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Understanding Coatings Raw Materials

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V. Mannari, C.J. Patel: Understanding 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.

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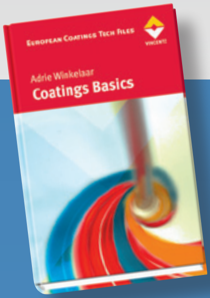
Ypsilanti, MI/USA, January 2015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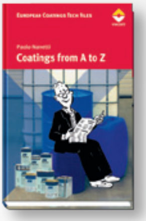
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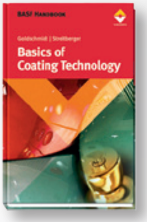
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Basics of Coating Technology

Contents

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,

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- 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 provided 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 ~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.

2 Binders

2.1 Introduction

2.1.1 Introduction to polymers

In the previous chapter, binders or film formers were described as one of the most important components of paints and coatings. Binders are essentially polymeric materials and thus presenting some concepts and definitions related to polymers will be useful in understanding the different types of binders used in paints and coatings.

Simply put, polymers are giant molecules. Unlike small molecules such as H_2O, benzoic acid, and glucose that we are more familiar with, polymers are large molecules with a chain-like structure. This long chain-like polymer structure is formed by bonding between small molecular units called **monomers**. The chemical process by which monomers bond with each other and form long chain-like structures is a reaction called **polymerization** (Figure 2.1).

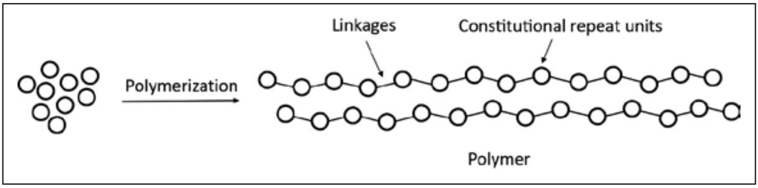

Figure 2.1: Simplified schematic representation of polymerization reaction

It should be noted that in a polymerization reaction, many polymer chains are formed, and these chains are not all of the same size, but rather a distribution of chains having a different chain length.

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The average number of monomeric units in a sample of a polymer is known as the **average degree of polymerization**, expressed as DP bar. Similarly, the molecular weight (MW) of a polymer sample is also calculated by averaging the MW of individual chains, which is expressed as the **average MW**, or Mn bar. A number average MW can be calculated by multiplying the number average DP bar value with the MW of the repeat unit structure.

Equation 2.1: $\overline{\mathrm{Mn}} = \overline{\mathrm{DP}} * \mathrm{MW}$ of repeat unit structure

Depending on the type of monomers and the polymerization process, the average MW of polymers can be from a few thousands to hundreds of thousands of grams per mole. Polymers with very low average MW, on the order of a few hundreds grams per mole, are frequently referred to as **oligomers**. Many polymers are available in nature or synthesized by living organisms and are called **natural polymers**, whereas those prepared from monomers by polymerization reactions are called man-made or synthetic polymers. Both natural and synthetic polymers are used in paints and coatings. In the paint and coating industry, the term **resin** is frequently used for polymeric materials. In this book, the terms polymers, resins, and binders are used interchangeably.

There are two basic types of polymerization reactions, as briefly described below.

Chain-growth polymerization (addition polymerization)

In this process, high MW polymers are formed by chemical bonding between monomers through a very fast polymerization reaction. This polymerization process requires an initiator compound that produces active species, such as free radicals or ions, which initiate the polymerization reaction. Once initiated, monomers combine to form a growing chain with a large number of monomer units, called a propagation step. Propagating chains then terminate by a number of different routes. Figure 2.2 shows polymerization of methyl methacrylate monomer to poly(methyl methacrylate) by chain-growth polymerization. The most common polymers used in paints and coatings that are prepared by this process are acrylics and vinyl polymers.

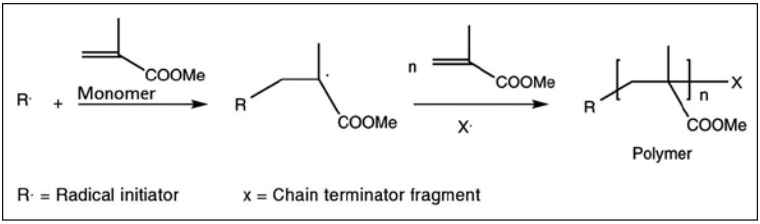


Figure 2.2: Chain growth polymerization of methyl methacrylate

Step-growth polymerization (condensation polymerization)

In this type of polymerization, monomers with at least two functional groups are used, and the linkages between monomeric units are formed by reaction between the functional groups of monomers that generally produce a low MW by-product, such as water. The polymer MW grows in a step-wise manner at a much slower rate compared to that for chain-growth polymerization. This type of polymerization does not produce a very high MW polymer. Figure 2.3 shows a polyesterification reaction, an example of step-growth polymerization.

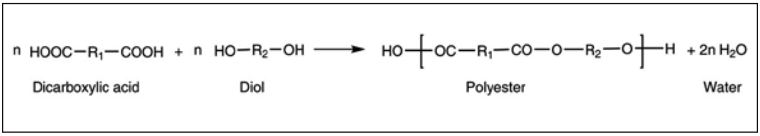


Figure 2.3: Example of step-growth polymerization

2.1.2 Thermoplastic and thermosetting polymers

As mentioned in the previous chapter, resins are polymeric materials capable of forming useful films after application of coatings. For good film formation, a high MW resin is necessary. In general, in the paint and coating industry, two types of resins are used:

(1) those with very high MW that are capable of forming useful films on their own after application of coatings, without any need for a chemical reaction, and

(2) those with low MW that require, after application of coatings, a chemical reaction to increase their MW and become capable of film formation.

These two fundamental film formation mechanisms form the basis of their classification. In general, all resins, and hence all coatings, can be classified into two distinct types, **thermoplastic resins** and **thermosetting resins**.

Thermoplastic resins are high MW polymers that are capable of forming useful films without requiring any chemical reactions during or after film formation. Thermoplastic resins are essentially linear or branched polymers. The film formation of coatings based on such polymers primarily involves only the evaporation of solvent. The dry films of such resins are essentially stacks of entangled long chain amorphous polymers physically interacting with each other through Van der Waals forces. Due to their long chains, the degree of entanglement and physical interactions are strong enough to provide some useful properties, but in general, they lack some desired mechanical properties and resistance to attack by solvents. As the viscosity of a polymer solution is dependent on its MW, the high MWs of thermoplastic resins give them high solution viscosities. This requires use of higher amounts of solvents in their coatings to bring their viscosities down to acceptable levels. However, thermoplastic resin **latexes** (dispersions of thermoplastic resins in water) can afford coatings without necessarily using solvents. Such systems are very popular and form a major category of today’s waterborne coatings.

