperature but exhibit some attack by concentrated acid solutions. The normally protective layer of silicon oxide that forms on the surface of silicon carbide and silicon nitride can exhibit accelerated corrosion when various molten salts are present. None of the carbides or nitrides are stable in oxygen-containing environments. Under certain conditions some carbides and nitrides form a protective metal oxide layer that allows them to exhibit reasonably good oxidation resistance. Silicon carbide and nitride are reasonably inert to most silicate liquors as long as they do not contain significant amounts of iron oxide.

Quartz (silica) is not attacked by hydrochloric, nitric, or sulfuric acids at room temperature but will be slowly attacked by alkaline solutions. At elevated temperatures, quartz is readily attacked by sodium hydroxide, potassium hydroxide, sodium carbonate, and sodium borate. The presence of organics dissolved in the water increases the solubility of silica. Fused silica is attacked by molten sodium sulfate.

Tables C.13a, 13b, and 13c show the compatibility of various ceramic materials with selected corrodents.

#### **Glassy Materials**

Typical glassy materials consist of silicate glasses, borosilicate glasses, lead-containing glasses, phosphor-containing glasses, fluoride glasses, and chalcogenide-halide glasses.

Glassy materials corrode primarily through the action of aqueous media. In general, the very high silica glasses (96% Si0<sub>2</sub>) such as aluminosilicate and borosilicate compositions have excellent resistance to a variety of corrodents.

Borosilicate glass is the primary composition used in the corrosion resistance field. It is resistant to all chemicals except hydrofluoric acid, fluorides, and such strong caustics as sodium or potassium hydroxide. However, caustics of even up to 50% concentration at room temperature will not be detrimental to borosilicate glass.

Because of its inertness, borosilicate glass has found wide usage in contact with high-purity products. The glass will not impart contamination to the material it comes into contact with. See "Borosilicate Glass."

There are many glass compositions. A list of about 30 glass compositions with their resistance to weathering, water, and acid may be found on page 572 of *Encyclopedia of Glass Technology*, 2nd ed., vol. 10, published by Wiley in New York.

See Refs. 12 and 13.

# C-GLASS

This is a calcium aluminosilicate glass used for reinforcing thermosetting resins. See "Thermoset Reinforcing Materials."

			R	lesistar	ice to			
	Sl	ags			Molter	1 meta	s	
Material	Acid	Basic	Al	Fe	Na	Pb	Zn	Mg
Zircon	G	F	G	G	Р	G	G	F
Bonded 99% alumina	G	G	G	G	Р	G	G	G
Fused cast alumina	EX	G	G	G	F	G	G	ΕX
Zirconia stabilized	G	Р	G	G	Р	G	G	F
Silicon carbide	G	F	G	Р	Р		EX	G
Silicon nitride								
bonded silicon carbide	EX	F	ΕX	Р	Р		EX	G
Magnesite	Р	G	F	G	Р	G	F	F
Chrome	Р	F	Р	G	Р	G	F	F
Fosterite	Р	F	F	G	Р	G	F	F
Synthetic mullite	G	G	F	G	Р	G	G	F
Converted mullite	G	F	F	G	Р	G	G	F
Silica	G	F	Р	G	Р	F	G	Р
Fireclay	G	F	F	G	Р	F	G	Р

Table C.13a Chemical Resistance of Various Ceramic Materials

EX = Excellent, G = Good, F = Fair, P = Poor.

Material	CO <sub>2</sub>	СО	Steam	$Cl_2$	H <sub>2</sub>	HCl	NH3	SO <sub>2</sub>	S
Zircon	А	А	А	B–D	E	А	А	А	B–D
Bonded 99% alumina	А	А	А	А	А	А	А	А	А
Fused cast alumina	А	А	А	A–D	А	А	А	А	A–C
Zirconia stabilized	А	А	B–C	В	Е	А	Е	А	A–B
Silicon carbide	В	В	В	D		А	А	А	D
Silicon nitride									
bonded silicon carbide	В	В	В	D		А	А	А	A–C
Magnesite	А	B-C	А	D		D	А	C–D	B-D
Chrome	А	B–C	А	C–D		C–D	А	C–D	B–C
Fosterite	А	А	А	C–D		C–D	А	C–D	B–C
Synthetic mullite	А	А	А	B–D		А	A–C	А	А
Converted mullite	А	B–C	А	B–E		А	A–C	A–C	A–C
Silica	А	А	А	C–E		А	A–C	B–C	B–C
Fireclay	А	С	А	C–E		А	A–C	B-C	B-C

 Table C.13b
 Chemical Resistance of Various Ceramic Materials: Resistance to Gases

A = No reaction, material stable; B = Slight reaction, material suitable; C = Reaction, material suitable under certain conditions: D = Reaction, material not suited unless tested under operating conditions; E = Rapid reaction, material not suitable.

- 1. Chlorine attacks silicates above 1300°F (704°C).
- 2. Nascent or atomic hydrogen attacks silica and iron.
- 3. Sulfur in strong concentrations reacts with silica above 1700°F (927°C).

Material	Nitric	Sulfuric	Hydrochloric	Hydrofluoric	Phosphoric	Hydrocarbons
Zircon	А	А	А	B–C	A–B	A–D
Bonded 99% alumina	А	А	А	A–C	А	А
Fused cast alumina	А	А	А	A–C	А	А
Zirconia stabilized	А	А	А	B-C	А	А
Silicon carbide	А	А	А	B–D	A–B	A–D
Silicon nitride						
bonded silicon carbide	А	А	А	C–D	А	A–C
Magnesite	D	D	D	D	D	B-C
Chrome	B-C	B–D	B-D	B–E	B–D	B-C
Fosterite	B–D	B–D	B-D	B–E	B–E	B-C
Synthetic mullite	А	А	А	C–E	A–B	A–D
Converted mullite	А	А	А	C–E	A–B	A–D
Silica	A–C	A–C	A–C	Е	A–C	B-D
Fireclay	A–C	A–C	A–C	E	A–C	B–D

Table C.13c Chemical Resistance of Various Ceramic Materials: Resistance to Heated Acids

A = No reaction, material stable; B = Slight reaction, material suitable; C = Reaction, material suitable under certain conditions; D = Reaction, material not suited unless tested under operating conditions; F = Rapid reaction, material not suitable.

## CHECKING

Checking is the development of slight breaks in a coating film that do not penetrate to the underlying surface. It is also cracking in a crosshatch manner resembling mud cracking. It usually forms as the coating ages and becomes harder and more brittle as a result of shrinkage of the film.

# CHEMICAL SYNONYMS

Chemical	Synonym
Acetic acid, crude	Pyroligneous acid
Acetic acid amide	Acetamide
Acetic ether	Ethyl acetate
Acetol	Diacetone alcohol
Acetylbenzene	Acetophenone
Acetylene tetrachloride	Tetrachloroethane
Almond oil	Benzaldehyde
Aluminum hydrate	Aluminum hydroxide
Aluminum potassium chrome	Chrome alum
Alum potash	Aluminum potassium sulfate
Amino benzene	Aniline
Ammonium fluoride, acid	Ammonium bifluoride
Baking soda	Sodium carbonate
Benzene carbonal	Benzaldehyde
Benzene carboxylic acid	Benzoic acid
Benzol	Benzene
Boracic acid	Boric acid

### CHEMICAL SYNONYMS

Chemical	Synonym
Bromomethane	Methyl bromide
Butanoic acid	Butyric acid
Butanol-1	Butyl alcohol
Butanone	Methyl ethyl ketone
Butter of antimony	Antimony trichloride
Butyl phthalate	Dibutyl phthalate
Calcium sulfide	Lime sulfur
Carbamide	Urea
Carbolic acid	Phenol
Carbonyl chloride	Phosgene
Caustic potash	Potassium hydroxide
Caustic soda	Sodium hydroxide
Chlorobenzene	Monochlorobenzene
1-Chlorobutane	Butyl chloride
Chloroethane	Ethyl chloride
Chloroethanoic acid	Chloroacetic acid
Chloromethane	Methyl chloride
Chloropentane	Amyl chloride
3-Chloropropene-1	Allyl chloride
Chlorotoluene	Benzyl chloride
Chromium trioxide	Chromic acid
Cupric acetate	Copper acetate
Cupric carbonate	Copper carbonate
Cupric fluoride	Copper fluoride
Cupric nitrate	Copper nitrate
Cupric sulfate	Copper sulfate
Cuprous chloride	Copper chloride
Diacetone	Diacetone alcohol
Dibromomethane	Ethylene bromide
Dibutyl ether	Butyl ether
Dichloroethane	Ethylene dichloride
Dichloroethane	Dichloroethylene
Dichloromethane	Methylene chloride
Diethyl	Butane
Diethylene dioxide	Dioxane
Diethylenimide oxide	Morpholine
Dihydroxy ethane	Ethylene glycol
Dimethylbenzene	Xylene
Dimethyl polysiloxane	Silicone oil
Dipropyl	Hexane
Dipropyl ether	Isopropyl ether
Dowtherm	Diphenyl
Epsom salt	Magnesium sulfate
Ethanal	Acetaldehyde
Ethanamide	Acetamide
Ethanoic acid	Acetic acid
Ethnoic anhydride	Acetic anhydride
Ethanol	Ethyl alcohol
	-
Ethanonitrile	Acetonitrile
Ethanonitrile Ethanoxy ethanol	Acetonitrile Cellosolve

133

С

Chemical	Synonym
Ethylene chloride	Ethylene dichloride
Ethyl ether	Diethyl ether
Formalin	Formaldehyde
Furfuraldehyde	Furfural
Furfurol	Furfural
Glucose	Dextrose
Glycerol	Glycerine
Glycol	Ethylene glycol
Glycol ether	Diethylene glycol
Glycol methyl ether	Methyl Cellosolve
Hexamethylene	Cyclohexane
Hexandioic acid	Adipic acid
Hexose	Dextrose
Hexyl alcohol	Hexanol
Hydroxybenzoic acid	Salicylic acid
Hypo photographic solution	Sodium bisulfate
Lime	Calcium oxide
Marsh gas	Methane
Methanal	Formaldehyde
Methanoic acid	Formic acid
Methanol	Methyl alcohol
Methylbenzene	Toluene
Methyl chloroform	Trichloroethane
Methyl cyanide	Acetonitrile
Methyl phenol	Cresol
Methyl l phenol ketone	Acetophenone
Methyl phthalate	Dimethyl phthalate
Methyl propane–2	Butyl alcohol, tertiary
Muriatic acid	Hydrochloric acid
Nitrogen trioxide	Nitrous acid
Oil of mirbane	Nitrobenzene
Oil of wintergreen	Methyl salicylate
Oxalic nitrile	Cyanogen
	Aniline
Phenylamine Phenyl bromide	Bromobenzene
· · · · · · · · · · · · · · · · · · ·	
Phenyl carbinol Phenyl chlorida	Benzyl alcohol Chlorobenzene
Phenyl chloride Phenyl ethane	
Pimelic ketone	Ethylbenzene
	Cyclohexanone
Propanoic acid	Propionic acid
Propanol	Propyl alcohol
Propanone	Acetone
Propenyl alcohol	Allyl alcohol
Propenoic acid	Acrylic acid
Propyl acetate	Isopropyl acetate
Prussic acid	Hydrocyanic acid
Pyrogallol	Progallic acid
Red oil	Oleic acid
Sal ammoniac	Ammonium chloride
Sodium borate, tetra	Borax
Sodium phosphate, diabasic	Disodium phosphate

Chemical	Synonym
Starch gum	Dextrin
Sugar of lead	Lead acetate
Sulfuric chlorohydrin	Chlorosulfonic acid
Tannin	Tannic acid
Tetrachloroethylene	Perchloroethylene
Tetrachloromethane	Carbon tetrachloride
Trichloromethane	Chloroform
Trihydroxybenzene	Pyrogaflic acid
Trihydroxybenzoic acid	Gallic acid
Trinitrophenol	Picric acid
Vinyl cyanide	Acrylonitrile
Water glass	Sodium silicate

## CHLORINATED POLYVINYL CHLORIDE (CPVC)

See also "Polymers." When acetylene and hydrochloric acid are reacted to produce polyvinyl chloride, the chlorination is approximately 56.8%. Further chlorination of the PVC to approximately 67% produces CPVC, whose chemical structure is as follows

The additional chlorine increases the heat deflection temperature and permits a higher allowable operating temperature. While PVC is limited to a maximum operating temperature of 140°F (60°C), CPVC has a maximum operating temperature of 180°F (82°C). Because of the higher operating temperature. CPVC finds application as piping for condensate return lines in areas having corrosive external conditions. It has also found application for hot water piping. The physical and mechanical properties are given in Table C.14.

The corrosion resistance of CPVC is similar to that of PVC but not identical. CPVC can be used to handle most acids, alkalies, salts, halogens, and many corrosive wastes. In general it cannot be used in contact with most polar organic materials, including chlorinated or aromatic hydrocarbons, esters, and ketones. Refer to Table C.15 for the compatibility of CPVC with selected corrodents. Reference 4 provides a more comprehensive listing of the compatibility of CPVC with selected corrodents.

See also Ref. 14.

#### CHLOROBUTYL RUBBER

See "Butyl Rubber and Chlorobutyl Rubber."

#### CHLOROSULFONATED POLYETHYLENE RUBBER (HYPALON)

Chlorosulfonated polyethylene rubber (CSM) is manufactured by DuPont under the trade name Hypalon. In many respects it is similar to neoprene, but it does possess some advantages over neoprene in certain types of service. It has better heat and ozone resistance, better electrical properties, better color stability, and better chemical resistance.

135

Specific gravity	155
Water absorption 24 h at 73°F (23°C), %	0.03
Tensile strength at 73°F (23°C), psi	8000
Modulus of elasticity in tension at 73°F (23°C) $\times 10^5$	4.15
Compressive strength at 73°F (23°C), psi	9000
Flexural strength, psi	15,100
Izod impact strength at 73°F (23°C)	1.5
Coefficient of thermal expansion	
in./in.–°F $\times 10^{-5}$	3.4
in./10°F/100 ft	0.034
Thermal conductivity Btu/h/sq ft/°F/in.	0.95
Heat distortion temperature, °F/°C	
at 66 psi	238/114
at 264 psi	217/102
Resistance to heat at continuous drainage, °F/°C	200/93
Limiting oxygen index, %	60
Flame spread	15
Underwriters lab rating (U.L. 94)	VO;5VA;5VB

Table C.14 Physical and Mechanical Properties of CPVC

Source: Courtesy of B. F. Goodrich. Specialty Polymers and Chemical Division.

	Maxi	mum		Maxi	mum
	ten	ıp.		temp.	
Chemical	°F	°C	Chemical	°F	°C
Acetaldehyde	х	x	Ammonium carbonate	200	93
Acetic acid 10%	90	32	Ammonium chloride 10%	180	82
Acetic acid 50%	Х	x	Ammonium chloride 50%	180	82
Acetic acid 80%	х	x	Ammonium chloride, sat.	200	93
Acetic acid, glacial	Х	x	Ammonium fluoride 10%	200	93
Acetic anhydride	х	x	Ammonium fluoride 25%	200	93
Acetone	х	x	Ammonium hydroxide 25%	х	х
Acetyl chloride	х	x	Ammonium hydroxide, sat.	х	x
Acrylic acid	х	x	Ammonium nitrate	200	93
Acrylonitrile	х	x	Ammonium persulfate	200	93
Adipic acid	200	93	Ammonium phosphate	200	93
Allyl alcohol 96%	200	93	Ammonium sulfate 10–40%	200	93
Allyl chloride	х	x	Ammonium sulfide	200	93
Alum	200	93	Ammonium sulfite	160	71
Aluminum acetate	100	38	Amyl acetate	х	х
Aluminum chloride, aqueous	200	93	Amyl alcohol	130	54
Aluminum chloride, dry	180	82	Amyl chloride	х	х
Aluminum fluoride	200	93	Aniline	х	x
Aluminum hydroxide	200	93	Antimony trichloride	200	93
Aluminum nitrate	200	93	Aqua regia 3:1	80	27
Aluminum oxychloride	200	93	Barium carbonate	200	93
Aluminum sulfate	200	93	Barium chloride	180	82
Ammonia gas, dry	200	93	Barium hydroxide	180	82
Ammonium bifluoride	140	60	Barium sulfate	180	82

 Table C.15
 Compatibility of CPVC with Selected Corrodents<sup>a</sup>

	Maxin	num		Maxi	mum
	terr	np.		temp.	
Chemical	°F	°C	Chemical	°F	°C
Barium sulfide	180	82	Citric acid 15%	180	82
Benzaldehyde	х	x	Citric acid, conc.	180	82
Benzene	х	x	Copper acetate	80	27
Benzene sulfonic acid 10%	180	82	Copper carbonate	180	82
Benzoic acid	200	93	Copper chloride	210	99
Benzyl alcohol	х	x	Copper cyanide	180	82
Benzyl chloride	х	x	Copper sulfate	210	99
Borax	200	93	Cresol	х	x
Boric acid	210	99	Cupric chloride 5%	180	82
Bromine gas, dry	х	x	Cupric chloride 50%	180	82
Bromine gas, moist	x	x	Cyclohexane	x	х
Bromine liquid	х	x	Cyclohexanol	х	х
Butadiene	150	66	Dichloroacetic acid, 20%	100	38
Butyl acetate	x	х	Dichloroethane (ethylene dichloride)	x	x
Butyl alcohol	140	60	Ethylene glycol	210	99
<i>n</i> -Butylamine	х	х	Ferric chloride	210	99
Butyric acid	140	60	Ferric chloride 50% in water	180	82
Calcium bisulfide	180	82	Ferric nitrate 10–50%	180	82
Calcium bisulfite	210	99	Ferrous chloride	210	99
Calcium carbonate	210	99	Ferrous nitrate	180	82
Calcium chlorate	180	82	Fluorine gas, dry	x	x
Calcium chloride	180	82	Fluorine gas, moist	80	27
Calcium hydroxide 10%	170	77	Hydrobromic acid, dilute	130	54
Calcium hydroxide, sat.	210	99	Hydrobromic acid 20%	180	82
Calcium hypochlorite	200	93	Hydrobromic acid 50%	190	88
Calcium nitrate	180	82	Hydrochloric acid 20%	180	82
Calcium oxide	180	82	Hydrochloric acid 38%	170	77
Calcium sulfate	180	82	Hydrocyanic acid 10%	80	27
Caprylic acid	180	82	Hydrofluoric acid 30%	x	x
Carbon bisulfide	X	x	Hydrofluoric acid 70%	90	32
Carbon dioxide, dry	210	99	Hydrofluoric acid 100%	x	x
Carbon dioxide, wet	160	71	Hypochlorous acid	180	82
Carbon disulfide	x	x	Ketones, general	x	x
Carbon monoxide	210	99	Lactic acid 25%	180	82
Carbon tetrachloride	x	x	Lactic acid, concentrated	100	38
Carbonic acid	180	82	Magnesium chloride	230	110
Cellosolve	180	82	Malic acid	180	82
Chloracetic acid, 50% water	100	38	Manganese chloride	180	82
Chloracetic acid	x	x	Methyl chloride	x	x
Chlorine gas, dry	140	60	Methyl ethyl ketone	x	x
Chlorine gas, wet	x	x	Methyl isobutyl ketone	x	x
Chlorine, liquid	X	x	Muriatic acid	170	77
Chlorobenzene	X	x	Nitric acid 5%	180	82
Chloroform	X	x	Nitric acid 20%	160	71
Chlorosulfonic acid	X	x	Nitric acid 70%	180	82
Chromic acid 10%	x 210	x 99	Nitric acid, anhydrous		
Chromic acid 50%	210	99 99	Nitrous acid, concentrated	x 80	x 27
Chronine actu 7070	210	22	i vicious aciu, concentrateu	00	41

137

	Maxi	num		Maxii	mum
	ten	np.		temp.	
Chemical	°F	°C	Chemical	°F	°C
Perchloric acid 10%	180	82	Stannic chloride	180	82
Perchloric acid 70%	180	82	Stannous chloride	180	82
Phenol	140	60	Sulfuric acid 10%	180	82
Phosphoric acid 50–80%	180	82	Sulfuric acid 50%	180	82
Picric acid	х	x	Sulfuric acid 70%	200	93
Potassium bromide 30%	180	82	Sulfuric acid 90%	х	x
Salicylic acid	х	x	Sulfuric acid 98%	х	x
Silver bromide 10%	170	77	Sulfuric acid 100%	х	x
Sodium carbonate	210	99	Sulfuric acid, fuming	x	x
Sodium chloride	210	99	Sulfurous acid	180	82
Sodium hydroxide 10%	190	88	Thionyl chloride	х	x
Sodium hydroxide 50%	180	82	Toluene	x	x
Sodium hydroxide, concentrated	190	88	Trichloroacetic acid, 20%	140	60
Sodium hypochlorite 20%	190	88	White liquor	180	82
Sodium hypochlorite, concentrated	180	82	Zinc chloride	180	82
Sodium sulfide to 50%	180	82			

 Table C.15
 Compatibility of CPVC with Selected Corrodents<sup>a</sup> (Continued)

The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated. Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x.

