Chapter 1

Introduction to Coatings

Coatings have been used since prehistoric times to protect objects and convey information, and they are ubiquitous in modern society as they serve to both protect substrates and impart aesthetic qualities to improve objects’ appearance. If you are reading this text in a traditional paper book, the paper is coated. Look up and the walls of your room are coated, as are the windows. If you are wearing glasses, the lenses are likely coated to improve the plastic’s scratch resistance and absorb UV radiation. If you are reading this text on a computer screen, the screen is coated to prevent glare and perhaps reduce fingerprints. The CPU inside your computer exists because of coatings used during the printing of nanometer-sized circuits. If you are outside, the buildings, cars, airplanes, roads, and bridges are all coated. Objects without coatings are less common than those with coatings!

Just because coatings science is an ancient technology does not mean that innovation has ceased. Today many coatings scientists and formulators are working diligently to improve the performance of coatings, reduce the environmental impact of their manufacture and application, and create coatings that provide functionality beyond today’s coatings.

1.1 DEFINITIONS AND SCOPE

Coatings are typically thought of as thin layers that are applied to an object, which is often referred to as the substrate. Thus, one of the defining characteristics of a coating is its thinness. While the thickness of a coating depends on the purpose it serves, typical coating thicknesses range from a few microns to a few hundred microns, but of course, exceptions to this are common. Historically, the thickness of a coating was often quoted in terms of mils, where 1 mil equals one thousandth of an inch or 25.4 µm.

While coatings can be made from any material, this book is primarily concerned with organic coatings. Thus, we leave for other books coatings such as the zinc coatings used to galvanize steel, ceramic coatings that are formed from metal oxides or when metals such as aluminum are anodized, and the many other inorganic coatings used to impart hardness, scratch resistance, or corrosion protection. While these coatings are both technically and economically important, they lie mostly beyond the scope of this book.

Organic coatings are often composite materials in that they are composed of more than one distinct phase. The matrix, called the binder, holds the other components of the coating composition together and typically forms the continuous phase in the dry coating. As stated previously, we are mostly concerned with organic coatings, where the binder is typically an organic polymer.

A confusing situation results from multiple meanings of the term coating. As a noun coating is used to describe both the material (usually a liquid) that is applied to a substrate and the resultant “dry” film. As a verb, coating means the process of application. Usually, the intended meaning of the word coating can be inferred from the context. The terms paint and finish often mean the same thing as coating and also are used both as nouns and verbs. What is the difference between a coating and a paint? Not much—the terms are often used interchangeably. However, it is fairly common practice to use “coatings” as the broader term and to restrict “paints” to the familiar architectural and household coatings and sometimes to maintenance coatings for bridges and tanks. Some prefer to call sophisticated materials that are used to coat automobiles and computer components “coatings,” and others call them “paints.” Consumers are often familiar with the terms varnish or stain. These are types of coatings that are used to protect and beautify wood...
and are certainly within the scope of this book as they are typically made from polymeric binders with or without pigments.

Because we are limiting the scope of this book to organic coatings that are historically associated with paints, we are also choosing not to cover important materials such as coatings applied to paper and fabrics, decals, laminates and cosmetics, and printing inks, even though one could argue that these coatings share much in common with traditional paints. However, readers interested in those materials will find that many of the basic principles discussed in this text are applicable to such materials. Restrictions of scope are necessary if the book is to be kept to a reasonable length, but our restrictions are not entirely arbitrary. The way in which we are defining coatings is based on common usage of the term in worldwide business. For classification purposes, coatings are often divided into three categories: architectural coatings, original equipment manufacturer (OEM) coatings, and special purpose coatings.

As the coatings industry is a relatively mature industry, its growth rate typically paces that of the general economy. Like many other industries, growth has slowed in North America and Europe and has dramatically increased in Asia and South America as those economies have boomed. An estimate of the value of coatings used in each region is shown in Figure 1.1. The total value of the global coatings market was estimated to be approximately $112 billion in 2014 (American Coatings Association and Chemquest Group, 2015).

