7 Metal Packaging Materials

7.1 INTRODUCTION

Four metals are commonly used for the packaging of foods: steel, aluminum, tin and chromium. Tin and steel, and chromium and steel, are used as composite materials in the form of tinplate and electrolytically chromium-coated steel (ECCS), the latter being somewhat unhelpfully referred to as tin-free steel (TFS). Aluminum is used in the form of purified alloys containing small and carefully controlled amounts of magnesium and manganese. Copper is used as a wire electrode during the welding of three-piece tinplate containers but does not become part of the finished container. The safety aspects of these different metals, together with can coatings, are discussed in Chapter 22.

The first commercial manufacture of tinplate commenced in England in 1699 and in France in 1720, where it was used for a variety of purposes including household utensils such as plates. Some time in about the middle of the eighteenth century, the Dutch navy began to use foods preserved by packing them in fat in tinned iron canisters (Thorne, 1986). After cooking and while still hot, the material to be preserved was placed into the canister, covered with hot fat and the lid immediately soldered on. Records show that from 1772 to 1777, the Dutch Government supplied its navy (which had been sent out to Suriname [formerly Dutch Guiana in South America] to quell a revolt) with roast beef packed in this way (Farrer, 1980).

Before the end of the eighteenth century, the Dutch had also established a small industry to preserve salmon in a similar manner. Freshly caught salmon were cleaned, cooked in boiling brine, smoked over a wood fire for 2 days and then placed in a tinplated iron box. The spaces were filled up with hot salted butter or olive oil and a lid was soldered onto the box (Thorne, 1986). A famous London firm of snuff merchants supplied 13 tins of Dutch salmon to one of its clients in 1797 (Farrer, 1980). Thus, a canning industry of sorts had been established in Holland independently of, and prior to, Appert's work.

The French confectioner Nicolas Appert discovered a method of "conserving all kinds of food substances in containers," and, in 1804, produced preserved meat for the French navy by packing it in glass champagne bottles, sealing them with a cork held in place with wire and heating in boiling water for several hours (Garcia and Adrian, 2009). Appert received an ex gratia payment of 12,000 francs in 1810 from the Ministry of the Interior's Bureau of Arts and Manufactures on condition that he publish details of his process; Appert obliged and 200 copies of his book were printed the same year. Appert deliberately avoided tinplate in his early work because of the poor quality of the French product, according to the fourth (1831) and fifth (1858) editions of his book. However, the quality of tinplate in England was good and it was freely available.

After almost two centuries of history, there is still controversy as to who introduced the tin can as a package. The latest account, based on extensive research of early-nineteenth-century archives (Cowell, 2007), has thrown additional light on those involved in the genesis of the canning industry and has revealed a new name: the French inventor Phillipe de Girard. It appears that he got Durand (a broker in London) to patent the process in 1810, the patent referring to the substitution of glass jars and bottles with tin cases. A successful trial with the Royal Navy was undertaken at Durand's request in 1811, and the patent was acquired by Bryan Donkin in 1812 for which Girard received £1000. Donkin had become interested in the tinning of iron as early as 1808 and, as mentioned in Chapter 6, was involved with John Gamble in developing the Fourdrinier papermaking machine.

Donkin applied to the British Admiralty for a test of his product and the first substantial orders were placed in 1814 with the London firm of Donkin, Hall and Gamble for meat preserved in tinplate canisters (John Hall was the founder of the famous Dartford Iron Works). By the 1820s, canned foods were a recognized article of commerce in Britain and France.

To complete the historical record, William Underwood left London and arrived in New Orleans in 1817. He traveled up to Boston where he started a business preserving food in glass jars by Appert's method. In 1819, Thomas Kennsett, also from England, started a similar business in preserved foods in New York in partnership with his father-in-law Ezra Daggett. The first offering of preserved provisions in tin cans in America is assumed to be the announcement by Daggett and Kensett in the New York *Evening Post* of July 18, 1822 (Bishop, 1978), although it was not until 1825 that they took out a patent in which "vessels of tin" were mentioned.

The American Civil War provided the opportunity for canning to become a great industry, and by the end of the war in 1865, canners had increased their output sixfold. For many years, the cans were made slowly and laboriously by hand. Both ends were soldered to the can with a hole of about 25 mm in diameter left in the top. After the can was filled through this hole, a metal disc was soldered into place. The mechanical roll crimping (commonly known as double seaming) of the can ends onto a body with a soldered side seam was patented in 1896 by Max Ams of New York (Thorne, 1986), making it possible to develop high-speed equipment for the making, filling and closing of these cans. In 1892, the first pineapple cannery was established in Hawaii. The first canned soup was produced in the United States in 1897.

Today, materials like tinplate and aluminum have become universally adopted for the manufacture of containers and closures for foods and beverages, largely due to several important qualities of these metals. These include their mechanical strength and resistance to working, low toxicity, superior barrier properties to gases, moisture and light, ability to withstand wide extremes of temperature and ideal surfaces for decoration and lacquering.

7.2 MANUFACTURE OF TINPLATE

The term tinplate refers to low-carbon, mild steel sheet varying in thickness from around 0.15–0.5 mm with a coating of tin between 2.8 and 17 gsm (g m^{-2}) (0.4–2.5 μm thick) on each surface of the material. The combination of tin and steel produces a material that has good strength, combined with excellent fabrication qualities such as ductility (the capability to undergo extensive deformation without fracture) and drawability (these attributes arise from the grade of steel selected and the processing conditions employed in its manufacture) as well as good weldability, nontoxicity, lubricity, lacquerability and a corrosion-resistant surface of bright appearance (these latter properties are due to the unique properties of tin). Furthermore, the tin coating adheres sufficiently to the steel base so that it will withstand any degree of deformation that the steel is able to withstand without flaking.

Continuous demand for improved quality and more economic production has led to the development of highly sophisticated manufacturing techniques. These are outlined in this section, together with their effects on the metallurgical and mechanical characteristics. The chemical composition of the base steel has a very significant effect on the subsequent corrosion resistance and mechanical properties of the tinplate.

7.2.1 Manufacture of Pig Iron

The iron ores used are generally hematite (Fe_2O_3) with some magnetite (Fe_3O_4). Commercial extraction of iron from its ores is carried out in blast furnaces, where a mixture of iron ores, solid fuel (coke) and fluxes (limestone and dolomite) are heated to around 1800°C. This results in the reduction of most of the iron oxides to metallic iron (m.p. ≈ 1200°C). Today, modern blast furnaces are capable of producing molten iron of near constant composition at high rates.

7.2.2 Steelmaking

The pig iron from a blast furnace contains 3.5%–5.0% carbon, 0.3%–1.0% silicon and up to 2.5% manganese, 1% phosphorous and 0.08% sulfur depending on the ore. Carbon is the most important alloying element for steel and effects the strength of cans. A higher carbon content is usually combined with a higher manganese content, resulting in higher strength steel. Lower carbon content improves material formability and weldability. These metalloids must be substantially reduced in the steelmaking stage, and this is commonly accomplished using a basic oxygen furnace. From the furnace, the steel is cast into ingots, which are subsequently rolled into slabs about 250 mm thick or, more commonly today, continuously cast into slab form.

The thick slabs are hot rolled down to about 2 mm and, during this process, substantial layers (0.01 mm thick) of oxides or scale are formed as a consequence of the steel being heated to elevated temperatures for rolling. Next, the scale is removed by a process called "pickling," which uses a dilute aqueous solution of acid (traditionally sulfuric acid but now mainly hydrochloric acid) near its boiling point. After pickling, the oxide-free strip is recoiled and coated with an oil to prevent rust formation and act as a lubricant in subsequent operations.

The final stage of thickness reduction (typically 90% from about 2 mm to <0.2 mm) is carried out by cold rolling. The effects of cold rolling are to increase the strength and hardness of the steel, but this is done at the expense of ductility.

Cold rolling is followed by annealing where the steel is heated to temperatures of 600°C–700°C to relieve the stresses from the rolling process; annealing results in recrystallization of the elongated ferrite grains into new fine grains. Two different annealing processes are used after cold rolling: continuous annealing (which results in a strong material with a fine grain structure) and batch annealing (which has a coarse grain structure but excellent formability).

After annealing, the material is either temper rolled or cold rolled for the second time. Steel that is temper rolled is known as "single reduced" (one cold rolling operation); steel that is cold rolled after annealing is known as "double reduced." Double reduced (DR) material is very strong and stiff and has a higher hardness for a given thickness, allowing the use of comparatively thin gauges for many applications. However, it has only limited forming possibilities. Minimum thicknesses currently in use are 0.18 mm for single reduced (SR) and 0.12 mm for DR plate.

Some types of tinplate display excellent deep-drawing behavior thanks to a high Lankford coefficient (or coefficient of anisotropy), which is a measure of the plastic anisotropy of rolled sheet metal; it is used as an indicator of the formability of recrystallized low-carbon steel sheets. It ensures near-identical behavior, irrespective of the orientation of the deformation in relation to the rolling direction, an important consideration in drawn and redrawn (DRD) can manufacture.

To reduce the possibility of severe fluting, paneling or creasing, and to impart the desired surface finish, the steel is given a final, very light cold rolling (generally a reduction of less than or equal to 5.0% in thickness) in a "Temper" mill. This imparts "springiness" to the steel but changes the temper or surface hardness only slightly. Temper refers to an arbitrary number designation that indicates the forming properties of tin mill products and is the summation of interrelated mechanical properties such as elasticity, stiffness, springiness and fluting tendency (Kraus and Tarulis, 2009).

At this stage, the uncoated steel sheet is referred to as *blackplate*, thus called because some of the early production was covered with black iron oxide. It is the raw material for electrolytic tinplate (ETP) and ECCS. The Rockwell hardness test has been adopted as the industry standard to express temper because of its simplicity and overall good correlation with fabrication requirements. A 1.6 mm diameter ball penetrator with a 30 kg load is impressed into the plate surface and the measurement is expressed as a Rockwell 30 T reading, which is then converted into plate temper values using an arbitrary scale. Typical temper values for blackplate and ETP are presented in Table 7.1, where both the former and current designations are listed as the former designations are still used in some countries. The four main grades of steel product for subsequent use in tinplate production are shown in Table 7.2.

TABLE 7.1
Tinplate Temper Designations

Temper			Rockwell Hardness 30T Scale	Formability	Applications
TS230	T50	T1	46–52	Soft for extra-deep drawing	Nozzles, spouts and closures;
TS245	T52	T2	50–56	Moderate deep drawing	Rings and plugs, dome tops, closures and shallow-drawn cans
TS275	T57	T3	54–63	Shallow drawing and general purpose	Can ends and bodies, large-diameter closures and crown caps
TH415	T61	T4	58–64	General purpose where increased stiffness required	Crown caps, can ends and bodies for noncorrosive products
TH435	T65	T5	62–68	Increased stiffness to resist buckling	Can ends and bodies
—	T70	T6	67–73	Very stiff	
TH550	DR550	DR8	70–76	High strength and stiffness	Small diameter round can bodies and ends
TH620	DR620	DR9	73–79	High strength and stiffness	Large diameter round can bodies and ends
—	DR660	DR9M	74–80	High strength and stiffness	Beer and carbonated beverage ends and DRD cans
—	DR690	DR10	77–83	Maximum strength and stiffness	Ends

Note: Some products may be either batch annealed or continuously annealed. Although the temper of the plate will be the same, the mechanical properties may differ as continuously annealed plate has a finer grain structure.

TABLE 7.2
Types of Steel Produced for Subsequent Use in Tinplate

Type	Composition (%) (Maximum)							Properties	Application
	C	Mn	P	S	Si	Cu	Al		
D	0.12	0.60	0.02	0.05	0.02	0.20	0.06	Stabilized steel and, therefore, nonaging Less C than other tinplate steels	Used for severe drawing operations (e.g., D&I cans)
L	0.13	0.60	0.015	0.05	0.01	0.06	0.08	High purity; low in residual elements	Used where high internal corrosion resistance is required
MR	0.13	0.60	0.02	0.05	0.01	0.20	0.08	Similar to L but Cu and P maxima are raised. Is most widely used tinplate steel	Vegetable and meat packs where internal corrosion resistance is not too critical
N	0.13	0.60	0.015	0.05	0.01	0.06	0.06	Nitrogenized steel with up to 0.02% N to increase strength	Used where high strength and rigidity required (e.g. can ends)

Packaging steels generally fall into two groups: those that are created specifically for strength and those that are created for formability. Higher strength steels are suitable for welded food cans, while softer, more formable grades are better for drawn cans and components such as aerosol tops and bottoms, fish or beverage cans.

7.2.3 Tinplating

The traditional method for tinplating involved dipping or passing the steel through a bath of molten pure tin, but, since the 1930s, the process of depositing tin by electroplating has been used. The introduction of the electroplating process enabled a different thickness of tin to be applied to the two surfaces of the steel. This "differential tinplate" is of economic benefit to the user because it enables the most cost-effective coating to be selected to withstand the different conditions of the interior and exterior of the container.

There are a number of methods of electroplating, but the two principal methods are the acid stannous sulfate process (generally known as the Ferrostan process) and the halogen process (Morgan, 1985). Plating by either method is preceded by cleaning in a pickling and degreasing unit, followed by thorough washing to prepare the surface. After the plating stage, the coating is flow melted, passivated and then lightly oiled.

Flow melting consists of heating the strip to a temperature above the melting point of tin (typically, 260°C–270°C), followed by rapid quenching in water. During this treatment, a small quantity of the tin–iron compound $FeSn_2$ is formed; the weight and structure depend on the time and temperature, as well as other factors such as the surface condition of the steel. The structure and weight of this alloy layer plays an important role in several forms of corrosion behavior.

Because the naturally formed oxide layer on the surface of the tin will readily grow in the atmosphere to form a yellow stain (especially when heated, e.g., during stoving after the application of organic enamels, which are also known as lacquers or varnishes), the steel strip is given a passivation treatment to render its surface more stable and resistant to the atmosphere. Many types of treatments have been developed, but an electrolytic treatment in a sodium dichromate electrolyte is the most widespread. It results in the formation of a film (usually <1 μm thick), consisting of chromium, chromium oxides and tin oxides, the quantity and form of these basic constituents determining the varying properties of the film. The process ensures that the only species present are Cr^O and Cr^{III} and not Cr^{IV}, which is the toxicologically important species. Although the level of migration from uncoated tinplate cans is negligible, work on alternative passivation treatments is continuing (Whitaker, 2007). These include titanium sulfate, titanium and potassium oxalates, and zirconium sulfate and fluoride treatments (Catalá et al., 2005).

After passivation, the plate is given a light oiling (oil film weights are generally in the range of 5–10 mg m^{-2}) to help preserve it from attack, and to assist the passage of sheets through container-forming machines without damaging the soft tin layer. It is obviously essential that the oil used is approved for use in food packaging; cotton seed oil was used for many years but this has now been largely superseded by dioctyl sebacate (DOS). The oil is applied by electrostatic precipitation or direct plate immersion. The quantity of oil (applied uniformly to both sides) is carefully controlled because an excessive oil film can cause dewetting of enamels and printing inks, which are applied during subsequent container manufacture. Finally, the strips are sheared into sheets or coiled, and then packed for shipment to the can manufacturers.

The final structure of the completed coating is shown in Figure 7.1, and consists of a tin/iron alloy layer (principally $FeSn_2$) adjacent to the steel base, free tin, a film of mixed oxides formed by the passivation process and an oil film.