Thermosetting resins, the another important resin type, are polymeric materials that must undergo some chemical reaction after coatings are applied to form useful films. These chemical reactions, called cross-linking reactions or curing reactions, essentially connect relatively smaller polymer chains, leading to an increase in MW and formation of a cross-linked or network polymer structure. Thus, the structure of the polymer in the cured films of thermosetting systems, unlike thermoplastic ones, is formed by strong chemical linkages connecting polymer chains, making these films strong and resistant to chemical and solvent attack. In general, the binders for thermosetting coatings are comprised of relatively low

MW resins with reactive functional groups and an added cross-linking agent (cross-linker). After the coating is applied, under suitable reaction conditions, cross-linkers react with functional groups of resins, forming a dry film with a cross-linked network structure. Some thermosetting resins have functional groups that are capable of cross-linking by reacting with themselves (self-cross-linking) or with the components of the atmosphere, such as moisture or oxygen, without the need for an added cross-linking agent. Thus, it follows that the structure of the film formed and the properties of the coatings based on thermosetting and thermoplastic resins are fundamentally different and find application in different end uses. Table 2.1 shows typical examples and applications of resin types.

Table 2.1: Typical examples and applications of resin types

Resin type	Examples	Film formation	Applications
Thermoplastic resin	Thermoplastic acrylic resin solutions	Physical drying	Acrylic coatings, wood finishes
	Acrylic latex	Coalescence	Architectural coatings
	Nitrocellulose resin	Physical drying	NC refinishes, nail lacquers
Thermosetting resin	Alkyd resins	Air oxidation	Architectural enamels, primers
	Epoxy resins	Crosslinkers, amines, acids	Industrial coatings, anticorrosive coatings, industrial maintenance coatings
	Polyurethanes	Crosslinkers, co-curing resins, moisture	Industrial coatings, wood finishes
	Polyesters	Crosslinkers, co-curing resins	Industrial coatings
	Acrylate functional	UV curing	Coatings, printing inks

2.1.3 Requirements of resins and binders

The primary role of paints and coatings is to enhance appearance and protect the surface from environmental damage during their service life. Paints and coatings are used for a myriad of applications, and hence their service environment and the degree of protection expected vary to a large extent. Since binders and resins are the actual film formers, their proper selection in formulation is very important. Depending upon the requirements of the final dry film properties, very careful selection of resins is required. In general, resins and binders used for coatings should have the following desirable properties.

- A high MW or capability of cross-linking (curing) after application of coatings
- Solubility in solvents or dispersible in water for efficient formulation, processing and application
- Capability of forming a continuous, adherent and uniform film after application of coatings
- Physical, thermo-mechanical and optical properties as required by coating applications
- Broad range of compatibility with different resins, cross-linkers, additives, solvents and water
- Good shelf-life under normal storage conditions
- Requirement for low or no VOCs for their processing or use in coatings
- Ability to offer paint and coatings products that are compliant to regulatory requirements
- Preferably made from sustainable resources
- Be cost competitive.

2.2 Natural binders

In IS0 4618/3, natural resins are defined as resins obtained from a vegetable or animal origin. Natural resins have been used in coatings for a long time. In recent times, although technologically advanced synthetic resins have replaced these materials, certain natural resins have maintained their place for particular uses as modifiers. They are classified, based on their source, as recent resins, fossil resins and recent-fossil resins. Recent resins are typically obtained by collecting exudations from plants, while fossil resins are those that have been buried underground over geological time. In general, natural resins are low MW compared to many synthetic resins used in coatings, and chemically, they are mixture of various polycyclic and aromatic compounds. As their applications in coatings have been limited in recent years, we will briefly discuss some important natural resins in the subsequent sections.

2.2.1 Rosin (colophony)

Rosin, also known as colophony, and its derivatives are among the most important and widely used natural resins. Rosin is obtained from pine trees either by collecting exudations from the tree (known as **gum rosin**) or by solvent extraction of aged pine stumps (known as **wood rosin**). It can also be obtained as a by-product of the paper industry, where soluble salts of rosin and fatty acid along with lignin are formed as a by-product, which is further distilled to obtain fatty acid and rosin as a residue (known as **tall oil *rosin***). Chemically, rosin is mixture of monocarboxylic acids (~90 %), with the main component being abietic acid and the remainder (~10 %) being neutral materials such as hydrocarbons, oxidized terpenes and saponifiable esters (see Figure 2.4). When heated at ~150 °C, abietic acid isomerizes to levopimaric acid. The unsaturated abietic acid can be readily oxidized, but levopimaric acid is more resistant to oxidation. Rosin is a light yellow to brown brittle solid material (softening point ~70 to 80 °C) having good solubility in aliphatic solvents and good compatibility with drying oils. But due to its high acid content, it is sensitive to water and alkali. Therefore, rosin is frequently chemically modified to increase its softening point and lower its acidity. The important chemical modifications of rosin involve either neutralization of acid groups with calcium oxide (lime) or zinc oxide to form calcium or zinc soaps, respectively, or its esterification with polyols such as glycerol or pentaerythritol for necessary molecular enlargement to the product commonly known as ester gum. The carboxylic acid group of rosin acid is sterically hindered and hence requires a higher temperature (~250 °C) for esterification, but on the other hand, its esters have better resistance to hydrolysis.

Maleic modified rosin is a commercial product and widely used as a binder in the printing ink industry. Levopimaric acid with its conjugated double bonds can undergo a Diels-Alder reaction with maleic anhydride, maleic acid or fumaric acid to produce **maleic**

modified rosin adduct, which is a tricarboxylic acid derivative. The adduct is then reacted with a polyol such as glycerol or pentaerythritol to produce **maleic resins**, which are characterized by their light color, higher melting point, improved light fastness, better hardness and oxidation resistance than rosin. A wide range of such products are commercially available, mainly varying in softening point and excess hydroxyl content.