Source: PA Schweitzer. Corrosion Resistance Tables. 4th ed. Vols. 1-3. New York: Marcel Dekker, 1995.

Hypalon, when properly compounded, also exhibits good resistance to wear and abrasion, good flex life, high impact resistance, and good resistance to permanent deformation under heavy loading.

#### Physical and Mechanical Properties

The ability of Hypalon to retain its electrical properties after long-term exposure to heat, water immersion, and weathering is outstanding. These properties make the elastomer useful as insulation for low-voltage applications (less than 600 V), particularly as a covering for power and control cable, mine trailing cable, locomotive wire, nuclear power station cable, and motor lead wire. Because of Hypalon's outstanding weathering resistance, it is used as an outer protective jacket in high-voltage applications. The elastomer also exhibits excellent resistance to corona discharge.

Another property of Hypalon that is important in electrical applications is its ability to be colored and not discolor or fade when exposed to sunlight and ultraviolet light for long periods of time. The white raw polymer will accept any color, including light pastels, without impairing the true brilliance or hue. Because of the polymer's natural ozone resistance, it is not necessary to add antiozonates during compounding. The antiozonates are strong discoloring agents and when added to elastomers will cause colors to fade and become unstable.

When coloring agents are added to most elastomers it is usually necessary to sacrifice some physical properties. This is not the case with Hypalon. Except in cases where the elastomer is being specially compounded for exceptionally high heat resistance or set characteristics, its physical properties will be unaffected by the addition of coloring agents. In these special cases a black material must be used if the maximum performance is to be gotten from the elastomer.

Hypalon will burn in an actual fire situation but is classified as self-extinguishing. If the flame is removed, the elastomer will stop burning. This phenomenon is due to its chlorine content, which makes it more resistant to burning than exclusively hydrocarbon polymers.

The chlorine content of the elastomer protects it against the attack of microorganisms, and it will not promote the growth of mold, mildew, fungus, or bacteria. This feature is important when the elastomer is to be used in coating fabrics. To maintain this property it is important that proper compounding procedures be followed. The addition of wax and those plasticizers that provide food for microorganisms should be avoided if the maximum resistance to mold, mildew, and fungus is to be maintained.

On the low-temperature side, conventional compounds can be used continuously down to 0 to  $-20^{\circ}$ F (-18 to  $-28^{\circ}$ C). Special compounds can be produced that will retain their flexibility down to  $-40^{\circ}$ F ( $-40^{\circ}$ C), but to produce such a compound it is necessary to sacrifice performance of some of the other properties.

Heat aging does not have any effect on the tensile strength of Hypalon, since it acts as additional heat curing. However, the elongation at break does not decrease as the temperature increases.

Hypalon exhibits good recovery from deformation after being subjected to a heavy load or a prolonged deflection. Refer to Table C.16 for compression set values.

## Resistance to Sun, Weather, and Ozone

Hypalon is one of the most weather-resistant elastomers available. Oxidation takes place at a very slow rate. Sunlight and ultraviolet light have little if any adverse effect on its physical properties. It is also inherently resistant to ozone attack without the need for the addition of special antioxidants or antiozonates to the formulation.

, , , , , , , , , , , , , , , , , , , ,	
Specific gravity	1.08-1.28
Brittle point	-40 to -80°F
	(-40 to -62°C)
Dielectric strength, V/mil	500
Dielectric constant at 1000 Hz	8 <sup>-10</sup>
Dissipation factor at 1000 Hz	0.05-0.07
Tensile strength, psi	2500
Elongation, % at break	430-540
Hardness, Shore A	60
Abrasion resistance	Excellent
Maximum temperature, continuous use	250°F (121°C)
Impact resistance	Good
Compression set, %	
at 158°F (70°C)	16
at 212°F (100°C)	25
at 250°F (121°C)	44
Resistance to sunlight	Excellent
Effect of aging	None
Resistance to heat	Good
Effect of aging	None

**Table C.16**Physical and Mechanical Properties ofChlorosulfonated Polyethylene (Hypalon; CSM)<sup>a</sup>

<sup>a</sup>These are representative values since they may be altered by compounding.

Many elastomers are degraded by ozone concentrations of less than 1 part per million parts of air. Hypalon, however, is unaffected by concentrations as high as 1 part per 100 parts of air.

#### Chemical Resistance

When properly compounded, Hypalon is highly resistant to attack by hydrocarbon oils and fuels, even at elevated temperatures. It is also resistant to such oxidizing chemicals as sodium hypochlorite, sodium peroxide, ferric chloride, and sulfuric, chromic, and hydrofluoric acids. Concentrated hydrochloric acid (37%) at elevated temperatures above 158°F (70°C) will attack Hypalon, but it can be handled without adverse effect at all concentrations below this temperature. Nitric acid at room temperature and up to 60% concentration can also be handled without adverse effects.

Hypalon is also resistant to salt solutions, alcohols, and both weak and concentrated alkalies and is generally unaffected by soil chemicals, moisture, and other deteriorating factors associated with burial in the earth. Long-term contact with water has little or no effect on Hypalon. It is also resistant to radiation.

Hypalon has poor resistance to aliphatic, aromatic, and chlorinated hydrocarbons, aldehydes, and ketones.

Fabrics coated with Hypalon are highly resistant to soiling and staining from atmospheric deposits and from abrasive contact with soiling agents. Most deposits left on the elastomeric surface can he removed by the application of soap and water. Stubborn deposits can he removed when necessary with detergents, dry cleaning fluids, bleaches, and other cleaning agents without causing damage to the elastomers.

Table C.16 lists the physical and mechanical properties of Hypalon.

Hypalon has a broad range of service temperatures with excellent thermal properties. General-purpose compounds can operate continuously at temperatures of 248–275°F (120–135°C). Special compounds can be formulated that can be used intermittently up to 302°F (150°C).

Refer to Table C.17 for the compatibility of Hypalon with selected corrodents.

	Maxin	num		Maximum temp.	
	tem	p.			
Chemical	°F	°C	Chemical	°F	°C
Acetaldehyde	60	16	Aluminum sulfate	180	82
Acetamide	х	х	Ammonia gas	90	32
Acetic acid 10%	200	93	Ammonia carbonate	140	60
Acetic acid 50%	200	93	Ammonium chloride 10%	190	88
Acetic acid 80%	200	93	Ammonium chloride 50%	190	88
Acetic acid, glacial	х	х	Ammonium chloride, sat.	190	88
Acetic anhydride	200	93	Ammonium fluoride 10%	200	93
Acetone	х	х	Ammonium hydroxide 25%	200	93
Acetyl chloride	х	x	Ammonium hydroxide, sat.	200	93
Acrylonitrile	140	60	Ammonium nitrate	200	93
Adipic acid	140	60	Ammonium persulfate	80	27
Allyl alcohol	200	93	Ammonium phosphate	140	60
Aluminum fluoride	200	93	Ammonium sulfate 10–40%	200	93
Aluminum hydroxide	200	93	Ammonium sulfide	200	93
Aluminum nitrate	200	93	Amyl acetate	60	16

 Table C.17
 Compatibility of Hypalon with Selected Corrodents<sup>a</sup>

	Maximum			Maximum temp.	
Chaminal	°F °C				
Chemical			Chemical	°F	°C
Amyl alcohol	200	93	Chromyl chloride		
Amyl chloride	х	х	Citric acid 15%	200	93
Aniline	140	60	Citric acid, concentrated	200	93
Antimony trichloride	140	60	Copper chloride	200	93
Barium carbonate	200	93	Copper acetate	х	х
Barium chloride	200	93	Copper cyanide	200	93
Barium hydroxide	200	93	Copper sulfate	200	93
Barium sulfate	200	93	Cresol	х	x
Barium sulfide	200	93	Cupric chloride 5%	200	93
Benzaldehyde	х	x	Cupric chloride 50%	200	93
Benzene	х	x	Cyclohexane	х	x
Benzene sulfonic acid 10%	х	x	Cyclohexanol	х	x
Benzoic acid	200	93	Dichloroethane (ethylene dichloride)	х	x
Benzyl alcohol	140	60	Ethylene glycol	200	93
Benzyl chloride	x	x	Ferric chloride	200	93
Borax	200	93	Ferric chloride 50% in water	200	93
Boric acid	200	93	Ferric nitrate 10–50%	200	93
Bromine gas, dry	60	16	Ferrous chloride	200	93
Bromine gas, moist	60	16	Fluorine gas, dry	140	60
Bromine liquid	60	16	Hydrobromic acid, dilute	90	32
Butadiene	x	x	Hydrobromic acid 20%	100	38
	x 60	x 16	Hydrobromic acid 50%	100	38
Butyl acetate					
Butyl alcohol	200	93	Hydrochloric acid 20%	160	71 60
Butyric acid	x 200	X Q2	Hydrochloric acid 38%	140	
Calcium bisulfite	200	93 22	Hydrocyanic acid 10%	90	32
Calcium carbonate	90	32	Hydrofluoric acid 30%	90	32
Calcium chlorate	90	32	Hydrofluoric acid 70%	90	32
Calcium chloride	200	93	Hydrofluoric acid 100%	90	32
Calcium hydroxide 10%	200	93	Hypochlorous acid	х	х
Calcium hydroxide, sat.	200	93	Ketones, general	x	х
Calcium hypochlorite	200	93	Lactic acid 25%	140	60
Calcium nitrate	100	38	Lactic acid, concentrated	80	27
Calcium oxide	200	93	Magnesium chloride	200	93
Calcium sulfate	200	93	Manganese chloride	180	82
Caprylic acid	х	х	Methyl chloride	х	х
Carbon dioxide, dry	200	93	Methyl ethyl ketone	х	x
Carbon dioxide, wet	200	93	Methyl isobutyl ketone	х	x
Carbon disulfide	200	93	Muriatic acid	140	60
Carbon monoxide	х	x	Nitric acid 5%	100	38
Carbon tetrachloride	200	93	Nitric acid 20%	100	38
Carbonic acid	х	x	Nitric acid 70%	х	x
Chloracetic acid	х	х	Nitric acid, anhydrous	х	х
Chlorine gas, dry	х	х	Oleum	x	x
Chlorine gas, wet	90	32	Perchloric acid 10%	100	38
Chlorobenzene	x	x	Perchloric acid 70%	90	32
Chloroform	x	x	Phenol	x	2
Chlorosulfonic acid	x	x	Phosphoric acid 50–80%	200	93
Chromic acid 10%	150	66	Picric acid	80	27
(hromic acid 10%)					

 Table C.17
 Compatibility of Hypalon with Selected Corrodents<sup>a</sup> (Continued)

	Maxir	num		Maximum	
	temp.			temp.	
Chemical	°F °C		Chemical	°F	°C
Sodium carbonate	200	93	Sulfuric acid 10%	200	93
Sodium chloride	200	93	Sulfuric acid 50%	200	93
Sodium hydroxide 10%	200	93	Sulfuric acid 70%	160	71
Sodium hydroxide 50%	200	93	Sulfuric acid 90%	х	x
Sodium hydroxide, concentrated	200	93	Sulfuric acid 98%	х	x
Sodium hypochlorite 20%	200	93	Sulfuric acid 100%	х	x
Sodium hypochlorite, concentrated			Sulfurous acid	160	71
Sodium sulfide to 50%	200	93	Toluene	х	x
Stannic chloride	90	32	Zinc chloride	200	93
Stannous chloride	200	93			

 Table C.17
 Compatibility of Hypalon with Selected Corrodents<sup>a</sup> (Continued)

<sup>a</sup>The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated. Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x. A blank space indicates data unavailable.

Source: PA Schweitzer. Corrosion Resistance Tables, 4th ed Vols. 1-3. New York: Marcel Dekker, 1995.

### Applications

Hypalon finds useful applications in many industries and many fields. Because of its outstanding resistance to oxidizing acids, it has found widespread use as acid transfer hose. For the same reason it is used to line railroad tank cars and other tanks containing acids and other oxidizing chemicals. Its physical and mechanical properties make it suitable for use in hoses undergoing continuous flexing and/or those carrying hot water or steam.

The electrical industry makes use of Hypalon to cover automotive ignition and primary wire, nuclear power station cable, control cable, and welding cable. As an added protection from storms at sea, power and lighting cable on off-shore oil platforms is sheathed with Hypalon. Because of its heat and radiation resistance, it is also used as a jacketing material on heating cable imbedded in roadways to melt ice and on x-ray machine cable leads. It is also used in appliance cord, insulating hoods and blankets, and many other electrical accessories.

In the automotive industry, advantage is taken of Hypalon's color stability and good weathering properties by using the elastomer for exterior parts on cars, trucks, and other commercial vehicles. Its resistance to heat, ozone, oil, and grease makes it useful for application under the hood for such components as emission control hose, tubing, ignition wire jacketing. spark plug boots, and air-conditioning and power steering hoses. The ability to remain soil-free and easily cleanable makes it suitable for tire whitewalls.

When combined with cork, Hypalon provides a compressible set-resistant gasket suitable for automobile crankcase and rocker pans. The Hypalon protects the cork from oxidation at elevated temperatures and also provides excellent resistance to oil, grease, and fuels.

The construction industry has made use of Hypalon for sheet roofing, pond liners, reservoir covers, curtain wall gaskets, floor tiles, escalator rails, and decorative and maintenance coatings. In these applications the properties of color stability, excellent weatherability, abrasion resistance, useful temperature range, light weight, flexibility, and good aging characteristics are of importance.

Application is also found in the coating of fabrics that are used for inflatable structures, flexible fuel tanks, tarpaulins, and hatch and boat covers. These products offer the advantages of being lightweight and colorful. Consumer items such as awnings, boating garb, convertible tops, and other products also make use of fabrics coated with this elastomer.

See Refs. 4, 15.

# CHROMATING

Chromating is a process for producing a conversion coating containing chromium compounds on metal surfaces. The chromate conversion coatings are applied to the protective top coats of metallic products and are the bases for organic coatings. The coating processes are dipping, electrolysis, and roll coating. The metals usually chromated include aluminum, copper, magnesium, cadmium, silver, zinc, and their alloys.

See Ref. 1.

# CHROMIUM COATINGS

Chromium coatings are for decorative purposes; they are used mostly on duplex nickel or copper strike undercoat. Decorative chromium coatings are used for bicycle parts and electric components.

See Ref. 1.

# **CLAD STEELS**

A clad steel plate is a composite plate made of carbon steel with a cladding of corrosionresistant or heat-resistant metal on one or both sides. The clad steels are used in place of solid corrosion-resistant or heat-resistant materials, particularly when relatively thick sections are required because of high-pressure applications in processing vessels, in order to reduce the cost. They also find application where corrosion is a minor problem but where freedom from contamination of the materials handled is essential. In addition to the savings in material costs, the clad steels are frequently easier to fabricate than solid plates of the cladding material, resulting in reduced labor costs. Their high heat conductivity is another reason for their selection for many applications.

Various grades of stainless steels, nickel, Monel, Inconel, cupronickel, titanium, or silver may be used as a cladding material. The thickness of the cladding material is normally held to 10% to 20% of the thickness of the clad plate, but it may vary from 5% to 50%. Clad steels are available in the form of sheet, plate, and strip and may be obtained also as wire.

Clad steels are used for processing equipment in the chemical, food, beverage, drug, paper, textile, oil, and associated industries.

Cladding can be applied in any one of six methods, from the insertion of a loose liner to explosion cladding.

The least expensive form of cladding is the installation of a thin corrosion-resistant liner inside a process vessel constructed of a less expensive base metal. With this type of cladding the liner is normally relatively thin, anywhere from 0.3 to 2 mm thick, and is used only for corrosion resistance. The base metal provides all of the structural strength. The advantages of this method are

- 1. Relatively low cost.
- **2.** Availability. When the base metal and the liner material are available, the finished piece of equipment can be produced in a short time.

- **3.** Repairs can be made relatively easily.
- 4. Base metal and liner material do not have to be metallurgically compatible.

The disadvantages of a loose liner are

- 1. Heat transfer is reduced.
- **2.** The liner is easily damaged.
- **3.** A vacuum will cause the liner to collapse. This disadvantage can be overcome by periodically attaching the liner to the base metal or by increasing its thickness, but this does increase the cost.

## **Roll Cladding**

Roll cladding produces full-sized sheets of clad material that a fabricator then forms into a finished product. These sheets are rolled at the mill. The bond formed is partly mechanical and partly metallurgical, and consequently metallurgically incompatible materials normally cannot be produced. One exception is the production of titaniumclad sheets by Nippon Kokan KK of Tokyo. Cladding thicknesses range from 5% to 50% of the compatible thickness.

Composites are produced with cladding designed to resist wear, abrasion, or corrosion.

## Explosion Cladding

Explosion cladding produces full-sized sheets of clad material, as roll cladding does, that a fabricator then forms and welds into a finished product.

The explosion bonding technique was originally developed by DuPont. In this process, detonation of an explosive presses the plates together with such force that the lower elastic limit of the metals is exceeded, and the unmelted surface metal is jetted through the rapidly closing space between the plates, destroying interfering layers of metal and resulting in a metallurgical bond with a relatively smooth surface.

Metallurgically incompatible metals can be coupled by use of an intermediate material.

Thick plates up to 510 mm may be produced by this method, but unless relatively thick sections are required, this process is not economical.

## Weld Overlaying

Weld overlaying is used with cladding materials and base metals that are metallurgically compatible and is best restricted for use on small, complex parts. Readily available commercial alloys, such as stainless steels and nickel- and copper-based alloys, can be used to provide a corrosion-resistant overlay.

Because of the heat required for welding, care must be taken not to distort the member being clad.

## Thermal Spraying

Thermal spraying can also produce a clad material. It is accomplished by heating the metal cladding (or nonmetallic) particles to a molten state and spraying them on the prepared surface of the base metal. As the molten particles impact on the surface of the base metal, they form an overlapping multilayered cladding, ranging in thickness from 0.2 to 2.5 mm, One of the advantages of this process is that the temperature of

C

the base metal normally does not exceed 300 to 410°F (150 to 200°C), which minimizes thermal distortion of the base metal. This also does not permit the coating to become diluted, which is essential when the cladding material and the base metal are not metallurgically compatible. Combinations of certain metals form mixtures that are affected adversely by the intermixing or interaction of the components. For example, nickel and copper are metallurgically compatible, whereas steel and zirconium are not. This process is relatively inexpensive and is a common operation performed by many shops.

Certain disadvantages are prevalent with these spraying processes. The claddings or coatings have a tendency to be porous. This can be overcome somewhat by increasing the density of the coating. In addition, the bond between the coating/cladding is mechanical, and any leakage of corrodent to the base metal through a porous section of the coating can cause the coating to spall off. It is also very difficult, and at times impossible, to clad complex shapes.

## **Resistance Cladding**

Resistance cladding provides a means of applying a lining to a base metal regardless of whether the base metal and the liner material are metallurgically compatible. In this process, use is made of resistance welding and proprietary intermediate materials to bond thin-gauge corrosion-resistant materials to heavier, less expensive base metals.

This type of cladding can be applied to completed fabrications of equipment or to components during fabrication. It is also possible to apply this cladding to existing used equipment. Completed fabrications are relatively inexpensive.

Because of the relatively thin layer of cladding, the corrosion rate of the process must be low. The process also does not lend itself to providing a finished surface. Economics do not favor this process unless the cladding material is expensive.

### COATINGS

The development of new and improved coatings has been increasing over the past several years. New technologies have evolved that have expanded the usage of these materials. By incorporating these coatings with a substrate having the required physical and mechanical properties, it is possible to obtain the desired strength and the optimum corrosion resistance at an economical cost.

The available coatings can be categorized as metallic, inorganic, or organic in nature. Each category has its own specific area of application, with a range of properties dependent on the specific material.

#### Metallic Coatings

There are several methods by which metallic coatings may be applied:

- 1. Brief immersion in a molten bath of metal, called hot dipping
- 2. Electroplating from an aqueous electrolyte
- **3.** Spraying, in which a gun is used that simultaneously melts and propels small droplets of metal onto the surface to be coated, as with spray painting
- **4.** Cementation, in which the material to be coated is tumbled in a mixture of metal powder and an appropriate flux at elevated temperatures, which allows the metal to diffuse into the base metal

- 5. Gas phase reaction
- 6. Chemical reduction of metal-salt solutions, the precipitated metal forming an overlay on the base metal (nickel coatings of this type are referred to as "electroless" nickel plate)

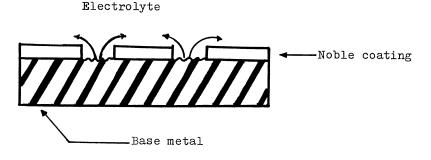
Coatings from a corrosion viewpoint are classified as either noble or sacrificial. All metal coatings contain some degree of porosity. Coating performance is therefore determined by the degree of galvanic action that takes place at the base of a pore, scratch, or other imperfection in the coating.

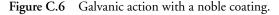
Noble coatings, consisting of nickel, silver, copper, lead, or chromium on steel, are noble in the galvanic series with respect to steel, resulting in galvanic current attack at the base of the pores of the base metal and eventually undermining the coating. See Fig. C.6.

