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FAILURE ANALYSIS OF PAINTS AND COATINGS

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**To my son Andy,
who is always able to make me smile**

Preface

From the author's point of view there are few things more satisfying than solving a problem. The failure analysis of paints and coatings is all about problem solving, and is both a fascinating and a challenging endeavor. It requires the blending of polymer chemistry, analytical chemistry, coatings science and microscopy with the curiosity of a detective. All of these skills, with the possible exception of the last, can be studied in school or learned from books. It is putting them all together that is the trick, and which was the impetus for writing this present book.

Perhaps the most difficult part of writing this book was deciding how to organize it. A thorough knowledge of analytical techniques, including weaknesses as well as strengths, is essential in solving a coatings failure problem. However, an understanding of the chemical and physical properties of the substrate/coating system is equally important, as are the more mundane areas of samples and background information.

The approach finally decided upon was to begin with a basic review of coatings technology. Without this knowledge, it is virtually impossible to decide what to look for in the laboratory. While there are several excellent and expansive texts on the subject, it seemed impossible to write a manuscript on failure analysis without first describing the nature of what it is that we are investigating. Readers familiar with the technology may wish to skip some of these chapters, although it should be pointed out that the chapter on resins and polymers contains some specific information on failure mechanisms.

Likewise, it seemed impossible to write about the various analytical methods without first discussing their theoretical background. These discussions are admittedly very brief, as entire volumes have been written about each and every technique. Indeed, as I am personally particularly fond of analytical chemistry, it was tempting not to be more expansive here. I hope that I have adequately resisted the temptation, and have written a failure analysis book rather than an analytical chemistry one. It is, however, important to understand the basics of the various techniques, in order to appreciate their limitations. Without knowing what a technique cannot do, it is possible to make serious errors in judgment.

In a perfect world there would be no paint failures and I would have to find a different line of work. In a nearly perfect world, one would have unlimited time, excellent samples, and a handsome budget with which to solve the problems that occur. Usually, none of these three conditions exist. Furthermore, although great strides have been made there are still substantial gaps in our basic knowledge of paints and coatings. Without knowing exactly why something works, it can be difficult to say exactly why it doesn't.

As a consequence of the above, there are times when it is not possible to unequivocally determine the cause of a coating failure. However, starting with a firm understanding of coatings technology, applying the many powerful analytical techniques available, and keeping an open and inquisitive mind, the majority of coating failures can be solved. It is hoped that this text will be a step forward in that direction.

Acknowledgements

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1 General Principles of Coating Formulation

1.1 Introduction

Before discussing the chemistry or mechanics of formulating a coating, the reader needs to take a minute or two to think about all of the coated articles encountered in everyday life. The list is a very long one, including bridges, water tanks (both inside and out), cars, planes, structural steel for any number of uses, chemical process vessels, wood of all types, plastic bumpers, furniture, concrete block, cement floors, ships' hulls, electrical equipment, plaster, drywall, appliances and food containers. The list seems almost endless. It is not surprising that the first step in formulating a coating is to ask a simple question – i.e. what is this coating going to be used for?

This is a critical question, since every coating is a compromise. A coating cannot be both soft and hard, or both glossy and flat. A coating that might have superb corrosion resistance on structural steel, such as an ethyl silicate-zinc-rich primer, would be a failure as a coating for a backyard deck. Once the purpose of the coating has been identified, there are certain basic principles that can be followed to produce an effective coating.

Most coatings consist of four basic ingredients, namely a binder, pigments, solvents, and additives. Some coatings may not have all of these ingredients. For example, a 100 % solids plural spray epoxy contains no solvents, while an automotive clear coat contains no pigments. Nevertheless, it is important for the formulator to understand the roles of these basic ingredients and how they interact with one another.

The purpose of this present chapter is not to enable the reader to formulate a coating, but rather to serve as a useful starting point in understanding the mechanisms of how paints work and therefore, how they can fail.

1.2 Binder

In simple terms, a coating's binder is the 'glue' which holds it together, and which is principally responsible for providing adhesion to the substrate. With a few exceptions, the binder is nearly always organic, consisting of natural resins or man-made polymers or pre-polymers.

There are numerous types of binders for various applications such as alkyds, vinyls, natural resins and oils, epoxies and urethanes. Specific properties of many of these resins and polymers will be discussed later in this volume. However, some general properties of binders will be discussed here.

It is common practice to classify binders into one of two types, depending on how they cure. Those that cure solely by solvent evaporation are referred to as thermoplastic, or sometimes non-convertible. Those that cure via a chemical reaction during or after application are referred to as thermosetting.

As simple as this nomenclature seems, there are still a few areas of confusion in the industry. Two such examples are enamels and alkyds. To a chemist, the term 'enamel' is synonymous with a thermoset coating, i.e. one that cures by chemical reaction. To a marketing or advertising person, however, the term is used to conjure up the vision of a hard, glossy coating, regardless of its curing mechanism. It is possible to have thermoset coatings that are soft, and even to have thermoplastic coatings that are relatively hard. Therefore, 'enamel' is more of a descriptive term than a scientific one.