Rosin modified phenolic resin, another important rosin derivative used in the coating industry, is derived by reacting rosin with a resole type phenolic resin. The extent of modification, the type of phenolic resin used (in terms of the phenolic compound used), and

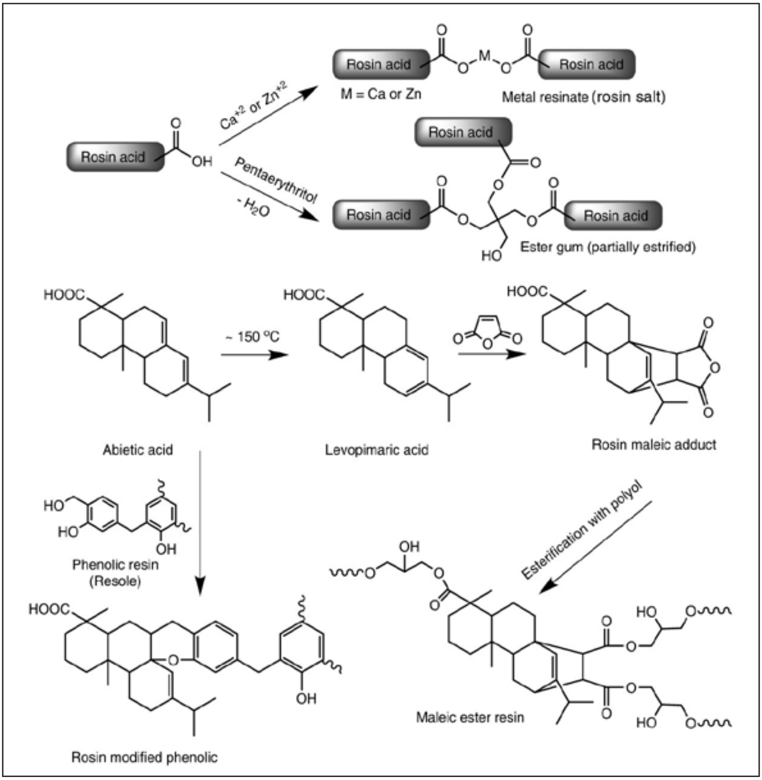


Figure 2.4: Schematic representation of some modifications of rosin

the formaldehyde to phenol (f:p) ratio are the main variations offering different grades of these products. Please see Section 2.6.3 for further discussion of this topic.

The main applications of rosin and its derivatives are in printing inks, oleoresinous varnishes, and modified alkyds to improve hardness and physical drying.

2.2.2 Bituminous binders

Bituminous binders are a crude type of hydrocarbon resin, generally produced as a by-product during distillation of crude oil or coal. Bituminous resins, based on their chemical composition, are categorized as asphalt-based and coal-tar pitch-based products. We will briefly discuss some important bituminous binders used in coatings and related industries.

Bituminous vehicles are chemically complex mixtures of hydrocarbon resins with varying content of paraffins, cycloparaffins, naphthenes and olefinic materials, depending upon their source. The asphalts are rich in aliphatic components while coal tars are mainly composed of aromatic components. Asphalts are soluble in aliphatic hydrocarbon solvents while coal tars are soluble in aromatic hydrocarbon solvents. They are very black in color due to the presence of colloidal carbon. Important properties for their use in coatings are their chemical inertness, excellent water repellency, electrical resistivity, barrier properties and most importantly, lower cost. On the limiting side, they have poor UV resistance and a tendency to bleed in solventbased topcoats, and therefore their usage is restricted to underground structures, coatings for immersed conditions and areas not exposed to UV light.

Petroleum asphalts, obtained as a residue in distillation of asphaltic crude, are used in protective coatings for buried structures and pipelines, coatings for pavements and parking lots, roof coatings and water proofing applications.

Coal tars, obtained from destructive distillation of bituminous coal, are widely used in thick, thermoplastic, hot-applied barrier coatings and linings for the interior as well as exterior of pipelines. Another important use is with other synthetic binders including epoxy-coal tar hybrids and occasionally polyurethane coal-tar hybrids for protecting steel structures in contact with water, soil and back-fills.

Bituminous emulsions are produced by emulsifying an asphalt or coal tar in water using suitable combinations of surfactants along with colloidal clays. After application as coatings, with subsequent evaporation of water, the emulsified bituminous particles coalesce to form a continuous film. Being waterbased, such systems have the potential to comply with VOC regulations.

While bituminous vehicles have been extensively used in barrier coatings over the years, their use is decreasing in recent years due to toxicity issues, especially with coal tars.

2.2.3 Natural oils for surface coatings

There is much historical evidence that plant oils and animal fats were among the first binders to be used for paints and coatings. Their easy availability and ability to form a coherent film when applied to a surface and exposed to air, which oxidizes them, have made them very attractive as a coating raw material from historical and earlier times. With the availability of synthetic resins of a wide variety and higher performance during and after The Second World War, usage of oils as the sole binders has diminished, but they are still used considerably as raw material for various synthetic binders such as alkyd resins, epoxy esters and uralkyds. In recent years, with increasing awareness of environmental issues and the need for sustainable coatings, natural oilbased resins have made a significant comeback as green materials.

2.2.3.1 Composition of natural oils

Natural oils, used as components of binders for surface coatings, are generally derived from oilseeds, though occasionally they are of animal origin, such as fish oil. Compositionally they are triglycerides of fatty acids. They are sometimes described as **fixed oils** to distinguish them from **essential oils**, which are volatile aromatic oils found in some plants. The physical and chemical properties of triglyceride oils are governed by the composition of fatty acids in them. The generic structure of a triglyceride oil is shown in Figure 2.5.

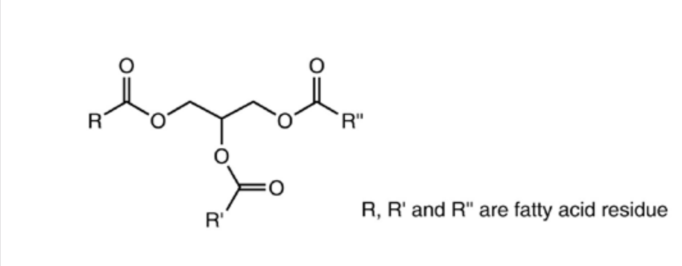


Figure 2.5: General structure of triglyceride oil

R, R' and R'' are fatty acid chains, which may or may not be of one type in a given triglyceride molecule. The fatty acid distribution is broad and characteristic in specific plant oils. Some of the important natural fatty acids commonly found in vegetable oils are shown in Figure 2.6.