In order to reduce this rate of attack it is important that this type of coating be prepared with a minimum number of pores and that any pores present be as small as possible. This can be accomplished by increased coating thickness.

In sacrificial coatings, consisting of zinc, cadmium, and in certain environments aluminum and tin on steel, the base metal is noble in the galvanic series to the coating material, resulting in cathodic protection to the base metal and attack on the coating material. See Fig. C.7.

As long as sufficient current flows and the coating remains in electrical contact, the base metal willbe protected from corrosion. Contrary to noble coatings, the degree of





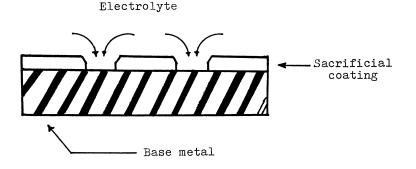


Figure C.7 Galvanic action with a sacrificial coating.

147

porosity of sacrificial coatings is relatively insignificant. However, the thicker the coating, the longer cathodic protection will be provided to the base metal.

## **Nickel Coatings**

The most common method of applying nickel coatings is by electroplating, either directly on steel or over an intermediate coating of copper. Copper is used as an underlayer to facilitate buffing, since it is softer than steel, and to increase the required coating thickness with a material less expensive than nickel.

## Zinc Coatings

Galvanized or zinc coating is probably one of the most common coatings. It is applied by either hot dipping or electrodeposition. Electrodeposited coatings tend to be more ductile than hot-dipped coatings, but otherwise they are comparable in corrosion resistance, with one exception. Hot-dipped coatings tend to pit less in hot or cold water and soils than coatings applied by other methods.

Zinc coatings stand up extremely well in rural atmospheres and in marine atmospheres except when salt water spray comes into direct contact with the coating.

In aqueous environments at room temperatures within a pH range of 7 to 12, good corrosion resistance will be obtained.

Any welding or forming should, if possible, be performed prior to the galvanizing operation.

## **Cadmium Coatings**

These coatings are produced almost exclusively by electrodeposition. A cadmium coating on steel does not provide as much cathodic protection to the steel as does a zinc coating, since the potential between cadmium and iron is not as great as between zinc and iron. Therefore it becomes important to minimize defects in the cadmium coating.

Unlike zinc, a cadmium coating will retain a bright metallic appearance. It is more resistant to attack by salt spray and atmospheric condensation. In aqueous solutions cadmium will resist attack by strong alkalies but will be corroded by dilute acids and aqueous ammonia.

Since cadmium salts are toxic, these coatings should not be allowed to come into contact with food products. This coating is commonly used on nuts and bolts.

#### Tin Coatings

Most of the tinplate (tin coating on steel) is used for the manufacture of food containers (tin cans). The nontoxic nature of tin salts makes tinplate an ideal material for the handling of foods and beverages.

An inspection of the galvanic series will indicate that tin is more noble than steel and consequently the steel corrodes at the base of the pores. On the outside of the tinned container this is what happens—the tin is cathodic to the steel. However, on the inside of the container there is a reversal of the polarity due to the complexing of the stannous ions by many food products. This greatly reduces the activity of the stannous ion, resulting in a change in the potential of tin in the active direction.

This change in polarity is absolutely necessary, since most tin coatings are thin and therefore porous. In order to avoid perforation of the can, the tin must act as a sacrificial

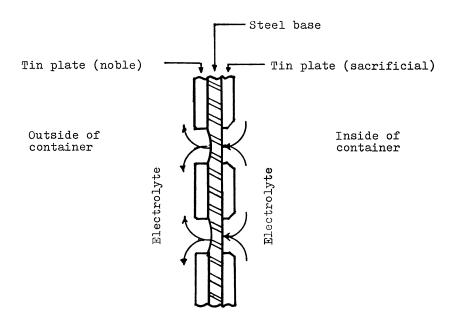


Figure C.8 Tin acting as both a noble and a sacrificial coating.

coating. Figure C.8 illustrates this reversal of activity between the outside and inside of the can.

Tin will react with both acids and alkalies but is relatively resistant to neutral or near neutral media.

It is extremely resistant to soft waters and consequently has found wide usage as a piping material for distilled water. Only its cost and availability have precluded it from monopolizing this market.

## Aluminum Coatings

Aluminum coatings on steel are applied primarily by hot dipping or by spraying. Silicon is usually added to the molten bath so as to retard the formation of a brittle alloy layer. Organic lacquers or paints are used as sealers over sprayed coatings.

Hot-dipped coatings are used mostly to provide oxidation resistance at moderately elevated temperatures (e.g., oven construction). They find limited applications as protection against atmospheric corrosion because they are more expensive than zinc and have a variable performance.

## Vitreous Enamels

Vitreous enamels, glass linings, or porcelain enamels are all essentially glass coatings that have been fused on metals. Powdered glass is applied to a pickled or otherwise prepared metal surface and heated in a furnace at a temperature that softens the glass and permits it to bond to the metal. Several thin coats are applied to provide the required final thickness. These coatings are normally applied to steel, but some coatings can be applied to brass, aluminum, and copper.

There are many glass formulations, but those with very high silica (<96% SiO<sub>2</sub>), aluminosilicate, and borosilicate compositions have the highest corrosion resistance to a

С

wide range of corrosive environments. Glass is assumed to be inert to most liquids, but in reality it slowly dissolves.

The greatest danger of failure of a glass coating comes from mechanical damage or from cracking as a result of thermal shock. Thus care must be taken in handling glassed equipment so as not to damage the lining, and sudden temperature changes in the operation must be avoided, particularly cold shock, which poses a greater danger of failure than hot shock.

Cold shock is the sudden introduction of a cold material onto a hot glassed surface; hot shock is the reverse. Manufacturers of this type of equipment will specify the maximum allowable thermal shock. These precautions must be followed.

# Masonry

Monolithic corrosion-resistant masonry linings are normally applied by means of pneumatic gunning (guniting), although they may be troweled on. Thicknesses vary from 1/2 in. up to several inches. When a thickness greater than 1 in. is to be applied, it is necessary to anchor the lining in place using wire mesh and studs. There should be a minimum of 1/2 in. cover over the highest point.

This type of lining has three main advantages:

- 1. Curved or irregular surfaces can be covered uniformly.
- 2. Monolithic linings bond to steel, brick, and concrete.
- **3.** Monolithic linings can be gunited horizontally, vertically, or overhead without the need for complex forms, supports, or scaffolds.

# Sodium Silicate Base Monolithics

This material is supplied as two separate components, a powder and a liquid. The two components are mixed and applied for use. Hardening occurs as a result of a chemical reaction. Application can be by means of casting, pouring into forms, or guniting. Its resistance to acid is excellent over a pH range of 0.0 to 7.0.

# **Modified Silicate Base Monolithics**

There are two types of modified silicate base materials available, both of which are supplied in powder form and must be mixed with water prior to application. Application is by guniting.

The first type is unaffected by acids (except hydrofluoric), mild alkalies, water, and solvents and can be operated up to a temperature of 1740°F (950°C) through a pH range of 0.0 to 9.0. It weighs approximately 135 lb/ft<sup>3</sup>.

The second type is lighter in weight, weighing approximately 98 lb/ft<sup>3</sup>, and is thermally insulating. It has a K factor of 2.25 to 2.50. This type can be operated up to a temperature of 1695°F (925°C) through a pH range of 0.0 to 9.0.

# **Calcium Aluminate Base Monolithics**

This type consists of a calcium aluminate base cement to which various inert aggregates have been added. It is supplied in powder form and mixed with water when used, and may be cast, poured, or gunited into place. These monolithics are similar to portland cement in that they are hydraulic in nature and consume water in their reaction mechanism to form hydrated phases. In contrast to portland cement, their rates of hardening are very rapid, and full strength is usually attained within 24 hours at room temperatures of 73°F (23°C).

They are not useful in contact with acids below a pH of 5, although they do exhibit better mild acid resistance than portland cement. These types should not be used for halogen service or for alkali service above a pH of 12.

#### Portland Cement Coatings

Although portland cement does not have the corrosion resistance of other monolithics, it does have the advantage of low cost and ease of repair when accessible. The coatings can be applied by centrifugal casting, troweling, or guniting. Thicknesses usually range from 1/4 to more than 1 in. The thicker coatings are reinforced with wire mesh.

Primary applications for portland cement linings are the protection of hot or cold water tanks, oil tanks, and chemical storage tanks. The disadvantage of portland cement coatings is their sensitivity to damage by mechanical shock.

Since cement compositions may vary, care should he taken that the proper selection is made for the specific application.

### **Chemical Conversion Coatings**

These are protective coatings formed by a chemical reaction taking place on the surface of the metal. Included in this category are phosphate coatings on steel (sometimes referred to as "parkerizing" or "bonderizing"), oxide coatings on steel and aluminum, and chromate coatings on zinc.

#### Phosphate Coatings

These coatings are not used to provide corrosion protection since they offer little. They are used to provide a base for the application of paints, by providing good adherence of the paint to the steel and decreasing the tendency for corrosion to undercut the paint film at scratches or defects.

#### Oxide Coatings

Oxide coatings are not applied for providing increased corrosion resistance since they do not appreciably improve the resistance of the base metal. Oxide coatings produced on aluminum result in a product known as anodized aluminum. During this process the oxide coating can be dyed various colors, for aesthetic purposes.

As with phosphate coatings, the main advantage lies in providing an improved base for paints.

#### Chromate Coatings

These coatings are produced on zinc, imparting a slight yellow color and protecting the metal against spotting or staining by condensed moisture. The coating will extend the life of zinc somewhat, when exposed to the atmosphere.

## **Organic Coatings**

Organic coatings are widely used to protect metallic surfaces from corrosion. The effectiveness of such coatings is dependent not only on the properties of the coatings, which are related to the polymeric network and possible flaws in this network, but also on the character of the metal substrate, the surface pretreatment, and the application procedures. Therefore, when considering the application of a coating it is necessary to take into account the properties of the entire system.

Organic coatings provide protection either by the formation of a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating. In actual practice the barrier properties are limited since all organic coatings are permeable to water and oxygen to some extent. The average transmission rate of water through a coating is about 10 to 100 times larger than the water consumption rate of a freely corroding surface, and in normal outdoor conditions an organic coating is saturated with water at least half its service life. For the remainder of the time it contains a quantity of water comparable in its behavior to an atmosphere of high humidity. It has also been determined that in most cases the diffusion of oxygen through the coating is large enough to allow unlimited corrosion. Taking these factors into account indicates that the physical barrier properties alone do not account for the protective action of coatings.

Additional protection may be supplied by resistance inhibition, which is also a part of the barrier mechanism. Retardation of the corrosion action is accomplished by inhibiting the charge transport between cathodic and anodic sites. The reaction rate may be reduced by an increase in the electronic resistance and/or the ionic resistance in the corrosion cycle. Applying an organic coating on a metal surface increases the ionic resistance. The electronic resistance may be increased by the formation of an oxide film on the metal. This is the case for aluminum substrates.

Organic coatings are relatively easily damaged under mechanical and thermal load, which may lead to corrosion under the paint film at or near the site. Under these conditions the otherwise adequate barrier properties of the coating will no longer provide adequate protection. In an attempt to compensate for this, active pigments are incorporated in the matrix of the primer (first coating layer). These pigments provide protection through an active inhibitive mechanism immediately when water and some corrosive agent reach the metal surface. The protection provided is of a passivating, blocking, or galvanic action.

In order for the coating to provide protection, the adhesion of the coating must be good. The quality of the coating is determined to some extent by the mechanical properties of the polymer that determine the formability of coated substances and also the sensitivity to external damage.

# Water Permeation and Underfilm Corrosion Initiation

In order for corrosion to take place under a coating it is necessary for an electrochemical double layer to be established. In order for this to occur it is necessary for the adhesion between the coating and the substrate to be broken. When this happens a thin water layer at the interface can be formed when the water permeates the coating. All organic coatings are permeable to water to some degree. The permeability of a coating is often given in terms of the permeation coefficient P. This is defined as the product of the solubility of water in the coating (S, kg/cm<sup>3</sup>), the diffusion coefficient of water in the coating (D, m<sup>2</sup>/s), and the specific mass of water (p, kg/m<sup>2</sup>). Therefore, different coatings can have the same permeation coefficient even though the solubility and the diffusion coefficient, both being material constants, are very different. This limits the usefulness of the permeation coefficient. Water permeation takes place under the influence of several driving forces:

- **1.** A concentration gradient during immersion or during exposure to a humid atmosphere, resulting in true diffusion through the polymer
- **2.** Capillary forces in the coating resulting from poor curing, improper solvent evaporation, bad interaction between binder and additives, or entrapment of air during application
- **3.** Osmosis due to impurities, or corrosion products at the interface between the metal and the coating

Given sufficient time a coating system that is exposed to an aqueous solution or a humid atmosphere will be permeated. Water molecules will eventually reach the coating's substrate interface. Saturation will occur after a relatively short period of time (of the order of one hour) depending on the values for D and S and the thickness of the layer. Typical values for D and S are  $10^{-13}$  m<sup>2</sup>/s and 3%. Periods of saturation under atmospheric exposure are determined by the actual cyclic behavior of the temperature and the humidity. In any case, situations will develop in which water molecules reach the coating and the substrate, eventually resulting in loss of adhesion and corrosion initiation, provided that a cathodic reaction can take place. A constant supply of water or oxygen is required for the corrosion reaction to proceed. Water permeation may also result in the build-up of high osmotic pressures, resulting in blistering and delamination.

## Wet Adhesion

Adhesion between the coating and the substrate may be affected when water molecules have reached the substrate—coating interface. The degree to which permeated water may change the adhesion properties of a coated system is referred to as wet adhesion. Two different theories have been proposed for the mechanism for the loss of adhesion due to water:

- 1. Chemical disbondment resulting from the chemical interaction of water molecules with covalent hydrogen, or polar bonds between polymer and metal (oxide)
- **2.** Mechanical or hydrodynamic disbondment as a result of forces caused by accumulation of water and osmotic pressure

For chemical disbondment to take place it is not necessary that there be any sites of poorly bonded coating. This is not the case for mechanical disbonding, where water is supposed to condense at existing sites of bad adhesion. Water volume at the interface may subsequently increase due to osmosis. As the water volume increases under the coating, hydrodynamic stresses develop. These stresses eventually result in an increase of the nonadherent surface area.

## Osmosis

Osmotic pressure may result from one or more of the following conditions:

- 1. Presence of soluble salts as contaminants at the original metal surface.
- **2.** Inhomogeneities in the metal surface such as precipitates, grain boundaries, or particles from blasting pretreatment.

**3.** Surface roughness due to abrasion. Once corrosion has started at the interface, the corrosion products produced can be responsible for the increase in osmotic pressure.

# Blistering

Various phenomena may be responsible for the formation of blisters and the start of underfilm corrosion. These include the presence of voids, wet adhesion problems, swelling of the coating during water uptake, gas inclusions, impurity ions in the coating, poor general adhesion properties, and defects in the coating.

When a coating is exposed to an aqueous solution, water vapor molecules and some oxygen diffuse into the film and end up at the substrate interface. Eventually a thin film of water may develop at sites of poor adhesion or at sites where wet adhesion problems arise. A corrosion reaction can start with the presence of an aqueous electrolyte with an electrochemical double layer, oxygen and the metal. This reaction will cause the formation of macroscopic blisters. Depending on the specific materials and circumstances, the blisters may grow out because of the hydrodynamic pressure, in combination with one of the chemical propagation mechanisms such as cathodic delamination or anodic undermining.

# Cathodic Delamination

Loss of adhesion of the paint film adjacent to defects on a coated metal to which cathodic protection is applied is known as cathodic delamination. It derives its name from the fact that the driving force is the cathodic reaction taking place at the interface. As a result of the high pH values resulting from the cathodic reactions, delamination occurs. In the case of cathodic overprotection, blistering, due to the evolution of hydrogen gas, can take place.

# Anodic Undermining

This is a class of corrosion reactions underneath an organic coating in which loss of adhesion is caused by anodic dissolution of the substrate metal or its oxide in contrast to cathodic delamination. In this case the metal is anodic at the blister edges. Anodic undermining usually is initiated at a corrosion-sensitive site underneath the coating such as an enclosed particle, or a section of the metal with potentially increased activity caused by scratches. These sites become active once corrodents have penetrated to the metal surfaces. The corrosion rates start out low, but as corrosion products are formed osmotic pressure develops, which stimulates blister growth. Once formed, the blister will grow due to a type of anodic crevice corrosion at the edge of the blister.

In general, coated aluminum tends to be susceptible to anodic undermining, while coated steel is more susceptible to cathodic delamination.

# **Filiform Corrosion**

Filiform corrosion is a threadlike undermining of the coating and is sometimes referred to as worm track corrosion. It generally occurs in humid chloride-containing environments and is common under organic coatings on steel, aluminum, magnesium, and galvanized steel. The majority of problems occur on coated aluminum and represent a special form of anodic undermining. Filiform corrosion takes place when the following conditions are present:

- **1.** The coating has defects.
- **2.** The coating is permeable to water.
- 3. High relative humidity, specifically in the range 80–95%.
- 4. Contaminants are present on or in the coating or at the coating-substrate interface.

#### Early Rusting

When a latex paint is applied to a cold steel substrate under high-moisture conditions, a measles-like, rusty appearance may develop immediately when the coating is touch dry. This corrosion takes place when the following conditions are met:

- **1.** The air humidity is high.
- 2. The substrate temperature is low.
- **3.** A thin (up to  $40 \mu$ m) latex coating has been applied.

#### **Flash Rusting**

Flash rusting is the appearance of brown rust stains on a blasted steel surface immediately after application of a water-based primer. Contaminants remaining on the metal surface after blast cleaning are responsible for this corrosion. The grit on the surface provides crevices or local galvanic cells that activate the corrosion process as soon as the surface is wetted by the water-based primer.

#### Stages of Corrosion

To prevent excessive corrosion, good inspection procedures and preventive maintenance practices are required. Proper design considerations are also necessary as well as selection of the proper coating system. Regular inspections of coatings should be conducted. Since corrosion of substrates under coatings takes place in stages, early detection will permit correction of the problem, thereby preventing ultimate failure.

#### First Stages of Corrosion

The first stages of corrosion are indicated by rust spotting or the appearance of a few small blisters. Rust spotting is the very earliest stage of corrosion and in many cases is left unattended. Standards have been established for evaluating the degree of rust spotting and may be found in ASTM D-610-68 or "Steel Structures Painting Council Vis-2." One rust spot in 1 square foot may provide a 9+ rating, but three or four rust spots drop the rating to 8. If the rust spots go unattended, a mechanism for further corrosion is provided.

Blistering is another form of early corrosion. Frequently, blistering occurs without external evidence of rusting or corrosion. The mechanism of blistering is attributed to osmotic attack or a dilution of the coating film at the interface with the steel under the influence of moisture. Water and gases pass through the film and dissolve ionic material from either the film or the substrate, causing an osmotic pressure greater than that of the external face of the coating. This produces a solution concentration gradient, with water building up at these sites until the film eventually blisters. Visual blistering standards are found in ASTM D-714-56.

Electrochemical reactions also assist in the formation of blisters. Water diffuses through a coating also by an electro-endesmotic gradient. Once corrosion has started,

moisture is pulled through the coating by an electrical potential gradient between the corroding areas and the protected areas that are in electrical contact. Therefore, osmosis starts the blistering, and once corrosion begins, electro-endesmotic reactions accelerate the corrosion process. The addition of heat and acidic chemicals increases the rate of breakdown. Temperatures of 150 to 200°F (66 to 93°C) accelerate the chemical reaction. Under these conditions steel will literally dissolve in a chemical environment. Moisture is always present and often condenses on the surface behind the blister. This condensation offers a solute for gaseous penetrants to dissolve. When the environment is acidic, the pH of the water behind the blister can be as low as 1.0 to 2.0, subjecting the steel to severe attack.

# Second Stage of Corrosion

After the initial one or two rust spots have been observed, or after a few blisters are found, a general rusting in the form of multiple rust spots develops. This rusting is predominantly  $Fe_2O_3$ , a red rust. In atmospheres lacking sufficient oxygen, such as in sulfur dioxide scrubbers, a black FeO rust develops. Once the unit has been shut down and more oxygen becomes available, the FeO will eventually convert to  $Fe_2O_3$ .

# Third Stage of Corrosion

This advanced stage of corrosion is the total disbondment of the coating from the substrate, exposing the substrate directly to the corrodents. Corrosion can occur at an uninhibited rate since the coating is no longer protecting the steel.

# Fourth Stage of Corrosion

Attack of the metal substrate after the removal of the coating is not usually of a uniform nature, but rather that of a localized attack, resulting in pitting.

# Fifth Stage of Corrosion

Deep pits formed in the substrate during the fourth stage of attack may eventually penetrate completely to cause holes. Within the corrosion cell, pitting has occurred to such a degree that undercutting, flaking, and delamination of the substrate take place. As the small hole develops, the electrolyte has access to the reverse side and corrosion now takes place on both sides of the substrate.

