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Understanding Coatings Raw Materials



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Understanding Coatings Raw Materials

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Foreword

The coating industry is highly raw material intensive and uses a wide range of these raw materials, from relatively inexpensive minerals to high performance polymers and pigments to highly engineered specialty additives. *Understanding Coatings Raw Materials* intends to provide a comprehensive overview of the raw materials used in contemporary paints and coatings.

Significant advances have been made in the field of polymeric materials and coatings during the past few decades. Ever since the negative impacts of solventbased coatings on the environment and human health were recognized, the coating industry has been striving not only to address these impacts but also to offer better performing products to meet the ever growing demands to decorate, protect, and provide new functionalities to surfaces. This has led to the emergence and commercialization of such advanced technologies as waterborne coatings, high-solid coatings, powder coatings, radiation curable coatings, and bio-based as well as nanomaterial based coatings, to name a few. The raw materials used in today's advanced coatings are incredibly diverse and innovative compared to those used a few decades before. Understanding this growing palette of coating raw materials and their specific roles and interactions with each other is increasingly challenging, both for new entrants as well as those already working in the coating industry.

This book is divided into five chapters. The first chapter introduces readers to the historical development and fundamentals of coatings and their compositions, thus putting the topics that follow into perspective. The following chapters cover individual families of raw materials – resins, pigments and extenders, solvents and additives – with adequate detail and practical examples in keeping with the scope of this book.

This book in hand is intended for people involved in sectors of the industry related to research and product development, production, quality assurance and testing, the supply chain, coating system

specifications, technical service and marketing. Due to the extensive coverage of these topics, this book will also be very useful for undergraduate and graduate students seeking to learn the fundamentals of coating raw materials. It will also serve as a reference book for any reader interested in paints and coatings.

Vijay Mannari, Ph.D.

Chintankumar J. Patel, Ph.D.

Ypsilanti, MI/USA, January 2015

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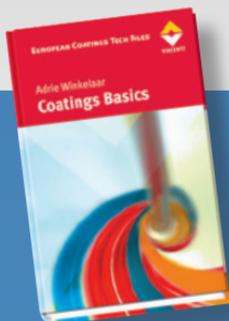
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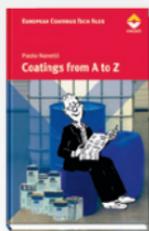
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1 Introduction to paints and coatings

1.1 Why paints and coatings?

Looking around, we find paints and coatings virtually everywhere. We see paint on the walls of our homes or offices, and on furniture, refrigerators, washing machines, and toasters with nice colorful finishes. Outdoors, we see cars with an increasing variety of coatings. Building exteriors, equipment, bridges, pipelines, superstructures, and monuments are all painted with a variety of paints and coatings. If we examine them carefully, we can also find coatings on CDs and DVDs, fruits and vegetables, medical equipment such as catheters and surgical materials, reading glasses, electronic gadgets such as iPod tablets and cell phones... coatings are everywhere! There are virtually limitless products that use some kind of paint or coating on their surface.

Paints and coatings are not useful products by themselves, but they make other products better, more durable, more attractive, safer, and more saleable. Paints and coatings are therefore considered enabling materials that add value to manufactured products. Think of a car without paint on it, or your nice teakwood furniture without a finish. Thin coats of paint, coating, or varnish bring life to these products and make them acceptable and durable.

In general, paints and coatings are used for three primary reasons:

- providing aesthetic appeal or decorative value to surfaces and products,

- providing protection from damage by the external environment, and
- providing specific attributes to the product.

Many coatings satisfy more than one of the above reasons.