Three important attributes of the structure of these fatty acids are: The length of the fatty chain, the degree of unsaturation (number of double bonds) of the chain and the position of the double bonds in polyunsaturated chains.

The chain length of fatty acids can vary from C_8 to C_{22}, but C_{18} is the most common fatty acid in the case of vegetable oils. Fish oil is the only animal oil that has an even broader range of fatty chain length, from C_{12} to C_{30} with variation in unsaturation. The saponification value of triglyceride oils is an indirect measurement of their chain length.

The double bonds in the chain are the reactive centers responsible for thermal and oxidative polymerization properties of the oils. A quantitative measure of the average degree of unsaturation present in a given oil is expressed by its iodine value (IV), which increases with an increasing number of double bonds. Therefore, highly unsaturated oils having the ability to form a solid or semisolid polymeric structure by means of oxidative or thermal polymerization are invaluable for coatings.

In addition to the number of double bonds, their placement in the fatty chain with respect to each other also has a considerable influ-

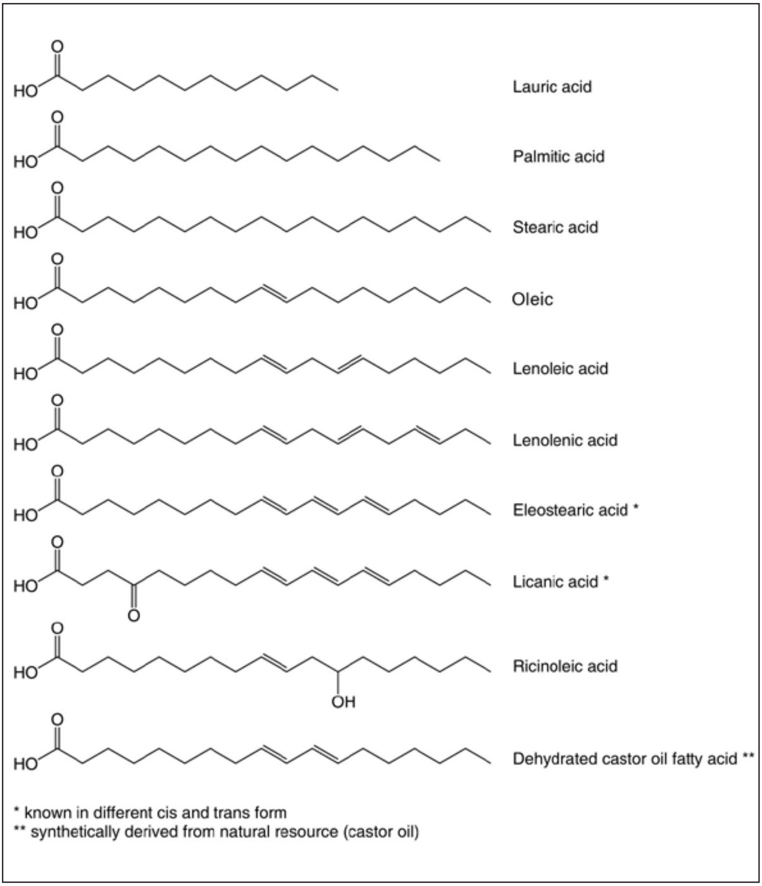


Figure 2.6: Chemical structures of some common fatty acids

ence on properties of oils. Based on this, oils are classified as conjugated or unconjugated; in the former, two or more double bonds are arranged to give a system of alternating single and double bonds (–CH=CH–CH=CH–), while in the latter, double bonds are separated by two or more single bonds (–CH=CH–CH–CH=CH–). A conjugated molecule is much more reactive than an unconjugated one with the same degree of unsaturation. This is the reason for the reactivity of dehydrated castor oil (a conjugated diene) and the extreme reactivity of tung oil (conjugated triene), compared to, for instance, soybean oil (an unconjugated oil).

Certain oils contain characteristic fatty acids, such as ricinoleic acid in castor oil, with hydroxyoleic acid (12-hydroxy-9-octadecenoic acid); eleostearic acid in tung oil, with a conjugated triene; licanic acid in oiticica oil, with a conjugated triene keto acid, which are responsible for the high reactivity of the parent oils.

Raw oils are obtained from oilseeds by solvent extraction or by mechanical pressing. They contain a variable amount of non-glyceride impurities that are not desirable for their applications in paints and coatings. Therefore, refined oils with considerably low odor, color and impurities are commercially supplied for use in coatings and related industries.

2.2.3.2 Classification of oils in the coating industry

There are many ways in which oils can be classified, but in the surface coating industry, oils are mainly classified according to their film forming ability, which is primarily governed by their degree of unsaturation. Therefore, oils are classified according to their iodine value (IV) as:

- **Non-drying oil:** IV < 120 (for example, coconut oil, castor oil, rapeseed oil)
- **Semi-drying oil:** IV = 120 to 150 (for example, soybean oil, safflower oil, sunflower oil)
- **Drying oil**: IV > 150 (for example, linseed oil, tung oil, oticica oil).

Although non-drying oils are not suitable for film formation, they are used in the coating industry for their plasticizing effects.

Various oils used in the coating industry are listed in Table 2.2 with their respective fatty acid compositions.

Among the most important drying and semidrying oils with commercial significance for the modern coating industry are linseed oil, soybean oil, sunflower oil, dehydrated castor oil, tall oil and fish oil, while important non-drying oils are coconut oil, castor oil and palm oil. Tall oil is a misnomer; this oil is actually supplied as a mixture of fatty acids obtained as a by-product in the production of wood pulp in the paper industry.