# Final Stage of Corrosion

Corrosion is now taking place at its most rapid and aggressive rate. Large, gaping holes are formed, causing severe structural damage.

# **Composition of Coatings**

The most commonly used organic coating is paint. When applied for corrosion protection, paints are referred to as coatings. Paints consist of binders, pigments, fillers, additives, and solvents.

# Binder

The binder forms the continuous polymeric phase in which all of the other ingredients are incorporated. Its density and composition determine the permeability, chemical resistance,

and ultraviolet resistance of the coating. The protective film is formed through physical curing, chemical curing, or a combination of these.

### Pigments

Pigments are added to the coating for two reasons: to provide color and to improve the corrosion resistance of the coating. The improvement in corrosion resistance may be accomplished by one or more of the following:

- 1. Anticorrosion pigments dissolve slowly in the coating and provide protection by covering corrosion-sensitive sites under the coating, or by sacrificially corroding themselves, thereby protecting the substrate metal, or by passivating the surface.
- 2. Blocking pigments absorb at the active metal surface, reducing the active area for corrosion, and form a transport barrier for ionic species to and from the substrate.
- **3.** Galvanic pigments are nonnoble metal particles (relative to the substrate). These particles when exposed corrode preferentially, while at the original metal surface only the cathodic reaction occurs.
- **4.** Passivating pigments stabilize the oxide film on the exposed metal substrate. Chromates with limited water solubility are generally used.

### Fillers

Fillers are used to increase the volume of the coating. They are also used to improve such properties as impact, abrasion resistance, and water permeability.

### Additives

Additives are made up of numerous materials that are added in small amounts to enhance certain specific properties. They consist of thickeners, antifungal agents, dispersing agents, antifoam agents, anticoalescence agents, UV absorbers, and fire-retarding agents.

#### Solvents

Solvents have two different roles to perform in a coating. Prior to application, the solvent has to function to reduce viscosity of the binder and other components to permit their homogeneous mixing. The reduced viscosity also enables the coating to be applied in a thin, smooth, continuous film. Prior to application, the liquid mixture should be a solution or stable dispersion or emulsion of binder, pigments, and additives in the solvent. After the paint has been applied, a major attractive force between the components is necessary for the formation of a continuous film. There should be no interaction between the solvent and other components, so that the solvent is free to evaporate from the curing film.

Two-component epoxy coatings do not require the use of a solvent. These coatings have a low viscosity. The two components are mixed, usually at elevated temperatures, to reduce the viscosity as much as possible.

## **Complex Coating Systems**

Because of poor adhesion, the corrosion protection supplied by organic coatings is not always satisfactory. To compensate for this, conversion layers are applied to the substrate metal. These layers provide ions, which become part of the protective coating after (electro)chemical reaction of the substrate with a reactive medium. Common conversion layers are phosphate layers on steel and zinc, chromate layers on zinc and aluminum, and anodized layers on aluminum,

157

the latter without an organic topcoat. Anodizing is an electrochemical treatment of a metal (mainly aluminum) while the metal itself is the anode. This produces a reasonably thick oxide layer, which is passive.

Pretreatment layers are used for a variety of reasons:

- **1.** To provide a uniform grease-free surface
- 2. To obtain electrically insulating barrier layers
- 3. To improve the adherence of the organic layer
- **4.** To provide active corrosion inhibition by passivating the metallic substrate or by reducing the rate of oxygen reduction reaction.

There are two types of resin systems, thermoplastic and thermosetting. Thermoplastic solvent-deposited coatings do not undergo any chemical change from the time of application until the attainment of final properties as a protective film. Thermosetting resins differ in that a chemical change takes place after application and solvent evaporation. The coating is said to cure as the chemical reaction is taking place. This curing can take place at room temperature or, in the case of baked coatings, at elevated temperatures. The reaction is irreversible and unlike with thermoplastic coatings, high temperatures or exposure to solvents does not cause the coating to melt or soften. The more commonly used industrial paints are discussed.

# Vinyls (Thermoplastic)

These are polyvinyls dissolved in aromatics, ketones, or ester solvents.

- 1. Resistance: insoluble in oils, greases, aliphatic hydrocarbons, and alcohols; resistant to water and aqueous salt solutions; at room temperature resistant to inorganic acids and alkalies; fire resistant
- 2. Temperature resistance: 180°F (82°C) dry; 140°F (60°C) wet
- 3. Limitations: dissolved by ketones, aromatics, and ester solvents
- 4. Applications: used on surfaces exposed to potable water and on sanitary equipment

# Chlorinated Rubbers (Thermoplastic)

These are resins dissolved in hydrocarbon solvents.

- **1.** Resistance: chemically resistant to acids and alkalies; low permeability to water vapor; abrasion resistant; fire resistant
- 2. Temperature resistance: 200°F (93°C) dry; 120°F (49°C) wet
- 3. Limitations: degraded by ultraviolet light; attacked by hydrocarbons
- **4.** Applications: used on structures exposed to water and marine atmospheres (swimming pools, etc.); excellent adherence to concrete and masonry

# Epoxy (Thermoset)

These are a series of various epoxy paints, all of which are of the thermoset variety.

# Epoxy (Thermoset)

This is a polyamine plus epoxy resin (amine epoxy).

- 1. Resistance: resistant to acids, acid salts, alkalies, and organic solvents
- 2. Temperature resistance: 225°F (107°C) dry; 190°F (88°C) wet

- **3.** Limitations: harder and less flexible than other epoxies; less tolerant of moisture during application
- **4.** Applications: widest range of chemical and solvent resistance of epoxies; used for piping and vessels

# Epoxy (Thermoset)

This is polyamide plus epoxy resin.

- **1.** Resistance: partially resistant to acids, acid salts, alkalies, and organic solvents; resistant to moisture
- 2. Temperature resistance: 150°F (66°C) dry; 225°F (107°C) wet
- 3. Limitations: chemical resistance inferior to that of the polyamine epoxies
- **4.** Applications: used on wet surfaces or underwater, as in tidal zone areas of pilings, oil rigs, etc.

# Epoxy (Thermoset)

This is aliphatic polyamine plus partially prepolymerized epoxy.

- 1. Resistance: partially resistant to acids, acid salts, and organic solvents
- 2. Temperature resistance: 225°F (107°C) dry; 150°F (66°C) wet
- **3.** Limitations: film formed has greater permeability than the other amine epoxies
- 4. Applications: used for protection against mild atmospheric corrosion

# Epoxy (Thermoset)

Esters of epoxies and fatty acids are modified (epoxy ester).

- **1.** Resistance: resistant to weathering; attacked by alkalies
- 2. Temperature resistance: 225°F (107°C) dry; 150°F (66°C) wet
- 3. Limitations: chemical resistance generally poor
- 4. Applications: used where properties of a high-quality oil base paint are required

# Epoxy (Thermoset)

This is a cool tar plus epoxy resin (amine or polyamide cured).

- 1. Resistance: excellent resistance to fresh water, salt water, and inorganic acids
- 2. Temperature resistance: 225°F (107°C) dry; 150°F (66°C ) wet
- 3. Limitations: attacked by organic solvents
- 4. Application: used on steel for immersion or below-grade service

# Oil Base

This comprises coating formulations with vehicles (alkyd), epoxy (urethane), combined with drying oils.

- 1. Resistance: resistant to weathering
- 2. Temperature resistance: 225°F (107°C) dry; 150°F (66°C) wet
- 3. Limitations: chemical resistance generally poor
- 4. Applications: used on wood exterior surfaces because of its penetrating power

# Urethanes

This is a moisture-cured isocyanate prepolymer reacting with atmospheric moisture.

159

- 1. Resistance: abrasion resistant; if cross-linked, resistant to chemicals and solvents
- **2.** Temperature resistance: 250°F (121°C) dry; 150°F (66°C) wet
- 3. Limitations: may yellow under ultraviolet light; poor chemical resistance
- **4.** Applications: used on furniture and floors

# Urethanes

These are catalyzed aliphatic or aromatic isocyanate reacted with polyesters, epoxy, or acrylic polyhydroxyls.

- **1.** Resistance: good chemical resistance; similar to polyamide epoxy
- 2. Temperature resistance: 225°F (107°C) dry; 150°F (66°C) wet
- **3.** Limitations: not recommended for exposure to or immersion in strong acids or alkalies
- **4.** Applications: used as a decorative coating of tank cars and steel in highly corrosive atmospheres

# Silicones

Consider the high-temperature type.

- 1. Resistance: water repellent
- 2. Temperature resistance: 1200°F (649°C) dry and wet
- 3. Requires baking for good cure; not chemically resistant
- 4. Applications: water solvent formulations used on limestone, cement, and nonsilaceous materials; solvent formulations used on bricks and noncalcaceous masonry

# Water Base

These are aqueous emulsions of polyvinyl acetate, acrylic, or styrene-butadiene latex.

- 1. Resistance: poor chemical resistance; resistant to weather
- 2. Temperature resistance: 150°F (66°C) dry and wet
- **3.** Limitations: not suitable for immersion service
- 4. Applications: used in general decorative applications, primarily on wood

# Polyesters

These are organic acids condensed with polybasic alcohols. Styrene is a reactive diluent.

- 1. Resistance: excellent resistance to acids and aliphatic solvents; good resistance to weathering
- 2. Temperature resistance: 180°F (82°C) dry and wet
- **3.** Limitations: not suitable for use with alkalies and most aromatic solvents, since they swell and soften these coatings
- 4. Applications: lining materials for tanks and chemical process equipment

# Coal Tar

This is a distilled coking by-product in aromatic solvent.

- **1.** Resistance: excellent resistance to moisture; good resistance to weak acids, weak alkalies, petroleum oils, and salts
- 2. Temperature resistance: 100°F (38°C) dry and wet

- **3.** Limitations: ultraviolet light and weathering will degrade
- 4. Applications: used on submerged or buried steel and concrete

### Asphalt

These are solids from crude oil refining in aliphatic solvents.

- 1. Resistance: good resistance to weak acids, alkalies, and salts
- 2. Temperature resistance: 230°F (110°C) dry and wet
- **3.** Applications: used in above-ground weathering environments and chemical fume atmospheres

## Zinc Rich

This is metallic zinc in a vehicle of organic or inorganic type.

- 1. Resistance: highly resistant to galvanic and pitting-type corrosion
- 2. Temperature resistance: 700°F (371°C) dry and wet
- **3.** Limitations: must have top coat in severe environments or when pH is below 6 or above 10.5
- 4. Applications: jet fuel storage tanks; petroleum products

See Refs. 1, 2, 8, 16–20.

## **COBALT ALLOYS**

Cobalt alloys are primarily used for hard-face applications such as in valve seats. The purpose of hard facing is to improve resistance to abrasion, friction, galling, and/or impact. The cobalt hard-face alloys usually contain 30–60% cobalt with additives of carbon, nickel, chromium, tungsten, and/or molybdenum. Application is made by either welding or thermal spray processes. Their corrosion resistance is approximately that of the 300 series stainless steels. A typical alloy is Stellite.

See Ref. 4.

## **COLD WATER PITTING**

Cold water pitting is the electrochemical pitting of copper tubes and fittings in domestic water systems that transport groundwaters containing free carbon dioxide in conjunction with dissolved oxygen. The action may be accelerated by the presence of chlorides and sulfates in the water.

## COLUMBIUM

In 1801 an English chemist, C. Hatchett, found a new element. Since he found the element in a black stone discovered near Connecticut, he named it columbium after the country of origin, Columbia, a synonym for America.

A Swedish chemist, Ekeberg, discovered tantalum only one year later, in 1802. He gave it the name tantalum because of the tantalizing difficulty he had dissolving the oxide of the new metal in acids.

The discoveries of niobium and tantalum were almost simultaneous; however, the similarity of their chemical properties caused great confusion for the early scientists who tried to establish their separate identities. The confusion was compounded by some scientists' use of two different names for the same discovery—columbium and niobium.

It was not until 1865 that Mangnac separated niobium and tantalum by using the difference in solubilities of their double fluorides of potassium. In 1905 Dr. W. von Bolton introduced both tantalum and niobium to industry.

The dual nomenclature of niobium and columbium caused confusion and controversy. Niobium was preferred in Europe, and columbium was preferred in the United States. Finally, at the Fifteenth International Union of Chemistry Congress in Amsterdam in 1949, the name niobium was chosen as the recognized international name.

For more details see "Niobium."

## **COMPOSITE LAMINATES**

Composite laminates are two composite materials joined to form a dual laminate, one material being on the exterior and the other on the interior. Typical combinations include ABS and polyester, bisphenol and isophthalic fibrous glass systems, vinyl ester and polyester, epoxy and polyester, glass and reinforced polyester, polypropylene-lined reinforced polyester, and PVC and polyester composite.

When applying a composite laminate, it is necessary to evaluate each member of the composite as to its compatibility with the corrosive environment.

See also "Composites."

### COMPOSITES

For the purpose of corrosion-resisting materials, a composite is defined as a mixture of two or more materials that are distinct in composition and form, all being present in significant quantities (e.g., greater than 5 volume percent). By this definition, conventional alloyed steel would not be considered a composite since the alloying ingredients are present in quantities of much less than 1% by weight or volume, and most often less than 0.1%.

The object of composite materials is to achieve properties in composite form that exceed those of their individual components alone. In forming composites at times it is necessary to accept a trade-off. For example, combining a strong but brittle ceramic fiber in a ductile and weaker metal matrix results in a composite whose strength lies somewhere between the strength of the ceramic fiber and that of the metal matrix, but which is not as brittle as the ceramic alone.

The possibilities of forming composites are quite extensive. The duplex stainless steels, which contain approximately equal amounts of ferrite and austenite, are examples of metallic composites (see "Duplex Stainless Steels").

Glass fiber–reinforced polyesters are considered the first engineered composites. In addition to glass fiber, other types of fibers used to produce composites include boron, carbon, silicon carbide, and aramid fibers. For more detailed information on composites, refer to the following topics in this book:

Composite Laminates Duplex Stainless Steels Thermoset Reinforcing Materials

See Ref. 21.

## CONCENTRATION CELLS

These are the cause of pitting and crevice corrosion. The primary factors causing pitting are electrical contact between dissimilar materials or areas of the same metal where oxygen or conductive salts in water differ. Such a coupling is sufficient to cause a difference of potential, causing an electric current to flow through the water, or across moist steel, from the metallic anode to a nearby cathode. The cathode may be mill scale or any other portion of the metal surface that is cathodic to the more active metal areas. Mill scale is cathodic to steel and is one of the more common causes of pitting. If the cathodic area is relatively large compared with the anodic area, the damage is spread out and usually negligible. When the anode area is relatively small, the metal loss is concentrated and may be serious.

Concentration cells are capable of causing severe corrosion, leading to pitting, when differences in dissolved oxygen concentrations occur. That portion of the metal that is in contact with water relatively low in dissolved oxygen concentration is anodic to adjoining areas with water higher in dissolved oxygen concentration. This lack of oxygen may be caused by exhaustion of dissolved oxygen in a crevice. The low-oxygen area is always anodic. This type of cell is responsible for corrosion at crevices that are formed at the interface of two coupled pipes, or at threaded connections, since the oxygen concentration is lower within the crevice or at the threads than elsewhere. It also is responsible for pitting damage under rust or at the water line (air–water interface). These differential aeration cells are responsible for initiating pits in stainless steel, aluminum, nickel, and other so-called passive metals when they are exposed to aqueous environments such as seawater.

See Ref. 22.

#### **CONVERSION COATINGS**

Conversion coatings are coatings formed on metal either naturally by reaction with the environment or artificially using chemical or electrochemical treatment. The films or coatings formed by these treatments serve two purposes. They not only improve the corrosion resistance of the metal, but also increase the adhesive bonding of paint coatings.

Typical examples of this type of coating include anodizing of aluminum, magnesium, and titanium alloys; phosphate coatings on iron and steel, aluminum, and zinc; chromate coatings on zinc, aluminum, and cadmium; oxide bluing of iron and steel; oxide coatings on cadmium, iron, steel, copper, and zinc alloys; and pack cementation to form diffusion coatings on various metals.

See Refs. 1 and 2.

#### COPOLYMER

A copolymer is a polymer produced from two or more types of different monomers.

#### **COPPER AND COPPER ALLOYS**

Since before the dawn of history, when primitive people first discovered the red metal, copper has been serving mankind. The craftsmen who built the Great Pyramid for the Egyptian pharaoh Cheops used copper pipe to convey water to the royal bath. A remnant

#### COPPER AND COPPER ALLOYS

Copper UNS no.	Cu	Ag min.	Р	As	Sb	Te	Other
C10200	99.95						
C10300	99.95		0.001-0.005				
C10400	99.95	0.027					
C10800	99.95		0.005-0.012				
C11000	99.90						
C11300	99.90	0.027					
C12000	99.90		0.004-0.012				
C12200	99.90		0.015-0.040				
Cl 2500	99.88			0.012	0.003	0.025	0.050 Ni,
							0.003 Bi,
							0.004 Pb
C13000	99.88	0.085		0.012	0.003	0.025	0.050 Ni,
							0.003 Bi,
							0.004 Pb
C14200	99.40		0.015-0.040	0.15-0.50			

 Table C.18
 Chemical Composition of Coppers: Maximum<sup>a</sup> Composition (%)

<sup>a</sup>Except for Ag and when shown as a range. Source: Ref. 3.

of this pipe was unearthed some years ago, still in usable condition, a testimonial to copper's durability and resistance to corrosion. Today, nearly 5000 years after Cheops, copper is still used to convey water and is a prime material for this purpose.

To be classified as a copper, the alloy must contain a minimum of 99.3% copper. Elements such as silver, arsenic, lead, phosphorus, antimony, tellurium, nickel, cadmium, sulfur, zirconium, manganese, boron, and bismuth may be present singly or in any combination. Since copper is a noble metal, it finds many applications in corrosive environments. Table C.18 gives the chemical compositions of some of the coppers used in corrosion applications.

Copper itself is inherently corrosion resistant. It is noble to hydrogen in the emf series and thermodynamically stable with no tendency to corrode in water and in nonoxidizing acids free of dissolved oxygen. With copper and its alloys the predominant cathode reaction is the reduction of oxygen to form hydroxide ions. Therefore, oxygen or other oxidizing agents are necessary for corrosion to take place. In oxidizing acids or in aerated solutions of ions that form copper complexes (e.g., CN,  $MH_A$ ), corrosion can be severe. Copper is also subject to attack by turbulently flowing solutions, even though the metal may be resistant to the solution in a stagnant condition. Most of the corrosion products that form on copper and copper alloys produce adherent, relatively impervious films with low solubility that provide the corrosion protection.

Copper finds many applications in the handling of seawater and/or fresh water. The corrosion resistance of copper, when in contact with fresh water or seawater, is dependent on the surface oxide film that forms. In order for corrosion to continue, oxygen must diffuse through this film. High-velocity water will disturb this film, while carbonic acid or organic acids, which are present in some fresh waters and soils, will dissolve the film. Either situation leads to an appreciably high corrosion rate. If the water velocity is limited to 4–5 ft/s, the film will not be disturbed.

Sodium and potassium hydroxide solutions can be handled at room temperature by copper in all concentrations. Copper is not corroded by perfectly dry ammonia, but it may be rapidly corroded by moist ammonia and ammonium hydroxide solutions. Alkaline salts, such as sodium carbonate, sodium phosphate, or sodium silicate, act like hydroxides but are less corrosive.

When exposed to the atmosphere over a long period of time, the protective film that forms is initially dark in color, gradually turning green. This corrosion product is known as patina. Since the coloration is given by copper hydroxide products, the length of time required to form this coloration is dependent on the atmosphere. In marine atmospheres the compound is a mixture of copper hydroxide and chloride and in urban or industrial atmospheres a mixture of copper hydroxide and sulfate.

Pure copper is immune to stress corrosion cracking. However, alloys of copper containing more than 15% zinc are particularly subject to this type of corrosion.

The coppers are resistant to urban, marine, and industrial atmospheres. For this reason copper is used in many architectural applications such as building fronts, downspouts, flashing, gutters, roofing, and screening. In addition to corrosion resistance, their good thermal conductivity properties make the coppers ideal for use in solar panels and related tubing and piping used in solar energy conversion. These same properties plus their resistance to engine coolants make the coppers suitable for use as radiators.

Large amounts of copper are used in the beverage industry, particularly in the brewing and distilling operations.

In general, the coppers are resistant to

- 1. Seawater
- **2.** Fresh waters, hot or cold
- **3.** De-aererated, hot or cold, dilute sulfuric acid, phosphoric acid, acetic acid, and other nonoxidizing acids
- 4. Atmospheric exposure

The coppers are not resistant to

- 1. Oxidizing acids such as nitric and hot concentrated sulfuric acid, and aerated nonoxidizing acids (including carbonic acid).
- 2. Ammonium hydroxide (plus oxygen). A complex ion,  $Cu(NH_3)_4^{2^+}$ , forms. Substituted ammonia compounds (amines) are also corrosive.
- **3.** High-velocity aerated waters and aqueous solutions.
- **4.** Oxidizing heavy metal salts (ferric chloride, ferric sulfate, etc.).
- 5. Hydrogen sulfide and some sulfur compounds.