Tinplate sheets are described in terms of a base box, a hangover from earlier times when tinplate was sold in units of 112 sheets, each 356 × 508 mm (14 × 20 in.). Such a package was known as a base box, and the area it contained (20.2325 m^2 or 31,360 in.^{2}) survives today as the unit area for the
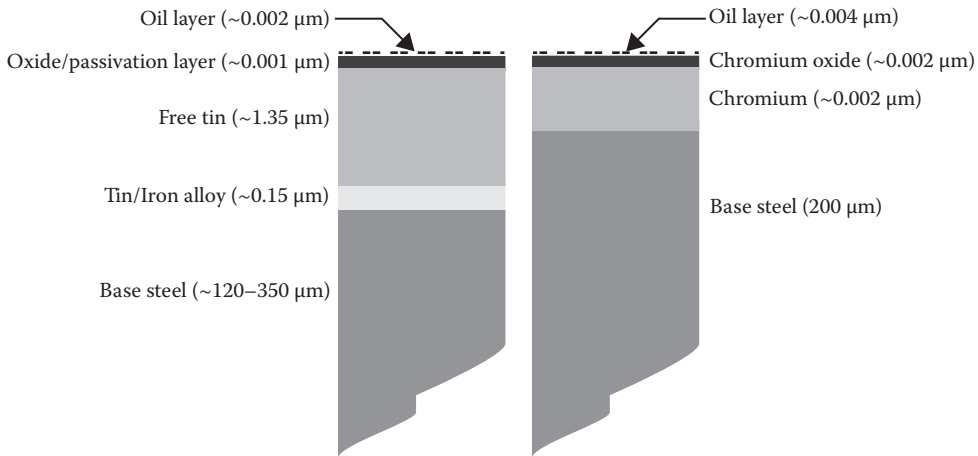
FIGURE 7.1   Schematic structure (not to scale) of tinplate and ECCS showing the main functional layers.

selling of tinplate. In the original system, a 1 lb base box meant that 1 lb of tin was applied evenly to both sides of the plate, that is, each side received 0.5 lb (equivalent to 11.2 gsm) of tinplate. This was given the designation in the United States of No. 100 (Turner, 2001).

The standard grades of ETP available in most countries, together with their nominal tin coating masses, are given in Table 7.3. The designation of ETP with 11.2 gsm of tin on each surface of the sheet is shown as E.11.2/11.2, and this represents a thickness of tin of ~1.54 μm on each surface. Tinplate is now commonly graded using the metric unit SITA (Système International Tinplate Area), which is based on 100 m^2. One SITA equals 4.9426 base boxes. The standard method for determining the mass of tin coating is the iodine titration procedure.

TABLE 7.3
Standard Grades and Nominal Masses of ETP

Code		Nominal Coating Mass per Surface	
Euronorms (145–146)	**ASTM (624–626)**	**(gsm)**	**(lb/Base Box)**
	No. 10	1.1/1.1	0.05/0.05
E.2.8/2.8	No. 25	2.8/2.8	0.125/0.125
E.5.6/5.6	No. 50	5.6/5.6	0.25/0.25
E.8.4/8.4	No. 75	8.4/8.4	0.375/0.375
E.11.2/11.2	No. 100	11.2/11.2	0.50/0.50
D.2.8/0	—	2.8/0	0.125/0
D.5.6/2.8	No. 50/25	5.6/2.8	0.25/0.125
D.8.4/2.8	No. 75/25	8.4/2.8	0.375/0.125
D.11.2/2.8	No. 100/25	11.2/2.8	0.50/0.125
—	No. 135/25	15.1/2.8	0.675/0.125
D.8.4/5.6	No. 75/50	8.4/5.6	0.375/0.25
D.11.2/5.6	No. 100/50	11.2/5.6	0.50/0.25
D.15.1/5.6	—	15.1/5.6	0.675/0.25

E, equal coatings on each surface; D, differential coatings on
    each surface.

7.3 MANUFACTURE OF ECCS

The production of electrolytic chromium/chromium-oxide-coated low-carbon steel sheet (to give ECCS its full name) is very similar to electrotinning, the only essential differences being that, in the former case, flow melting and chemical passivation are not involved. The initial development work was carried out in Japan in the 1960s when tin was on occasions in short supply, and the price extremely variable.

The process involves cathodic deposition in a dilute chromium plating electrolyte (e.g., $50 g L^{-1}$ CrO_3 and $0.5 g L^{-1} H_2SO_4$) at a temperature in the range of 50°C–70°C. As shown in Figure 7.1, ECCS consists of a duplex coating of metallic chromium and chromium sesquioxide. The ideal range of coating weights for ECCS is between 0.07 and 0.15 gsm chromium metal and between 0.03 and 0.06 gsm trivalent chromium present as oxide, giving a total coating weight of approximately 0.15 gsm. This is much thinner than the lowest grade of electrolytic tinplate which has a tin thickness of 5.6 gsm. ECCS is coated equally on both sides of the steel. Unlike tinplate, ECCS is not subject to a passivation treatment. Finally, an oil coating of either DOS or butyl stearate oil (BSO) is applied.

Recently Li et al. (2011) showed that the different modes of annealing and rolling have remarkable effects on the surface morphology and grain size of ECCS products. In compact surface chromium-coating of batch-annealed (BA) plate with low porosity, the grains were larger and coarser in comparison with that of continuously annealed (CA) plate. Evidence of microcracks was found on the surface of chromium-coated DR plate. The chemical composition of ECCS oxide film on steel consisted of CrOOH or $Cr(OH)_3$ as the main components, plus Cr_2O_3 and a small amount of H_2O. $Cr(OH)_3$ is mainly formed from cathodic films generated in the electroplating process. CrOOH was an intermediate product formed in process of $Cr(OH)_3$ losing water to generate Cr_2O_3.

The surface of ECCS is more acceptable for protective enamel coatings or printing inks and varnishes than tinplate, and the lack of a low melting point (232°C) tin layer means that higher stoving temperatures and consequently shorter stoving times can be used for the enameling of ECCS. Unlike flow-brightened tinplate, ECCS is a dull bluish color, which necessitates modification of decoration processes to allow for its poor reflection.

ECCS is less resistant to corrosion than tinplate as it has no sacrificial tin layer and, therefore, must be coated on both sides with an enamel or polymer coating. Polymer coatings are applied either by laminating film or extruding polymer directly onto the substrate; this is normally done on both sides.

ECCS containers cannot be soldered and, therefore, bonding of ECCS components must be by welding or the use of organic adhesives. If welded, then ECCS must be edge cleaned prior to welding to remove the chromium layer. This is a slow, costly and mechanically inefficient process. Typically, ECCS is used for components that do not have to be welded, such as ends for tinplate bodies, lids, crown corks, twist-off caps and aerosol bottoms and tops.

7.4 MANUFACTURE OF ALUMINUM

Aluminum is the earth's most abundant metallic constituent, comprising 8.8% of the earth's crust, with only the nonmetals O_2 and silicon being more abundant. Alumina or aluminum oxide (Al_2O_3) is the only oxide formed by aluminum and is found in nature as the minerals corundum (Al_2O_3), diaspore ($Al_2O_3 \cdot H_2O$), gibbsite ($Al_2O_3 \cdot 3H_2O$) and, most commonly, bauxite, an impure form of gibbsite. Because bauxite contains only 30%–54% alumina (the remainder is a mixture of silica, various iron oxides and titanium dioxide), it must be purified before it can be refined to aluminum. The Bayer process (invented in 1887 by Karl Bayer in St. Petersburg, Russia) is the principal industrial means of refining bauxite. A solution of NaOH at 175°C converts alumina to $Al(OH)_3$, which dissolves in the hydroxide solution; the other components that remain insoluble are filtered off. On cooling, the dissolved $Al(OH)_3$ precipitates as a white, fluffy solid and, when heated to 980°C (calcined), decomposes to alumina.

Hans Christian Oersted, a Danish physicist and chemist, first isolated aluminum in 1825 using a chemical process involving potassium amalgam. Between 1827 and 1845, Friedrich Wöhler, a German chemist, improved Oersted's process by using metallic potassium. In 1854, a French chemist Henri-Étienne Sainte-Claire Deville obtained the metal by reducing aluminum chloride with sodium. Aided by the financial backing of Napoleon III, Deville established a large-scale experimental plant and displayed pure aluminum at the Exposition Universelle of 1885 in Paris, where it was considered a precious metal (more valuable than gold or platinum) and used mainly for jewelry. In 1886, Charles Martin Hall in the United States and Paul Héroult in France independently and almost simultaneously discovered that alumina would dissolve in fused cryolite (Na_3AlF_6), and could then be decomposed electrolytically to a crude molten metal. A low-cost technique (the Hall-Héroult process) is currently the only method used for the commercial production of aluminum, although new methods are under study. In 1888, Hall opened the first large-scale aluminum production plant in Pittsburgh, which would eventually evolve into the Alcoa Corporation, the world's leading producer of aluminum.

Owing to the chemical stability of its oxides, the energy requirements for smelting are extremely high. This has led to the production of aluminum in areas where cheap electrical power is available. Currently, a typical aluminum process can be described as follows. First, alumina is dissolved in cryolite in carbon-lined steel boxes called cells. Then a carbon electrode or anode is lowered into the solution and an electric current of 50–150 MA is passed through the mixture to the carbon cathode lining of the cell. The current reduces the alumina into aluminum and O_2, the latter combining with the anode's carbon to form CO_2, while the aluminum (denser than cryolite) settles to the bottom of the cell.

Most commercial uses of aluminum require special properties that the pure metal cannot provide. Therefore, alloying agents are added to impart strength, improve formability characteristics and influence corrosion characteristics. A wide range of aluminum alloys is commercially available for packaging applications, depending on the container design and fabrication method used. The chemical composition and typical usage of some of the more commonly used aluminum alloys (the aluminum is at least 99% pure) are shown in Table 7.4. The alloys are identified by four-digit numbers where the first digit 1–8 gives the series family and indicates the alloy type and principal alloying element. Commercially pure (unalloyed) aluminum (e.g., 1050) contains different levels of impurities, with Fe and Si being the most common. It is used for the manufacture of foil and extruded containers since it is the least susceptible to work hardening. Type 3xxx alloy contains Mn, and type 5xxx alloy contains 4%–5% Mg and 0.5% Mn, producing a very rigid material suitable for manufacturing beverage can ends. Type 8xxx series includes miscellaneous alloys that cannot be placed within the other series designations (Reboul and Baroux, 2011).

The general effect of several alloying elements on the corrosion behavior of aluminum is as follows:

- Copper reduces the corrosion resistance of aluminum more than any other alloying element and leads to a higher rate of general corrosion.
- Manganese slightly increases corrosion resistance.
- Magnesium has a beneficial influence and Al–Mg alloys have good corrosion resistance.

TABLE 7.4

Some Aluminum Alloy Composition Limits (% Weight) and Applications

Alloy	Typical Application	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
1050	Foils and flexible tubes	0.25	0.4	0.05	0.05	0.05	0.05	0.03	0.03
3104	Beverage can ends and D&I can bodies	0.60	0.7	0.25	1.4	1.3	—	0.25	0.10
5042	Full panel EOE and DRD can bodies	0.20	0.35	0.15	0.5	4.0	0.10	0.25	0.10
5182	Easy-open beverage can ends and tabs	0.20	0.35	0.15	0.5	5.0	0.10	0.25	0.10
8011	Pilfer-proof caps	0.90	1.00	0.10	0.20	0.05	0.05	0.10	0.08
8079	Foil for lamination	0.30	1.3	0.05	—	—	—	0.10	—

- Zinc has only a small influence on corrosion resistance in most environments, tending to reduce the resistance of alloys to acid media and increase their resistance to alkalis.
- Silicon slightly decreases corrosion resistance, depending on its form and location in the alloy microstructure.
- Chromium increases corrosion resistance in the usual amounts added to alloys.
- Iron reduces corrosion resistance and is probably the most common cause of pitting in aluminum alloys; a high iron content increases the bursting strength but reduces the corrosion resistance.
- Titanium has little influence on corrosion resistance of aluminum alloys.

Compared with tinplate and ECCS, aluminum is a lighter, weaker but more ductile material that cannot be soldered. The reduction in metal thickness of the can body has continued incrementally over the past 30 years, at times facilitated by alloy development but mostly through optimization of can design, and continues today in many parts of the world.

7.5 CONTAINER-MAKING PROCESSES

7.5.1 END MANUFACTURE

The can end or lid is of complex design developed for optimum deformation behavior, the latter being dependent on plate thickness, the precise contour of the expansion rings and the countersink depth. It is important that the ends are able to deform under internal and external pressure without becoming permanently distorted. In effect, they must act like diaphragms, expanding during thermal processing and returning to a concave profile when vacuum develops inside the can on cooling. The cross-section of a typical end design is shown in Figure 7.2.

The ends are stamped on power presses from tinplate sheet (generally of high temper grade), which has been previously enameled. After stamping, the ends fall through the press into the curler to form the outside curl and diameter.

A lining or sealing compound is then applied into the seaming panel; the sealant used is based on natural or synthetic rubber and is dispersed in water or solvent. Its constituents are subject to stringent food regulations. The purpose of the sealant is to assist the formation of a hermetic seal by providing a gasket between adjacent layers of metal.

Several types of easy-opening devices, such as the key-opening scored strip found in solid meat or shallow fish cans, have been available for many years. However, an increased demand for convenience features has seen the development of easy-open ends (EOEs) of two broad types: those that provide a pouring aperture for dispensing liquid products, and those that give a near-full aperture opening for removing more solid products. The first EOE for canned beverages was patented in 1962 by Ermal Cleon Fraze of Dayton, Ohio who, in the late 1950s, was forced to open a beverage can on a car bumper at a family picnic because no one had brought along a can opener.
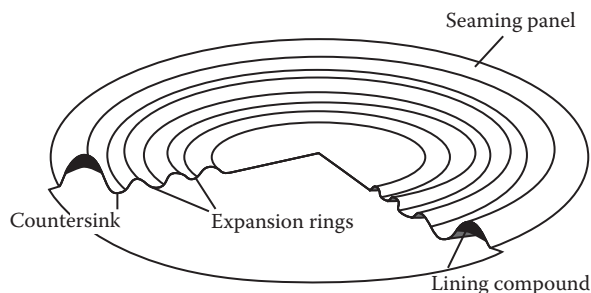

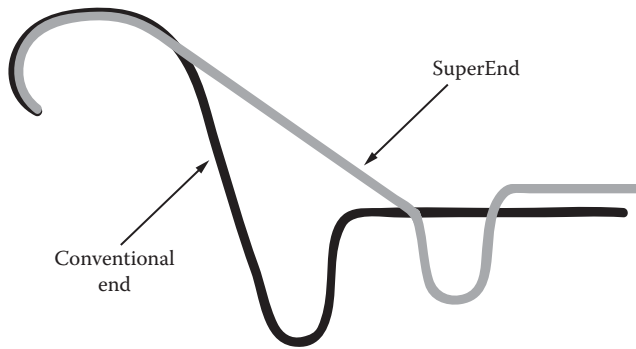**FIGURE 7.2** Profile of a typical can end.

FIGURE 7.3   Cross-section of the end profile of a conventional end and a SuperEnd®.

Being intimately familiar with working metal, he knew there had to be a better way. By the early 1960s, he had refined a technology for attaching a tab to the top of the can end, using nothing but the parent material of the end itself. It was test marketed and emerged in 1965 as the familiar ring-pull tab. However, because it was detachable it resulted in litter and, in 1975, a patent was granted to Daniel F. Cudzik from Reynolds Metals in Richmond, Virginia for a can end with an inseparable tear strip; this soon became the industry standard, and, in various formats, is known as the stay-on tab.

Most designs incorporate an EOE consisting of a scored portion in the end panel and a levering tab (formed separately) that is riveted onto a bubble-like structure fabricated during pressing. Most (but not all) of the entire aperture circumference is scored, leaving sufficient unscored portion to function as a hinge when the tab is pressed in. Close control of scoring conditions is vital to ensure adequate resistance to bursting without requiring an unduly high tearing load to open. Particular attention must be paid to metal exposure resulting from enamel fracture at the score.

Because of the greater ease of fabrication, integrated rivet ends have usually been made from aluminum, but this presents problems when such ends are used with steel cans. For example, the corrosion of carbonated soft drinks in such cans is accelerated because of the bimetallic container. These problems have led to the development of steel EOEs.

A significant reduction in the amount of material required to make an aluminum end became commercial in 2001 when Crown Cork and Seal introduced the SuperEnd®, achieving about a 10% decrease in weight while increasing the buckle failure strength of the end. Figure 7.3 shows a comparison of profiles of the new SuperEnd and the older designs. The innovative ends utilize a unique angled chuck-wall design, which significantly reduces metal use and improves end performance. This unique design provides 20% more finger access to lift the opening tab, thus making it easier to open; it has become an industry standard for beverage ends.

7.5.2   Three-Piece Can Manufacture

7.5.2.1   Welded Side Seams

In developed countries, the majority of three-piece tinplate cans used for food have welded side seams. Compared to soldered side seams (see below Section 7.5.2.2), welding offers savings in material, since the overlap needed to produce a weld uses less metal than an interlocked soldered seam. In addition, the side seam is stronger, it is easier to seam on the ends and a greater surface area is available for external decorating.