Table 2.2: Typical fatty acid composition of common oils used in surface coatings

Oil	**% of fatty acids**					**Iodine value**
	$C_{8:0}$–$C_{18:0}$	**$C_{18:1}$**	**$C_{18:2}$**	**$C_{18:3}$**	**Others**	
Coconut	92	6	2	–	–	7–10
Palm	46	45	9	–	–	44–51
Peanut	10	64	20	–	6[a]	84–105
Castor	3	3	4	–	90[b]	85–90
Tall*	7	45	35	12	1[c]	128–138
Soybean	15	25	51	9		120–140
Sunflower	10	42	47	1		125–144
Safflower	7	20	70			140–150
Cottonseed	23	35	42	–	–	99–113
Linseed	10	22	16	52		170–190
Tung	5	7	10	78[d]		160–175
Oiticica	10	8	8	–	74[e]	140–160
Dehydrated castor	2	2	85f	–	11[b]	130–145
Fish	20	10	15	–	55[g]	165–195

*a – Arachic acid and behenic acid (C_{20} and C_{21} saturated fatty acids); b – ricinoleic acid; c – rosin; d – eleostearic acid (conjugated double bond); e – licanic acid; f – mixture of conjugated and unconjugated linoleic acid; g – predominantly a mixture of arachidonic acid ($C_{20:4}$) and clupanodonic acid ($C_{22:5}$) with some $C_{20:1}$, $C_{22:1}$; * not a triglyceride but a mixture of fatty acids obtained as a by-product of the paper industry*

Note: compositions are representative; actual composition may vary from source to source

2.2.3.3 Modified oils

The relatively slow drying speed of oils was the main limitation for their use in paints and coatings, and therefore for practical applications, a number of oils modified either chemically and/or structurally were introduced to improve their drying time and other performance factors. These modifications involving reactions of oils in other resins such as alkyds, epoxy esters and uralkyds will be covered in relevant chapters. Here we will briefly describe the chemical modification of an oil itself.

Polymerized oil: One of the common approaches used to improve drying time of coatings is to increase the MW of the oil by partial polymerization so that it will take less time to form a fully crosslinked network. In earlier times, when synthetic resins were not available, this approach was frequently used to make practically useful binders. Partial polymerization can be carried out by thermal polymerization of an oil simply by application of heat (~300 °C) and use of peroxide initiators (in the case of non-conjugated systems) via a Diels-Alder reaction. Such products are called stand oil or bodied oil. In another approach, oil can also be partially polymerized at 130 to 140 °C by passing air through it, frequently in the presence of a catalyst, a process called **oxidative polymerization**. While the usage of such types of polymerized oils has decreased over the years, they still find some applications in the modern coating industry for certain cost-effective oleoresinous media for printing inks and varnishes.

Dehydrated castor oil: Castor oil, a non-drying oil, can be dehydrated in the presence of a catalyst at a temperature of 260 to 280 °C to produce dehydrated castor oil, a drying oil. Dehydrated castor oil has additional unsaturation, giving a mixture of conjugated and unconjugated linoleic acid chains. Dehydrated castor oil is marketed as a product with different levels of conjugated fatty acid chains. Because of the substantial amount of conjugated chains, dehydrated castor oil shows a much faster drying time

Maleinized oils: Traditional oils with conjugated as well as unconjugated unsaturation can be modified with up to 8 % of maleic anhydride. A conjugated system reacts more readily at a moderate temperature, while an unconjugated system needs a higher temperature. Among other applications, maleinized oils are useful in preparation of resins with high carboxylic acid content, especially for water-reducible types of systems.

Epoxidized vegetable oil: This is another interesting modification of oil that involves epoxidation of carbon-carbon double bonds in fatty acid chains using peracids or hydrogen peroxide to generate internal epoxy groups. While epoxidized vegetable oils have been known for their use as plasticizers and stabilizers for PVC plastics, in recent years, there has been considerable interest in deriving sustainable, green polyols from epoxidized soybean oil as a replacement for petroleum derived polyols. Some such polyols will be discussed in Section 2.9.1.8.

2.3 Alkyd resins

Alkyd resins have been used in surface coatings for more than eight decades. They have been the workhorse of the binders for solventbased architectural coatings and to a considerable extent for industrial coatings because of their low cost, good performance properties, and versatility of applications. In the beginning of the 20th century, the esterification product of glycerine with phthalic anhydride (glyptal) was produced as a synthetic hard resin. However, owing to its brittleness and incompatibility with oils, it was of not practical utility in coatings at that time. In the late 1920s, *Kienle* et al. made a significant contribution to alkyd resin technology by developing a process to chemically incorporate vegetable oil in the polymer backbone using an alcoholysis technique. This development led to the commercial availability of alkyd resins with good solubility and film forming characteristics. The term alkyd resin originally was proposed to describe the reaction product of polyhydric alcohols with a polybasic acid as a euphonic contraction of 'al' from 'alcohol' and 'cid' from 'acid' (changed to 'kyd' for aiding pronunciation). Although this does not make any reference to the fatty acid component, alkyd resins are generally understood as oil modified polyesters.

According to DIN 53183, "Alkyd resins are synthetic polyester resins produced by esterifying polyhydric alcohols with polybasic carboxylic acids where at least one of the alcohols must be trihydric or higher. Alkyd resins are always modified with natural fatty acids or oils and/or synthetic fatty acids and may be additionally modified with compounds such as resin acids, benzoic acid, styrene, vinyltoluene, isocyanates, acrylic, epoxy, or silicone compounds."

Despite the development of a vast variety of other synthetic resins, alkyd resins have remained a large fraction of the resins for the paint industry because of a number of reasons. They are a single-pack system with excellent storage stability; they are relatively inexpensive as well as soluble in inexpensive solvents; they are versatile and can be engineered for a wide variety of properties ranging from hard, fast-drying compositions to softer, more flexible slow-drying resins; they can be chemically modified by a number of other resins to improve their film properties; and they possess excellent wetting characteristics for pigments as well as the surfaces they're applied to. On the other hand, being polyesters, their main limitation is their sensitivity to water, alkali and acid due to hydrolysis of ester linkages of the polymer backbone.

2.3.1 Chemistry of alkyd resins

Chemically, all alkyds are polyesters and are derived from a polycondensation reaction of polyhydric alcohols and polybasic acids with a certain degree of modification by some kind of oil or fatty acid. Among the important chemical reactions involved in alkyd resin technology are direct esterification of carboxylic acids with alcoholic hydroxyl groups, transesterification reactions, and reaction of an alcoholic hydroxyl with an acid anhydride. These reactions are shown in Figure 2.7.