The compatibility of copper with selected corrodents is shown in Table C.19.

Copper has excellent electrical and thermal conductivity properties, is malleable, and is machinable, but has low mechanical properties. The mechanical and physical properties are given in Table C.20. To obtain strength, the metal must be cold worked or alloyed. As a result, there are hundreds of copper alloys. The Copper Development Association, together with the American Society of Testing and Materials and the Society of Automotive Engineers, has developed a five-digit system to identify these alloys. This system is part of the unified numbering system for metals and alloys. The numbers C10000 through C79999 denote the wrought alloys, whereas the cast copper and copper alloys are numbered C80000 through C99999.

See Refs. 23, 24.

		Maximum temperature (°I	E/°C)
Chemical	Copper	Aluminum bronze	Red brass
Acetaldehyde	х	х	х
Acetamide		60/16	
Acetic acid 10%	100/38		х
Acetic acid 50%	х	х	х
Acetic acid 80%	х	х	х
Acetic acid, glacial	х	х	х
Acetic anhydride	80/27	90/32	х
Acetone	140/60	90/32	220/104
Acetyl chloride	х	60/16	х
Acrylonitrile	80/27	90/32	210/99
Adipic acid	80/27	,	/
Allyl alcohol	90/32	90/32	90/32
Alum	90/32	60/16	80/27
Aluminum acetate	60/16	00/10	00/2/
Aluminum acctate Aluminum chloride, aqueous	x	х	х
Aluminum chloride, dry	60/16	А	А
Aluminum fluoride	x	90/32	
Aluminum hydroxide	x 90/32		80/27
Aluminum nitrate	90192	X	
		Х	х
Aluminum oxychloride	<u>80/27</u>		
Aluminum sulfate	80/27	x 90/32	X
Ammonia gas	х	90/32	х
Ammonium bifluoride	х		х
Ammonium carbonate	х		х
Ammonium chloride 10%	х	Х	
Ammonium chloride 50%	х	х	
Ammonium chloride, sat.	х	х	х
Ammonium fluoride 10%	х		х
Ammonium fluoride 25%	Х	Х	х
Ammonium hydroxide 25%	Х	х	х
Ammonium hydroxide, sat.	х	Х	х
Ammonium nitrate	х	Х	х
Ammonium persulfate	90/32	Х	х
Ammonium phosphate	х	90/32	х
Ammonium sulfate 10–40%	х	х	х
Ammonium sulfide	х	х	х
Ammonium sulfite	х		х
Amyl acetate	90/32	х	400/204
Amyl alcohol	80/27	90/32	90/32
Amyl chloride	80/27	90/32	80/27
Aniline	х	90/32	x
Antimony trichloride	80/27	х	x
Aqua regia 3:1	х	х	x
Barium carbonate	80/27	90/32	90/32
Barium chloride	80/27	80/27	80/27
Barium hydroxide	80/27	x	80/27
Barium sulfate	80/27	60/16	210/99
Barium sulfide	x	X	X
Benzaldehyde	80/27	90/32	210/99

 Table C.19
 Compatibility of Copper, Aluminum Bronze, and Red Brass

 with Selected Corrodents<sup>a</sup>

Chemical	Connor		
<u>ן</u>	Copper	Aluminum bronze	Red brass
Benzene	100/38	80/27	210/99
Benzene sulfonic acid 10%			90/32
Benzoic acid 10%	80/27	90/32	210/99
Benzyl alcohol	80/27	90/32	210/99
Benzyl chloride	х		х
Borax	80/27	90/32	80/27
Boric acid	100/38	90/32	х
Bromine gas, dry	60/16	х	
Bromine gas, moist	х	х	
Bromine liquid		х	
Butadiene	80/27		80/27
Butyl acetate	80/27		300/149
Butyl alcohol	80/27	90/32	90/32
Butyl phthalate	80/27		210/99
Butyric acid	60/16	90/32	80/27
Calcium bisulfite	80/27	x	x
Calcium carbonate	80/27	x	80/27
Calcium chlorate	x	x	x
Calcium chloride	210/99	x	80/27
Calcium hydroxide 10%	210/99	80/27	00,2,
Calcium hydroxide. sat.	210/99	60/16	210/99
Calcium hypochlorite	X	X	210/ <i>)</i> /
Calcium nitrate	A	x	x
Calcium sulfate	80/27	x	80/27
Caprylic acid	x	А	x
Carbon bisulfide	80/27		x
Carbon dioxide, dry	90/32	90/32	570/299
Carbon dioxide, wet	90/32	90/32	x
Carbon disulfide	80/27	90192	X
Carbon monoxide	00/2/	60/16	570/299
Carbon tetrachloride	210/99	90/32	180/82
Carbonic acid	80/27	x	210/99
Cellosolve	80/27	60/16	210/99
Chloracetic acid, 50% water	x	00/10	210/))
Chloracetic acid	x	80/27	х
Chlorine gas, dry	210/99	90/32	570/299
Chlorine gas, wet			
Chlorine, liquid	х	х	х
Chlorobenzene	90/32	60/16	210/99
Chloroform	80/27	90/32	80/27
Chlorosulfonic acid			
Chromic acid 10%	X	X	X
Chromic acid, 50%	X	x	x
Citric acid 15%	x 210/99	x 90/32	Х
-		90/32	x
Citric acid, concentrated	x 00/22	X	Х
Copper acetate	90/32	х	х
Copper carbonate Copper chloride	90/32 x	x	х

Table C.19Compatibility of Copper, Aluminum Bronze, and Red Brasswith Selected Corrodents<sup>a</sup> (Continued)

		Maximum temperature (°I	F/°C)
Chemical	Copper	Aluminum bronze	Red brass
Copper cyanide	х	х	х
Copper sulfate	х	х	х
Cupric chloride 5%	х		
Cupric chloride 50%			
Cyclohexane	80/27	80/27	80/27
Cyclohexanol	80/27		80/27
Dichloroethane			210/99
Ethylene glycol	100/38	80/27	80/27
Ferric chloride	80/27	х	х
Ferric chloride 50% in water	х	х	х
Ferric nitrate 10–50%	х	х	х
Ferrous chloride		х	х
Ferrous nitrate			
Fluorine gas, dry	х	х	х
Fluorine gas, moist	x		
Hydrobromic acid, dilute	x	х	х
Hydrobromic acid 20%	x	x	x
Hydrobromic acid 50%	x	X	x
Hydrochloric acid 20%	x	X	x
Hydrochloric acid 38%	x	X	x
Hydrocyanic acid 10%	x	x	x
Hydrofluoric acid 30%	x	x	x
Hydrofluoric acid 70%	X	x	X
Hydrofluoric acid 100%	x	x	X
Hypochlorous acid	x	А	X
Iodine solution 10%	х		А
		00/22	100/20
Ketones, general		90/32	100/38
Lactic acid 25%	00/00	X	90/32
Lactic acid, concentrated	90/32	90/32	90/32
Magnesium chloride	300/149	90/32	х
Malic acid	х		
Manganese chloride	х		
Methyl chloride	90/32	Х	210/99
Methyl ethyl ketone	80/27	60/16	210/99
Methyl isobutyl ketone	90/32		210/99
Muriatic acid	х		
Nitric acid 5%	х	х	х
Nitric acid 20%	х	х	х
Nitric acid 70%	х	х	х
Nitric acid, anhydrous	х	х	х
Nitrous acid, concentrated	80/27	х	
Oleum		х	х
Perchloric acid 10%			х
Perchloric acid 70%			х
Phenol	х	х	570/299
Phosphoric acid 50–80%	х	х	х
Picric acid	х	х	х
Potassium bromide 30%	80/27		

Table C.19Compatibility of Copper, Aluminum Bronze, and Red Brasswith Selected Corrodents<sup>a</sup> (Continued)

	М	aximum temperature (°F/	′°C)
Chemical	Copper	Aluminum bronze	Red brass
Salicylic acid	90/32		210/99
Silver bromide 10%	х		
Sodium carbonate	120/49	60/16	90/32
Sodium chloride to 30%	210/99	60/16	210/99
Sodium hydroxide 10%	210/99	60/16	210/99
Sodium hydroxide 50%	х	х	х
Sodium hydroxide, concentrated	х	х	х
Sodium hypochlorite 20%	х	х	80/27
Sodium hypochlorite, concentrated	х	х	х
Sodium sulfide to 50%	х	х	х
Stannic chloride	х	х	х
Stannous chloride	х	х	х
Sulfuric acid 10%	х	х	200/93
Sulfuric acid 50%	х	х	х
Sulfuric acid 70%	х	х	х
Sulfuric acid 90%	х	х	х
Sulfuric acid 98%	х	х	х
Sulfuric acid 100%	х	х	х
Sulfuric acid, fuming	х	х	х
Sulfurous acid	х	х	90/32
Toluene	210/99	90/32	210/99
Trichloroacetic acid	80/27	х	80/27
Zinc chloride	х	х	х

 Table C.19
 Compatibility of Copper, Aluminum Bronze, and Red Brass

 with Selected Corrodents<sup>a</sup> (Continued)

<sup>a</sup>The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated. Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x. A blank space indicates that data are unavailable. When compatible, corrosion rate is <20 mpy.

Source: PA Schweitzer. Corrosion Resistance Tables, 4th ed. Vols. 1-3. New York: Marcel Dekker, 1995.

Property	Annealed	Hard-drawn
Modulus of elasticity $ imes 10^6$ , psi	17	17
Tensile strength $\times 10^3$ psi	33	45
Yield strength 0.2% offset $\times 10^3$ , psi	10	40
Elongation in 2 in., %	45	10
Hardness, Rockwell	F-45	B-40
Density, lb/in. <sup>3</sup>	0.323	0.323
Specific gravity	8.91	8.91
Specific heat, Btu/hr °F	0.092	0.092
Thermal conductivity at 68°F		
Btu/hr ft <sup>2</sup> °F	2364	2364
Coefficient of thermal expansion at 77–572°F in/in. °F $\times 10^{-6}$	9.8	9.8

 Table C.20
 Mechanical and Physical Properties of Copper

# **High-Copper Alloys**

Wrought high-copper alloys contain a minimum of 96% copper. Table C.21 lists the chemical compositions of some of the high-copper alloys. High-copper alloys are used primarily for electrical and electronic applications.

UNS no.	Cu	Fe	Ni	Co	Be	Pb	Р	Zn	Sn	Si	Al
C1700	Balance		b	b	1.6–1.79	_		_	_	0.20	0.20
C17200	Balance	b	b	b	1.8-2.00	_	_	_		0.20	0.20
C17300	Balance	Ь	Ь	Ь	1.8 - 2.00	0.20-0.60	_	_	_	0.20	0.20
C1800 <sup>c</sup>	Balance	0.10	2.5	_	_	_	_	_	0.4	0.7	
C19200	96.7 min.	0.8-1.2	_	_	_	—	0.01 - 0.04	_	_	_	_
C19400	97.0 min.	2.1–2.6	—	—	—	0.03	0.015-0.15	0.05-0.20	—	—	—

Table C.21High-Copper Alloys: Maximum<sup>a</sup> Composition (%)

<sup>a</sup>Unless shown as a range or minimum.

 ${}^{b}M$  + Co: 0.20 min.; Ni + Fe + Co: 0.60 max.

<sup>c</sup>Also available in cast form as copper alloy UNS C81540.

Source: Ref. 25.

The corrosion resistance of the high-copper alloys is approximately the same as that of the coppers. These alloys are used in corrosion service when mechanical strength is needed as well as corrosion resistance. Alloy C19400 is basically copper that has about 2.4% iron added to improve corrosion resistance. It is used in seam-welded condenser tubing in desalting services.

#### **Copper-Aluminum Alloys**

These are alloys commonly referred to as aluminum bronzes. They are available in both wrought and cast forms. The ability of copper to withstand the corrosive effects of salt and brackish water is well known. Copper artifacts recovered from sunken ships have been identifiable and in many cases usable after hundreds of years under the sea. During the early 1900s aluminum was added to copper as an alloying ingredient. It was originally added to give strength to copper while maintaining the corrosion resistance of the base metal. As it developed, the aluminum bronzes were more resistant to direct chemical attack because aluminum oxide plus copper oxide were formed. The two oxides are complementary and often give the alloy superior corrosion resistance. Table C.22 lists the alloys generally used for corrosion resistance.

UNS no.	Cu	Al	Fe	Ni	Mn	Si	Sn	Zn	Other
C60800	92.5–94.8	5.0–6.5	0.010	_	—	—	—	_	0.02–0.25 As, 0.10 Pb
C61000	90.0-93.0	6.0-8.5	0.50	_		0.10		0.20	0.02 Pb
C61300	88.6–92.0	6.0-8.5	2.0-3.0	0.15	0.10	0.10	0.20-0.50	0.05	0.01 Pb
C61400	88.0-92.5	6.0-8.0	1.5–3.5	_	0.10			0.20	0.01 Pb
C61500	89.0–90.5	7.7-8.3	_	1.8-2.2	_			_	0.015 Pb
C61800	86.9–91.0	8.5-11.0	0.5-1.5	_	_	0.10		0.02	0.02 Pb
C62300	82.2-89.5	8.5-11.0	2.0-4.0	1.0	0.50	0.25	0.60	_	_
C63000	78.0-85.0	9.0-11.0	2.0-4.0	4.0-5.5	1.5	0.25	0.20	0.30	_
C63200	75.9–84.5	8.5–9.5	3.0-5.0	4.0–5.5	3.5	0.10	—	—	0.02 Pb

 Table C.22
 Wrought Copper-Aluminum Alloys: Maximum<sup>a</sup> Composition (%)

<sup>a</sup>Unless shown as a range.

Source: Ref. 25

Aluminum bronzes have progressed from simple copper-aluminum alloys to more complex alloys with the addition of iron, nickel, silicon, manganese, tin, and other elements.

Aluminum bronzes are resistant to nonoxidizing mineral acids such as phosphoric and sulfuric. The presence of an oxidizing agent controls their resistance.

These alloys are resistant to many organic acids, such as acetic, citric, formic, and lactic. The possibility of copper pickup by the finished product may limit their use. Such a pickup may discolor the product even though it is very low. Refer to Table C.19 for the compatibility of aluminum bronze with selected corrodents.

Dealloying is rarely seen in all alpha, single-phase alloys such as UNS C60800, C61300, or C61400. When dealloying does occur, it is in conditions of low pH and high temperature.

Alloy C61300 is used to fabricate vessels to handle acetic acid because its good corrosion resistance, strength, and heat conductivity make it a good choice for acetic acid processing. Alkalies such as sodium and potassium hydroxides can also be handled by aluminum bronze alloys.

Aluminum bronzes are also used as condenser tube sheets in both fossil fuel and nuclear power plants to handle fresh, brackish, and seawaters for cooling, particularly alloys C61300, C61400, and C63000.

#### **Copper-Nickel Alloys**

These are referred to as cupronickels. The copper nickels are single-phase alloys, with nickel as the principal alloying ingredient. The alloys most important for corrosion resistance are those containing 10% and 30% nickel. Table C.23 lists these alloys. Iron, manganese, silicon, and niobium may be added. Iron improves the impingement resistance of these alloys if it is in solid solution. Iron present in small microprecipitates can be detrimental to corrosion resistance. To aid weldability, niobium is added.

Of the several commercial copper-nickel alloys available, alloy C70600 offers the best combination of properties for marine application and has the broadest application in seawater service. Alloy 706 has been used aboard ships for seawater distribution and shipboard fire protection. It is also used in many desalting plants. Exposed to seawater, alloy 706 forms a thin but tightly adhering oxide film on its surface. To the extent that this film forms, copper-nickel does in fact "corrode" in marine environments. However, the copper-nickel oxide film is firmly bonded to the underlying metal and is nearly insoluble in seawater. It therefore protects the alloy against further attack once it is formed. Initial corrosion rates may be in the range of less than 1.0 to about 2.5 mpy. In the absence of turbulence, as would be the case in a properly designed piping system, the copper-nickel's corrosion rate will decrease with time, eventually dropping to as low as 0.05 mpy after several years of service.

UNS no.	Cu	Ni	Fe	Mn	Other
C70600	Balance	9.0–11.0	1.0–1.8	1.0 max.	Pb 0.05 max., Zn 1.0 max.
C71500	Balance	29.0–33.0	0.40–0.7	1.0 max.	Pb 0.05 max., Zn 1.0 max.
C71900	Balance	29.0–32.0	0.25 max.	0.5–1.0	Cr 2.6–3.2, Zr 0.08–0.2, Ti 0.02–0.08

 Table C.23
 Chemical Composition of Wrought Cupronickels (%)

11 ,	
Modulus of elasticity $\times$ 10 <sup>6</sup> , psi	18
Tensile strength $\times 10^3$ psi	
4½ in. O.D.	40
5½ in. O.D.	38
Yield strength at 0.5% extension under load $ imes 10^3$ psi	
4½ in. O.D.	15
5½ in. O.D.	13
Elongation in 2 in., %	25
Density, lb/in. <sup>3</sup>	0.323
Specific heat, Btu/lb °F	0.09
Thermal conductivity, Btu/h/ft/at ft. <sup>2</sup> /°F	26
Coefficient of thermal expansion at 68–572°F. in/in. °F $\times 10^{-6}$	9.5

Table C.24Mechanical and Physical Properties of 90–10Copper-Nickel Alloy 706

Another important advantage of the oxide film developed on alloy 706 is that it is an extremely poor medium for the adherence and growth of marine life forms. Algae and bromades, the two most common forms of marine biofouling, simply will not grow on alloy 706. Alloy 706 piping therefore remains clean and smooth, neither corroding appreciably nor becoming encrusted with growth. Refer to Table C.24 for the mechanical and physical properties of alloy 706.

Alloy C71500 finds use in many of the same applications as alloy C70600. Sulfides as low as 0.007 ppm in seawater can induce pitting in both alloys, and both alloys are highly susceptible to accelerated corrosion as the sulfide concentration exceeds 0.01 ppm.

Alloy C71900 is a cupronickel to which chromium has been added. It was developed for naval use. The chromium addition strengthens the alloy by spinodal decomposition. This increases the yield strength from 20.5 ksi for C71500 to 45 ksi for C71900. This alloy has improved resistance to impingement. There is, however, some sacrifice in general corrosion resistance, pitting, and crevice corrosion under stagnant or low-velocity conditions.

The copper-nickels are highly resistant to stress corrosion cracking. Of all the copper alloys, they are the most resistant to stress corrosion cracking in ammonia and ammoniacal environments. Although not used in these environments because of cost, they are resistant to some nonoxidizing acids, alkalies, neutral salts, and organics.

# **Copper-Tin Alloys**

These alloys are known as tin bronzes or phosphor bronzes. Although tin is the principal alloying ingredient, phosphorus is always present in small amounts, usually less than 0.5%, because of its use as an oxidizer.

These alloys are probably the oldest alloys known, having been the bronzes of the Bronze Age. Even today many of the artifacts produced during that age are still in existence. Items such as statues, vases, bells, and swords have survived hundreds of years of exposure to a wide variety of environments, testifying to the corrosion resistance of these materials.

Alloys that contain more than 5% tin are especially resistant to impingement attack. In general, the tin bronzes are noted for their high strength. Their main application is in water service for such items as valves, valve components, pump casings, and similar items. Because of their corrosion resistance in stagnant waters, they also find wide application as components of fire protection systems.

### Copper-Zinc Alloys (Brasses)

Brasses contain zinc as their principal alloying ingredient. Other alloying additions are lead, tin, and aluminum. Lead is added to improve machinability and does not improve the corrosion resistance. The addition of approximately 1% tin increases the dealloying resistance of the alloys. Aluminum is added to stabilize the protective surface film. Alloys containing in excess of 15% zinc are susceptible to dealloying in environments such as acids, both organic and inorganic, dilute and concentrated alkalies, neutral solutions of chlorides and sulfates, and mild oxidizing agents.

This is a type of corrosion in which the brass dissolves as an alloy and the copper constituent redeposits from the solution onto the surface of the brass as a metal in porous form. The zinc constituent may be deposited in place of an insoluble compound or carried away from the brass as a soluble salt. The corrosion can take place uniformly or be local. Uniform corrosion is more apt to take place in acid environments while local corrosion is more apt to take place in alkaline, neutral, or slightly acid environments. The addition of tin or arsenic will inhibit this form of corrosion.

Conditions of the environment that favor dezincification are high-temperature, stagnant solutions, especially acid, and porous inorganic scale formation. Other factors that stimulate the process are increasing zinc concentrations and the presence of both cuprous and chloride ions.

As the dealloying proceeds, a porous layer of pure or almost pure copper is left behind. This reaction layer is of poor mechanical strength. The dezincification process on copper-zinc alloys is therefore very detrimental. These alloys are also subject to stress corrosion cracking. Moist ammonia in the presence of air will cause this form of corrosion. The quantity of ammonia present need not be great, as long as the other factors are present.