Prior to welding, sheets of steel are enameled and, if necessary, printed, with the area where the weld will be made left bare. The sheets are then slit into individual blanks. Each blank is rolled into a cylinder with the two longitudinal edges overlapping. The two edges are then welded together.

The wire-welded operation used today for the high-speed welding of tinplate and ECCS containers utilizes a sine wave alternating current (and in the case of tinplate, a continuous copper wire
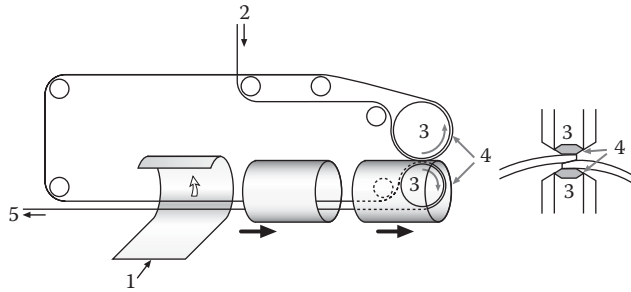
FIGURE 7.4 Stages in the formation of a three-piece welded can: (1) blank rolled to cylindrical shape, (2) copper wire, (3) welding electrodes, (4) copper wire contacts and (5) used wire to recycling. (Redrawn from Turner, T.A., *Canmaking: The Technology of Metal Protection and Decoration*, Blackie Academic & Professional, London, U.K., 1998.)

electrode) to produce a weld with an extremely low (0.4–0.8 mm) metal overlap (Turner, 2001). The use of copper wire as an intermediate electrode is necessary to remove the small amount of tin picked up from the tinplate during the welding process, which would otherwise reduce welding efficiency (Kraus and Tarulis, 2009). High electrical resistance causes the interface temperature to rise rapidly to at least 900°C, resulting in solid phase bonding at all locations along the seam (see Figure 7.4). The tensile strength of a good weld is equal to that of the base plate.

To prevent traces of iron being picked up by some types of beverages and acidic foods, repair side striping (enameling) of the internal surface of the weld is required. The side stripe generally comprises polymer resin powders that are applied by fusing or the like to the inside and/or the outside seam areas. Powder coating is usually applied electrostatically to the interior of the side seam.

A system of chemical bonding of side seams has been developed, mainly for dry or otherwise neutral products such as powders and oils. It utilizes a thermoplastic polyamide adhesive, which is applied to one edge of the preheated body blank before it is rolled into a cylinder, providing complete protection of the raw edges of the blank. A strong bonded lap seam is produced that is able to withstand the high in-can pressures generated by beers and carbonated soft drinks during can warming or pasteurization. This method can only be used with ECCS cans because the melting point of tin is close to the fusion temperature of the plastic. However, since the advent of high-speed welding operations, the use of chemically bonded side seams has declined.

7.5.2.2 Soldered Side Seams

With the exception of some developing countries, very few food cans are produced with soldered side seams, the concern of public health authorities being that lead from the tin/lead (2:98) solder would migrate into the food. Since the 1970s, most countries insisted that only pure tin solder be used on cans intended for baby foods, which added significantly to the cost of such cans. The use of tin/lead solder ceased when the U.S. FDA issued a final rule in July 1995 prohibiting its use in food containers.

7.5.2.3 Double Seaming

After the side seam has been welded, the bodies are transferred to a flanger for the final metal forming operation: necking and flanging for beverage cans, and beading and flanging for food cans. The can rim is flanged outward to enable ends to be seamed on. The top of beverage cans is necked to reduce the overall diameter across the seamed end to below that of the can body wall, yielding savings in the cost of metal through the use of smaller diameter ends. This allows more effective packing and stacking methods to be adopted, and prevents damage to the seams from rubbing against each other. Simultaneous creation of the neck and flange using a spin process is used. Double-, triple- and quadruple-neckings are now quite common, the latter reducing the end diameter from 68 to 54 mm for the common beverage can.
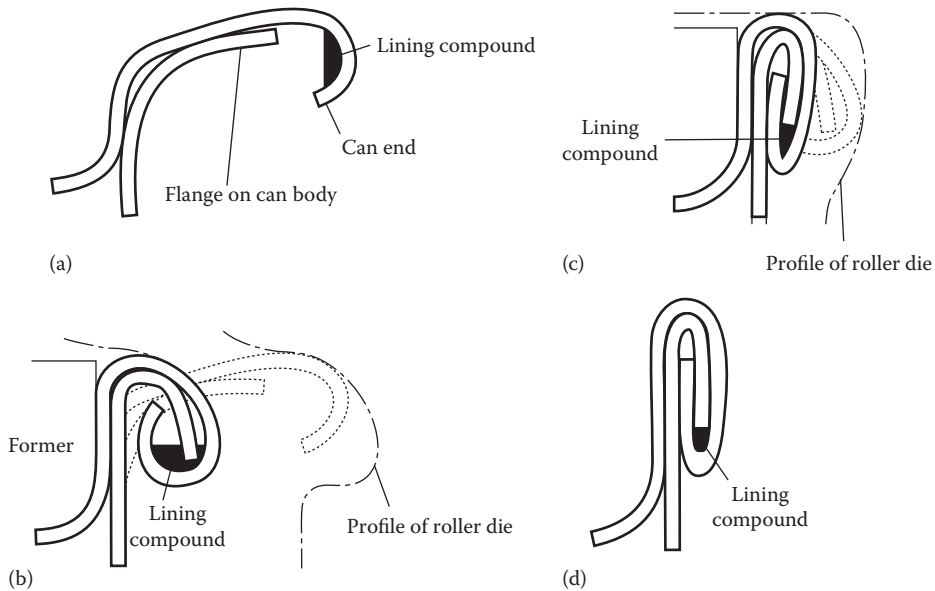
FIGURE 7.5 Double seaming of metal ends on to metal containers: (a) end and body are brought together, (b) first seaming operation, (c) second seaming operation and (d) section through final seam.

For food products where the cans may be subjected to external pressure during retorting or where they remain under high internal vacuum during storage, the cylinder wall may be beaded or ribbed for radial strength. There are many bead designs and arrangements, all of which are attempts to meet certain performance criteria. In essence, circumferential beading produces shorter can segments that are more resistant to paneling (implosion), but such beads reduce the axial load resistance by acting as failure rings.

The end is then mechanically joined to the cylinder by a double seaming operation. This is illustrated in Figure 7.5 and involves mechanically interlocking the two flanges or hooks of the body cylinder and end. It is carried out in two stages. In the first operation, the end curl is gradually rolled inward radially so that its flange is well tucked up underneath the body hook, the final contour being governed by the shape of the seaming roll. In the second operation, the seam is tightened (closed up) by a shallower seaming roll. The final quality of the double seam is defined by its length, thickness and the extent of the overlap of the end hook with the body hook. Rigid standards are laid down for an acceptable degree of overlap and seam tightness. The main components of a double seam are shown in Figure 7.6. Finally, the cans are tested for leakage using air pressure in large wheel-type testers; leaking cans are automatically rejected.

7.5.3 Two-Piece Can Manufacture

A major innovation in canmaking was the introduction of the seamless or two-piece aluminum can in the 1950s and tinplate can in the 1970s. For many years, canmakers have manufactured in a single pressing, shallow-drawn two-piece containers such as the familiar oval fish can. However, the technology to produce deep-drawn cans is a more recent innovation, although the basic concept dates back to the Kellver system for producing cartridge cases developed in Switzerland during World War II.

There are two main methods used commercially to make two-piece cans: the drawn and ironed (D&I) process, which can be adapted to produce a can for pressure packs (including carbonated beverages) and for food containers, and the DRD process, which is a multistage operation and produces a can mainly suitable for food products. Both processes depend on the property of the metal to
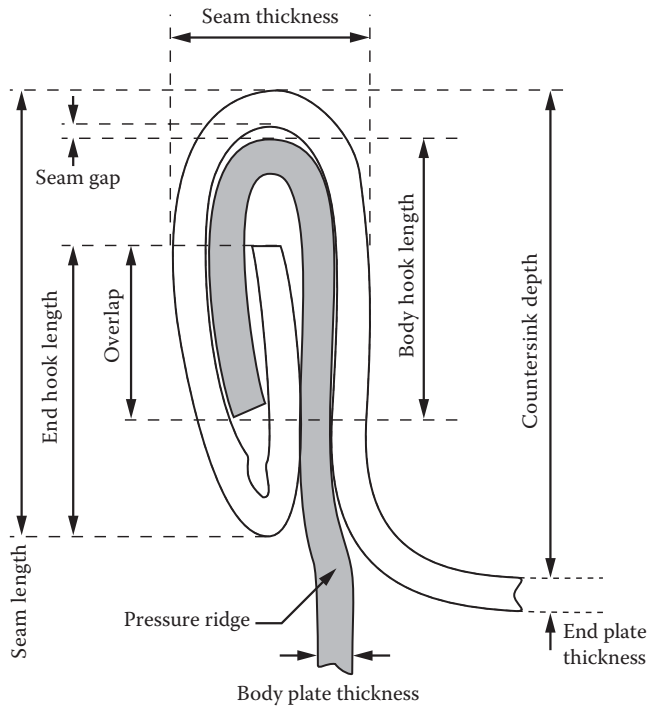
FIGURE 7.6   Main components of a double seam.

"flow" by rearrangement of the crystal structure under the influence of compound stresses, without rupturing the material.

The first aluminum D&I cans were introduced in the United States by a brewery in 1958, but it was not until 1971 that the first tinplate D&I can was launched. By comparison, the first three-piece soldered tinplate can for beer was introduced by the Krueger Brewing Company in the United States in 1935.

Two-piece cans have technical, economic and aesthetic advantages in comparison with soldered or welded three-piece cans. In terms of integrity, the two-piece can has no side seam and only one double seam, which is more easily formed and controlled because of the absence of a side seam lap juncture. The internal enamel does not have to protect a soldered side seam or weld cut edge, and there are material savings in solder and (in the case of D&I cans) plate, the latter being up to 35% lighter than a standard three-piece can. Since 1970, through the conversion of three- to two-piece cans and subsequent lightweighting, the weight of a 350 mL tinplate soft drink can has been reduced by 50% to 30 g, and that of the inherently lighter two-piece aluminum can by 39% to 13 g. Technology exists to continue this trend, especially with tinplate cans. Finally, the absence of a side seam permits all-round decoration of the outside of the can, increasing the effective printing area and leading to a more aesthetically pleasing appearance.

7.5.3.1   Drawn and Ironed

The D&I (also known as *drawn and wall ironed* [DWI]) tinplate or aluminum container is made from a circular disc stamped from a sheet or coil of uncoated plate, formed into a shallow cup with effectively the same side wall and base thicknesses as the starting material, as shown in Figure 7.7. The forming process involves a flat sheet being formed into a cup or cylinder by the action of a punch drawing it through a circular die (Silbereis, 2009), the wall thickness of the cup being uniform throughout. The plate is covered with a thin film of water-soluble synthetic lubricant prior to forming.
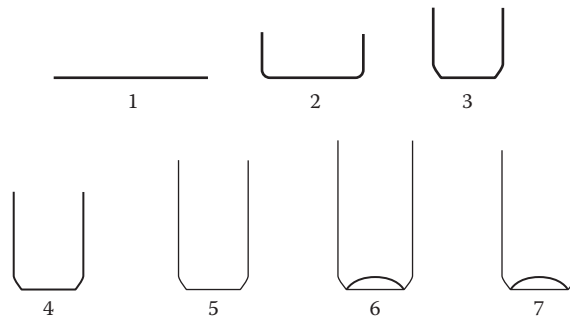
FIGURE 7.7 Sequential stages in the production of two-piece D&I cans: (1) disc cut from coil, (2) drawn into shallow cup, (3) redrawn into smaller diameter cup, (4, 5 and 6) wall thinning by ironing (diameter remains constant) and (7) finished can trimmed to required height.

The cup is transferred to an ironing press where it is held on a punch and passed successively through a series of ironing dies. As a consequence of the ironing process, the wall thickness is reduced (typically from 0.30 to 0.10 mm) and the body height is correspondingly increased. Concurrently, the integral bottom end is domed and profiled to provide added strength, with the end retaining essentially the original sheet thickness. Because the can wall may not iron to the same height all around the circumference due to slight variation in material properties, cans are "overdrawn" and then trimmed to the correct height.

The trimmed cans are chemically cleaned to remove drawing lubricants and prepare the surface for receiving exterior and interior coatings. If the cans are to be used for beverages, they are then necked; D&I food cans are commonly beaded for added strength against body collapse under partial vacuum conditions. The cans are then flanged.

Tinplate is the best material for D&I cans as the tin coating is soft and ductile and imparts lubricity to the steel while remaining bonded to it throughout. ECCS plate is not suitable for ironing as the chromium-based coating is too hard. Some aluminum is made into D&I cans for food packaging, but these are mainly shallow-drawn containers. Most D&I aluminum cans are used for beverage packaging (i.e., beer and soft drinks). Aluminum beverage bottles having screw tops with diameters of 28 and 38 mm were launched in the Japanese market in 2000 in keeping with the modern-day drinking habits of consumers and to compete with the reclosable PET bottles. However, a majority of consumers feel that the 28 mm opening is too small and the 38 mm opening is too large (Chihara and Yamazaki, 2012). Results of an optimization study showed that when the opening diameters are 35.4 and 34.4 mm in the case of green tea and carbonated beverage, respectively, the actual volume of fluid in the mouth is closest to the ideal volume and the participants feel most comfortable. These results were in agreement with the results of an earlier study by the same authors that found that an opening diameter of 33 mm was optimum for young Japanese adults.

TULC (Toyo Ultimate Can) is a two-piece can developed by Toyo Seikan Kaisha in Japan in 1991. ECCS, laminated with PET film on the interior and exterior surfaces, is processed into cups, similar to how D&I cans are processed. It is then drawn, stretched and ironed to reduce the thickness of the side walls but, unlike D&I cans, no coolant (lubricant) is used during the forming process, thus eliminating the need for coolant rinsing and wastewater treatment. Due to the internal layer of PET, no internal enamel/lacquer coating is required, resulting in a significant reduction in CO_2 emissions, a by-product of the internal lacquer curing process. More recently, a PET-laminated aluminum two-piece can known as aTULC has been developed.

7.5.3.2 Drawn and Redrawn

For many years, canmakers have manufactured shallow-drawn containers. However, the novelty of the DRD process is the use of multistage drawing to produce a can with a higher height-to-diameter ratio. This process is essentially identical to the initial stages of the D&I technique, except that the
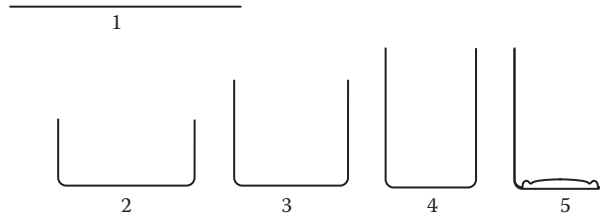
FIGURE 7.8 Sequential stages in the production of DRD cans: (1) body blank, (2) drawn cup, (3 and 4) diameter decreases as cup is redrawn and (5) finished trimmed can with profiled base.

final height and diameter of the container is produced by sequentially drawing cups to a smaller diameter—that is, causing metal to flow from the base to the wall of the container rather than ironing the container wall. As a consequence, the wall and base thickness, as well as the surface area, are identical to the original blank. This contrasts to the D&I can where the wall thickness is much less than the base thickness. A typical DRD process is illustrated in Figure 7.8.

In the D&I process, the internal diameter of the body remains constant throughout the ironing stages, whereas the internal diameter of the DRD can is progressively reduced as the height is increased during the various redrawing stages. Therefore, the DRD cans do not offer the same economies as D&I cans because, in the former, the metal cannot be selectively distributed as it can during wall ironing. Because the end is integral and is normally the thickest region, this governs the material gauge and the result is often excessive side wall thickness. Typically, 0.2 mm thick prelacquered tinplate and ECCS is used for the DRD process. DRD cans are currently used in the packaging of food rather than beverages since a greater wall thickness is required to withstand pressure reversals. The body is beaded, and ECCS is used more than tinplate since better enamel adhesion is achieved with the former.

7.5.4 Protective and Decorative Coatings

Container coatings provide a number of important basic functions (Turner, 1998):

- They protect the metal from the contents.
- They avoid contamination of the product by metal ions from the container.
- They facilitate manufacture.
- They provide a basis for decoration and product identification.
- They form a barrier to external corrosion or abrasion.