Satisfying an aesthetic need is a human instinct and there is much evidence indicating the use of some paints and coatings during the prehistoric era. In present times, many products must have aesthetic appeal for their acceptance and sale. Therefore, decorative value is one of the primary requirements of many paints and coatings. Since industrialization, we have been using a large quantity of metals and alloys, besides materials such as wood and masonry. After World War II, many polymeric materials, such as plastics, alloys, and composites, have been increasingly used. All of these materials, when exposed to the environment – heat, moisture, sunlight, wind, rain – are prone to degradation due to corrosion, erosion, or other forms of physical abuse reducing their service life. As a result, there has been a considerable need to protect these surfaces from environmental attack. Coatings are used as a barrier between the surfaces of such products and the environment to provide them with long-term protection.

Since there is a variety of material surfaces, such as wood, ceramic, masonry, metals, alloys, plastics, and glass, that have a wide range of physical and chemical characteristics, it is not surprising that we need a diverse range of coatings to protect them from the external environment. In addition to functioning in decoration and protection, many coatings are formulated to provide specific attributes to the product. For example, anti-microbial coatings on interior walls of hospitals control bacterial infections in addition to making buildings aesthetically appealing. The anti-fouling coatings on ship hulls keep barnacles under control, thus keeping ship surfaces clean. Without such a coating, growth of a thick layer of attached barnacles would keep increasing ship weight, leading to reduced fuel economy. A coating intended for a gym floor has, apart from giving it an attractive look and having general protective value, a specific property – anti-skidding – that is essential for such applications. Thus, paints and coatings are used for many different reasons and are expected to meet the specific requirements of particular products.

While the terms paint and coating are frequently used interchangeably, in general, the term **paint** is used to describe materials that have the major role of improving product aesthetics or decoration, such as interior wall paints. The term coating generally refers to materials that have a more protective role and provide long-term durability to products. In this book, the term coatings will be used most frequently to refer to both paints and coatings.

1.2 *Historical perspective*

The earliest known use of paints dates back to the prehistoric era. Humans, by nature, have a sense of aesthetics and there is considerable evidence of human beings using some type of paint for decoration of their dwellings or their bodies. The Greek and Roman civilizations (from ~ 4000 BC) used paints to decorate buildings, statues and other objects. These paints were composed of a variety of natural gums, hide glue, starches, beeswax, charcoal and various clays and minerals. Jumping forward in time, it was around 1000 AD when *Rodgerus von Helmershausen*, also known as Theophilus, first described coatings and gave detailed recommendations for formulas in his book *Schedula Diversarium Artium*. These coatings were primarily based on linseed oil and natural resins (amber), without use of any volatiles due to their unavailability. The art of extracting turpentine oil from plants became known around the 10th century, and it is believed that turpentine was first used as a solvent for reducing the viscosity of coating compositions in the early 15th century. This is an important landmark in the history of coatings because on one hand, use of a volatile solvent expanded coating applications rapidly, while on the other hand, it can be considered the beginning of the era of environmental problems due to solvent emissions that the industry is struggling hard to address even today. The development of coatings by what was known as the *paint boiling* process (as it required heating natural resin and linseed oil for a long time) continued, and by the 17th century, the art of making different types of coatings using different combinations of natural resins, linseed oil and volatiles was available.

The Industrial Revolution in the 18th century brought about a dramatic change in coating demand. An increasing number of coatings were now required for protection of iron, which was used in buildings and other products. This was the time when coating materials started slowly moving from their role of **decoration** to **protection**. Even in the 19th century, with the exception of a few pigments, the raw materials for coatings were all of natural origin. After heavily exploiting petroleum-based synthetic raw materials for more than a century, it is interesting that one of the major initiatives of the coating industry today in the early 21st century, for sustainability reasons, is to go back to natural-based raw materials.

Introduction of the continuous production line by Henry Ford in the early 20th century represented the industrial-scale painting technology, which required quicker drying and more durable coatings and faster coating processes. This led to the development of quick-drying cellulose-based paints and replacement of brush-application processes by spray processes. After the launch of the first entirely synthetic resin – phenol-formaldehyde – in 1907, rapid development of other synthetic polymers such as vinyl resins, urea resins, alkyds, acrylic resins, polyurethanes, melamine resins and epoxy resins, especially during and after World War II, made available a wide range of binder for coatings. It was in 1919 when titanium dioxide, the key raw material for coatings even today, was commercially available for the first time. Many synthetic pigments, both organic and inorganic types, were also commercialized during this time.