Transesterification can occur either by alcoholysis or by acidolysis; the latter is less important commercially. When acid anhydrides are used, they react in two steps: first, the anhydride ring opening by a hydroxyl, giving a half ester of acid, followed by condensation of the acid group with another hydroxyl. The first reaction occurs at

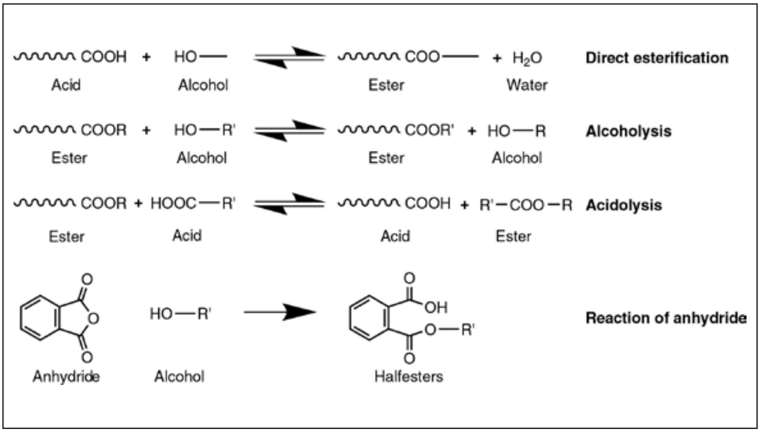


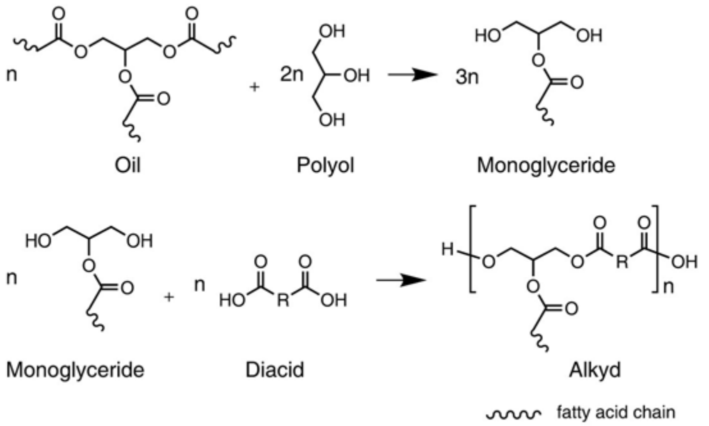
Figure 2.7: Alkyd resin reactions

relatively low temperature, as it does not generate any water as a by-product that needs to be removed in order to get a high yield of resin; therefore, the most important commercial route is to use anhydrides whenever possible. In addition to the desired esterification reaction, a competing side reaction is etherification by condensation of two alcohol groups.

Alkyds are made by different processes, depending upon the available raw materials, final product properties and cost. The alcoholysis process (also called the monoglyceride process) or acidolysis process is used when oil is one of the starting materials, while direct esterification uses fatty acids as starting materials, with better control of final resin properties, but generally at higher cost.

2.3.1.1 Alcoholysis process

This is the most commonly used route in alkyd resin manufacturing. Oils, being cheaper raw materials as compared to corresponding fatty acids, are naturally preferred for alkyd resins, but the oil does not react readily with acid or alcohol. Therefore, to avoid a heteroge-



Note: this is the simplest and representative scheme, actual polymer structure is more complex and branched

Figure 2.8: Schematic representation of alcoholysis process for alkyd resins

neous mixture of unmodified polyester and unreacted oil, first the oil is reacted with a polyol by transesterification (alcoholysis) in the presence of a basic catalyst (such as sodium hydroxide or lithium hydroxide) into a hydroxyl functional intermediate, monoglyceride. The monoglyceride is then reacted with phthalic anhydride and other polybasic acids to form alkyd resins. Generally, the alcoholysis product of oil and polyol contains a mixture predominantly containing a-monoglyceride and b-monoglyceride with some diglyceride, triglyceride and glycerol. The simplest possible representation of the process is shown in Figure 2.8.

2.3.1.2 Acidolysis process

This route for manufacture of alkyds, shown in Figure 2.9, is not widely used, and is only used when the diacid is insoluble in a reaction mixture or has a high melting point, for example, long oil alkyds based on terephthaleic acid or isophthalic acid. The reaction requires high temperature (270 to 290 °C) to attain perfect compatibility. Due to high temperature, some side reactions such as dimerization of the oil are inevitable.

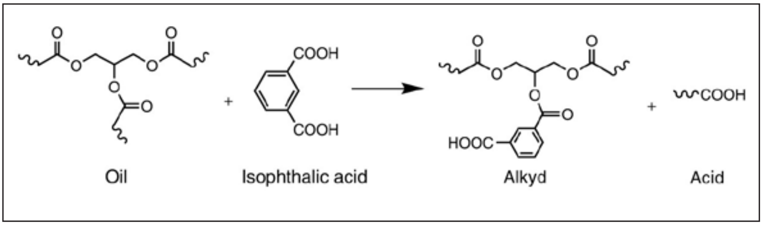


Figure 2.9: Schematic representation of acidolysis process for alkyd resins

2.3.1.3 Fatty acid process

This process is faster and involves only one stage. As the name suggests, fatty acids along with polyol and dibasic acid are reacted in a single step via direct esterification. This process gives more latitude for selection of polyol component and is useful when polyols other than glycerol are to be used in a formulation. Also, this process gives better control over MW, MW distribution and acid number, which gives a better product in a shorter processing time. Therefore, despite the higher cost of fatty acids, this process is widely used in the industry, especially in high-solid resin applications.

2.3.2 Raw materials for alkyd resins

2.3.2.1 Fatty acids and oils

Fatty acids and oils are one category of primary raw materials for alkyd resins. Their chemistry and compositions have been discussed in Section 2.2.3. Soybean oil, linseed oil, tall oil, sunflower oil, and safflower oil are common raw materials for air-drying alkyds, while coconut oil and castor oil are important for nondrying alkyds.

2.3.2.2 Polyhydric alcohols

A diverse range of compounds are used as polyols for alkyd resins (see Figure 2.10). Polyols used in alkyds are generally at least trifunctional to permit branching and can provide the alkyd with hydroxyl groups for further reaction. Glycerol, having two primary and one secondary hydroxyl, is the traditional polyol used in alkyds; however, it is generally limited to use in short and medium oil, oxidatively and thermally curing alkyd resins. Other important triols used to replace glycerol are trimethylol propane and trimethylol ethane, which have three equally reactive hydroxyl groups that produce alkyds with more branching and low viscosity, suitable for high-solid applications, along with better solubility in non-polar