7.5.4.1 Protective Coatings

Internally enameled metal containers are used when the product and the plain container would interact to reduce the shelf life or the quality of the product to an unacceptable level. Thus, most vegetables, colored berry fruits, flesh foods and beer and soft drinks are packed in enameled containers; that is, containers in which organic coatings have been applied to the inside (and sometimes the outside) surfaces. The primary function of interior can coatings is to prevent interaction between the can and its contents, although some enamels have special properties that allow products such as meat loaf to be easily removed from the cans, while others are used merely to improve the appearance of the pack. Exterior can coatings may be used to provide protection against the environment (e.g., when the cans will be marketed in particularly humid or salt-laden climates), or as decoration to give product identity as well as protection. Generally, some external coating of tinplate and ECCS containers is necessary for products stored in hot humid atmospheres to prevent external corrosion, particularly at the side seam region for three-piece cans.

There are several essential requirements needed in an interior coating: it has to act as an inert barrier, separating the container from its contents and not imparting any flavor to the contents; it

must resist physical deformation during fabrication of the container and still provide the required chemical resistance; and the enamel must be flexible, spread evenly, completely cover the substrate and adhere to the metal surface. Adhesion failure may occur during, or as a result of, mechanical deformation during heat processing or undermining by corrosion.

For most containers, the enamel is applied to the metal in the flat before fabrication, typical film masses being in the range between 3 and 9 gsm (4–12 µm thick). However, because of the considerable amount of metal deformation with substantial disruption of the surface that takes place in the D&I operation, such containers must be coated internally after fabrication. Control of the dry film weight is essential if the enamel is to function correctly. A dry film that is too thin may not cover the surface completely, while an overly thick film leads to brittleness and impaired protection, as well as being uneconomical. As the enamel film has imperfections and is damaged during container manufacture, it does not give complete protection to the can. Where it is essential to minimize product–container interactions, for example, for canned beer and soft drinks where metal pickup can affect flavor and clarity, the cans are given a post-fabrication repair lacquering.

Many types of internal enamel coatings are available for food containers including epoxy–phenolic, epoxy–amino, epoxy–acrylate, epoxy–anhydrite, vinyl organosol, thermoset polyester, thermoset polymer coated, phenolic and oleoresinous (see Table 7.5). The original can coatings were based on oleoresinous products that include all those materials made by fusing natural gums and rosins and blending them with drying oils such as linseed or tung (Chinese wood oil). Oleoresinous coatings were popular largely because of their low applied cost, but their open micellar structure made them prone to corrosion/staining problems with sulfur-bearing products unless they were pigmented with zinc oxide. In addition, they lacked resistance to retorting processes and had poor color retention and taste characteristics. For these reasons, a move has been made to synthetic epoxy-based resins and, apart from some specific applications, oleoresinous-based coatings find little general usage today.

The terminology used for epoxies can be confusing. Epoxy groups (also called epoxides) are three-membered cyclic ethers that, strictly speaking, should be called oxiranes. Most commercially important epoxy resins are derived from (chloromethyl)oxirane, more commonly known as epichlorohydrin (ECH). The resins generally contain oxiranylmethyl ethers or esters, usually called glycidyl ethers or esters (Wicks et al., 2007).

The first epoxy resins used in coatings were bisphenol A (BPA) epoxies made by reacting BPA with ECH. Under basic conditions, the initial reaction is formation of a BPA anion (BPA$^-$), which attacks ECH and results in the elimination of a chloride anion (Cl$^-$) and the formation of the monoglycidyl ether of BPA (MGEBPA). Analogous reaction of the phenolic group of MGEBPA with NaOH and ECH gives the diglycidyl ether of BPA (DGEBPA) commonly known as bisphenol A diglycidyl ether (BADGE). The epoxy groups of MGEBPA and DGEBPA react with BPA$^-$ to extend the chain. These reactions introduce alcohol groups on the backbone and continuation of these reactions results in linear polymers, since both the BPA and ECH are difunctional. Bisphenol A epoxy resins are made with excess ECH, so the end groups are glycidyl ethers (Wicks et al., 2007). MW is controlled by the ratio of ECH to BPA, and as the ratio of ECH to BPA is reduced, the MW increases. The lowest MW epoxy resin used is BADGE.

Epoxy resins based on BPA and ECH have been used in coatings for metal packaging since the 1950s and are the single most widely used class of resin in use today for metal packaging, with epoxy–phenolic coatings finding the largest application (Oldring and Nehring, 2007). Epoxy resins are cross-linked through both their hydroxyl and oxirane functionalities, using phenolic or amino resins and occasionally an anhydride oligomer. The success of epoxies as coatings for food cans is due to their desirable flavor-retaining characteristics, their excellent chemical resistance and their outstanding mechanical properties. Some epoxy components and the by-products of epoxy resins are known to migrate from the cured epoxy-based can coating into foods. Particular interest and concern has been given to BPA, BADGE, BADGE derivatives and epoxidized soya bean oil (ESBO). The safety aspects of these chemicals are discussed in Chapter 22.

TABLE 7.5
Metal Can Coatings

Coating Type	Properties	Main Applications
Epoxy–phenolic	High-MW epoxy resins cross-linked with phenolic resole resins	Most widely used coating
	Provides good flexibility and very good pack resistance for aggressive acid products	Universal golden coating for three-piece and shallow-drawn cans
Epoxy–amine and epoxy–acrylate	High-MW epoxy resins cross-linked with amino or acrylate resins	Universal lacquer for beer and beverage cans
	Employed now in waterborne coatings	Sideseam stripe in high solids form for welded cans
Epoxy–anhydride	High-MW epoxy resins cross-linked with anhydride hardeners	Internal white coating for three-piece cans and ends
	Good fabricability; withstands beading	
	Very good chemical resistance	
Vinyl organosol	PVC dispersed in an appropriate solvent and stabilized with low-MW epoxy resin or ESBO	Drawn cans
		Easy-open ends
		Often used over epoxy-phenolic base coat
	Good fabricability; superior corrosion resistance	
Thermoset polyester	Polyester resins cross-linked with phenolic or amino resins	Internal and external coating for two-piece and three-piece cans and ends for meat, fish and vegetables
	May contain low-MW epoxy resins	
	Very good chemical resistance	
	Good fabricability and withstands beading	
Thermoplastic polymer coated	Extrusion coated or laminated film of polypropylene, polyester, polyamide or combinations thereof	Shallow drawn cans
		Easy-open and standard ends
Phenolic	Low cost	Drums and pails where flexibility is not a critical factor
	Poor flexibility but excellent resistance, particularly for aggressive foods	
Oleoresinous	Naturally occurring oils and fatty acids with synthetic modification	A general-purpose, golden-colored, inexpensive coating
		Once very common but now very limited use

Source: Adapted from Whitaker, R., Metal packaging and chemical migration into food, in: *Chemical Migration and Food Contact Materials*, Barnes, K.A., Sinclair, C., Watson, D.H. (Eds), CRC Press, Boca Raton, FL, pp. 251–270, 2007; Hernandez, R.J. and Giacin, J.R., Factors affecting permeation, sorption, and migration processes in package-product systems, in: *Food Storage Stability*, Taub, I.A. and Singh R.P. (Eds), CRC Press, Boca Raton, FL, pp. 269–330, 1998.

Although their importance has waned, phenolic resins still have significant uses. Phenolics are made by reacting formaldehyde with phenolic monomers such as phenol, cresols, xylenols and substituted phenols. The products depend on the phenol(s) used, the stoichiometric ratio of phenol to formaldehyde and the pH during the reaction. Phenolic resins are divided into two broad classes: *resole* phenolics, which are made using alkaline catalysts and high ratios of formaldehyde to phenol,

and *novolac* phenolics, which are made using acid catalysts and low ratios of formaldehyde to phenol (Wicks et al., 2007). Phenolic coatings are low cost and have exceptional acid resistance and good sulfur resistance. Film thickness is restricted by their inflexibility and they have a tendency to impart off-flavor and odor to some foods.

Resole phenolic resins are used in interior can coatings and require baking using an acid catalyst to cure in short times. To enhance flexibility and adhesion, they are commonly blended with low MW poly(vinyl butyral) as a plasticizer. The films are resistant to swelling by oils, such as encountered in canned fish, and are completely resistant to hydrolysis. These resins and other heat-reactive phenolics discolor during baking due to quinone methide formation, which restricts their use to applications for which development of a yellow-brown color is acceptable (Wicks et al., 2007).

For most applications, phenolic resins are plasticized with epoxy resins with which they react to yield a cured film. A three-dimensional structure (normally golden in appearance) is formed during curing and baking, which combines the good adhesion properties of the epoxy resin with the high chemical resistance properties of the phenolic resin. The balanced properties of epoxy–phenolic coatings have made them almost universal in their application on food cans with the exception of deep multistage DRD cans. Epoxy–phenolics are among the most chemically resistant known coatings and are the predominant protective coatings used for lining the interior of metal food cans. They are made either by straight blending of a solid epoxy resin with a phenolic resin, or by the precondensation of a mixture of two resins in appropriate solvents. These resins are often polymerization products of BADGE or novolac diglycidyl ether (NOGE, also known as epoxy novolac) and the lowest MW component of NOGE is bisphenol F diglycidyl ether (BFDGE).

Vinyl coatings to improve retort resistance are based on copolymers of vinyl chloride and vinyl acetate of low MW (frequently with a small amount of a third monomer to impart special properties) dissolved in strong ketonic and aromatic hydrocarbon solvents. The vinyl acetate lowers the T_g. Vinyl chloride copolymers require stabilization to prevent thermal and photochemical degradation as they undergo dehydrochlorination in an autocatalytic chain reaction. The long carbon–carbon chains make them thermoplastic, and they can be blended with alkyd, epoxy and phenolic resins to enhance their performance. The essential qualities of vinyl coatings are adhesion, high flexibility and a complete absence of taste. Their flexibility allows them to be used for caps and closures as well as drawn cans. Their main disadvantage is their high sensitivity to heat and retorting processes, restricting their application to cans that are hot filled rather than retorted, and to beer and beverage products.

An organosol is a colloidal suspension or dispersion of very finely divided, insoluble material suspended in an organic liquid in which it cannot dissolve at normal temperatures. Vinyl organosol coatings incorporate a dispersion of high MW PVC resins in hydrocarbon solvents with a plasticizer such as dioctyl phthalate to aid film formation. Organosol have all the desirable properties found in vinyl coatings, together with better process resistance. Soluble thermosetting resins (including epoxy, phenolic, acrylic and polyesters) are added in order to enhance the film's chemical resistance, thermal stability and adhesion. BADGE and NOGE have been used as additives to vinyl organosols to scavenge the HCl formed during heat treatment in the coating procedure and they can migrate into the food during retorting if the curing process is unsuccessful.

Polyester-based coatings provide an alternative to epoxy-based resins. In these systems, the three-dimensional coating network is built up from any combination of a number of polyfunctional alcohol and carboxylic acid monomers. Polyester-based coatings can be thermoplastic, as used in sideseam stripes, or they can undergo cross-linking reactions (typically through their hydroxyl functionality) with a number of systems, such as phenolic resins, amino resins (particularly melamine formaldehyde resins) or polyisocyanates (Oldring and Nehring, 2007). It is desirable that the product arising from such modification should be free from migrating components and by-products, but possible candidates for migration include cyclic oligomers of the initial polyester resins. Among attempts to reduce this migration potential, polyester–polyurethane (PEPU) coatings were developed. Such coatings commonly contain a hardener precursor such as a polyisocyanate, resulting in coatings that develop urethane linkages during the curing process (Jiang et al., 2010).

Amino resins are based on the reaction products of urea, melamine or benzoguanamine with formaldehyde and frequently a low MW aliphatic alcohol. Their prime use in coatings for metal packaging is as a cross-linking resin for either epoxy or polyester resins. Amino resins typically undergo some degree of self-condensation reaction during their manufacture. During the curing process, they react with functionalities in the other resins present in the coating, as well as undergoing some self-condensation reactions, which can give rise to "clusters" of amino resin moieties in the cured coating (Oldring and Nehring, 2007). They are a universal coating for beer and beverage cans.

Trimellitic acid (TMA) and its anhydride are used as curing agents for the manufacture of epoxy–anhydride coatings, for example, a few percent of TMA is added to BADGE-type resins as a cross-linker. They are often based on the reaction product of trimellitic anhydride with an aliphatic glycol such as ethylene glycol and the anhydride functionality is retained. The resulting coating, typically white owing to added titanium oxide, is used in some 10% of all food cans.

As an alternative to applying coatings on metal, thermoplastic films can be laminated or extruded onto the metal and the coated metal formed into cans or can components. Films may consist of PP, PA, a PP/PA coextruded combination or PET, the latter being the most common.

PET coatings provide waterproof protection to ECCS plate, prevent physicochemical interactions with the environment, and offer resistance to surface mechanical damage during handling and transport of the metal sheets. However, the polymer-coated sheets can undergo damage during rolling and forming resulting in fracture, detachment of the polymer layer, discontinuities between coating and substrates, and the presence of surface microdeformations after these processes. All of these features are of considerable importance in determining the formability limits of ECCS plate. The PET layer can be subject to thermomechanical deformation during the processing and manufacturing of plates, such as extrusion, drawing, and molding, but during these processes, microstructural and mechanical properties of PET coatings are for the most part independent (Zumelzu et al., 2009).

Novel, highly functional biobased epoxy compounds, epoxidized sucrose esters of fatty acids (ESEFAs), have recently been cross-linked with a liquid cycloaliphatic anhydride to prepare polyester thermosets with a high biobased content (71%–77% in theory). They have excellent properties in the equivalent ratio of epoxides to anhydrides of 1:0.5. Because of the high performance achieved, they may have wide-ranging applications in areas where thermally cured materials are used such as in protective coatings (Pan et al., 2011).

Instead of using enamels, there is considerable interest in using different organic (heterocyclic) compounds that can act as cathodic or anodic corrosion inhibitors. Essential onion oil (EOO) has been proposed as a potential inhibitor of tin and chromium dissolution from tinplate sheets. The influence of EOO on the dissolution of iron and the porosity of tinplate was investigated by Grassino et al. (2010) who reported that EOO improved the protection of tinplate compared with DOS oil, and was almost as effective as epoxy–phenolic lacquer. They recommended the addition of EOO due to the lower cost of canned food production and enhanced organoleptic properties, but the storage temperature has to be lower than 36°C to avoid accelerating the corrosion process.

Sulfur-resistant enamels are used to prevent the staining of tinplate surfaces by sulfur compounds released from foods such as meat, fish and vegetables with sulfur-containing amino acids that breakdown during heat processing and storage to release sulfides. These react with tin to form black tin sulfide, or accumulate in the headspace and give out an unpleasant odor. To overcome this problem, two approaches have been used. Enamels are pigmented with zinc oxide or zinc carbonate that reacts with the sulfur compounds to form white zinc sulfide (these are known as the sulfur-absorbing enamels), or the enamels are pigmented with aluminum powder or white pigment to obscure any unsightly black tin sulfide that might form (these are known as sulfur-resisting enamels).

In the United States, most fruits and vegetables are packed in cans with an interior coating called an R enamel (from R for regular). Historically, R enamel was a phenolic varnish but now it is more commonly a phenolic resin or an epoxy–phenolic coating (a resole phenolic), with a BPA epoxy

and phosphoric acid catalyst (Wicks et al., 2007). For packing vegetables such as corn that give off sulfides during retorting, fine-particle-size zinc oxide pigment is dispersed in the coating, which is called a C enamel (from C for corn). Acidic products should not be permitted to come into contact with coatings containing zinc oxide because the reaction may produce zinc salts that could destroy the continuity of the film (Oldring and Nehring, 2007).

Coatings obtain their final color in various ways. Epoxy–phenolic coatings normally generate a golden color when cured due to the chromophores in the phenolic resin; the color is a useful indicator of the degree of cure for a given system. White coatings are made by the addition of titanium dioxide, often in an epoxy–anhydride coating or sometimes an organosol, for example, vinyl organosol coatings are typically white or buff colored due to the addition of titanium dioxide. Aluminum powder is added to a coating to give a grey "aluminumized" appearance to the final film (Oldring and Nehring, 2007). Enamels pigmented with aluminum powder or other materials were described earlier as sulfur-resisting enamels, but they are also used in premium quality packs (where sulfur staining is not a problem), simply to improve the appearance of the inside can surface.