With continued industrialization and demand for coatings for a myriad of applications, the industry witnessed a steady increase in demand. It should, however, be noted that up until mid-20th century, all coating materials were almost entirely of the **solventbased** type. Prior to 1960, there were hardly any regulations that restricted the use of toxic substances or volatile organic compounds (VOCs) in coatings. The increased usage of such coating materials, with high VOC content, resulted in high emissions, and consequently, their harmful effects on safety, health and the environment were recognized. These concerns generated a need for regulation of paints and coatings.

Rising concerns for safety, health and the environment and establishment of agencies and regulations across developed nations heralded a new era for the paint and coating industry. Toxic materials such as lead and chrome were restricted and limits on use of VOCs for paints and coatings were established during the 1960s and later. These limits became increasingly stringent over the years and required coating formulators to think of new ways to offer coatings that satisfied customers' needs while meeting the needs of regulatory requirements and cost. To address the issues of VOC reduction, three important approaches emerged:

- high-solid coatings, which are essentially solvent-based systems but formulated using a reduced amount of solvent (made possible by using low-viscosity binders),
- waterborne coatings, by replacing the majority of the solvents (VOCs) with water, and
- powder coatings, by eliminating volatiles and offering coatings in fine powder form.

These approaches required entirely new types of coating raw materials to meet their formulation, application, cure and performance requirements. They also required new crosslinking technologies that provided faster curing. For instance, ultraviolet (UV) radiation curable technology was developed that offered very short curing times to formulations that are ~100 % solid. All the above-mentioned approaches developed into the full-fledged coating technologies of today. Due to highly diverse product offerings based on these technologies, combined with increasingly demanding requirements both by customers and regulators, has resulted in an ever-widening palette of coating raw materials.

Today's coating raw materials are comprised of a range of organic, inorganic and special-effect pigments, offered both in dry form as well as dispersions in water. Resins and binders are offered as traditional solutions in organic solvents, or as advanced aqueous dispersions with a variety of particle sizes and morphologies. The above development has also resulted in the availability of a wide range of additives specific for waterbased, powder, or UV-cure coatings for optimum performance.

As with many other fields of material technology, use of nanomaterials in formulations of advanced paints and coatings has been very promising. Nanoparticle size pigments and fillers, nanopolymer dispersions, and nanoadditives are now commercially available and many more such products are in the development stage. Another important challenge for the coating raw material industry in recent years has been to offer “green” raw materials that reduce the environmental footprint of coatings. With increasing awareness and consumer interest for using bio-based and greener raw materials, researchers and industries are trying to provide such raw materials at affordable costs without compromising their performance. The outlook for future coating raw materials seems to be highly advanced, multifunctional, and with a significantly lower carbon footprint, and hence more sustainable.

1.3 Anatomy of paints and coatings

We now know the primary functions of paints and coatings and their importance in enhancing and protecting many industrial and consumer products. Now let’s look at what paints and coatings are composed of. In general, paints and coatings are liquid mixtures that are applied onto the surfaces of products using a brush, roller or spray. These mixtures are supplied in a variety of forms, such as waterborne or solventborne, low viscosity or paste-like consistency, sprayable or brushable, to meet the end use application requirements. Simply put, coatings are liquid mixtures that are spread onto a surface as a thin uniform wet layer that dries to a hard and adherent film. After application, the wet liquid film is then converted to a dry and adherent coating through a **physical drying or chemical curing process**. The nature of the films formed depends upon the composition of the paint, and varies, for example from transparent to opaque, glossy to matte, and hard to soft.