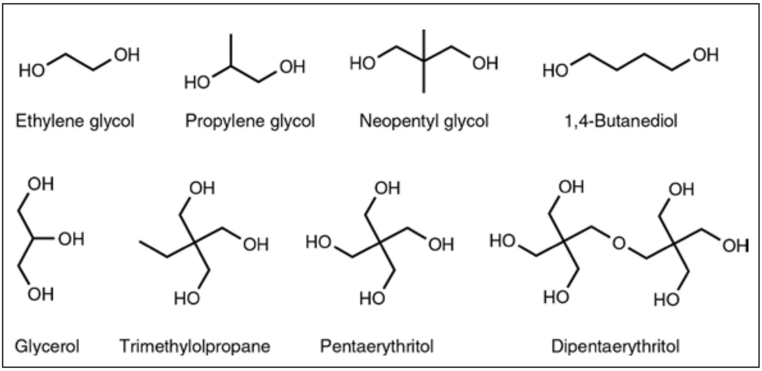


Figure 2.10: Polyols for alkyd resins

solvents, improved exterior durability and water resistance. Pentaerythritol, with four primary hydroxyl groups, is the most common polyol for long oil and medium/long oil alkyd resins; however, their use as the sole polyol in short to medium oil alkyds is prone to gelation due to its high functionality. Long oil alkyd resins from pentaerythritol have superior adhesion, hardness, gloss retention, weather resistance, water resistance and chemical resistance properties. Diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol and neopentyl glycol are not commonly used as the main polyols, but they may be used as a modifier or to balance the average functionality of the mixture.

2.3.2.3 Polybasic acids

Although they are not the only type used, difunctional aromatic acids are most commonly used in alkyd resins, of which phthalic anhydride is the most important and commonly used diacid because of its availability, low cost, relatively low melting point, and high reactivity. Isophthalic acid is another dibasic acid that is frequently used for alkyds with improved hardness and heat resistance, but its high melting point (342 °C) makes it difficult to process resins at normal temperatures. Partial replacement of phthalic anhydride with maleic anhydride improves drying time and color of resins. Aromatic acids and maleic anhydride contribute to hardness, chemical resistance, and durability of alkyds. On the other hand, long-chain dibasic acids, such as adipic acid, sebacic acid and azelaic acid, are sometimes used in minor quantities to plasticize alkyds and provide flexibility. Bio-based succinic acid has recently gained interest among alkyd manufacturers due to its renewable nature and sustainability. An important trifunctional acid worth mentioning is trimellitic anhydride, which is often employed in water-reducible alkyd resins and in high-solids alkyds. Some examples of commonly used carboxylic acids and anhydride are shown in Figure 2.11.

2.3.2.4 Monobasic acids

Besides fatty acids, other monofunctional acids are often used in small quantities in certain alkyd resins (Figure 2.11). Rosin was initially used to modify the drying time of alkyd resins because of its low cost, but it impairs durability of coatings. Some aromatic monofunctional acids such as benzoic acid or *p-tert*-butylbenzoic acid are used in small quantities, mainly to control functionality and to avoid gelation during resin processing. Some synthetic monofunctional aliphatic acids such as 2-ethylhexanoic acid and isononanic acid are also used in some special cases.

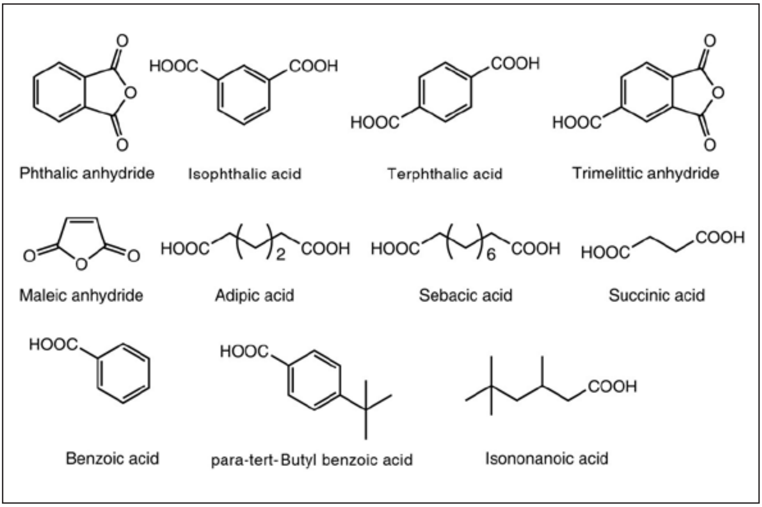


Figure 2.11: Common polybasic and monobasic acids for alkyd resins

2.3.3 Processing of alkyd resins

There are two major chemical processes used for manufacturing alkyds: the **fusion process** and the **azeotrope process** (solvent process). The fusion process is an old method of manufacturing alkyd that involves **fusing** all components at elevated temperature. An inert gas is continuously purged in the system to avoid oxidation as well as to drive off water of the reaction. Alkyds made by this process are often darker in color. Due to the possibilities of sublimation of phthalic anhydride and loss of polyols, this process suffers from poor reproducibility. In the solvent process, poly condensation is carried out in the presence of a small quantity (5 to 10 % of reaction mass) of hydrocarbon solvents (normally xylene or toluene) in the reaction mixture. Thus, water of the reaction is carried to the condenser as an azeotrope with the solvent, and upon condensation, being immiscible, water is separated from the solvent and the solvent is returned to the reactor. While the process requires complex condensation and separation equipment, most of the alkyds currently manufactured use the solvent process because it reduces the loss of components, allows a lower esterification temperature, gives superior color to the product, and is a faster reaction due to better agitation resulting from viscosity reduction by the solvent. In both processes, the progress of the reaction is monitored by intermittent measurement of viscosity increase and decrease in acid number of samples of the reaction mixture.

2.3.4 Classification of alkyd resins

Most common and traditional alkyd resins are classified on the basis of their oil content (wt% of oil in final resin) as:

- Short oil alkyd resin: oil content <40 %
- Medium oil alkyd resin: oil content 40 to 60 %
- Long oil alkyd resin: oil content 60 to 70 %
- Very long oil alkyd resin: oil content 70 to 85 %.

Long oil alkyd resins have been the workhorse as binders for architectural and do-it-yourself paints, anticorrosive coatings (linseed oil based), metal primers and intermediate coats. They are mainly based on such oils as soybean oil, linseed oil, dehydrated castor oil and safflower oil.

Medium oil alkyd resins are based on drying oils or fatty acid mixtures, and are useful as binders for architectural coatings and industrial coatings, including cost-effective auto refinishes, metal primers, and original equipment manufacturing (OEM) finishes for air-drying as well as force-drying applications. Due to their compatibility, they are frequently used in combination with such other film formers as nitrocellulose to improve drying, other hard resins to increase hardness and gloss, chlorinated rubber for improved chemical resistance and amino resins for heat cured (stoving) finishes.