In coatings for meats such as ham, a key requirement is that the coatings permit the release of the product from the can. This requires that a release agent such as petroleum or polyamide wax be incorporated into the coating.

Two methods are used for the application of protective coatings to metal containers: roller coating and spraying, the former being the most widespread. Roller coating is used if physical contact is possible; thus, it finds use in the coating of material in sheet and coil form, and the external coating of cylindrical can bodies. Spraying techniques are used if physical contact is impossible or difficult; thus, it finds use mainly to coat the inside surface of can bodies, including two-piece D&I and sometimes DRD cans.

Because the coating is generally applied wet (i.e., the resin is suspended in a carrier such as an organic or aqueous solvent for ease of application), it must be dried after application by solvent removal, oxidation or heat polymerization. This process (known as baking or curing) is usually carried out in a forced convection oven using hot air at up to 210°C for up to 15 min. Today's resin formulations require lower temperatures and shorter curing times, and this is achieved through the use of UV radiation to accelerate polymerization. Such UV-cured resins are virtually solvent free. They contain photosensitive molecules that absorb the UV radiation and release free radicals, which polymerize or cross-link the liquid resin to form a solid coating almost instantly. Because the substrate is not heated, it can be handled immediately for further operations, and substantial savings (up to 50%) in energy and space are possible. UV-curable coatings based on low-viscosity aromatic, aliphatic and cyclo-aliphatic epoxy resins are used to coat the exterior and ends of cans.

Powder coating, where the resin is applied "dry" in the form of a fine powder under the direction of an electrostatic field, is used mainly where heavy coatings are required, such as in the protection of welded side seams where the bare metal that exists in the weld area (most of the tin is removed during the welding process) must be covered. Curing is usually by gas heating or high-frequency induction heating. Powdered coatings contain little or no volatile effluents and require low energy consumption for application and cure.

Electrophoretic deposition, a process originally developed for protecting automobile bodies, has been used for coating both two-piece and three-piece cans (Silbereis, 2009). A resin film is deposited electrically from an aqueous suspension, providing a far more even distribution than that obtained by spraying. Moreover, its throwing power enables it to coat regions inaccessible to spray. The process overcomes the current wasteful spray techniques with almost 99% coating utilization achieved.

Owing to environmental concerns and legislation concerning VOCs, the trend is for waterborne coatings to replace organic coatings that can consist of up to 70% solvent. The aqueous coatings contain only a small amount of organic solvents, and can be applied using essentially the same coating and curing equipment.

7.5.4.2 Decorative Coatings

Although the primary purpose in decorating the external surface of a metal container is to improve its appearance and assist its marketability, it also significantly improves the container's external corrosion resistance. In many respects, decoration of the external surface is similar to the process used to protect the internal surface, with the constituents generally being dispersed in volatile solvents, applied on roller coating machines (apart from the printed image) and baked in tunnel ovens.

Offset lithography (see Chapter 9 for a description) has been used for over a century for decorating sheet metal. Because metal is nonabsorbent, the coatings and prints cure by internal chemical reactions involving oxidation, polymerization or both. By adjusting the tack properties of the ink, it is possible to print one wet ink onto the previous wet ink ("wet-on-wet") without the second blanket picking off the first layer. Methods used to "set" the ink in between single color presses in tandem include high temperature air blasts, flame treatment and, more recently, the application of UV radiation to the print. The development of UV-curable resins has found application in the metal decorating industries for both printing inks and coatings that give instantaneous curing, reducing costs, space and production time. This has necessitated a new approach to ink formulation. The print process is usually carried out with sheet stock prior to slitting into can body blanks or scroll shearing into end stock. With the advent of two-piece cans, less elaborate designs are used on beer and beverage cans because of the necessity to use presses that can print completely fabricated cans.

7.6 ALUMINUM FOILS AND CONTAINERS

7.6.1 Aluminum Foil

Aluminum foil is a thin-rolled sheet of alloyed aluminum varying in thickness from about 4–150 μm. It was first produced commercially in the United States in 1913 where it was used for wrapping Life Savers™, candy bars and chewing gum. In 1921, it was laminated on paperboard for folding cartons. Household foil was marketed in the late 1920s, and the first heat sealable foil was developed in 1938. Formed or semirigid containers appeared on the market in 1949.

Foil can be produced by two methods: either by passing heated aluminum sheet ingot between rollers in a mill under pressure and then rerolling on sheet and plate mills until the desired gauge is obtained or continuously casting and cold rolling. This latter method is much less energy intensive and has become the preferred process.

Aluminum foil is available in a variety of alloys (see Table 7.4), with the alloys 1100, 1145 and 1235 most commonly used in flexible packaging and 3003 when heavier gauges are required for stiffness. In the softest temper, aluminum foil exhibits dead fold characteristics—that is, when wrapped around an object it will assume the profile of the object with no spring back. Although this is frequently advantageous, soft temper foil also wrinkles very easily, which necessitates the use of great care during handling.

Aluminum foil is essentially impermeable to gases and water vapor when it is thicker than 15 μm, but it is permeable at lower thicknesses due to the presence of minute pinholes. For example, 12 μm thick foil has a WVTR of ≤ 0.01 g m^{-2} day^{-1}, and 8–9 μm thick generally of 0.07–0.1 g m^{-2} day^{-1} (Lamberti and Escher, 2007). These values are still far below those of most plastic films used for food packaging and, at thicknesses below 15 μm, aluminum foil is mainly used with polymers or lacquers, thus making the effect due to pores negligible.

Aluminum foil can be converted into a wide range of shapes and products including semirigid containers with formed foil lids, caps and cap liners, composite cans and canisters, laminates containing plastic and sometimes paper or paperboard where it acts as a gas and light barrier and foil lidding, the latter being sealed using inductive sealing (see Chapter 10). Processes involved may include converting, forming, laminating, coloring, printing and coating. It can also be embossed to provide textured surfaces.

7.6.2 TUBE

The collapsible aluminum tube is a unique food package that allows the user to apply the product directly and in precise amounts when required. Typical applications include condiments such as mustards, mayonnaises and sauces, as well as dessert sauces, cheese spreads and pâté.

The aluminum tube is formed by the cold impact extrusion of an aluminum slug using a plunger. To relieve the hardness, the tube is annealed in an oven at 600°C, after which the inside is enameled with an epoxy–phenolic or acrylic lacquer. Aluminum tubes are printed by a dry offset process (see Chapter 9) using either thermally or UV-cured inks. Aluminum tubes are closed by folding after the application of latex or heat sealable lacquer inside the fold area, and heat applied, which ensures a hermetic seal. Currently, the aluminum tube is relatively rare with most food tubes being made of plastic laminates.

Foil laminate tubes are sealed using a high frequency, which generates an eddy current in the aluminum, heating up the surrounding plastic layers and forming a hermetic seal. Although early plastic tubes contained aluminum foil as a barrier layer, it is now common to coextrude LDPE with EVOH to obtain a tube that provides an excellent barrier to air and moisture. Plastic tubes are also printed by a dry offset process.

7.6.3 RETORT POUCH

Developed in the 1950s, the retort pouch is a flexible package, hermetically sealed on three or four sides and made from one or more layers of plastic or foil, each layer having a specific functionality. The choice of barrier layers, sealant layers and food contact layers depends on the processing conditions, product application and desired shelf life. Typical processing conditions involve temperatures of 121°C for times of up to 30 min (60 min for the large [3.5 kg] catering packs). One of the attractions of the retort pouch compared to the metal can is the thin profile of the package (12–33 mm for 200–1000 g pouches), enabling retorting times to be reduced by up to 60%, final quality to be improved, as well as rapid reheating prior to consumption. Other advantages include the ease of carrying, reheating and serving, as well as weight and space saving. Finally, disposal of the used pouch is much simpler than for the metal can as it can be easily flattened. It is for all of these reasons that retort pouches have found wide acceptance by military forces, the U.S. military term for this type of package being "Meal, Ready-To-Eat" (MRE). NASA began using retort pouch food for space missions in the 1970s and the U.S. Army began delivering large quantities of MREs to the troops in 1981 (Lampi, 2009). The current packaging material specification for MREs (MIL-PRF-44073F, 2006) includes performance requirements for OTR $\leq$ 0.06 mL m^{-2} day^{-1} atm^{-1} and WVTR $\leq$ 0.01 g m^{-2} day^{-1}.

A typical three-layer pouch structure would consist of an outer layer of 13 μm PET for strength and toughness; a middle layer of 9–18 μm aluminum foil as a moisture, light and gas barrier and an inner layer of 70–100 μm CPP for heat sealability, strength and compatibility with all foods. An additional inner layer of 15–25 μm BON-6 is used when a longer shelf life is required. Traditionally, a three-sided seal pouch was used for MREs and other commercial products, but this has been superseded by a multilayer four-side-seal pouch. Stand-up pouch designs having a gusseted bottom have also been commercialized.

Transparent retort pouches can be produced by replacing the aluminum foil layer. Typical structures including PET-OPA-CPP, SiO$_x$ PET-OPA-CPP, AlO$_x$ PET-OPA-CPP, OPA-PVdC-CPP and OPA-EVOH-CPP. These materials allow the pouch to be reheated in a microwave oven.

Unlike the metal can, retort pouches are susceptible to rupture or seal separation during retorting if the internal pressure exceeds the external process pressure. This is most likely to occur at the start of the cooling cycle when the product is at its hottest. The use of superimposed air pressure to counter balance the buildup in internal pressure in the pouch and control pouch integrity is necessary. Retorts used in processing pouches can be batch or continuous, and

agitating or static. It is also necessary to use trays that support the pouches and ensure uniform thickness and, thus, an adequate thermal process.

The shelf life of foods packaged in retort pouches is very dependent on storage temperature. If stored at 16°C, they will have a shelf life of about 130 months. If they are stored at 27°C, then shelf life will be 76 months; at 38°C, 22 months and at 50°C, only a month. Because of this, military MREs are stored in climate-controlled warehouses where they can be kept for up to 10 years at chill temperatures before being used.

Pouches are reverse printed on the PET layer using any of the standard plastic printing techniques (see Chapter 9). However, the highest quality printing is generally obtained using rotogravure, with the high gloss of the PET adding a reflective sparkle to the surface of the package.

A recent development has been the incorporation of zippers into the pouch to make it easier to open and reseal. Conventional zippers are made of LDPE that will not withstand retort temperatures, forcing zipper manufacturers to design zippers made from PP resins and match them with compatible pouch film. Aesthetic considerations have also had to be addressed. Because food migrates to the edges of the pouch during retorting, a secondary barrier to shield the zipper and prevent food from crusting around it had to be designed.

Laser scoring (done on either the exterior or interior surface) can withstand the conditions in a retort and maintain pouch integrity. With laser-scored packages, the laser beam "burns off" a portion of the substrate, providing a line for easy, uniform tearing of the pouch. However, the laser should only remove enough substrata to allow easy opening while not providing a route for O_2 migration through the pouch, which would decrease shelf life.

Several investigations on the effect of retorting on the O_2 barrier of packages containing EVOH have shown a significant deterioration. In a recent review, Mokwena and Tang (2012) summarized reported results. An increase in OTR of more than 10 times has been reported for a PET/EVOH/PP pouch and about 47 times for PET/PP/PA-6/EVOH/PA-6/PP pouch after retorting for 28 min at 125°C. Generally, a larger increase has been observed for film containing EVOH than for other barrier materials such as PVdC copolymer. The OTR for film containing EVOH increased by more than 60 times compared to only 1.4 times for SiO_x-coated and PVdC copolymer films under similar retort conditions. The effect of retort processing on EVOH has been explained on the basis of both plasticization of the polymer matrix and alteration in polymer morphology. An irreversible partial dissolution of EVOH crystalline regions occurs due to pressurized heated water entering the polymer and disrupting the intermolecular hydrogen bonding between EVOH chains.

In general, part of the O_2 barrier of multilayer EVOH films lost during retorting is recovered during long-term storage. Thus, while the O_2 barrier of such films decreased considerably during the first 2 months of storage, it remained relatively constant for the rest of the storage period (up to 12 months), although the preprocessing OTR values were not reached during the entire storage period. At steady-state (i.e., after 2 months), the OTR for PET/EVOH/PP film was about four times that of the initial preprocessing value, while that of PET/PP/PA-6/EVOH/PA-6/PP film was about eight times the initial preprocessing value. The OTRs for both films processed by combined microwave-hot water processing remained below $2 \, mL \, m^{-2} \, day^{-1}$ over 12 months of storage, a value that is comparable to commercially available PVdC copolymer-laminated films currently used in the United States as lidstock film for shelf stable products. Others have reported that during long-term storage of rigid containers of polyolefin/tie/EVOH/tie/polyolefin, steady-state was reached after 200 days of storage, at which time the OTR was four times higher than the preprocessing value. In contrast, others have reported that the OTR was only four times the initial value 6 days after retorting at 121°C for 20 min. In practice, the lack of full barrier recovery during storage can result in substantial additional quantities of O_2 permeating into the package, leading to possible deterioration of O_2 sensitive foods, especially during the first few weeks of storage.

Although the O_2 barrier properties of EVOH are compromised when exposed to high moisture conditions, EVOH acts as an effective O_2 barrier in rigid retort packages when used in combination with water-resistant polymers such as PP. For thin film structures (<0.254 mm),

EVOH is vulnerable to the effects of high moisture and high temperature conditions encountered during retorting. Therefore, a properly designed package that incorporates both good material selection and their correct positioning in the multilayer structure is essential to achieve the optimal O_2 barrier.

7.6.4 BOTTLE

The aluminum beverage bottle (also referred to as a bottlecan) was launched by two Japanese breweries in 2000 and in the United States for energy drinks in 2001. The bottles are made by either an impact extrusion (IE) or, since 2008, a Coil-to-Can (C2C) process, resulting in a wide range of shapes and sizes. A variety of standard finishes is available including a 26 mm standard crown cap, 38 mm lug finish, 38 mm continuous thread with plastic sleeve, 38 mm ROPP and 28 mm continuous thread.

IE is a technique originally developed to produce a heavier-wall aerosol container that could withstand greater internal pressure. The process involves pushing a mandrel into a die cylinder containing an aluminum slug with up to 3.5×10^8 kg m^{-2} of force. Through the impact, the metal of the slug is forced to flow up along the inside of the die, creating a seamless can body. As IE evolved, manufacturers took advantage of the softness of the aluminum alloy to add shaping capabilities to the necking area, resulting in threaded bottle openings that have essentially brought resealable aluminum cans to the beverage market to compete with resealable PET bottles.

The key to the C2C process is combining traditional D&I beverage canmaking technology on the front end with the IE shaping capabilities on the back end. IE bottles are produced with three times the aluminum of a traditional beer can; C2C bottles use 30%–40% less aluminum than IE bottles. The 3104 alloy used for the C2C process is lighter but stronger and harder than the 1070 pure virgin aluminum alloy used for IE that is much harder to shape.

7.7 CORROSION OF METAL PACKAGING MATERIALS

7.7.1 FUNDAMENTAL CONCEPTS

7.7.1.1 Introduction

Metals are important materials for the packaging of foods, combining properties of strength, toughness, ductility and impermeability. However, the chemical structure that gives them their valuable practical properties is also responsible for their main weakness—their susceptibility to corrosion. Corrosion is the term used to describe the chemical reaction between a metal and its environment to form compounds; it is a universal process affecting all metals to some extent. Because the reaction takes place at the metal surface, the rate of attack can be reduced and controlled by modifying the conditions at the surface.

Metals are chemically reactive and can be readily oxidized by O_2 and other agents to form largely useless corrosion products. This vulnerability to oxidation accounts for the fact that with few exceptions (copper, silver and gold), metals do not occur naturally in the metallic state but are found combined with O_2 or sulfur in their ores. A considerable amount of energy is required to extract metals from their ores, and the reverse process (which releases energy) is strongly favored as the metal reverts back to its natural state. Generally, it can be said that the more difficult it has been to win the metal from its natural form, the greater will be its tendency to return to that form by corroding, but the rate of return will, of course, depend on the environment.

7.7.1.2 Electrochemical Corrosion

The reaction of metals in aqueous solutions or under moist conditions (known as wet corrosion) is electrochemical in nature, involving the transfer of electrical charges across the boundary formed by the metal surface and its environment. An electrolyte is a medium that conducts electricity by

the movement of ions, the cations (e.g., Fe^{2+}) and anions (e.g., Cl^-) moving in opposite directions. When an electrode reaction takes place at a metal surface, the electron flow in the metal corresponds to an ion flow in the electrolyte.