Figure 1.2 summarizes the estimated value and volume of coating shipments in the United States for a recent 10-year period. The effect of the economic downturn in 2008–2009 is evident (Data from American Coatings Association and Chemquest Group, 2015).

**Figure 1.1** The value of coatings used in 2014. Source: Reproduced with permission of American Coatings Association.

**Figure 1.2** Ten-year trend in coating shipments in the United States (both gallons and dollar value). Source: Reproduced with permission of American Coatings Association.
1.2 Types of Coatings

Architectural coatings include paints and varnishes (transparent paints) used to decorate and protect buildings, outside and inside. They also include other paints and varnishes sold for use in the home and by small businesses for application to such things as cabinets and household furniture (not those sold to furniture factories). Architectural coatings are often called trade sales paints. They are sold directly to painting contractors and do-it-yourself users through paint stores and other retail outlets. In 2014 in the United States, architectural coatings accounted for about 60% of the total volume of coatings; however, the unit value of these coatings was lower than for the other categories, so they made up about 49% of the total value. This market is the least cyclical of the three categories. While the annual amount of new construction drops during recessions, the resulting decrease in paint requirements tends to be offset by increased repainting of older housing, furniture, and so forth during at least mild recessions. Latex-based coatings make up about 77% of architectural coatings. Interior paints are approximately 2/3 of all architectural coatings, exterior paints 23%, and stains 7%, with the remained split among varnishes, clear coats, and others.

OEM coatings are applied in factories on products such as automobiles, appliances, magnet wire, aircraft, furniture, metal cans, and chewing gum wrappers—the list is almost endless. In 2014 in the United States, product coatings were about 29% of the volume and 31% of the value of all coatings. The volume of product coatings depends directly on the level of manufacturing activity. This category of the business is cyclical, varying with OEM cycles. Often, product coatings are custom designed for a particular customer’s manufacturing conditions and performance requirements. The number of different types of products in this category is much larger than in the others; research and development (R&D) requirements are also high.

Special purpose coatings are industrial coatings that are applied outside a factory, along with a few miscellaneous coatings, such as coatings packed in aerosol containers. This category includes refinish coatings for cars and trucks that are applied outside the OEM factory (usually in body repair shops), marine coatings for ships (they are too big to fit into a factory), and striping on highways and parking lots. It also includes maintenance paints for steel bridges, storage tanks, chemical factories, and so forth. In 2012 in the United States, special purpose coatings made up about 11% of the total volume and 20% of the total value of all coatings, making them the most valuable class. Many of today’s special purpose coatings are the product of sophisticated R&D, and investment in further improvements remains substantial.

Coatings are used for one or more of three reasons: (1) for decoration, (2) for protection, and/or (3) for some functional purpose. The low gloss paint on the ceiling of a room not only fills a decorative need but also has a function. It reflects and diffuses light to help provide even illumination. The coating on the outside of an automobile adds beauty to a car and also helps protect it from rusting. The coating on the inside of a beverage can have little or no decorative value, but it protects the beverage from the can. (Contact with metal affects flavor.) In some cases, the interior coating also protects the can from the beverage. (Some soft drinks are so acidic that they can dissolve the metal.) Other coatings reduce the growth of algae and barnacles on ship bottoms, protect optical fibers for telecommunications against abrasion and guide the light within the fiber, retard corrosion of bridges, protect wind turbine blades from erosion due to the impact of raindrops, and so on. While the public most commonly thinks of house paint when talking about coatings, all kinds of coatings are important throughout the economy, and they make essential contributions to most high-tech fields. As already mentioned, computer technology depends on microlithographic coatings to pattern the circuits in CPU and memory chips.

1.3 Composition of Coatings

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories: (1) binders, (2) volatile components, (3) pigments, and (4) additives.