The relative resistance of the brasses to stress corrosion cracking is as given in the table.

Low resistance
Brasses containing >15% zinc
Brasses containing >15% zinc and small amounts of lead, tin, or aluminum
Intermediate resistance
Brasses containing <15% zinc
Aluminum bronzes
Nickel-silvers
Phosphor bronzes
Good resistance
Silicon bronzes
Phosphorized copper
High resistance
Commercially pure copper
Cupronickels

If the metal is cold formed, residual stresses may be present that can also cause stress corrosion cracking. By heating the metal to a temperature high enough to permit recrystallization, the stresses will be removed. It is also possible to provide a stress-relieving anneal at a lower temperature without substantially changing the mechanical properties of the cold-worked metal. As stated earlier, the addition of small amounts of tin improves the dezincification resistance of these alloys. The brasses most commonly used for corrosion-resistant applications are

Copper Alloy UNS No.
C27000
C28000
C44300
C44400
C44500
C46400
C46500
C46600
C46700
C68700

Copper alloys UNS C44300 through C44500 are known as admiralty brasses. They are resistant to dealloying as a result of the presence of tin in the alloy.

Admiralty brass finds application mainly in the handling of seawater and/or fresh water, particularly in condensers. These brasses are also resistant to hydrogen sulfide and therefore find application in petroleum refineries.

The high-zinc brasses, such as C27000, C28000, C44300, and C46400, resist sulfides better than do the low-zinc brasses. Dry hydrogen sulfide is well resisted.

Alloys containing 15% or less of zinc resist dealloying and are generally more corrosion resistant than the high-zinc-bearing alloys. These alloys are resistant to many acids, alkalies, and salt solutions that cause dealloying in the high-zinc brasses. Dissolved air, oxidizing materials such as chlorine and ferric salts, compounds that form soluble copper complexes (e.g., ammonia) and compounds that react directly with copper (e.g., sulfur and mercury) are corrosive to the low-zinc brasses. These alloys are more resistant to stress corrosion cracking than the high-zinc-containing alloys.

Red brass (C23000) is a typical alloy in this group, containing 15% zinc and 85% copper. It has the basic corrosion resistance of copper but with greater tensile strength. Refer to Table C.19 for the compatibility of red brass with selected corrodents. The mechanical and physical properties of red brass are shown in Table C.25.

The leaded brasses (C31200 through C38500) have improved machinability as a result of the addition of lead.

Modulus of elasticity $\times 10^6$ , psi	17
Tensile strength $\times 10^3$ , psi	40
Yield strength 0.2% offset $\times 10^3$ psi	15
Elongation in 2 in., %	50
Hardness, Brinell	50
Density, lb/in. <sup>3</sup>	0.316
Specific gravity	8.75
Specific heat, Btu/lb °F	0.09
Thermal conductivity at 32–212°F Btu/ft <sup>2</sup> /h/ °F/in.	1100
Coefficient of thermal expansion at $31-212^{\circ}$ F in/in. $^{\circ}$ F $\times 10^{-6}$	9.8

Table C.25 Mechanical and Physical Properties of Red Brass

#### CORROSION ALLOWANCE

The required wall thickness of a pressure vessel or storage tank is determined by the physical and mechanical properties of the specific metal or alloy being used and the operating conditions of temperature and pressure. Calculations provide the minimum required thickness to which a safety factor is added. The corrosion allowance is an extra thickness of metal above that needed for mechanical strength. The extra thickness, which is determined by the corrosion rate of the metal or alloy, is added to the design thickness to compensate for the anticipated lifetime corrosion loss. In general, the corrosion allowance for vessels, heat exchangers, and tanks should provide for 20 years of corrosion. For piping 10 years of corrosion allowance should be required, based on the easier replaceability of piping.

A minimum of 3 mm  $(\frac{1}{8}$  in.) corrosion allowance should be provided for carbon steel and low-alloy vessels, heat exchangers, and tanks, unless the service is considered noncorrosive.

For high alloys a nominal corrosion allowance of 1.5 mm ( $\frac{1}{16}$  in.) may be specified. This would apply to alloy plate, the clad layer of clad plate, and the overlay of overlayed plate.

Some service may require different corrosion allowances for different sections of the same vessel. For example, the lower course and bottom of an oil storage tank may have a 3 mm ( $\frac{1}{8}$  in.) corrosion allowance for water corrosion, while the upper courses, which are not exposed to water corrosion, may have only a 1.5 mm ( $\frac{1}{16}$  in.) or even zero corrosion allowance.

In some instances an external corrosion allowance may be considered. Such circumstances would include buried piping or external insulation. Soils can be corrosive to buried piping and cause failure from the outside. When insulation is applied to a vessel, there is the possibility of corrosion taking place under the insulation. To guard against premature failure in these instances, a corrosion allowance may be applied.

#### **CORROSION COUPONS**

See "Corrosion Testing."

#### **CORROSION FATIGUE**

Corrosion fatigue is the cracking of a metal or alloy under the combined action of a corrosive environment and repeated or fluctuating stress. As in stress corrosion cracking (SCC), successive or alternate exposure to stress and corrosion does not lead to corrosion fatigue.

Metals and alloys fail by cracking when subjected to cyclic or repetitive stress even in the absence of a corrosive medium. This is known as fatigue failure. The greater the applied stress, the fewer the number of cycles required and the shorter the time to failure. In steels and other ferrous metals, no failure occurs for an infinite number of cycles at or below a stress level called the endurance limit or the fatigue limit. In a corrosive medium, failure occurs at any applied stress if the number of cycles is sufficiently large. Corrosive fatigue may therefore be defined as the reduction in fatigue life of a metal in a corrosive environment. Unlike SCC, corrosion fatigue is equally prevalent in pure metals and their alloys, and is not restricted to specific environments. Any environment causing general

С

attack in a metal or alloy is capable of causing corrosion fatigue. For steels the minimum corrosion rate required is approximately 1 mpy.

Corrosion fatigue increases almost proportionately with the increase of general aggressiveness of the corrodent. Consequently, an increase in temperature, a lowering of the pH, or an increase in the concentration of the corrodent leads to aggravation of corrosion fatigue.

Corrosion fatigue can be reduced or eliminated by

- **1.** Lowering of the stress
- **2.** Controlling the environment
- 3. Use of coatings
- **4.** Cathodic protection
- 5. Shot peening

See Refs. 10, 26, and 27.

#### **CORROSION INHIBITORS**

Corrosion of metallic surfaces can be reduced or controlled by the addition of chemical compounds to the corrodent. This form of corrosion control is called inhibition, and the compounds added are known as inhibitors. These inhibitors will reduce the rate of either anodic oxidation or cathodic reduction or both processes. The inhibitors themselves form a protective film on the surface of the metal. It has been postulated that the inhibitors are absorbed into the metal surface either by physical (electrostatic) adsorption or chemisorption.

Physical adsorption is the result of electrostatic attractive forces between the organic ions and the electrically charged metal surface. Chemisorption is the transfer of, or sharing of, the inhibitor molecule's charge to the metal surface, forming a coordinate bond. The adsorbed inhibitor reduces the corrosion rate of the metal surface either by retarding the anodic dissolution reaction of the metal or by cathodic evolution of hydrogen or both. Inhibitors can be used at pH values from acid to near neutral to alkaline.

Inhibitors can be classified in many different ways, according to

- 1. Their chemical nature (organic or inorganic substances)
- 2. Their characteristics (oxidizing or nonoxidizing compounds)
- **3.** Their technical field of application (pickling, descaling, acid cleaning, cooling water systems, and the like)

The most common and widely known use of inhibitors is their application in automobile cooling systems and boiler feedwaters.

## Inhibitor Evaluation

Since there may be more than one inhibitor suitable for a specific application, it is necessary to have a means of comparing their performance. This can be done by determining the inhibitor efficiency according to the correlation

$$I_{\rm eff} = \frac{R_0 - R_i}{R_0} \times 100$$

where

 $I_{\text{eff}} = \text{efficiency of inhibitor, \%}$  $R_0 = \text{corrosion rate of metal without inhibitor present}$  $R_i = \text{corrosion rate of metal with inhibitor present}$ 

 $R_0$  and  $R_i$  can be determined by any of the standard corrosion-testing techniques. The corrosion rate can be measured in any units, such as weight loss (mpy), as long as consistent units are used for all tests.

## **Classification of Inhibitors**

Inhibitors can be classified in several ways, as indicated previously. We will classify and discuss inhibitors under the headings

- 1. Passivation inhibitors
- 2. Organic inhibitors
- 3. Precipitation inhibitors

#### Passivation Inhibitors

Passivation inhibitors are chemical oxidizing materials such as chromate  $(Cr_2O_4^{2^-})$  and nitrite  $(NO_2^{-})$  or substances such as  $Na_3PO_4$  or  $NaBrO_7$ . These materials favor the adsorption on the metal surface of dissolved oxygen.

This type of inhibitor is the most effective and consequently widely used. Chromatics are the least expensive inhibitors for use in water systems and are widely used in the recirculation—cooling—systems of internal combustion engines, rectifiers, and cooling towers. Sodium chromate in concentrations of 0.04 to 0.1% is used for this purpose. At higher temperatures or in fresh water that has a chloride concentration above 10 ppm, higher concentrations are required. If necessary, sodium hydroxide is added to adjust the pH to a range of 7.5 to 9.5. If the concentration of chromate falls below a concentration of 0.016%, corrosion will be accelerated. Therefore, it is essential that periodic colorimetric analysis be conducted to prevent this from occurring.

Recent environmental regulations have been imposed on the use of chromates. They are toxic and on prolonged contact with the skin can cause a rash. It is usually required that the  $Cr^{+6}$  ion be converted to  $Cr^{+3}$  before discharge. The  $Cr^{+3}$  ion is water soluble and toxic. The  $Cr^{+3}$  sludge is classified as a hazardous waste and must be constantly monitored. Because of the cost of the conversion of the chromate ions, the constant monitoring required, and the disposal of the hazardous wastes, the economics of the use of these inhibitors are not as attractive as they formerly were.

Since most antifreeze solutions contain methanol or ethylene glycol, the chromates cannot be used in this application since the chromates have a tendency to react with organic compounds. In these applications borax ( $Na_2B_4O_7 \cdot 10H_2O$ ), to which have been added sulfonated oils to produce an oily coating, and mercaptobenzothiazole are used. The latter material is a specific inhibitor for the corrosion of copper.

Nitrites are also used in antifreeze-type cooling water systems since they have little tendency to react with alcohols or ethylene glvcol. Since they are gradually decomposed by bacteria, they are not recommended for use in cooling tower waters. Nitrites are the corrosion inhibitors of the internal surfaces of pipelines used to transport petroleum products or gasoline, which is accomplished by continuously injecting a 5–30% sodium nitrite solution into the line.

177

At lower temperatures, such as in underground storage tanks, gasoline can be corrosive to steel as dissolved water is released. This water, in contact with the large quantities of oxygen dissolved in the gasoline, corrodes the steel and forms large quantities of rust. The sodium nitrite enters the water phase and effectively inhibits corrosion.

The nitrites are also used to inhibit corrosion by cutting oil-water emulsions used in the machining of metals.

Passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason it is essential that constant monitoring of the inhibitor concentration be performed.

#### Organic Inhibitors

These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Since the metal surface covered is proportional to the inhibitor concentrates, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate, or 0.2% sodium cinnamate, is effective in water that has a pH of 7.5 and contains 17 ppm sodium chloride or 0.5% by weight of ethyl octanol.

The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

#### Precipitation Inhibitors

These are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water, which is high in calcium and magnesium, is less corrosive than soft water because of the tendency of the salts in hard water to precipitate on the surface of the metal and form a protective film.

If the water pH is adjusted in the range of 5 to 6, a concentration of 10 to 100 ppm of sodium pyrophosphate will cause a precipitate of calcium or magnesium orthophosphate to form on the metal surface, providing a protective film. The inhibition can be improved by the addition of zinc salts.

### Inhibition of Acid Solution

The inhibition of corrosion in acid solutions can be accomplished by the use of a variety of organic compounds. Among those used for this purpose are triple-bonded hydrocarbons; acetylenic alcohols; sulfoxides and mercaptans; aliphatic, aromatic, and heterocyclic compounds containing nitrogen; and many other families of simple organic compounds of condensation products formed by the reaction between two different species such as amines and aldehydes.

Incorrect choice or use of organic inhibitors in acid solutions can lead to corrosion stimulation and/or hydrogen penetration into the metal. In general, stimulation of corrosion is not related to the type and structure of the organic molecule. Stimulation of acid corrosion of iron has been found with mercaptans, sulfoxides, azole and treazole deratives, nitrites, and quinoline. This adverse action depends on the type of acid. For example, bis(4-dimethylaminophenyl) antipyrilcarbinol and its derivatives at a  $10^{-4}$  M concentration inhibited attack of steel in hydrochloric acid solutions but stimulated attack in sulfuric acid solutions. Much work has been done studying the inhibiting and

stimulating phenomena of organic compounds on ferrous as well as nonferrous metals. Organic inhibitors have a critical concentration value below which inhibition decreases and stimulation begins. Therefore, it is essential that when organic inhibitors are used, constant monitoring of the solution should take place to ensure that the inhibitor concentration does not fall below the critical value.

## Inhibition of Near-Neutral Solutions

Because of differences in the mechanisms of the corrosion process between acid and near-neutral solutions, the inhibitors used in acid solutions usually have little or no inhibition effect in near-neutral solutions. In acid solutions the inhibitor action is due to adsorption on oxide-free metal surfaces. In these media the main cathodic process is hydrogen evolution.

In almost neutral solutions the corrosion process of metals results in the formation of sparingly soluble surface products such as oxides, hydroxides, or salts. The cathodic partial reaction is oxygen reduction.

Inorganic or organic compounds as well as chelating agents are used as inhibitors in near-neutral aqueous solutions. Inorganic inhibitors can be classified according to their mechanism of action:

- **1.** Formation and maintenance of protective films can be accomplished by the addition of inorganic anions such as polyphosphates, phosphates, silicates, and borates.
- 2. Oxidizing inhibitors such as chromates and nitrites cause self-passivation of the metallic material. It is essential that the concentration of these inhibitors be maintained above a "safe" level. If not, severe corrosion can occur as a result of pitting or localized attack caused by the oxidizer.
- **3.** Precipitation of carbonates on the metal surfaces, forming a protective film. This usually occurs due to the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions usually present in industrial waters.
- **4.** Modification of surface film protective properties is accomplished by the addition of Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, or Fe<sup>2+</sup>.

The sodium salts of organic acids such as benzoate, salicylate, cinnamate, tartrate, and azelate can be used as alternatives to the inorganic inhibitors, particularly in ferrous solutions. When using these particular compounds in solutions containing certain anions such as chlorides or sulfates, the inhibitor concentration necessary for effective protection will depend on the concentration of the aggressive anions. Therefore, the critical pH value for inhibition must be considered rather than the critical concentration. Other formulations for organic inhibition of near-neutral solutions are given in Table C.26.

Inhibitor	Type of metal protected
Organic phosphorus-containing compounds, salts of aminomethylenephosphonic acid, hydroxyethylenediphosphonic acid. phosphenocarboxylic acid, polyacrylate, polymethacrylate	Ferrous
Borate or nitrocinnimate anions (dissolving oxygen in solution required)	Zinc, zinc alloys
Acetate or benzoate anions	Aluminum
Heterocylic compounds such as benzotriazole and its derivatives, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole,	Copper and copper-based alloys

 Table C.26
 Organic Inhibitors for Use in Near-Neutral Solutions

Chelating agent	Type of metal protected
Alkyl-catechol derivatives. sarcosine derivatives,	Steel in industrial cooling systems
carboxymethylated fatty amines, and mercaptocarboxylic acids	
Azo compounds, cupferron, and rubeanic acid	Aluminum alloys
Azole derivatives and alkyl esters of thioglycolic acid	Zinc and galvinized steel
Oximes and quinoline derivatives	Copper
Cresol phthalexon and thymol phthalexon derivatives	Titamium in sulfuric acid solutions

Table C.27 Chelating Agents Used as Corrosion Inhibitors in Near-Neutral Solution

Chelating agents of the surface-active variety also act as efficient corrosion inhibitors when insoluble surface chelates are formed. Various surface-acting chelating agents recommended for corrosion inhibition of different metals are given in Table C.27.

## Inhibition of Alkaline Solutions

All metals whose hydroxides are amphoteric and metals covered by protective oxides that are broken in the presence of alkalies are subject to caustic attack. Localized attack may also occur as a result of pitting and crevice formation.

Organic substances such as tannions, gelatin, saponin, and agar-agar are often used as inhibitors for the protection of aluminum, zinc, copper, and iron. Other materials that have been found to be effective are thiourea, substituted phenols and naphthols, betadiketones, 8-hydroxyquinoline, and quinalizarin.

## **Temporary Protection with Inhibitors**

Occasions arise when temporary protection of metallic surfaces against atmospheric corrosion is required. Typical instances are in the case of finished metallic materials or of machinery parts during transportation and/or storage prior to use. When ready to be used, the surface treatment or protective layer can be easily removed.

It is also possible to provide protection by controlling the aggressive environment either by eliminating the moisture and the aggressive gases or by introducing a vapor phase inhibitor. This latter procedure can only be accomplished in a closed environment such as a sealed container, a museum showcase, or a similar enclosure.

Organic substances used as contact inhibitors or vapor inhibitors are compounds belonging to the following classes:

- 1. Aliphatic, cycloaliphatic, aromatic, and heterocyclic amines
- 2. Amine salts with carbonic, carbamic, acetic, benzoic, nitrous, and chromic acids
- 3. Organic esters
- 4. Nitro derivatives
- 5. Acetylenic alcohols

### Summary

Corrosion inhibitors are usually able to prevent general or uniform corrosion. However, they are very limited in their ability to prevent localized corrosion such as pitting, crevice corrosion, galvanic corrosion, dezincification, or stress corrosion cracking. Additional research is being undertaken in the use of inhibitors to prevent these types of corrosion.

See Refs. 10, 28, and 29.

#### CORROSION MEASUREMENT

See "Monitoring Corrosion" and "Corrosion Testing."

#### CORROSION MECHANISMS

Most of the commonly used metals are unstable in the atmosphere. These unstable metals are produced by reducing ores artificially; therefore, they tend to return to their original state or to similar metallic compounds when exposed to the atmosphere. Exceptions to this are gold and platinum, which are already in their metal state.

Corrosion, in its simplest definition, is the process of a material returning to its thermodynamic state. For most materials this means the formation of the oxides or sulfides which they started out as when they were taken from the earth before being refined into useful engineering materials.

Most corrosion processes are electrochemical in nature, consisting of two or more electrode reactions: the oxidation of a metal (anode partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction). The study of electrochemical thermodynamics and electrochemical kinetics is necessary to understand corrosion reactions. For example, the corrosion of zinc in an acid medium proceeds according to the overall reaction

$$Zn + 2H^{+} \rightarrow Zn^{2+} + H_{2}$$
<sup>(1)</sup>

This breaks down into the anodic partial reaction

$$Zn \to Zn^{2+} + 2e \tag{2}$$

and the cathodic partial reaction

$$2H^{+} + 2e \rightarrow H_{2} \tag{3}$$

The corrosion rate depends on the electrode kinetics of both partial reactions. If all of the electrochemical parameters of the anodic and cathodic partial reactions are known, in principle the rate may be predicted.

According to Faraday's Law, a linear relationship exists between the metal dissolution rate at any potential  $V_{M}$ , and the partial anodic current density for metal dissolution  $i_{aM}$ .

$$V_M = \frac{l_{aM}}{nF} \tag{4}$$

where *n* is the charge number (dimensionless), which indicates the number of electrons exchanged in the dissolution reaction, and *F* is the Faraday constant (F = 96,485 C/mol). In the absence of external polarization, a metal in contact with an oxidizing electrolytic environment spontaneously acquires a certain potential, called the corrosion potential,  $E_{\text{corr}}$ . The partial anodic current density at the corrosion potential is equal to the corrosion current density  $i_{\text{corr}}$ 

Equation (4) then becomes

$$V_{\rm corr} = \frac{i_{\rm corr}}{nF} \tag{5}$$

The corrosion potential lies between the equilibrium potentials of the anodic and cathodic reactions.

The equilibrium potential of the partial reaction is predicted by electrochemical thermodynamics. The overall stoichiometry of any chemical reaction can be expressed by

$$0 = \sum V_i B_i \tag{6}$$

where *B* designates the reactants and products. The stoichiometric coefficients  $V_i$  of the products are positive and those of the reactants negative. The free enthalpy of reaction  $\Delta G$  is

$$\Delta G = \sum V_i m_i \tag{7}$$

where  $\mu_i$  is the chemical potential of the participating species. If reaction (6) is conducted in an electrochemical cell, the corresponding equilibrium potential  $E_{rev}$  is given by

$$\Delta G = -nFE_{\rm rev} \tag{8}$$

Under standard conditions (all activities equal to 1),

$$\Delta G^{\circ} = -nFE^{\circ} \tag{9}$$

where  $G^{\circ}$  represents the standard free enthalpy and  $E^{\circ}$  represents the standard potential of the reaction.