When a metal corrodes, atoms of the metal are lost from the surface as cations, leaving behind the requisite number of electrons in the body of the metal. This dissolution of the metal is called an *anodic reaction* and takes place at a surface termed an *anode*; an anodic reaction always involves the release of electrons or electrochemical oxidation. Thus, for the case of a metal, M,

$$\underset{\text{(reduced)}}{M} \rightarrow \underset{\text{(oxidized)}}{M^{n+}} + n \text{ electrons} \tag{7.1}$$

Simultaneously, reagents in the electrolyte solution react with the metal surface to remove electrons left behind by the departing metal ions. This removal of electrons is termed a *cathodic reaction* and takes place at a surface called a *cathode*. The cathodic reaction always involves the consumption of electrons or electrochemical reduction.

Since practically all metals are covered with an oxide film, this must be removed before the metal can be exposed to an electrolyte. A metal covered with an oxide has different properties in solution from a bare metal, but in studying electrochemical corrosion, it is simplest to begin with the ideal case of a pure, bare metal electrode on which the only reaction occurring is metal dissolution.

7.7.1.3 Electrochemical Series

The removal of electrons from a metal to form an ion involves energy. When a metal with a high reaction energy is in an electrolyte, and is connected to one of lower reaction energy in the same electrolyte, electrons will flow from the high to the low energy level. If an infinite resistance voltmeter is placed across the system, it will show the difference in potential (E) between the two metals; this is a measure of the relative tendencies of the metals to corrode in the particular environment involved.

Because only differences in potential are measurable and not absolute values, it is desirable to have some reaction equilibrium as a datum or reference zero of potential from which other potentials could be measured. This was chosen as hydrogen gas at a pressure of 1 atm in equilibrium with hydrogen ions at pH = 0 and 25°C, and is taken as zero. Potentials measured relative to this reaction are indicated as E_H in volts. A list of equilibria and standard electrode potentials obtained from such measurements is usually called the *electrochemical series* or the *electromotive force series*, and an abridged version is shown in Table 7.6. The gold or noble end of the series is the cathodic end, and the aluminum or base end the anodic end. The further down the series a metal appears, the more readily it will give up its electrons—that is, it is more electropositive and has a greater potential to corrode.

The potentials shown in Table 7.6 refer to metals free from an oxide film. Aluminum, which covers itself with a highly protective oxide film that can be difficult to remove, commonly gives values much less negative than that indicated in Table 7.6, so that aluminum is frequently "nobler" than, for example, chromium.

While oxide films on the metal tend to shift the potential in the positive (noble) direction, the presence of salts that form complex ions containing the metal in question renders the potential abnormally negative. This is particularly important in the case of tinplate and is discussed further in Section 7.7.2.1.

In many ways, hydrogen behaves like a metal, and the chemical reduction of hydrogen ions can balance the corrosion reaction or ionization of any metal whose potential occurs below the hydrogen/hydrogen-ion equilibrium potential. Iron and tin will always tend to corrode in aqueous

Practice

TABLE 7.6
Electrochemical Series

Equilibrium Reaction	E_H (volts)	
Cathodic end		
$Au^{2+} + 2e^- \Leftrightarrow Au$	+1.50	
$\frac{1}{2}O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O$	+1.23	
$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$	+0.77	
$\frac{1}{2}O_2 + H_2O + 2e^- \Leftrightarrow 2OH^-$	+0.40	
$Cu^{2+} + 2e^- \Leftrightarrow Cu$	+0.34	
$2H^+ + 2e^- \Leftrightarrow H_2$	0.00 by definition	Increasing potential to corrode
$Pb^{2+} + 2e^- \Leftrightarrow Pb$	−0.13	
$Sn^{2+} + 2e^- \Leftrightarrow Sn$	−0.14	
$Ni^{2+} + 2e^- \Leftrightarrow Ni$	−0.25	
$Fe^{2+} + 2e^- \Leftrightarrow Fe$	−0.44	
$Cr^{3+} + 3e^- \Leftrightarrow Cr$	−0.74	
$Al^{3+} + 3e^- \Leftrightarrow Al$	−1.66	
Anodic end		

environments since the ionization or corrosion reaction can be balanced by hydrogen-ion reduction (i.e., evolution of hydrogen gas):

$$2Fe \rightarrow Fe^{2+} + 2e^- \tag{7.2}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{7.3}$$

If the concentration of hydrogen ions is increased (i.e., the aqueous environment has a lower pH), then the rate of the reaction tends to increase.

For those metals above the hydrogen/hydrogen-ion equilibrium (i.e., those metals which have a positive E_H), hydrogen-ion reduction will not give a balancing reaction for their corrosion, and some other reaction must be available if they are to corrode. The reduction of gaseous O_2 is such a reaction, except in the case of gold. If free O_2 were available, the corrosion reaction would be balanced by O_2 absorption, and, in the case of tin, the balanced reactions would be

$$Sn \rightarrow Sn^{2+} + 2e^- \tag{7.4}$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{7.5}$$

It follows that the reduction of any available free O_2 will assist hydrogen-ion reduction in balancing the corrosion of metals that are below the hydrogen/hydrogen-ion potential (i.e., have a negative E_H). This explains why, for example, in the canning of foods, positive attempts are made to remove O_2 from the can prior to seaming on the can end.

It is important to realize that the thermodynamic approach, as embodied in the electrochemical series, has severe limitations if used as a single basis for any theory of corrosion. This is because the effect of films that may form on metals under a variety of conditions is not taken into account by theories based only on the electrochemical series. For example, since chromium and aluminum are both more basic than iron, the electrochemical series predicts

that they are both more liable to corrode. This is often interpreted as implying that they would both corrode more rapidly than iron. However, it is well known that these metals are far more corrosion resistant than iron in a wide variety of practical environments. In fact, chromium is added to steel in substantial quantities as an alloying constituent to produce corrosion-resistant stainless steels.

7.7.1.4 Factors Affecting the Rate of Corrosion

7.7.1.4.1 Polarization of the Electrodes

The potentials recorded in Table 7.6 represent equilibrium values. When a current flows, there is a change in the potential of an electrode; this is known as *polarization*. As the current begins to flow, the potential of the cathode becomes increasingly negative and the anode increasingly positive. Consequently, the potential difference between the anode and the cathode decreases until a steady state is reached when corrosion proceeds at a constant rate. Thus, the corrosion current and, therefore, the corrosion rate will be affected by anything that affects the polarization of the electrodes.

The potential at which the reaction takes place changes by an amount called the *overpotential*, η, which is defined as

$$\eta = E_{corr} - E_i \tag{7.6}$$

where E_{corr} is the corrosion potential and E_i is the polarized potential. The anodic overpotential η_a drives the metal dissolution process, and the cathodic overpotential η_c drives the cathodic deposition process (Mannheim and Passy, 1982).

The dominant polarization term controlling the corrosion rate of many metals in deaerated water is the hydrogen overpotential at cathodic areas of the metal. The hydrogen overpotential for iron at 16°C in 1N hydrochloric acid is 0.45 V, and for tin at 20°C in 1N hydrochloric acid, it is 0.75 V. The possible significance of this difference in hydrogen overpotential as it affects corrosion of tinplate is discussed in Section 7.7.2.1.

7.7.1.4.2 Supply of Oxygen

The rate at which O_2 is supplied largely governs the rate of corrosion, because corrosion by O_2 reduction requires the presence of O_2 for the cathodic reaction to proceed (see Equation 7.5). The rate of supply is proportional to the rate at which O_2 diffuses to the metal surface, and this depends on the concentration of dissolved O_2 in solution. This is further justification for the practice of attempting to remove all the O_2 from canned foods prior to seaming on the can end.

7.7.1.4.3 Temperature

The rate of corrosion generally increases with increase in temperature, as more reactant molecules or ions are activated and are able to cross over the energy barrier. Furthermore, increasing the temperature tends to increase the rate of diffusion of molecules or ions in a solution, although the solubility of O_2 in water decreases with increasing temperature.

7.7.1.5 Passivity

In Section 7.7.1.2, the dissolution process of a metal was described as an oxidation process of the general form $M \rightarrow M^{n+} + n$ electrons. If the metal can be oxidized to an oxide that is stable in the electrolyte, then the metal is rendered passive (i.e., passivated). Passivation usually requires strong oxidizing conditions.

Thus, corrosion-resistant metals and alloys can withstand an aggressive environment because of the presence of thin films of adherent oxides on their surfaces. The oxide layer will completely stop the anodic reaction, which is the direct cause of corrosion, and if the film is insoluble in

the electrolyte solution, then it will form an insulation barrier that will reduce the rate of the cathodic reaction.

For example, iron is readily attacked by dilute nitric acid, but is inert in concentrated nitric acid because a thin, protective film is formed. As a result, iron behaves in concentrated nitric acid like a much more noble metal than it actually is. Iron can also be passivated by chromate solutions, as can tinplate, the latter being a very important step in the manufacture of tinplate. Passivation of tinplate can be achieved using an aqueous solution of chromic acid, although an electrolytic treatment in a sodium dichromate electrolyte has gained widespread favor. The resultant film is composed of chromium and chromium oxides and tin oxide, and its properties vary depending on the quantity and form of these basic components.

7.7.1.6 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a type of localized corrosion that develops by way of the simultaneous action of particular media, which, in the absence of stress, may be only mildly aggressive or even nonaggressive, and a stress that is lower than that required for purely mechanical cracking. The metal may contain internal stresses due to cold working or be externally stressed. It is not possible to formulate general rules regarding the degree of susceptibility of a material to stress corrosion or the aggressive power of a food or beverage, since this type of corrosion only takes place under specific conditions.

Failure due to SCC often occurs without signs of appreciable shape deformation, which, on initial examination, gives the erroneous impression that the cracked material is intrinsically fragile. The cracks occur in a direction perpendicular to that of the maximum tensile stress and display practically no visible signs of corrosion. Depending on the metallic material and the environment, and on the extent and distribution of the stress, the cracks are predominantly intercrystalline or transcrystalline, and are often branched to varying extents (Gelati et al., 2006).

The failure of metal packaging because of SCC is a well-known phenomenon and occurs frequently in aluminum carbonated soft drink cans where the score areas of the EOEs are particularly susceptible in the presence of humid environments. The first failures from SCC of meat and fish cans in tinplate and ECCS were recorded in the early 1980s. The phenomenon of SCC seems to have been steadily increasing over the last few years and this has been attributed to the use of increasingly thin materials of high mechanical strength and lower-radius beaded profiles, the adoption of EOEs and, finally, the production of foods with complex formulations (Gelati et al., 2006). In order to maintain certain mechanical characteristics, a reduction in thickness must be accompanied by a modification in the design of the can (e.g., an increase in the number and a decrease in the radius of curvature of the beading or corrugations used to reinforce the can wall). These modifications can create deformation and residual stress that, combined with corrosive environments, can give rise to the conditions that trigger SCC.

7.7.2 Corrosion of Tinplate

7.7.2.1 Corrosion of Plain Tinplate Cans

7.7.2.1.1 Reversal of Polarity

The tinplate surface consists of a large area of tin and tiny areas of exposed tin–iron alloy ($FeSn_2$) and steel as a result of pores and scratches in the tin coating. Although the now obsolete hot-dipped tinplate had a substantial tin–iron alloy layer, ETP has a much thinner layer, which is electropositive to the base and also to the tin, thus acting as a chemically inert barrier to attack on the steel base. The effect of this barrier is to prevent a significant increase in the steel cathode area. Thus, the density or degree of continuity of the alloy layer has a material effect on the rate of corrosion. The alloy–tin couple test gives a good indication of the continuity of the alloy layer in tinplate.

In the case of tinplate exposed to an aerated aqueous environment, tin is noble (i.e., cathodic) to iron according to the electrochemical series. Therefore, all the anodic corrosion is concentrated on the minute areas of steel and the iron dissolves (i.e., rusts). In extreme cases, perforation of the sheet may occur. This is the process that occurs on the external surface of tinplate containers.

However, inside a tinplate can, the tin may be either the anode or the cathode, depending on the nature of the food. In a dilute, aerated acid medium, the iron is the anode and it dissolves, liberating H_2. In deaerated acidic food, iron is the anode initially, but later, reversal of polarity occurs and the tin becomes the anode, thus protecting the steel. Tin has been described in this situation as a *sacrificial anode*. This reversal occurs because certain constituents of foods can combine chemically with Sn^{2+} ions to form soluble tin complexes. Consequently, the activity of Sn^{2+} ions with which the tin is in equilibrium is greatly lowered, and the tin becomes less noble (i.e., more electropositive) than iron.

7.7.2.1.2 Rate of Tin Dissolution

Corrosion in deaerated acidic food cans comprises three stages as shown in Figure 7.9. During the first stage, the oil and tin oxide layers are removed from the can surface and the rate of tin dissolution is high. Oxygen and other depolarizers are reduced. This stage lasts from 4 to 15 days depending on the nature of the food. The mirror surface of the tin coating should change to one in which the shape of the individual tin crystals may be seen with the naked eye.

In the second stage, the corrosion rate is slow and almost constant. Continued dissolution of the tin causes enlargement of the existing pores and scratches, exposing the alloy layer and the steel. The exposed steel provides sites for cathodic reaction and the evolved H_2 is taken up by the depolarizers in the food. The area of exposed steel dictates the rate of H_2 evolution, and as the ratio between the areas of tin and steel decreases (i.e., as more steel is exposed), polarization decreases. This stage is slow and can last for over 2 years.

The third stage is characterized by a high rate of tin and iron dissolution. As large areas of steel become exposed, H_2 evolves at a faster rate and accumulates in the can causing swelling. Once the internal pressure in the can causes the ends of the can to bulge, the product is no longer saleable since consumers cannot distinguish between a swollen can caused by microbial spoilage or H_2 evolution. Moreover, the metal content of the food may have reached an unacceptable level by this stage. Therefore, this third stage is of little importance because, by this time, the food will have reached the end of its acceptable shelf life.
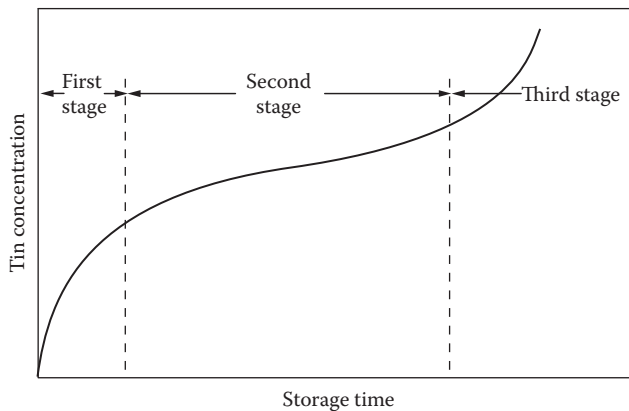

FIGURE 7.9 Schematic rate curve for tin dissolution in acidic foods. (From Mannheim, C. and Passy, N., *CRC Crit. Rev. Food Sci. Nutr.*, 17, 371, 1982.)
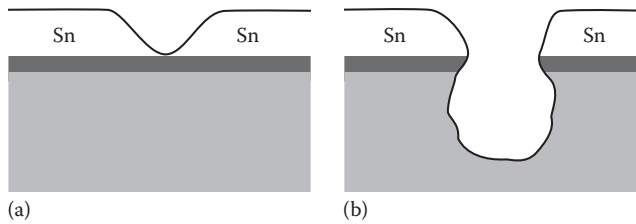
FIGURE 7.10 Schematic diagram illustrating two possible corrosion mechanisms of plain tinplate: (a) anodic tin and (b) cathodic tin.

7.7.2.1.3 Possible Tin–Iron Couple Situations

Four possible scenarios are possible in plain tinplate cans depending on the nature of the food and the presence of depolarizers.

7.7.2.1.3.1 Normal Detinning   Normal detinning is an essential process in plain cans of most foods. It has already been described earlier as the second stage and leads initially to etching and later detinning of the can. In this situation, the tin is anodic to iron and affords complete cathodic protection. Tin dissolution and H_2 evolution at the exposed steel are slow, with the area of exposed steel determining the couple current. The dissolved tin forms complexes with food components and the H_2 attaches itself to the depolarizers. Food products characteristic of this type of corrosion include low pH products such as citrus, pineapple, peach and apricot packed in plain tinplate cans.