Binders are the materials that form the continuous film that adheres to the substrate (the surface being coated), bind together the other substances in the coating to form a film, and present an adequately hard outer surface. The binders of coatings within the scope of this book are organic polymers—some made via synthetic organic chemistry and some derived from plant oils. In some cases, these polymers are prepared and incorporated into the coating before application; in other cases, lower molecular weight organic materials (monomers or oligomers) are mixed with the other components of the coating, and final polymerization takes place after the coating has been applied. Binder polymers and their precursors are often called resins. The binder governs, to a large extent, the properties of the coating film. The major resin types used in coatings as percentages of the total are given in Table 1.1. These numbers should be taken as approximations as different coating suppliers name their resins somewhat differently, and some coating contain more than one resin type.

Volatile components are included in a large majority of coatings and are often referred to as solvents. They play a major role in the synthesis, mixing, and application of coatings. They are liquids that make the coating fluid enough for
application, and they evaporate during and after application. Until about 1935, almost all of the volatile components were low molecular weight organic compounds that dissolved the binder components. However, the term solvent has become potentially misleading because many coatings have been developed for which the binder components are not fully soluble in the volatile components but instead act as a carrier to reduce viscosity, but not fully solvate the binder. Because of the need to reduce the environmental impact of coating manufacture and application, a major continuing drive in the coatings field is to reduce the use of volatile organic compounds (VOCs) by making the coatings more highly concentrated (higher solids coatings), by using water as a major part of the volatile components (waterborne coatings), and by eliminating solvents altogether.

Vehicle is a commonly encountered term. It usually means the combination of the binder and the volatile components of a coating. Today, most coatings, including waterborne coatings, contain at least some volatile organic solvents. Exceptions are powder coatings, certain solventless liquid coatings (also called 100% solids coatings), radiation-curable coatings, and a small but growing segment of architectural coatings.

Pigments are finely divided, insoluble solid particles, ranging from a few tens of nanometers to a few hundred microns in size, that are dispersed in the vehicle and remain suspended in the binder after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film. Additionally, pigments can provide other functions, such as corrosion-inhibiting pigments, which enhance the corrosion protecting properties of the coatings. Pigments also play a major role in the application characteristics and the mechanical behavior of coatings.

While most coatings contain pigments, there are important types of coatings that contain little or no pigment, commonly called clear coats, or just clears. Clear coats for automobiles and transparent varnishes are examples. Coating solids typically refer to the proportion of binder and pigment and are the part of the paint that remains after the volatile components have left the coating. Pigments are distinct from dyes, which are typically soluble in their binder and/or solvent and exist as individual molecules in that vehicle. Dyes are rarely used in the types of coatings discussed in this book.

Additives are materials that are included in small quantities to modify some property of the coating. Examples are catalysts for polymerization reactions, light and heat stabilizers, rheology modifiers, defoamers, and wetting agents.

## 1.4 COATING HISTORY

The chemistry of most coatings used today bears little resemblance to the coatings used prior to the industrial revolution. For centuries coatings were based on naturally occurring oils and pigments. 40,000 years ago ochre was processed for use as a pigment in Africa (Rosso et al., 2016). Cave paintings in northern Spain date from over 40,000 years ago and contain depictions of animals and people. While their true purpose is impossible to ascertain, the paintings demonstrate that even in prehistoric times people were using coatings to decorate their surroundings and to convey information to others.

In Asia, a traditional coating made from urushiol, the resin from a native tree, has been used since at least 1200 B.C. to produce beautiful clear lacquers for art objects. Egg yolk was often used as the binder for paintings in the West until the fourteenth or fifteenth century, when certain plant oils, such as linseed (also known as flax) and walnut oils, were introduced to protect and beautify wood. Those oils were also used as the binder for many of the great oil paintings made famous artists such as Michelangelo, and they continue to be favored by many artists today. During the nineteenth and early twentieth centuries, most architectural coatings employed linseed oil as the binder.