Electrode reactions are commonly written in the form

$$\sum V_{\text{ox}i} \bullet B_{\text{ox}i} + ne = \sum V_{\text{red}i} \bullet B_{\text{red}i}$$
(10)

where  $V_{\text{ox}i}$  represents the stoichiometric coefficient of the "oxidized" species,  $B_{\text{ox}i}$ , appearing on the left side of the equality sign with the free electrons, and  $V_{\text{red}i}$  indicates the stoichiometric coefficient of the reduced species,  $B_{\text{red}i}$  appearing on the right side of the equality sign, opposite the electrons. Equation (10) corresponds to a partial reduction reaction, and the stoichiometric coefficients  $V_{\text{ox}i}$  and  $V_{\text{red}i}$  are both positive.

By setting the standard chemical potential of the solvated proton and of the molecular hydrogen equal to zero— $\mu_{H^+}^{\circ} = 0$ ,  $\mu_{H_2}^{\circ} = 0$ , —it is possible to define the standard potential of the partial reduction reaction (10) with respect to the standard hydrogen electrode. The standard potential of an electrode reaction that corresponds to the overall reaction

$$\sum V_{\text{ox}i} B_{\text{ox}i} + \frac{n}{2} H_{2(PH_{2} = 1 \text{ bar})} = \sum V_{\text{red}i} B_{\text{red}i} + n H_{(aH^{+} = 1)}^{+}$$
(11)

Table C.28 indicates the standard potential of selected electrode ractions.

For a given reaction to take place, there must be a negative free energy change as calculated from equation

$$\Delta G = -nFE \tag{12}$$

For this to occur, the cell potential must be positive. The cell potential is taken as the difference between two half-cell reactions, the one at the cathode minus the one at the anode.

Electrode	E°/V
$\mathrm{Li}^{+} + \mathrm{e} = \mathrm{Li}$	-3.045
$Mg^{2+} + 2e = Mg$	-2.34
$Al^{3+} + 3e = Al$	-1.67
$\mathrm{Ti}^{2+} + 2\mathrm{e} = \mathrm{Ti}$	-1.63
$Cr^{2+} + 2e = Cr$	-0.90
$Zn^{2+} + 2e = Zn$	-0.76
$Cr^{3+} + 3e = Cr$	-0.74
$\mathrm{Fe}^{2+} + 2\mathrm{e} = \mathrm{Fe}$	-0.44
$Ni^{2+} + 2e = Ni$	-0.257
$Pb^{2+} + 2e = Pb$	-0.126
$2\mathrm{H}^{+} + 2\mathrm{e} = \mathrm{H}_2$	0
$Cu^{2+} + 2e = Cu$	0.34
$O_2 + 2H_2O + 4e = 4OH$	0.401
$\mathrm{Fe}^{3+} + \mathrm{e} = \mathrm{Fe}^{2+}$	0.771
$Ag^{+} + e = Ag$	0.799
$Pt^{2+} + 2e = Pt$	1.2
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$Au^{3+} + 3e = Au$	1.52

Table C.28Standard Potentials ofElectrode Actions at 25°C

If we place pure iron in hydrochloric acid, the chemical reaction can be expressed as  $Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow$  (13)

On the electrochemical side we have

$$Fe + 2H^{+} = 2Cl^{2-} \rightarrow Fe^{2+} = Cl^{2-} + H_{2} \uparrow$$
(14)

The cell potential is calculated to be

E = cathode half-cell minus anode half-cell

$$E = E(H^{+}/H_{2}) - E(Fe/Fe^{2+})$$
$$E = 0 - (-0.440) = +0.44$$

Since the cell is positive, the reaction can take place. The larger this potential difference, the greater the driving force of the reaction. Other factors will determine whether or not corrosion does take place and if so at what rate. For corrosion to take place, there must be a current flow and a completed circuit, which is then governed by Ohm's Law (I = E/R). The cell potential calculated here represents the peak value for the case of two independent reactions. If the resistance were infinite, the cell potential would remain as calculated but there would be no corrosion. If the resistance of the circuit were zero, the potentials of the half-cells would approach each other while the rate of corrosion would be infinite.

C

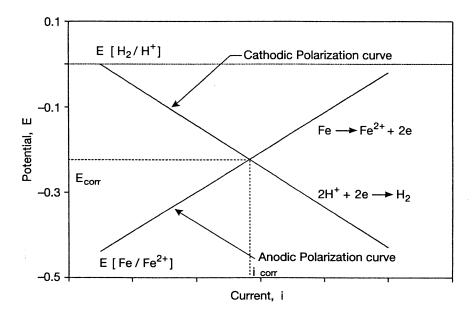


Figure C.9 Polarization of iron in acid.

At an intermediate resistance in the circuit, some current begins to flow and the potentials of the half-cells move slightly toward each other. This change in potential is called polarization. The resistance in the circuit is dependent on various factors, including the resistivity of the media, surface films, and the metal itself. Figure C.9 shows the relationship between the polarization reactions at the two half-cells. The intersection of the two polarization curves closely approximates the corrosion current and the combined cell potentials for the freely corroding situation.

The corrosion density can be calculated by determining the surface area once the corrosion current is determined. The corrosion rate in terms of metal loss per unit time can be determined using Faraday's laws.

In addition to estimating corrosion rates, the extent of polarization can help predict the type and severity of corrosion. As polarization increases, corrosion decreases. Understanding the influence of environmental changes on polarization can aid in controlling corrosion. For example, in the iron–hydrochloric acid example, hydrogen gas formation at the cathode can actually slow the reaction by blocking access of hydrogen ions to the cathode site, thereby increasing circuit resistance, resulting in cathodic polarization, lowering the current flow and corrosion rate. If the hydrogen is removed by bubbling oxygen through the solution, which combines with the hydrogen to form water, the corrosion rate will increase significantly.

There are three basic causes of polarization: concentration, activation, and potential drop. Concentration polarization is the effect resulting from the excess of a species that impedes the corrosion process (as in the previous hydrogen illustration) or from the depletion of a species critical to the corrosion process.

Activation polarization is the result of a rate-controlling step within the corrosion reaction. In the  $H^+/H_2$  conversion reaction the first step of the process,

 $2H^+ + 2e \rightarrow 2H$ 

proceeds rapidly, whereas the second step,

 $2H \rightarrow H_2$ 

takes place more slowly and can become a rate-controlling factor.

Potential drop is the change in voltage associated with effects of the environment and the circuit between the anode and cathode sites. Included are the effects of surface films, corrosion products, resistivity of the media, etc.

Other factors affecting corrosion include temperature, relative velocities between the metal and the media, surface finish, grain orientation, stresses, and time.

Since corrosion is an electrochemical reaction and reaction rates increase with increasing temperature, it is logical that corrosion rates will also increase with increasing temperature.

In some instances increasing the velocity of the corrodent over the surface of the metal will increase the corrosion rate when concentration polarization occurs. However, with passive metals, increasing the velocity can actually result in lower corrosion rates, since the increased velocity shifts the cathodic polarization curve so that it no longer intersects the anodic polarization curve in the active corrosion region.

Rough surfaces or tight crevices can promote the formation of concentration cells. Surface cleanliness is also a factor since deposits or films can act as initiation sites. Biological growths can behave as deposits or change the underlying surface chemistry to promote corrosion.

Variations within the metal surface on a microscopic level can influence the corrosion process. Microstructural differences such as secondary phases or grain orientation will affect the manner in which the corrosion process will take place. The grain size of the material plays an important role in determining how rapidly the material's properties deteriorate when the grain boundaries are attacked by corrosive environments.

Stress is a requirement for stress corrosion cracking or corrosion fatigue, but can also influence the rate of general corrosion.

The severity of corrosion is affected by time. Corrosion rates are expressed as a factor of time. Some corrosion rates are rapid and violent, while most are slow and almost imperceptible on a day-to-day basis.

Potential-pH diagrams (Pourbaix diagrams) represent graphically the stability of a metal and its corrosion products as a function of the potential and pH of an aqueous solution. The pH is shown on the horizontal axis and the potential on the vertical axis. Pourbaix diagrams are widely used in corrosion because they easily permit identification of the predominant species at equilibrium for a given potential and pH. However, being based on thermodynamic data, they provide no information on the rate of possible corrosion reactions.

In order to trace such a diagram, the concentration of the dissolved material must be fixed. Figure C.10 shows a simplified Pourbaix diagram for zinc. The numbers indicate the  $H_2CO_3$  content in the moisture film, for example,  $10^{-2}$  and  $10^{-4}$  mol/L. The diagram takes into account the formation of zinc hydroxide, of  $Zn^{2+}$ , and of the zincate ions  $HZnO_2^{-}$  and  $ZnO_2^{2-}$ . At high potentials  $ZnO_2$  may possibly be formed, but because the corresponding thermodynamic data are uncertain, they are not presented in the diagram. The broken lines indicate the domain of thermodynamic stability of water.

See Refs. 23 and 30.

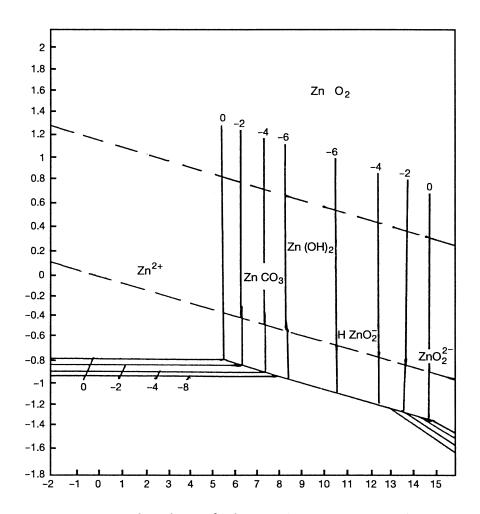


Figure C.10 Potential-pH diagram for the system Zn-CO<sub>2</sub>-H<sub>2</sub>O at 77°F/21°C.

#### **CORROSION MONITORING**

See "Monitoring Corrosion."

### **CORROSION TESTING**

When a corrosion test is designed and conducted properly, reliable corrosion data may be obtained. There are a number of testing techniques that may be employed. The simplest of these involve the determination of a change in weight or dimension and observation of the corroded surface. Other, more complex methods involve the measurement of hydrogen diffusion or electrical resistance or determining electrochemical characteristics.

### Weight Change

Corrosion testing utilizing weight change involves the use of corrosion coupons. Coupons can be made in any size or shape. They are carefully weighed and measured before

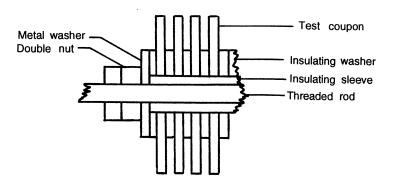


Figure C.11 Corrosion coupons insulated from each other and the coupon rack.

assembly on a test rack. They may be mounted in different configurations to study different types of corrosion mechanisms, such as galvanic attack, crevice corrosion, and stress corrosion. By mounting different materials of construction on the same test rack it is possible to evaluate the difference in resistance to corrosion of various materials. When assembling the coupons on the test rack it is necessary that they be insulated both from the test rack itself and from each other. This is to avoid galvanic corrosion taking place between the test pieces. See Fig. C.11.

When the test is completed the test rack is disassembled and the coupons are cleaned, weighed, and measured. The formula for calculating the uniform corrosion rate is

$$mpy = \frac{534W}{DAT}$$

where

W = weight loss, mg D = density of specimen, g/cm<sup>3</sup> A = area of specimen, in.<sup>2</sup> T = exposure time, h

The low cost, the ability to evaluate several materials at one time, and closer resemblance to actual conditions of the equipment are the main advantages to using corrosion coupons. The time involved in preparing and evaluating the coupons to determine the corrosion rates after sufficient exposure time, and the limited locations for placing the test coupons, are the primary disadvantages. The use of test coupons does not permit the engineer to evaluate the results of changing process conditions, which can also be a disadvantage.

Whenever possible, actual field conditions should be used to determine which metal is going to provide the best service. Coupons should be exposed to all conditions to which the metal will be subjected. Different locations in the process may have different corrosive effects. For example, the effects in the vapor space may vary from those in the liquid phase or in the condensing area. Because of this it is necessary to install test racks in each of the various locations.

If field testing is not possible, then laboratory tests should be planned to duplicate as closely as possible actual field conditions. Remember that very small changes in the environment can produce large changes in the corrosion rates of metals. Test apparatus must be used that will simulate the different conditions that will be faced in the actual equipment. For example, condensate is often more corrosive than the bulk of the liquid; also heat transfer surfaces can exhibit different corrosive effects from other surfaces.

Manufacturers of metals and new products usually have fairly large amounts of data available. These data are a good guide as to which materials should be considered, but testing should still be conducted to ensure that the material will be satisfactory for the specific application.

It is important that the proper data be recorded. This will vary depending on the purpose of the test. The following are guidelines as to what data should be recorded.

- 1. For corrosive media, the overall concentration and variation in concentration during the test; also any contaminants that may be present
- **2.** For test metals, the trade name, chemical composition, product type (plate, sheet, rod, etc.), metallurgical condition (cold rolled, hot rolled, quenched and tempered, solution heat treated, stabilized, cast, etc.), and the size and shape of the coupon
- **3.** Volume of test solution, for laboratory tests
- 4. The temperature: average, variation, and whether it was a heat transfer test
- **5.** For aeration, the technique or conditions for the laboratory test, process exposed to atmosphere for field test
- 6. The apparatus and test rack type
- 7. The test time
- **8.** The exposure location
- **9.** The cleaning technique
- **10.** The weight loss
- **11.** The type and nature of localized corrosion: stress corrosion cracking, intergranular corrosion, pitting (maximum and average depth), crevice corrosion, etc.
- **12.** The agitation: velocity for field tests, and technique for laboratory tests
- **13.** The corrosion rate (which, if localized corrosion is present, may be rnisleading)

#### **Dimension Change**

Changes in dimensions can be measured using ultrasonic measuring techniques, microscopic examination, or eddy current. The most straightforward is the ultrasonic measurement of parts.

1. Ultrasonic thickness measurement. This technique can be used to measure thickness ness either while the part is in service or after it has been removed from service. The thickness of the part is measured before testing starts, and thereafter at regular time intervals. After each measurement the thickness is plotted against time as shown in Fig. C.12. The difference between thickness measurements can be divided by the time interval to obtain the corrosion rate. This information is particularly useful in determining the remaining service life of a vessel.

Assume that the pressure vessel represented in Fig. C.12 had a corrosion allowance of 0.125 inches. During the initial plant start-up (A) the corrosion rate was 15 mpy based on the ultrasonic measurement. The corrosion rate during the second year (B) equals 5 mpy. The overall rate equals 10 mpy. The process changed C

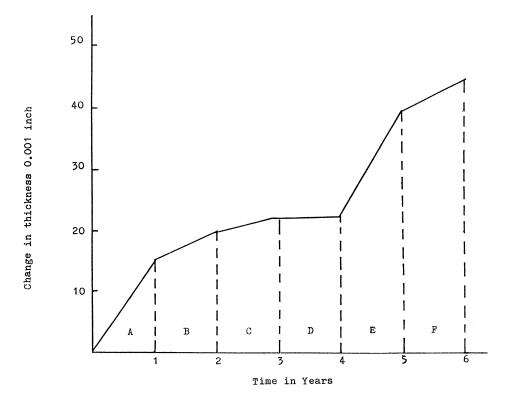


Figure C.12 Change in wall thickness plotted against time.

during the third year (*C*), with a corrosion rate equal to 2 mpy, making for an average corrosion rate of 7 mpy. During the fourth year (*D*) the plant was shut down. A new process was introduced in the fifth year (*E*) with an average corrosion rate equal to 18 mpy. The overall corrosion rate equals 8 mpy. The vessel continues in service during the sixth year with a corrosion rate equaling 6 mpy. Of the original corrosion allowance of 0.125 inches, there is now 0.080 inch remaining, or an expected life of 13 years based on the overall corrosion rate or 16 years based on the last year's corrosion rate.

This measurement technique is not accurate enough for most laboratory testing, but it is the most accurate technique that can be used to measure the thickness of parts while in service. It also has the advantage of being able to detect changes in corrosion rates when there are process changes, or if inhibitors are added. If there is a possibility of nonuniform corrosion, an instrument with a cathode ray tube should be used, since digital instruments can give misleading readings.

2. Microscopic examination. When testing for high-temperature corrosion or dealloying (dezincification), it is usually necessary to examine a polished cross-section to determine how much unaffected metal remains. In these types of corrosion, considerable damage can take place because of inward diffusion of a corrodent such as oxygen or sulfur or because of the removal of some of the elements from the solid alloy. A change in external dimensions or a loss of weight is not an indication of the amount of damage that may have taken place. To determine accurately how much metal is

 $\mathcal{C}$ 

left, it is necessary to prepare a cross-section of corroded metal for a metallographic examination and determine microscopically how much metal is left.

**3.** *Eddy current*. An eddy current instrument and a probe are used to measure the wall thickness of nonferromagnetic tubes. In this manner tubes in a heat exchanger may be inspected for corrosion while still in place. The instrument must first be calibrated on a tube of known thickness of the same metal as the tube to be inspected.

Changes in thickness can be measured with an accuracy of  $\pm 2\%$ . It is also possible to test for nonuniform corrosion.

# **Electrochemical Techniques**

The three most often used electrochemical techniques are zero-resistance ammeters, polarization curves, and linear polarization resistance curves.

- 1. *Zero-resistance ammeter.* A zero-resistance ammeter is a potentiostat that has been programmed to zero potential difference between the reference electrode and the test electrode. The current lead to the counterelectrode is connected to the reference electrode. This permits measurement of the amount and direction of the current that flows between the two electrodes that are electrically short-circuited. Corrosion rates of the anode cannot be calculated directly from the galvanic current because it is only a measure of how much faster the anode is corroding than the cathode.
- **2.** *Polarization curves.* This is primarily a laboratory technique to study corrosion, particularly pitting. A variety of methods and equipment are available to conduct these studies. The following types are generally used:

Potentiostatic

Potential held constant

Galvanostatic

Current held constant

Potentiodynamic

- a. Potential changed constantly at a specified rate
- **b.** Potential changed in steps and held constant at each step

Galvanodynamic

- a. Current changed continuously at a specified rate
- b. Current changed in steps and held constant at each step

As with all electrochemical techniques, they can only be used with sufficiently conductive media and when the area of the wetted electrode is known. Because of the high polarization potentials required, the estimation of corrosion rates is less precise than with linear polarization resistance methods.

**3.** *Linear polarization resistance.* The linear polarization technique permits measurement of the corrosion rate of a metal at any instant. In order to be utilized, the electrodes must be exposed to an electrolyte that has a continuous path between them. Laboratory or field testing can be conducted using either manual or automatic linear polarization equipment.

# Hydrogen Diffusion

Some corrosive reactions produce atomic hydrogen at the cathode, which can diffuse through steel and most other metals if it does not combine to form hydrogen molecules.

When sulfides are present, the atomic hydrogen produced by the corrosion reaction readily diffuses through steel. If hydrogen diffusion is detected, corrosion is taking place. Hydrogen diffusion can be measured using either a hydrogen probe (pressure measurement) or a hydrogen monitoring system (electrochemical).

#### **Electrical Resistance**

As the products of corrosion build up, small changes in electrical resistance occur. Low corrosion rates can be measured in this manner by not removing the products of corrosion. Probes are available with test elements made from all of the common alloys used to fabricate process equipment. Temperature changes can result in erroneous readings, since resistance changes with temperature. Although there have been modifications in probe design, it is still not possible to measure small changes in corrosion rate with a single reading unless you are absolutely sure that the temperature remained constant.

Corrosion is measured by first taking a reading on the test and check element. The probe is then inserted into the test environment and allowed to come to the test temperature. Another reading is then taken on the test and check element. Corrosion is allowed to take place for a few hours, after which a new set of readings is taken. The corrosion rate is calculated using the equation

Corrosion rate (mpy) = 
$$\frac{CR \times PM \times 0.365}{CT}$$

where

- CR = current reading minus the previous reading. If the reading is negative, the results are not related to corrosion. They are due to either the temperature of a conductive film or the test element.
- PM = probe multiplier supplied by the manufacturer

CT = change of time, in days

The overall corrosion rate (rate over the total exposed time) and the corrosion rate between readings should both be calculated to determine whether the corrosion rate is changing with time.

See Refs. 31 and 32.

## CORROSION TESTING FOR ENVIRONMENTALLY ASSISTED CRACKING (EAC)

There is no single testing technique that will take into account all the factors that come into play for a particular material and environment for the evaluation of EAC. The testing program undertaken will take into account as many of the factors as possible. This may require

- 1. Different alternative configurations of the same specimen
- 2. More than one type of test specimen
- 3. Several test techniques with the same specimen

It is also important that the laboratory and field or in-plant test data he correlated with service experience. There are three basic general types of tests that can be performed. They are constant load/deflection techniques, slow-strain-rate tests, and fracture mechanics tests.