7.7.2.1.3.2 Rapid Detinning   Rapid detinning occurs when the tin is sufficiently anodic to protect the steel but the couple current is high. This leads to a rapid rate of tin dissolution and hydrogen evolution as shown in Figure 7.10a. Rapid detinning is caused by the use of tinplate with a tin coating mass that is too light, or by a product that is intrinsically too corrosive or contains corrosion accelerators (also known as *depolarizers*) such as dissolved O_2 or anthocyanins, which are chemically reduced. Food products characteristic of this type of corrosion include tomato and aggressive citrus products such as lemon juice, as well as berry fruits.

7.7.2.1.3.3 Partial Detinning and Pitting   With partial detinning and pitting, the tin is anodic to iron, but protection is limited because local anodes on the latter are more anodic than the tin. Early failure occurs because of H_2 swelling or perforation as a result of the exposed steel continuing to corrode. This type of behavior is associated with products such as prunes or pear nectar, or with steel of inferior quality.

7.7.2.1.3.4 Pitting Corrosion   Pitting corrosion is a reversal of the normal situation, with iron being anodic to tin. Thus, the tin does not corrode, but pitting corrosion of the base steel occurs at imperfections in the tin coating as shown in Figure 7.10b. In rare cases, pitting corrosion also occurs when the tin is in fact corroding but at too slow a rate to provide sufficient electrochemical protection to the exposed steel. Pitting corrosion used to be rare, appearing in highly corrosive products such as pickles and carbonated beverages formulated with phosphoric acid. However, it is becoming more common and, for example, is the single greatest cause of failure in canned pears and pear products.

7.7.2.2 Corrosion of Enameled Cans

As discussed earlier in this chapter, food cans with enamel coatings are used to protect against excessive dissolution of tin, sulfide staining, local etching and change in color of pigmented products such as berry fruits. However, the use of enamels will not guarantee the prevention of corrosion and, in some cases, may actually accelerate it. Therefore, careful consideration must be given before selecting an enamel system for a particular canned food.

The general pattern of corrosion in enameled cans is very different from that in plain cans, and is generally more complex. It depends not only on the quality of the base steel plate, the tin–iron alloy layer and the tin coating, but also on the passivation layers and the nature of the enamel coating. The only exposure of metal in an enameled can is at pores and scratches in the enamel coating and at cracks along the side seam. Some of these discontinuities in the enamel coating may coincide with pores in the tin coating, thus resulting in exposure of the steel. Even if defects in the enamel film expose only the tin coating, the availability of all the corrosion promoters in the can for attack on the limited areas of tin ensures that steel is soon exposed. Because these areas of exposed steel are virtually unprotected either by the electromechanical action of a tin coating or by dissolved tin, corrosion may proceed at a rapid rate, resulting in H_2 swelling or perforation of the can. Thus, it is possible to actually reduce the shelf life of a canned product by using an enameled can instead of a plain one.

The effectiveness of an enamel coating is related directly to its ability to act as an impermeable barrier to gases, liquids and ions, thereby preventing corrosive action on the protected surface. The transport of ions through the enamel is governed by the electrochemical characteristics of the film. This is in contrast to the transport of gases and liquids, which involves dissolution in, and diffusion through, the enamel film under a concentration gradient. Because ions are electrically charged, their transfer through the enamel coating (actually the flow of an electric current) is complex and depends not only on their electric charge, but also on the concentration of the electrolyte. If the transport rate of cations and anions through the coating differs, the coating itself may become charged. Thus, the protection offered by the enamel coating depends on its resistance to ion transfer, which may take place even in the absence of pores, scratches or blisters.

The performance of enameled food cans is greatly affected by the thickness of the enamel coating. A thickness of 4–6 μm is sufficient for nonaggressive products such as apricots and beans, but aggressive products such as tomato paste require thicknesses of 8–12 μm, the heavier coatings having much lower porosities.

Two possible electrochemical corrosion mechanisms in enameled cans are presented in Figure 7.11. In a plain can, the product would attack the tin layer, causing it to dissolve. The presence of an enamel coating protects the surface, and tin dissolution occurs only from both sides of a scratch under the enamel or through a pore, causing anodic undermining (Figure 7.11a). Because only a very small area is in contact with the product in the can, dissolution is slow. With time, the exposed area increases, and detachment of the enamel may be observed, resulting in the appearance of enlarged pores in the enamel coating. The tin–iron alloy layer may also be visible as a grayish color. Because (in theory) the alloy layer is more passive than tin and iron, it should dissolve only after all the tin and iron. However, because of its extreme thinness and its coupling effect with the tin, the potential of the can may be nobler than that of iron, which may also go into solution. In this situation, the enamel coating may serve as the cathode due to diffusion of protons through it.
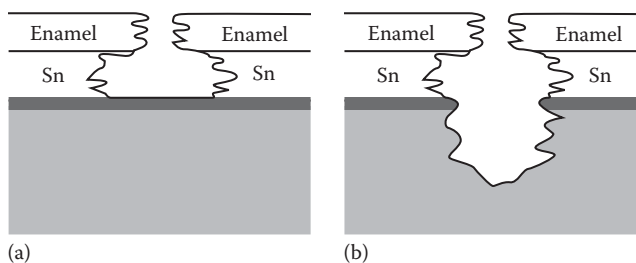

(a)

(b)

FIGURE 7.11 Schematic diagram illustrating two possible corrosion mechanisms of enameled tinplate: (a) anodic tin and (b) cathodic tin.

Mannheim and Passy (1982) used tomato concentrate as an example of the preceding scenario. Although the overall rate of tin dissolution is reduced in the presence of an enamel coating, protection of the steel by the tin is also impaired due to reduction in the ratio of exposed tin to steel areas. Corrosion is concentrated in small areas and strong local currents may occur. The presence of corrosion accelerators such as nitrates aggravates the situation.

Where the alloy and iron are more anodic than the tin (as illustrated in Figure 7.11b) the alloy layer dissolves rapidly and the iron is attacked. However, because no tin is dissolved, the alloy layer is not laid bare and, thus, has no influence on the corrosion process. Failure eventually occurs due to pinhole formation (also known as *pitting corrosion*) but there is no undermining of the enamel, with corrosion usually starting at a point of discontinuity such as a scratch or pore in the coating. Aggressive products such as beets in acetic acid and berries are responsible for this type of corrosion. The cans do not appear to be corroded, and it is only on closer inspection (usually with a hands lens) that spots of corrosion (often with deep penetration into the steel) are visible.

Failure of enameled cans is often due to a reduction in the bond between the enamel and the metal surface, resulting in eventual lifting of the enamel coating. Thus, good adhesion is required to prevent anodic reactions, to counteract forces developed under the coating due to physical or chemical factors and to ensure an aesthetic appearance.

7.7.2.3 Corrosiveness of Foods

Food products and beverages are extremely complex chemical systems covering a wide range of pH and buffering properties, as well as a variable content of corrosion inhibitors or accelerators. Factors that influence the corrosiveness of food products and beverages can be divided into two groups: intensity and type of corrosive attack inherent in the food itself, and corrosiveness due to the processing and storage conditions. All these factors are interrelated and may combine in a synergistic manner to accelerate corrosion.

The most important corrosion accelerators in foods include O_2, anthocyanins, nitrates, sulfur compounds and trimethylamine. Some typical corrosion reactions associated with these accelerators and their stoichiometric equivalents of dissolved tin are presented in Table 7.7.

From a corrosiveness point of view, it is convenient to divide foods into five classes:

1. Highly corrosive such as apple and grape juices, berries, cherries, prunes, pickles and sauerkraut
2. Moderately corrosive such as apples, peaches, pears, citrus fruits and tomato juice
3. Mildly corrosive such as peas, corn, meat and fish
4. Strong detinners such as green beans, spinach, asparagus and tomato products
5. Beverages are conveniently considered as a fifth class

TABLE 7.7

Some Corrosion-Promoting Agents and Their Mode of Reaction

Corrosion Accelerator	Reduction Product	Equivalent in Weight
Proton (H^+)	H_2	1 mL H_2 ≡ 5.3 mg Sn^{2+}
Oxygen (O_2)	H_2O	1 mL O_2 ≡ 10.6 mg Sn^{2+}
Sulfur dioxide (SO_2)	H_2S	1 mL SO_2 ≡ 5.5 mg Sn^{2+}
Sulfur (S)	H_2S	1 mg S ≡ 3.7 mg Sn^{2+}
Nitrate (NO_3)	NH_3	1 mg NO_3 ≡ 7.65 mg Sn^{2+}
Trimethylamine oxide (TMAO)	TMA	1 mg TMAO ≡ 1.57 mg Sn^{2+}

Source: Mannheim, C. and Passy, N., *CRC Crit. Rev. Food Sci. Nutr.*, 17, 371, 1982.

Although the aforementioned classification offers a broad guide, it is important to note that different lots or varieties of the same food can exhibit as much variation in their corrosiveness as may exist between different types of foods. Thus, for example, the same variety of fruit from different growing regions may vary significantly in terms of corrosiveness. The various factors that can influence the corrosiveness of food products and beverages are considered in more detail.

7.7.2.3.1   Acidity

No direct proportionality exists between the acidity of a product and the degree of corrosion of tinplate, that is, two products of the same acidity will not necessarily be equally corrosive. It also appears that pure solutions of organic acids are less corrosive than the fruit juices containing them, suggesting that fruit juices contain unidentified depolarizers that enhance the corrosive action of organic acids. It has been well established that the tendency of an acid to form a complex with dissolved tin has an important bearing on the relative polarity of tin and steel and, hence, the degree of corrosion (see Section 7.7.2.1).

7.7.2.3.2   pH

As is the case with acidity, no direct proportionality exists between pH and the degree of corrosion of tinplate. This is not surprising given that the reaction product when a metal is dissolved is not always an ionic species but often a solid oxide or hydroxide. The pH of the system also determines the relative cathodic protection given to steel. In some cases, tin is cathodic to steel over a certain pH range (in the case of acetic acid the range is pH 2.0–4.5), while in others, it offers protection up to pH 4; above that level it may accelerate corrosion.

7.7.2.3.3   Sulfur Compounds

Sulfur and sulfur compounds may be introduced into the can in a number of ways. They may be introduced in the form of spray residues from agricultural chemicals, residues from sulfur-containing preservatives or as components in sulfur-containing compounds such as proteins in meat, fish and certain vegetables. Proteins are degraded during heat processing, releasing free sulfide or hydrosulfide ions and evolving hydrogen sulfide gas into the headspace.

Trace amounts of sulfur compounds from agricultural chemicals (e.g., derivatives of thio- and dithiocarbamic acid fungicides) can lead to accelerated corrosion and failure of plain tinplate cans containing acid foods such as apricots and peaches. In addition, pitting corrosion can occur, and this has been attributed to inactivation of the tin coating by a protective film of sulfide having a more cathodic potential. Consequently, there is a significant reduction in the tin dissolution rate, and no electrochemical protection of the steel by the tin.

Sulfur dioxide may be directly reduced on the tin surface to sulfide or even to sulfur, with tin passing into solution and the development of unpleasant odors and flavors. Residual SO_2 accelerates corrosion through its action as a depolarizer, inducing a negative charge in the double layer. This repels the electrons from the electrode, thus shifting the potential in the positive direction (Mannheim and Passy, 1982). Trace amounts of SO_2 as low as 1 mg kg^{-1} are sufficient to accelerate corrosion, but such corrosion problems may be overcome by the use of enameled cans.

There are two types of sulfide staining. One involves iron sulfide (sometimes called sulfide black) and the other involves tin sulfides. These two types of staining do not constitute a health hazard or lead to failure of the can. However, both types may cause adverse reactions from the consumer on aesthetic grounds.
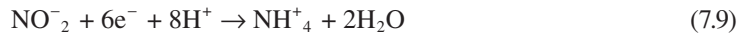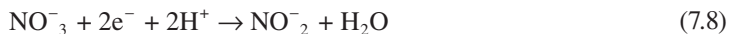
Iron sulfide stains are characteristically black, and usually occur at isolated points on the can (mainly in the headspace region) during or immediately after heat processing. Iron sulfide is not formed at pH values below about 6. Thus, it is uncommon to find iron sulfide in the portion of the can in contact with the contents. However, the pH of condensed volatile matter in the headspace may be above 6. The problem may be overcome by using enameled cans or plain cans with enameled ends.

Tin sulfide staining is usually widespread throughout the can and is blue-black or sometimes brown. Two stages are believed to be involved. The first stage is an oxidation of the tin, and the second is the deposition of an insoluble tin sulfide precipitate on the surface. It occurs during, or soon after, heat processing and shows little or no increase in intensity during storage. It may be prevented by using sulfur-resistant enamels into which quantities of zinc or aluminum compounds are added before being applied to the plate surface. These react with sulfur-bearing gases to form almost invisible white metal sulfides. However, this approach is not suitable for acid products since the acids may attack the coating to produce zinc or aluminum salts, which could be harmful to health.

7.7.2.3.4 Nitrates

Nitrates are found in fruits and vegetables grown in heavily fertilized soils, and may also occur in water supplies as a result of pollution by fertilizers. Vegetables such as green beans, spinach, turnips, lettuce, beets and radishes have often been shown to contain several thousand mg kg^{-1} of nitrates. Nitrates are very efficient cathode depolarizers since they are capable of being reduced all the way to ammonia. They have been responsible for serious economic and toxicological problems in some canned foods, notably tomato products. Although nitrates and nitrites are also present as intentional additives in processed meats, they present no problem because meat products are above the critical pH (5.5) for detinning to occur via the nitrate–tin reduction system.

Nitrates act as electron acceptors, replacing the H_2 evolution reaction with the electron–nitrate two-step reduction reaction and shifting the reaction toward increased tin dissolution. The reduction reactions involved are thought to be as follows:

$$4Sn \rightarrow 4Sn^{2+} + 8e^- \tag{7.7}$$

$$NO^-_3 + 2e^- + 2H^+ \rightarrow NO^-_2 + H_2O \tag{7.8}$$

$$NO^-_2 + 6e^- + 8H^+ \rightarrow NH^+_4 + 2H_2O \tag{7.9}$$

The first reduction reaction (Equation 7.8) is probably rate determining. The equations indicate that the rate of detinning depends on the nitrate concentration and pH. Nitrate does not immediately affect the corrosion rate, but begins to act after tin and iron ions have passed into solution. Although the ammonium ion is the major conversion product at pH 5 and less, above this pH other products are formed, including nitrous oxide (N_2O), nitric oxide (NO) and hydroxylamine. Oxygen present in the can at the time of processing triggers the nitrate-detinning reaction by increasing the initial rate of formation of Sn^{2+} (Equation 7.7).

Overcoming the problem by restricting the use of nitrate fertilizers has proved difficult, and instead efforts have been directed toward finding cultivars that do not accumulate high concentrations of nitrate. It is also possible to avoid the use of waters with high nitrate content for canning operations; a suggested maximum is 5 mg L^{-1} nitrate. The best solution to the problem at present is the use of enameled cans, although the development of corrosion inhibitors (the search for such substances is continuing) would offer an alternative solution.

7.7.2.3.5 Phosphates

Phosphates are naturally present in meat and are often intentionally added as polyphosphates to processed meat products such as hams to reduce the loss of water during processing. The presence of phosphates leads to increased discoloration due to iron phosphate and sulfide formation. One measure used to counter the effect of polyphosphate in cans of processed meats is the introduction of a small area of aluminum, which acts as a sacrificial anode, protecting the tin surface. This is not always completely successful, and parchment liners may be used in addition or as an alternative.

7.7.2.3.6   Plant Pigments

The anthocyanins and related pigments are among the most important potential corrosion accelerators (cathodic depolarizers) since they are easily reduced. Anthocyanin pigments can also act as anodic depolarizers through their ability to form complexes with cations, particularly those of iron and tin salts. Analysis of samples of canned fruits after a period of storage usually shows a greater amount of tin in the drained fruit than in the syrup, indicating that at least part of the tin is combined in an insoluble form with some constituent within the fruit.

The nature of the anthocyanin pigment is also important. For example, raspberries contain cyanidin glucosides that have *ortho*-dihydroxy groups in their structures. It is these groups that are involved in the formation of blue-tinted complexes with metals such as tin. The major pigment of strawberries is pelargonidin-3-glucoside, which does not possess the necessary *ortho*-dihydroxy groups for complex formation. Therefore, strawberries do not show the same shift to a blue color in the presence of tin salts as do raspberries.