Looking at the diversity of coating types, it is not surprising that different types of coatings would have different constituents. As one would expect, all coatings must have an ingredient that forms a film. These film forming ingredients, which are essentially polymeric materials, are called **resins** or **binders**. Resins and binders

have the capability of forming transparent and adherent films, but they cannot hide or destroy the surface on which they are applied. Pigments, which are finely divided insoluble particles, colored or white, have the capability of providing color and opacity when dispersed into a medium. In general, a paint or a coating consists of **pigment** dispersed in a resinous binder, reduced to an acceptable application viscosity with a **solvent**, sometimes water. The role of the solvent is essentially to provide a suitable consistency to the pigment/resin mixture such that it can be applied uniformly as a thin layer using application equipment, such as a spray gun. In order to control some properties of coatings such as viscosity, drying time, opacity, storage stability and ease of application, some specialty chemical compounds are added to the resin/pigment/volatile mixture, in small amounts, and are known as **additives**. A typical coating may have several such additives added to improve or modify specific properties. In general, all the ingredients of coatings are classified into the following four major raw material categories:

- Resins or binders
- Pigments
- Additives
- Solvents.

1.3.1 Resins or binders

Resins (film formers or binders) are the most important components of coatings since many important properties of dry films, such as hardness, adhesion, chemical and solvent resistance and durability, are primarily dependent on the nature of the resins used. After application of coatings, resins form useful films by a variety of physical and/or chemical mechanisms that convert liquid films into a dry coating. The term **binder** is frequently used to refer to a resin since one of its roles is to “bind” pigment particles in the dry film. Resins used for paints and coatings are polymeric materials with film forming capabilities. Resins control most of the physical, chemical and mechanical properties of the coatings. It is important to note that while there are hundreds of types of polymers commercially available, only a few are useful as binders for coatings because of the specific requirements for the successful use of binders in coatings.

More details on these requirements and different types of binders are covered in Chapter 2.

1.3.2 Pigments

Pigments are finely divided colored (or white) insoluble particles having a high refractive index, typically >1.70 . Pigments, when uniformly dispersed in the resin (medium), impart color and opacity to the cured film. Thus, color and opacity are the primary functions of pigments. In addition, some pigments (for example, chrome pigments, zinc phosphate pigments) exhibit functional properties such as corrosion resistance, resistance to UV light, and anti-fouling properties. Pigments are also used to control rheology, exterior durability and mechanical properties of the films. Pigments with high light reflectivity and specific particle size and shape are used in special effect coatings. Pigments are classified based on their origin, whether natural or synthetic, and on their functions as organic, inorganic, metallic, and special effect pigments.

1.3.3 Additives

In order to facilitate manufacturing, storage and satisfactory application and to improve durability and performance, it is essential to incorporate special additives to coatings. Additives are compounds added in small quantities (up to $\sim 5\%$ by weight) that substantially improve or modify properties of coatings. These compounds include wetting and dispersing agents, which help disperse the pigment particles in the medium, driers that help faster drying of coating films, plasticizers, UV stabilizers, rheology modifiers, preservatives, and others. Their types and amounts must be carefully selected, as they may have unintended results when used inappropriately. For their successful performance, the coating formulator must have good knowledge about the role of additives and their interactions with other components of coatings.

1.3.4 Solvents

Solvents are primarily used to control viscosity of the coatings for acceptable application. These are essentially volatile compounds

that must evaporate from the film after application. Solvents also affect such properties as flow and leveling, drying time, gloss etc. A wide range of organic solvent types are used in coatings. Many of these solvents are VOCs, which have harmful effects on human health and the environment. Over the past several decades, there have been significant efforts in developed nations to reduce VOC emissions, and there are increasingly stringent regulatory requirements for use of such solvents in coatings. **Waterborne coatings**, which use water as the primary carrier replacing organic solvents, have therefore significantly grown over **solventbased coatings** as the preferred coating types for a number of end-use applications.