Alkyds are basically polyesters modified with natural oils, such as linseed oil. They are widely used for a variety of applications, including exterior house paint, and are often referred to as thermoplastic, or non-convertible, coatings. This terminology, however, is usually incorrect.

While it is true that a linseed oil alkyd dries by solvent evaporation, this is only the first step in its curing process. The second step is not a chemical reaction with another ingredient in the paint, but rather a reaction with oxygen in the air. The reaction is not a rapid one, and may take weeks or months before it is essentially complete. The fact that the co-reactant is not part of the paint, and that the reaction is so slow, has led to some errors in classifying these types of coatings as thermoplastic, whereas they are actually thermosetting.

Another fundamental aspect of binders that needs to be understood by the formulator is viscosity. In intuitive terms, viscosity is a material's resistance to flow. Thick, viscous materials such as maple syrup do not flow out of a container nearly as easily as low-viscosity materials such as water. There are numerous ways of measuring a coating's viscosity, and therefore numerous units to describe it. While it is beyond the scope of this current text to present a detailed discussion of viscosity and rheology, an understanding of their practical significance is important.

A coating must be low enough in viscosity to be applied by conventional equipment (brush, roller or spray) and high enough in viscosity so as not to sag

or drip. It must also maintain, for at least a short length of time after application, a suitable viscosity such that the coating can flow and level. This is necessary not only for the elimination of imperfections such as brush marks, but also so that the coating can thermodynamically wet the substrate. This latter property is critical in achieving good adhesion.

The primary factor responsible for the viscosity of a binder is its molecular weight. Other things being equal, a polymer of high molecular weight will be more viscous than one of low molecular weight. This is an important fact, and basically leaves the coating formulator with two means of controlling viscosity: varying the molecular weight of the polymer or resin, or diluting it with solvent. The path taken can have significant consequences regarding the physical and chemical properties of the coating.

In simpler times, the choice was usually an easy one, i.e. dilute. Higher-molecular-weight polymers generally have superior properties to low-molecular-weight ones, and solvents are relatively cheap. However, in the modern era of regulation and environmental awareness, the move is towards lower-molecular-weight, higher-solids coatings. In many ways, this is synonymous with saying the trend is towards thermoset coatings and away from thermoplastic ones.

A typical poly(vinyl acetate)/poly(vinyl chloride) (PVA/PVC) coating, which has many architectural and light industrial uses, might have a molecular weight of 200 000 or more. It would have to, in fact, because, as a thermoplastic coating, 'what you get is what you start with', and lower-molecular-weight polymers would simply not have adequate physical properties once they dry and cure by solvent evaporation. A consequence of such high-molecular-weight material is its concomitant high viscosity. Such coatings may contain 70 % solvent to bring the viscosity into a workable range.

In contrast, let us consider amine-cured two-component epoxies. These coatings consist of an epoxy component (which may be clear or pigmented), and a separate can of 'activator' component that contains an amine. The two ingredients are mixed together shortly before application, and the amine reacts with the epoxy to produce a hard, tough, highly cross-linked coating. The molecular weight of the epoxy starting material might be only 500–1000, and that of the amine even less. Therefore, their initial viscosity is very low and such coatings might only contain 10 or 20 % solvent.

The previous discussion has focused on molecular weight as it relates to viscosity. Another important variable in formulation, at least for two-component coatings, is the equivalent weight. The equivalent weight of a polymer is its molecular weight divided by the number of reactive functional groups on the polymer molecule. Staying with the example of an amine-cured epoxy, the primary reactive functional group of an epoxy resin is the three-membered epoxy, or oxirane, group.

Figure 1.1 Structure of the epoxy (oxirane) group
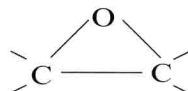
If a particular epoxy resin has a molecular weight of 380, and has two oxirane groups per molecule, its equivalent weight is 190. This is very important because although it is *sometimes true* that 'one molecule reacts with one molecule', it is *always* true that 'one equivalent reacts with one equivalent'.

If one were to select an amine-curing agent that has an equivalent weight of 43, then in order to completely react, or cross-link the above epoxy, one would have to mix 190 g of epoxy resin with 43 g of the amine-curing agent. While in some cases it may be desirable to have a slight excess of one component versus another, it is obvious that a knowledge of equivalent weights is critical in the formulation process.

1.3 Pigments

Pigments can affect a coating's corrosion resistance, physical properties, and appearance. They are commonly grouped into two categories, namely inorganic and organic.

Inorganic pigments consist of discreet particles, often crystalline in nature, which are dispersed in paints, often with the aid of special additives which improve their compatibility with various resin systems. They can contribute to all three of the pigment functions listed above, i.e. corrosion resistance, physical properties and aesthetics.