Combination of metal ions with tannins has been observed in other fruits. For example, discoloration in canned cranberry has been attributed to the formation of a complex between tannins present in the fruit and tin salts. Darkening in canned maraschino cherries has been observed to be more severe when fruit of high tannin content is used, where a high tannin content is often found in unripe fruit and fruit that has been stored in wooden barrels. It should be noted that not all reactions between plant pigments and metal ions will produce undesirable colors, although this is usually the case with anthocyanin pigments.

7.7.2.3.7   Synthetic Colorings

Canned products that most commonly contain synthetic colorings are soft drinks, which consist basically of sugar-based syrups and carbonated water containing flavors, acidulants and colors. The behavior of soft drinks largely depends on the presence of azo dyes (e.g., amaranth) and the amount of residual O_2 in the filled can. Both of these components are capable of acting as corrosion accelerators and are potentially active corrosive agents. Tin dissolution may adversely affect the color of some products, and iron dissolution may lead to perforation and flavor defects. Thus, fully enameled cans are essential, it being important to obtain near-perfect coverage by the enamel.

7.7.2.3.8   Copper

Foods containing dissolved copper will deposit it when put in a metallic container, and, in acid products, this can lead to accelerated corrosion, either by tending to strip the tin or by producing local attack on the steel. The basic reason why copper accelerates the corrosion of steel is because copper catalyzes the reduction of O_2.

In the past, copper entered products by the solution of copper oxide from copper-bearing metal food contact equipment. However, with the replacement of copper equipment with stainless steel, the problem of copper in canned foods has been dramatically reduced. Another possible source of copper is from certain fungicides. In some cases, cannery water supplies may have unacceptably high copper levels.

7.7.2.4   Effects of Processing and Storage

7.7.2.4.1   Oxygen

Oxygen may be dissolved in food products as it is naturally present in food tissues such as fruit and vegetable cells and is inevitably entrained or absorbed by particulate products prior to their being filled into cans. Removal of as much of this O_2 as possible is an essential part of good cannery practice, and a variety of methods are used including hot filling, vacuum filling, exhausting, closure under vacuum, steam flow closure and vacuum syruping. In addition, positive control of the headspace volume is essential.

A larger headspace is likely to contain a higher residual O_2 concentration than a smaller one. However, the larger the headspace, the more room there is for accumulation of H_2 resulting from corrosion, and, thus, the greater the time required to form an H_2 swell. In practice, the cannery technologist has little room to maneuver the headspace if the declared weight on the can label is to be met.

Despite the aforementioned procedures, there will always be some O_2 present in the headspace of newly filled cans. The rate of O_2 consumption at this stage is quite rapid but decreases with time, the rate being a function of initial concentration, headspace volume, can vacuum, nature of the product and type of container. Oxygen acts as a depolarizer, accelerating corrosion by reacting with the H_2 formed in the can through a cathodic reaction, as shown in Equation 7.3.

7.7.2.4.2   Thermal Processing

Little is known about the effect of heat sterilization processes on corrosion rates, except that the quantity of metal dissolved during the process is very small. This is hardly surprising given the comparatively short processing times (typically 30–120 min) relative to the total shelf life of the canned product (typically 2–5 years). However, degradation products formed during thermal processing can become involved in corrosion (e.g., nonenzymic browning intermediates and sugar derivatives).

The importance of correct cooling has been emphasized, where failure to cool cans adequately (generally a target temperature of 40°C when the cans leave the retort) can lead to increased corrosion because the can center temperatures may take several days to return to ambient. On the other hand, cooling to too low a temperature may cause paneling of the can walls as well as external corrosion (see Section 7.7.2.5) because complete drying of the can exteriors will not occur.

7.7.2.4.3   Storage Temperature

The rate of a chemical reaction increases as the temperature is raised, and for many reactions, the rate doubles for each 10°C increase in temperature (i.e., the temperature quotient Q_{10} equals 2). Therefore, to minimize undesirable reactions such as nonenzymic browning in canned foods, it is preferable that storage temperatures are kept as low as practicable.

7.7.2.5   External Corrosion of Cans

Although tinplate is very durable in a dry atmosphere, it rusts readily in the presence of moisture, where rusting occurs more readily the thinner the tin coating. The presence of sulfur dioxide or oxides of nitrogen in the atmosphere accelerates the rate of corrosion since they dissolve to form acids. Chlorides (present in locations close to the sea) can also cause a rapid increase in the rate of corrosion.

The mechanism of external corrosion is complex. Under normal conditions on the outside of a can, tin is cathodic to iron, and when a galvanic cell is set up at pore sites, the attack on the iron is accelerated by the presence of tin. Rust forms as a result of corrosion of the iron. Three stages of exposure to the risk of external rusting may be differentiated: thermal processing, cooling of cans and storage.

7.7.2.5.1   Thermal Processing

The essential ingredient for rusting of cans during thermal processing is the presence of O_2 in the processing vessel (typically a steam retort). When cans are processed in water at atmospheric pressure (as is quite common for high acid, low pH products such as fruits), the risk reaches a maximum at a temperature of about 80°C. Above this temperature, the loss of dissolved O_2 counteracts the acceleration of the reaction rate at the higher temperatures. Therefore, when full boiling is not required, the water should be deoxygenated and preferably treated with corrosion restrainers.

When cans are processed in steam, it is important that proper venting of the retort occurs so that all the O_2 initially present is displaced from the retort by the steam. In addition, bleeder

valves should be left open so that any residual or incoming O_2 may escape. As well as minimizing any external corrosion, the removal of air from the retort prevents pockets of air from surrounding individual cans and insulating them from the steam, the latter situation leading to underprocessing.

7.7.2.5.2 Cooling of Cans

Cans are typically cooled after thermal processing by passing water through the retort or placing the cans in cooling canals. However, in some canneries, hot cans are removed from the retort and left to cool in the air. If cans are cooled with water, it is a regulatory requirement in virtually every country that such water contain a measurable amount of bactericide (typically chlorine) when it exits the retort. In the case of chlorine, this usually means that incoming water has a free chlorine content of around $5–10\,mg\,L^{-1}$.

When cans are water cooled, they should be around 40°C when they are removed from the retort. If they are warmer than this, there is the risk of thermophilic spoilage, chemical degradation and significant internal corrosion. On the other hand, if they are cooler than this, insufficient heat will remain to evaporate any water adhering to the exterior of the can. Cans should be stacked in such a way so as to enable self-drying prior to labeling and packing.

The addition of a wetting agent to the cooling water, or the spraying of a dilute solution of a wetting agent onto the cans as they leave the cooling water, facilitates rapid drainage of the water and leaves it as a quickly evaporating thin layer rather than as isolated droplets. Accelerated drying methods such as the use of hot air, or a steam spray, or rolling cans over a sterile absorbent surface, have advantages in minimizing external corrosion of cans.

7.7.2.5.3 Storage

If corrosion is to be prevented during storage, then the atmosphere surrounding the can must be free of corrosive vapors or chemicals, and not promote condensation of moisture. In addition, packaging materials in contact with the cans (generally paperboard cartons closed with adhesives) should be as free as possible from soluble chlorides, sulfates or other salts that may promote condensation of moisture and corrosion. Cartons usually have a water content of 10%–12%, and when the air temperature rises, moisture evaporates from the cartons in the warmer outer zone and condenses in the cooler center of the stack. The time for rust to develop on wet cans held at various temperatures is presented in Table 7.8.

TABLE 7.8
Time–Temperature Profile for Rust to Develop on Wet Cans of Vegetables Held in a Saturated Moisture Atmosphere

Temperature (°C)	Storage Limits
26.7–37.8	4 h
15.6–21	1 day
10	2 days
4	4 days
0	6 days
−6.7 or below	≥90 days

Source: Yang, T.C.S., Ambient storage, in: *Food Storage Stability*, Taub, I.A. and Singh, R.P. (Eds), CRC Press, Boca Raton, FL, pp. 435–458, 1998.

The shrink or stretch wrapping of cans, while protecting them from promoters of corrosion found in the atmosphere, can cause problems of condensation. If the air inside the shrink wrap contains a considerable quantity of water vapor and the package is later subjected to a drop in temperature, condensation will occur.

Rusting can also be caused by unsuitable conditions of transport and storage where cycling of the humidity (described as "sweating") occurs (Yang, 1998). This is especially so when cans are transported from temperate to tropical areas, or temperate to temperate areas via the tropics (e.g., from Australia to North America). Attempts to prevent condensation of moisture by free movement of air have usually been unsuccessful because the center of a stack of cartons filled with cans takes a long time to respond to the external temperature change and may remain below the dew point for long periods.

7.7.3 CORROSION OF ECCS

Although the chromium/chromium oxide layer on ECCS cans is only ~1/30–1/50 the thickness of a typical tinplate coating, it transforms the base steel into an excellent canmaking material by providing rust protection, outstanding enamel coating adhesion and good resistance to underfilm sulfide staining. However, ECCS cannot be used in food packaging unless it is enameled because of its lack of resistance to corrosion. Two-piece ECCS cans have significantly lower product iron contents compared with three-piece tinplate cans.

7.7.4 CORROSION OF ALUMINUM

Unlike plain carbon steel, unalloyed aluminum has excellent corrosion resistance in natural environments. In aluminum alloys, alloying elements are not used to improve corrosion resistance as chromium does in steel, but to improve mechanical strength (Reboul and Baroux, 2011). Aluminum rapidly forms a protective oxide film when exposed to air or water:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \tag{7.10}$$

The film is extremely thin (about 10 nm) but it renders the metal completely passive in the pH range 4–9. Because aluminum oxide is amphoteric, it will dissolve in acid or alkali to give the soluble aluminum cation or anion, respectively:

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \tag{7.11}$$

$$Al_2O_3 + 2OH^- \rightarrow 2AlO^-_2 + H_2O \tag{7.12}$$

Although, in practice, aluminum will corrode in acid solutions (pH below 4) and alkali (pH above 9), its corrosion resistance is excellent in the neutral range of pH 4–9. Having a strongly negative electrode potential ($E_H = -1.66$), aluminum is liable to undergo severe corrosion if brought into metallic contact with copper, iron or other more positive metals in the presence of an electrolyte (e.g., fruit juice). Thus, care must be taken to ensure that situations that could lead to such corrosion (e.g., processing equipment having food contact surfaces that contain both aluminum and stainless steel parts) are avoided.

Aluminum levels are generally very low because of the very good enamel systems that prevent contact of the food with the metal. However, in certain products such as beer, even very low levels of aluminum can cause cloudiness or haze and render the product unacceptable.

Pitting corrosion of aluminum EOEs on cans of fruit juices has been experienced, with the corrosion taking place mainly along the depressed score line if the underside organic coating is torn or

damaged by the scoring operation. Corrosion takes place with high chloride content products such as tomato and vegetable juices and is accelerated when the end is used with a tinplated can body. This is because the aluminum end is anodic to the can body. This problem can be overcome by reapplying enamel to the end after scoring.

Products containing brine should not be packed in aluminum as they can produce rapid and dramatic corrosion, with such corrosion becoming apparent in the form of container or end perforation within 24 h (Turner, 1998).

Although no foods have a pH greater than 8, cleaning solutions used in food processing plants frequently have pH values of 13. It is, therefore, important that these solutions do not come into contact with aluminum packaging materials, and that any package-contact surfaces that are cleaned with these solutions are thoroughly rinsed with water afterward.

REFERENCES

Bishop P.W. 1978. Who introduced the tin can? *Food Technology* 32(4): 60–64, 67.

Catalá R., Alonso M., Gavara R., Almeida E., Bastidas J.M., Puente J.M., de Cristaforo N. 2005. Titanium-passivated tinplate for canning foods. *Food Science and Technology International* 11: 223–227.

Chihara T., Yamazaki K. 2012. Evaluation function of drinking ease from aluminum beverage bottles relative to optimum bottle opening diameter and beverage type. *Applied Ergonomics* 43: 157–165.

Cowell N.D. 2007. More light on the dawn of canning. *Food Technology* 61(5): 40–45.

Farrer K.T.H. 1980. *A Settlement Amply Supplied*. Victoria, Australia: Melbourne University Press.

Garcia R., Adrian J. 2009. Nicolas Appert: Inventor and manufacturer. *Food Reviews International* 25: 115–125.

Gelati S., Peňalba F., Gomez X., Ferretti C., Montanari A. 2006. Stress corrosion cracking in tinplate destined for legume and pet food packaging. *Corrosion Engineering Science and Technology* 41: 297–303.

Grassino A.N., Grabarić Z., Pezzani A., Squitieri G., Berković K. 2010. Corrosion inhibition with different protective layers in tinplate cans for food preservation. *Journal of the Science of Food and Agriculture* 90: 2419–2426.

Hernandez R.J., Giacin J.R. 1998. Factors affecting permeation, sorption, and migration processes in package-product systems. In: *Food Storage Stability*, Taub I.A., Singh R.P. (Eds). Boca Raton, FL: CRC Press, pp. 269–330.

Jiang C., Driffield M., Bradley E.L., Castle L., Oldring P.K.T., Guthrie J.T. 2010. The behavior of MEKO-blocked isocyanate compounds in aluminum flake pigmented, polyester–polyurethane can coating systems. *Journal of Coating Technology and Research* 7: 57–65.

Kraus F.J., Tarulis G.J. 2009. Cans, steel. In: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam K.L. (Ed.). New York: John Wiley & Sons, pp. 205–216.

Lamberti M., Escher F. 2007. Aluminium foil as a food packaging material in comparison with other materials. *Food Reviews International* 23: 407–433.

Lampi R. 2009. Military food packaging. In: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam K.L. (Ed.). New York: John Wiley & Sons, pp. 772–786.

Li J., Huang J., Zhou G., Tian Y., Li Y. 2011. Study on the growth mechanism of electrolytic chromium coated steel (ECCS). *Advanced Materials Research* 154–155: 663–666.

Mannheim C., Passy N. 1982. Internal corrosion and shelf-life of food cans and methods of evaluation. *CRC Critical Reviews in Food Science and Nutrition* 17: 371–407.

Mokwena K.K., Tang T. 2012. Ethylene vinyl alcohol: A review of barrier properties for packaging shelf stable foods. *Critical Reviews in Food Science and Nutrition* 52: 640–650.

Morgan E. 1985. *Tinplate and Modern Canmaking Technology*. Oxford, England: Pergamon Press.

Oldring P.K.T., Nehring U. 2007. *Packaging Materials. 7. Metal Packaging for Foodstuffs*. Brussels, Belgium: ILSI Europe.

Pan X., Sengupta P., Webster D.C. 2011. High biobased content epoxy-anhydride thermosets from epoxidized sucrose esters of fatty acids. *Biomacromolecules* 12: 2416–2428.

Reboul M.C., Baroux B. 2011. Metallurgical aspects of corrosion resistance of aluminium alloys. *Materials and Corrosion* 62: 215–233.

Silbereis, J. 2009. Metal cans, fabrication. In: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam K.L. (Ed.). New York: John Wiley & Sons, pp. 727–742.

Thorne S. 1986. *The History of Food Preservation*. London, England: Parthenon Publishing Group.

Turner T.A. 1998. *Canmaking: The Technology of Metal Protection and Decoration*. London, U.K.: Blackie Academic & Professional.

Turner T.A. 2001. *Canmaking for Can Fillers*. Boca Raton, FL: CRC Press.

Whitaker R. 2007. Metal packaging and chemical migration into food. In: *Chemical Migration and Food Contact Materials*, Barnes K.A., Sinclair C., Watson D.H. (Eds). Boca Raton, FL: CRC Press, pp. 251–270.

Wicks Z.W., Jones F.N., Pappas S.P., Wicks D.A. 2007. *Organic Coatings: Science and Technology*, 3rd edn. New York: John Wiley & Sons Inc.

Yang T.C.S. 1998. Ambient storage. In: *Food Storage Stability*, Taub I.A., Singh R.P. (Eds). Boca Raton, FL: CRC Press, pp. 435–458.

Zumelzu E., Rull F., Ortega C., Cabezas C. 2009. Effect of temperature on polyethylene terephthalate coated ECCS plates in acetic-acetate medium. *Journal of Applied Polymer Science* 113: 1853–1859.