## **Constant Load/Deflection Tests**

Types of tests in this category include

- 1. Tension tests per ASTM G-49
- **2.** Bent beam per ASTM G-38
- 3. C-ring tests per ASTM G-38
- **4.** U-bend tests per ASTM G-30

Each type of test provides data relating to the specific type of stress or strain to which the specimen will be subjected under constant load.

# **Slow-Strain-Rate Tests**

This test replaces the constant load with a slow extension of the sample until failure. A detailed description of this test method is given in ASTM G-129. The advantage of SSR testing is that it produces a result in a relatively short period of time. The primary benefit of SSR testing is that it permits the evaluation of the effect of alloy composition heat treatment and/or environmental changes such as aeration, concentration, and inhibition.

## **Fracture Mechanics Tests**

These tests are conducted to determine the effects of metallurgical or environmental changes on EAC when the specimen contains a sharp crack. There are several fracture mechanics techniques that can be used to evaluate EAC. Regardless of which technique is used, the specimen is usually one of constant load or deflection.

When a constant-load specimen is employed, a load is applied to a fracture mechanics specimen using a directly applied dead weight or through a pulley or lever system to magnify the dead weight load.

Alternatively, constant-deflection specimens may be used. In this situation either constant-tension or double-cantilever beam specimens are loaded to an initial level of crack tip stress intensity by deflection of the arms of the specimen. The deflection is obtained either by tightening a bolt arrangement that deflects the arms of the specimen or by inserting a wedge into the specimen. The initial stress intensity must be above the threshold stress for EAC that permits cracking to start. Once started, the stress intensity decreases as the crack proceeds through the specimen.

See Ref. 33.

#### **CORROSION UNDER INSULATION**

Insulation is applied to vessels and piping as a means of conserving heat or of providing personnel protection from hot surfaces. As a result, the selection of a particular insulating material is normally based on installed cost versus energy saved. However, there are other costs associated with insulation that are generally overlooked, namely the cost of corrosion and maintenance.

Corrosion that takes place under the insulation can be caused by the insulation itself or by improper application. If after a period it is necessary to remove sections of insulation to make repairs on the equipment, these costs and the cost of repairing the insulation should be considered during the selection process.

Thermal insulation, when exposed to water, can hold a reservoir of available moisture which together with the permeability of air causes severe attack, up to 200 to

191

300 mpy. This is particularly true on warm steel surfaces. Severe corrosion may occur on cold surfaces where structural members abut the insulated vessel or pipe, permitting rime ice to form. Depending upon the specific containment, insulation can cause stress corrosion cracking of high-strength copper alloys and external stress corrosion cracking of type 300 series stainless steels. Chlorides or alkaline containments will rapidly attack aluminum. The use of an appropriate coating system, such as a catalyzed epoxy-phenolic and modified silicone, will help to prevent such corrosion in the event of ingress of water. Zinc and chloride-free coatings should be used for stainless steels.

### Types of Corrosion Under Insulation

There are three types of corrosion that can take place under insulation:

- 1. Alkaline or acidic corrosion
- 2. Chloride corrosion
- 3. Galvanic corrosion

Alkaline or acidic corrosion takes place as a result of either acid or alkali being present in contact with moisture in the insulating material. When these materials are applied to hot surfaces at temperatures above 250°F (121°C), the water is driven off, but it may condense at the edge of the insulation, dissolving any alkaline or acidic materials present. This results in corrosion of aluminum with certain alkaline waters.

Some insulating cements, before drying, contain alkaline chemicals and water. During the drying operation these alkaline chemicals will attack such metals as stainless steel, copper, brass, and aluminum. If the vessel being insulated is constructed of one of these metals, it may be subject to corrosion. Under normal circumstances steel would not be affected during the time required for the cement to dry.

Foam insulations containing fire-retardant chemicals, such as brominated or chlorinated compounds, can produce acidic solutions. This has been found to be true with polyurethane and phenolic foams.

Steps can be taken to prevent this type of corrosion. When external corrosion of the jacket is a problem, a good all-weather plastic jacket should be considered. If a metal jacket is to be used, a moisture barrier should be installed on the inside of the insulation. It goes without saying that all joints must be tightly sealed to prevent external water from entering the insulation.

Care should be taken in selection of the insulating material. Insulating cements are best mixed with clean potable water. The use of distilled water will increase the aggressiveness of the attack.

Chloride corrosion results when the insulating material contains leachable chlorides, temperatures are above 140°F (60°C), and the substrate surface is a 300 series stainless steel. The attack will usually be a typical stress corrosion cracking. Corrosion is propagated when water enters the insulation and diffuses inward toward the hot surface, eventually finding a "dry" spot. Adjacent to this dry spot will be found an area in which the pores of the insulation are filled with a saturated salt solution in which chlorides may be present. As the vessel wall cools down, this saturated area "moves" into the metal wall. When the wall is reheated it will be temporarily in contact with the saturated salt solution and any chlorides present. This will initiate stress corrosion cracking.

193

As with acidic or alkaline corrosion, care must be taken when installing the outer insulation jacket and barrier, making sure that all joints are properly sealed.

Galvanic corrosion under insulation occurs when wet insulation that has an electrolyte salt present allows a current to flow between dissimilar metals such as the insulated metal surface and the outer metal jacket or other metallic accessories. This can result in corroding of the metal jacket or of the vessel, depending on which is the less noble metal.

Galvanic corrosion can be prevented by using a cellular insulation and applying a synthetic rubber or plastic jacket over the insulation. Hypalon performs well in this application.

# Summary

Corrosion under insulation can be prevented by taking into account

Insulation selection Equipment design Weather barriers

The type of insulation to be used will be dependent on the application, keeping in mind the types of corrosion that can occur. Equipment design also enters into the picture. Adequate insulation supports should be provided and additional protection should be considered where leakage or mechanical damage is possible. Additional flashing should also be installed where spills or hosing down is prevalent.

Weather barriers are a must because all corrosion under insulation requires moisture of some kind. Therefore, it becomes a necessity to make sure that all joints are properly sealed and that an adequate weather barrier is installed.

# **CRACK-INDUCING AGENTS**

Crack-inducing agents can be either active or passive. Most crack-inducing agents require the presence of an electrolyte to become active. Passive agents, though present, cause no harm. For example, hydrogen sulfide requires the presence of liquid water or some other electrolyte to become an active agent. On the other hand, ammonia does not require the presence of an electrolyte to attack copper.

# Hydrogen Sulfide

Wet hydrogen sulfide can cause several forms of hydrogen cracking, including sulfide stress corrosion cracking (SSCC) hydrogen-induced cracking (HIC), and stressoriented hydrogen-induced cracking (SOHIC). SSCC occurs in many steels and alloys. HIC occurs in "dirty" steels. It is not necessary for stress to be present for this cracking to initiate. SOHIC is a stress-assisted form of HIC. It usually occurs in the heataffected zones of restrained welds, where residual stresses probably assist the cracking operation. Wet hydrogen sulfide corrosion is the beginning of the hydrogen cracking. As the sulfide ion combines with iron to form iron sulfide, hydrogen is released as a corrosion by-product. The sulfide ion being a cathodic poison encourages two phenomena:

- 1. The nascent hydrogen tends to dissolve into the metal rather than combining with another hydrogen atom to form hydrogen gas.
- **2.** Under normal circumstances this type of corrosion is rapidly slowed by the formation of a polarizing layer of hydrogen gas at the anode. However, the sulfide ion prevents such polarization. As a result, large amounts of nascent hydrogen are produced, as corrosion continues, until a thick film of dense iron sulfide forms, stopping further corrosion.

## Sulfide Stress Cracking

Sulfide stress cracking is a form of hydrogen stress cracking. It can develop in areas of excessive metal hardness. The low- to medium-strength carbon steels are most resistant to SSCC. Microalloyed carbon steels should not be used in welded construction subject to SCC since they have a tendency to produce excessively hard weld heat-affected zones. Such heat-affected zones are difficult to temper by postweld heat treatment. It is difficult to generate weld metal or heat-affected zone hardnesses to cause SSCC in low- to medium-strength carbon steels. When welding ordinary carbon steels, preheat and proper welding procedures will provide the necessary control to prevent excessive hardness. Postweld heat treatment is usually not necessary unless other crack-inducing agents (such as amines) or other cathodic poisons (such as cyanide) are also present. In these situations reduction of resident stresses is necessary to reduce the susceptibility to stress cracking.

## Hydrogen-Induced Cracking

Hydrogen-induced cracking is not technically a form of stress corrosion cracking, but it is related. HIC occurs primarily in steel plates containing excessive amounts of nonmetallic inclusions (primarily manganese sulfides) which have been flattened by the rolling process. Hydrogen-induced cracking is essentially a crack initiation mechanism. Nascent hydrogen diffuses into the steel as a result of hydrogen sulfide corroding the surface of the steel. Catalyst sites are established by nonmetallic inclusions, causing the diffusing nascent hydrogen to recombine into hydrogen gas. Pressure builds up adjacent to the inclusions as a result of the accumulating hydrogen gas, causing the inclusion matrix to split, initiating an HIC crack. A split can develop parallel to the surfaces of the steel plate when multiple initiation sites are present and the plate is relatively thin, less than ½ inch. On relatively thick plates staggered internal HIC cracks can link up and in extreme cases can cause through-thickness cracks.

Hydrogen-induced cracking lakes place in the temperature range of 32 to 130°F (0 to 55°C). HIC damage proceeds slowly above 130°F (55°C).

## Stress-Oriented Hydrogen-Induced Cracking

Stress-oriented hydrogen-induced cracking (SOHIC) usually occurs in heat-affected zones associated with the residual stresses of welds. The mechanics involves two components:

1. HIC cracks form in a stacked manner, producing a crack plane perpendicular to the surface of the plane. The cracks are generally short but closely spaced.

**2.** By shearing the ligaments between the stacked HIC cracks, a through-thickness crack develops. These cracks can be minimized by postweld heat treatment and normalizing.

# Mercury

Intergranular cracking of copper alloys, as well as intergranular cracking and pitting corrosion of aluminum, can be caused by liquid mercury. This effect is known as liquid metal embrittlement.

# Zinc

Liquid metal embrittlement in iron and aluminum alloys can be caused by zinc. For this reason galvanized carbon steel should not be used at temperatures exceeding 390°F (200°C). Intergranular penetration of the steel substrate by zinc from the galvanized coating is possible. At temperatures exceeding 1380°F (750°C) molten zinc will rapidly attack the grain boundaries of austenitic stainless steel at a rate of inches per second.

The following conditions can cause failures:

- 1. Welding or cutting stainless steel components that have been coated with a zincrich product such as zinc paint
- **2.** Welding a galvanized steel part to an austenitic steel component without first removing the galvanizing adjacent to the weld preparation

Higher alloys such as alloy 20Cb-3 and alloy 276 are not as susceptible as the conventional austenitic stainless steels.

# Cyanides

Cyanides by themselves do not cause stress corrosion cracking. However, in combination with wet hydrogen sulfide they can increase the rate of sulfide stress corrosion cracking of carbon and low-alloy steels. The hydrogen sulfide need only be present at concentration greater than 20 ppm.

Cyanides can also accelerate the rate of wet hydrogen sulfide corrosion. Sulfide films are usually stable and limit corrosion, but the presence of cyanides converts the iron sulfide scale deposits into soluble salt complexes. This subjects the underlying carbon steel to rapid corrosion.

# Chlorides

Chlorides are capable of causing stress corrosion cracking of austenitic stainless steels, provided the exposed surface is in tension. Residual tensile stresses can be the result of welding or of cold work. Such stresses can be relieved by solution annealing, postweld heat treatment, stress relief heat treatment, and shot peening, which ensures that the exposed surface is in compression.

Austenitic stainless steels may be exposed to external chloride stress corrosion cracking as well as internal exposure from the process. External chloride attack can be the result of exposure to wet chlorides in atmospheric marine environments or to chlorides deposited externally by wind, dust, or water.

# Caustics

Caustics can cause stress corrosion cracking of carbon steel and low-alloy steels. Under severe conditions caustics can also cause cracking of stainless steels and nickel-based

alloys. For moderate temperatures and concentrations, carbon steel is the recommended material of construction. It is advisable to stress relieve or postweld heat treat carbon steel equipment to be used in caustic service.

#### **Carbonates and Bicarbonates**

Carbon steel is subject to stress corrosion cracking when combinations of carbonates and bicarbonates (either singly or in combination) exceed 1 weight percent. Postweld heat treatment does not prevent cracking since cracking generally occurs in the parent metal. A better choice is to upgrade to duplex or austenitic stainless steels, or for low-pressure applications to use a nonmetallic material. Coatings are not recommended.

#### Amines

Amines can cause alkaline stress corrosion cracking in carbon steel. If the amine concentration exceeds 2 weight percent, all carbon steel components should be postweld heat treated regardless of service temperature. If the amine is fresh and uncontaminated, the heat treating may be eliminated. Some amines are rich in hydrogen sulfide and can cause various types of hydrogen-related cracking.

#### Ammonia

Copper and copper alloys are subject to stress cracking in the presence of anhydrous liquid ammonia if there is less than 0.1 weight percent of water present.

See Refs. 10 and 34-37.

### **CREVICE CORROSION**

Crevice corrosion is a localized type of corrosion occurring within or adjacent to narrow gaps or openings formed by metal-to-metal or metal-to-nonmetal contact. It results from local differences in oxygen concentrations, associated deposits on the metal surface, gaskets, lap joints, or crevices under bolts or around rivet heads, where small amounts of liquid can collect and become stagnant.

The material responsible for the formation of the crevice need not be metallic. Wood, plastics, rubber, glass, concrete, asbestos, wax, and living organisms have been reported to cause crevice corrosion. Once the attack begins within the crevice, its progress is very rapid. It is frequently more intense in chloride environments.

Prevention can be accomplished by proper design and operating procedures. Nonabsorbant gasketing material should be used at flanged joints. Fully penetrated butt-welded joints are preferable to lap joints. If lap joints are used, the laps should be filled with fillet welding or a suitable caulking compound designed to prevent crevice corrosion.

See Refs. 10 and 38.

#### **CRITICAL CREVICE CORROSION TEMPERATURE**

The critical crevice corrosion temperature of an alloy is that temperature at which crevice corrosion is first observed when immersed in a ferric chloride solution. Listed below are the critical crevice corrosion temperatures of several alloys in 10% ferric chloride solution.

Alloy	Temperature (°F/°C)
Туре 316	27/-3
Alloy 825	27/-3
Type 317	36/2
Alloy 904L	59/15
Alloy 220S	68/20
E-Brite	70/21
Alloy G	86/30
Alloy 625	100/38
AL-6XN	100/38
Alloy 276	130/55

## **CRITICAL PITTING TEMPERATURE**

The critical pitting temperature of an alloy is the temperature of a solution at which pitting is first observed. These temperatures are usually determined in ferric chloride (10%  $FeCl_3-6H_2O$ ) and in an acidic mixture of chlorides and sulfates.

# CYCOLOY

Cycology is G. E. Plastics' trademark for their polycarhonate/acrylonitrile-butadiene-styrene thermoplastic alloy. It is available in several blends. The alloy can be formulated to maintain its impact and ductility below  $-40^{\circ}$ F ( $-40^{\circ}$ C). See Table C.29 for the range of physical and mechanical properties based on the specific formulation.

Property	Value	Units
Specific gravity	1.12-1.8	
Water absorption, 24 h at 73°F (23°C)	0.07-0.20	%
Tensile strength, type 1		
0.125 in. (3.2 mm) yield	6.5-9.1	psi $ imes 10^3$
break	7.25	$psi \times 10^3$
Tensile elongation, type 1		
0.125 in. (3.2 mm) yield	4.0-5.0	%
break		%
Tensile modulus, type 1		
0.125 in. (3.2 mm)	2.8-3.9	psi $ imes 10^5$
Flexural strength		1
0.125 in. (3.2 mm) yield	11.2-14.8	psi
break	12-13.2	psi
Flexural modulus		1
0. 125 in. (3.2 mm)	3.0-4.0	psi
0.250 in. (6.4 mm)	3.85	psi
Hardness. Rockwell R	115	1

**Table C.29**Range of Physical and Mechanical Properties ofCycoloy Based on the Specific Formulation

197

## REFERENCES

- 1. I Suzuki. Corrosion Resistant Coatings Technology. New York: Marcel Dekker, 1989.
- H Leidheiser Jr. Coatings. In: F Mansfield, ed. Corrosion Mechanisms. New York: Marcel Dekker, 1987, pp 165–209.
- PK Whitcraft. Corrosion of stainless steels. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 53–77.
- 4. PA Schweitzer. Corrosion Resistance Tables. 4th ed. Vols. 1-3. New York: Marcel Dekker, 1995.
- PF Lafyates. Carbon and graphite. In: BJ Moniz and WL Pollock, eds. Process Industries Corrosion— Theory and Practice. Houston: NACE International, 1986, pp 703–770.
- JL Gossett. Corrosion resistance of cast alloys. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 268–273.
- GW George and PG Breig. Cast alloys. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook. 2nd ed. New York: Marcel Dekker, 1989, pp 296–301.
- 8. FC Porter. Corrosion Resistance of Zinc and Zinc Alloys. New York: Marcel Dekker, 1994.
- 9. PA Schweitzer. Cathodic protection. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook. 2nd ed. New York: Marcel Dekker, 1989, pp 33–45.
- 10. HH Uhlig. Corrosion and Corrosion Control. New York: John Wiley, 1963.
- 11. PK Whitcraft. Fundamentals of metallic corrosion. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 11–12.
- 12. RA McCauley. Corrosion of Ceramics. New York: Marcel Dekker, 1995.
- EL Liening and JM Macki. Aqueous corrosion of advanced ceramics. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 419–458.
- 14. PA Schweitzer Corrosion Resistant Piping Systems. New York: Marcel Dekker, 1994.
- 15. PA Schweitzer. Corrosion Resistance of Elastomers. New York: Marcel Dekker, 1990.
- KR Tator. Coatings. In: PA Schweitzer, ed. Corrosion, and Corrosion Protection Handbook. New York: Marcel Dekker, 1989, pp 453–490.
- 17. W Funk. Prog Org Coating 9:29, 1981.
- 18. KR Gowers and D Scautlebury. Corros Sci 23:935, 1983.
- 19. W Funk. Ind Eng Chem Prod Res Dev 24:343, 1985.
- JHW de Wit. Inorganic and organic coatings. In: P Marcus and J Oudar, eds. Corrosion Mechanisms in Theory and Practice. New York: Marcel Dekker 1993, pp 581–628.
- 21. GT Murray. Introduction to Engineering Materials. New York: Marcel Dekker, 1993.
- 22. DM Berger. Fundamentals and prevention of metallic corrosion. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook. 2nd ed. New York: Marcel Dekker, 1989, pp 1–22.
- 23. P Marcus and J Oudar. Corrosion Mechanisms in Theory and Practice. New York: Marcel Dekker, 1995.
- 24. V Kucera and E Mattsson. Atmospheric corrosion. In: F Mansfield, ed. Corrosion Mechanisms. New York: Marcel Dekker, 1987.
- 25. JM Ciesiweicz. Copper and copper alloys. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook. 2nd ed. New York: Marcel Dekker, 1989, pp 125–152.
- DJ Duquette. Corrosion fatigue. In: M Florian, ed. Corrosion Mechanisms. New York: Marcel Dekker, 1987, pp 367–397.
- 27. UK Chatterjee, SK Buse, and SK Roy. Environmental Degradation of Metals. New York: Marcel Dekker, 2001.
- PA Schweitzer. Corrosion inhibitors. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook. 2nd ed. New York: Marcel Dekker, 1989 pp 47–50.
- C Trabanelli. Corrosion inhibitors. In: F Mansfield, ed. Corrosion Mechanisms. New York: Marcel Dekker, 1987, pp 119–163.
- 30. F Mansfield. Corrosion Mechanisms. New York: Marcel Dekker, 1987.

#### REFERENCES

С

199

- CG Arnold and PA Schweitzer. Corrosion-testing techniques. In: PA Schweitzer, ed. Corrosion and Corrosion Protection Handbook, 2nd ed. New York: Marcel Dekker, 1989, pp 587–618.
- 32. A Perkins. Corrosion monitoring. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker. 1996, pp 623–652.
- 33. RD Kane. Corrosion testing. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 607–621.
- 34. RC Newman. Stress corrosion cracking mechanisms. In: P Marcus and J Oudar, eds. Corrosion Mechanisms in Theory and Practice. New York: Marcel Dekker, 1995, pp 311–372.
- 35. CP Dillon. Corrosion Control in the Chemical Process Industries. 2nd ed. St. Louis: Materials Technology Institute of the Chemical Process Industries, 1994.
- 36. CP Dillon. Corrosion Resistance of Stainless Steels. New York: Marcel Dekker, 1995.
- 37. DA Hansen and RB Puyear. Materials Selection for Hydrocarbon and Chemical Plants. New York: Marcel Dekker, 1996.
- H Bohni. Localized corrosion. In: F Mansfield, ed. Corrosion Mechanisms. New York: Marcel Dekker, 1987, p 285.