Two of the most common inorganic pigments are titanium dioxide and iron oxide. Titanium dioxide is the most widely used white pigment, particularly for exterior coatings. It has a high refractive index, which means that it has excellent hiding strength, and also provides a measure of stability against the harsh ultraviolet rays of sunlight, which can degrade many coating binders. Iron oxide, of which there are many varieties, is perhaps the most common inorganic red pigment and is used in both primers and topcoats. Both synthetic and natural iron oxides exist.

Extender pigments are a subdivision of inorganic pigments. They provide little color or corrosion resistance, but can affect such coating properties as density, flow, hardness and permeability. The three most common extender pigments are calcium carbonate (also known as whiting, or chalk), various silicates such as china clay (kaolin) and talc, and barium sulfate (barytes).

There are a very large number of organic pigments on the market. These are generally fairly complicated organic molecules, some of which may be partially soluble in certain resins and solvents. They are seldom used in primers or heavy-duty industrial coatings, as their main advantage is the pallet of vibrant, rich colors that they can produce.

1.4 Solvents

With very few exceptions, most coatings require solvents to dissolve the binder and to modify the viscosity so that the coating can be applied by conventional methods. Solvents evaporate after the coating has been applied and aid in the flow and leveling of the coating, as well as the wetting of the substrate. Solvents are generally thought of as organic liquids, although in a latex paint the main solvent is water.

Certain solvents can dissolve or 'cut' some resins more effectively than others. The ability of a solvent to do this is reflected in its solubility parameter, a concept that can be applied to both solvents and resins. Solubility parameters share one of organic chemistry's simplest rules, namely the concept of 'like dissolves like'. For instance, polar solvents are more effective than non-polar ones in dissolving polar resins. Solubility parameters will be discussed in more detail later (see Section 4.2).

In addition to compatibility, the rate of evaporation of solvents is also very important. Solvents that have a high vapor pressure and evaporate rapidly are considered fast, or hot, solvents, while those that evaporate slowly are referred to as slow solvents. The rate of solvent evaporation can have a major influence on the properties of the coating, and several common defects can be traced to an inappropriate choice of solvents. If the solvent evaporates too quickly, the coating may not have a chance to flow into a smooth, continuous film. A common example of this is the 'orange peel' texture occasionally seen on certain automobile finishes. If the solvent evaporates too slowly, sagging can occur. Orange peel and sagging are just two of the more visually apparent defects related to improper choice of solvents. As we shall see in later chapters, there are several less obvious effects that can also have serious consequences.

1.5 Additives

Although additives will be dealt with more thoroughly in Section 4.1, they span such a wide range of chemistry and functions that they probably deserve their own text. Additives are various chemicals, typically added in small amounts, which can greatly affect the properties of a coating. These include surfactants, anti-settling agents, coalescing agents, anti-skinning agents, catalysts, de-foamers, ultraviolet light absorbers, dispersing agents, preservatives, driers, and plasticizers. Some chemists, however, would not consider a plasticizer to be an additive, since sometimes they constitute a major ingredient of the formulation.

1.6   Formulation Concepts: Pigment-to-Binder Ratio

Once the proper ingredients of a coating have been selected, they must be put together in the proper amounts. A fundamental parameter of a coating is its ratio of pigment to binder. The pigment-to-binder ratio (P/B) is simply the ratio of the weight of pigment to the weight of binder. A gallon of paint containing 8.0 lb of pigment and 4.0 lb of binder therefore has a P/B of 2.0. Topcoats typically have a P/B of 1.0 or less, while primers often have a P/B of 2.0–4.0 [1]. All other things being equal, gloss coatings will have a lower P/B than flat coatings.

1.7   Formulation Concepts: Pigment-Volume Concentration

The pigment-to-binder ratio is an easily measurable and helpful concept in paint formulation. A concept with more far-reaching consequences is the pigment-volume concentration (PVC). The latter is the ratio of the volume of pigment (V_p) to the volume of pigment plus the volume of solid binder (V_b), as shown in the following:

$$PVC = \frac{V_p}{V_p + V_b} \tag{1.1}$$

When multiplied by 100, this parameter is referred to as the % PVC. From the above, it is obvious that two coatings can have an identical P/B value, but dramatically different PVC values, simply by using pigments of different densities.

A term related to the PVC is the critical pigment volume concentration ($CPVC$). The latter is the PVC at which there is precisely the right amount of binder to provide a thin coating over the complete surface of each particle of pigment. At levels above the $CPVC$, there is insufficient binder to wet all of the pigment, while below the $CPVC$ there is an excess of binder.

Several properties of coatings can be significantly affected by varying the PVC of the formulation. Abrasion resistance and tensile strength, for example, are usually best below the $CPVC$ and can rapidly decrease when the $CPVC$ is approached. Permeability is usually low below the $CPVC$ and rapidly increases as the $CPVC$ is approached or exceeded. Therefore, because of the deterioration of a number of physical properties, most high-performance or exterior coatings should not be formulated above the $CPVC$.