Early pigments were made from ground bones or charcoal and other minerals such as iron oxide, ochre, and calcium carbonate. Simple chemical reactions were later used to produce other pigments such as lead white (lead carbonate) and red lead (lead oxide). More chromatic pigments such as ultramarine blue were rare and expensive for centuries owing to their limited supply.

These simple binders and pigments formed the basis for almost all coatings up until the twentieth century when an explosion in our knowledge of synthetic organic chemistry multiplied the number of binders, pigments, and additives that were used in coatings. Naturally sourced binders
gave way to nitrocellulose lacquers and later enamels based on synthetic polymers. Other organic and synthetic inorganic pigments displaced some, but not all, of the naturally occurring pigments. For example, white lead carbonate gave way to titanium dioxide due to TiO$_2$’s superior hiding and reduced toxicity; and highly chromatic red pigments based on quinacridone chemistry were developed to provide colors that were previously difficult to achieve. *Hiding* refers to the capability of a coating to screen or hide the substrate from view, which is generally desirable from both aesthetic and protective standpoints.

Most people’s interaction with coatings occurs when they paint the walls of their house or refinish an old piece of furniture; and they likely believe that coatings have changed little over the course of their lives. In many ways their thoughts are justified, as the process of painting with a brush has changed little over the past 100 years. However, as shown previously, advances in chemistry have resulted in dramatic changes in the formulation of paints. In addition, since 1965 the reduction of VOCs has been a major driving force because of the detrimental effect of VOCs on air quality. Coatings have been second only to the gasoline–automobile complex as a source of VOC pollutants responsible for excess ozone in the air of many cities on many days of the year. This situation has resulted in increasingly stringent regulatory controls on such emissions. The drive to reduce VOC emissions has also been fueled by the rising cost of organic solvents. Other important factors have also accelerated the rate of change in coatings. In particular, the increasing concern about toxic hazards has led to the need to change many raw materials that were traditionally used in coatings.

### 1.5 COMMERCIAL CONSIDERATIONS

The person who selects the components from which to make a coating is a *formulator*, and the overall composition he or she designs is called a *formulation*. Throughout history, formulators have been trying to understand the underlying scientific principles that control the performance of coatings. Most coating systems are so complex that our understanding of them today is still limited. Real progress has been made, but the formulator’s art is still a critical element in developing high performance coatings. Demands on suppliers of coatings to develop new and better coatings are accelerating. Therefore, time is now too limited to permit traditional trial-and-error formulation. Understanding the basic scientific principles can help a formulator design better coatings more quickly. In the chapters ahead, we present, to as great an extent as present knowledge permits, the current understanding of the scientific principles involved in coatings science.

We also identify areas in which our basic understanding remains inadequate and discuss approaches to more efficient and effective formulation despite inadequate understanding. In some cases, in which no hypotheses have been published to explain certain phenomena, we offer speculations. Such speculations are based on our understanding of related phenomena and on our cumulative experience acquired over several decades in the field. We recognize the risk that speculation tends to increase in scientific stature with passing time and may even be cited as evidence or adopted as an experimentally supported hypothesis. It is our intent, rather, that such speculations promote the advancement of coatings science and technology by stimulating discussion that leads to experimentation designed to disprove or support the speculative proposal. We believe that the latter purpose outweighs the former risk, and we endeavor to identify the speculative proposals as such.

Cost is an essential consideration in formulation. Novice formulators are inclined to think that the best coating is the one that will last the longest time without any change in properties, but such a coating may be very expensive and unable to compete with a less expensive coating, which provides adequate performance for particular application. Furthermore, it is seldom possible to maximize all of the performance characteristics of a coating in one formulation. Some of the desirable properties are antagonistic with others; formulators must balance many performance variables while keeping costs as low as possible.

### REFERENCES