Short oil alkyd resins can produce harder and more durable films in combination with amino resins for industrial stoving finishes, such as for appliances and OEM applications. Most such resins for stoving finishes are based on non-drying oils and have improved yellowing resistance. Short oil resins are also formulated with urea or melamine resins for two-component wood coatings (frequently known as catalyzed lacquers), in which the second component is a solution of acid catalyst (such as *p*-toluene sulfonic acid) in alcohol. They are also combined with nitrocellulose as plasticizing resins for inexpensive furniture lacquers and automotive refinishing systems. Chain-stop alkyd resins, based on linoleic-rich fatty acids, are also an example of short oil alkyd resins mainly used in OEM applications requiring fast-drying coatings (1/2 to 2 h). Shorter oil length generally results in a need for aromatic solvents.

2.3.5 Effect of oil modification on properties

The key properties of alkyd resins controlled by type and content of fatty acid or oil are drying time, hardness and yellowing properties. The degree of unsaturation and presence of conjugated unsaturation in fatty acids increases the curing rate and improves their drying time. Oils with a high content of linoleic acid produce non-yellowing films, while those with high linolenic acid or conjugated fatty acids cause yellowing of the film upon aging. Oil imparts flexibility to the films, and hence, hardness of alkyd films is proportional to the oil length. For a given oil content in an alkyd resin, the hardness of the film it forms is proportional to the polyunsaturated acid content. Also, as oil length decreases, solubility in aliphatic hydrocarbon solvents (mineral spirit) decreases. Thus, selection of fatty acids and their content is very important in formulating alkyd resins for specific end uses.

2.3.6 Modifications of alkyd resin

Despite the wide range of properties of unmodified alkyd resins mentioned above, alkyds suffer from some inherent limitations. In general, coatings based on alkyd resins have poor water, alkali and chemical resistance, yellowing tendency and poor exterior durability and gloss retention properties. In order to partly overcome these limitations, alkyds are frequently chemically modified. Chemical reactions with alkyd resins can take place via their hydroxyl groups, carboxyl groups or the double bonds of their unsaturated fatty acids. Though it is out of the scope of this book to discuss each of the modifications in detail, some of the most common ones are listed in Table 2.3 with their characteristic advantages.

Table 2.3: Common modified alkyd resins

Modified alkyd resins	Key improved properties
Rosin modified	Faster surface drying, adhesion, wetting, gloss
Phenolic modified	Adhesion, resistance to water and corrosion
Vinylated (styrene/vinyl toluene)	Surface drying, water and chemical resistance, hardness
Acrylated	Surface drying, weather resistance, hardness
Epoxy modified	Adhesion, chemical and corrosion resistance
Urethane modified	Chemical and corrosion resistance, weather resistance, good mechanical properties, abrasion resistance
Silicone modified	Heat and weather resistance, gloss retention
Polyamide modified	Thixotropic rheology, non-dripping

It should be noted that while these modifications will improve certain properties, they may also cause a compromise with other properties. For example, rosin modification causes brittleness, poor color retention and water sensitivity of the film. In vinylated alkyds, due to reduced residual unsaturation after grafting, the cross-link density is lower compared to the unmodified alkyd, and hence solvent resistance is reduced. Such resins also have an increased tendency for yellowing. Certain modifications, such as by urethane, silicone or acrylic components, increases the cost of the resin, rendering them only suitable for specific applications that justify their higher cost.

The modifications with urethane and silicone are discussed in Section 2.11.3.2 and 2.12.5 respectively. Alkyd resins are modified by reacting them with polyamide resins to achieve special rheological properties (Section 5.3.2.5) and are called thixotropic alkyds. Although epoxy esters are a class of epoxy resin, they are frequently considered alkyds rather than epoxies. They are also ester-based resins, but are derived by esterification of a secondary hydroxyl and oxirane group of epoxy resin and vegetable oil fatty acids. This class of resins is discussed in Section 2.9.2.1.

Vinylated alkyds are produced by copolymerization of unsaturated monomers such as styrene, vinyl toluene, a-methyl styrene and methyl methacrylate with an alkyd resin in the presence of free radical initiators such as benzoyl peroxide or di-*tert*-butyl peroxide. This modification involves free radical-initiated addition polymerization of the vinyl monomers in the presence of the alkyd resin, resulting in grafting of vinyl chains onto the fatty chains of the alkyd (at the unsaturation sites of alkyds). Grafting is favored on fatty chains with conjugated double bonds compared to unconjugated fatty chains. Type of initiator and temperature are also important factors for grafting efficiency. The mechanism of grafting is depicted in Figure 2.12.

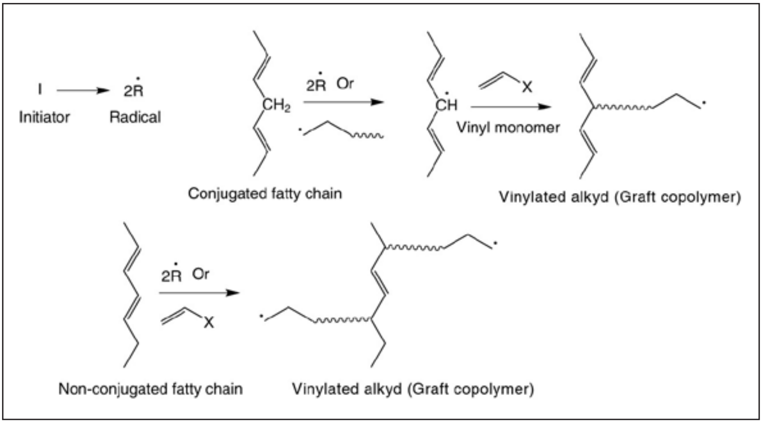


Figure 2.12: Vinylization of alkyd resin

2.3.7 High-solid alkyd resins

In order to meet environmental regulations pertaining to VOCs, high-solid alkyd resins have been developed with about 80 % by weight or more of the vehicle solids at acceptable viscosity. In high-solid resins, low viscosities are typically achieved by decreasing the MW of the polymers. The reduction in MW has a consequence of relatively poor mechanical and chemical resistance of their films. Additional cross-linking and MW buildup during curing is therefore necessary for acceptable performance. For the short oil alkyds that are used in stoving finishes, typically with amino resin cross-linkers, this approach is more feasible, as low MW alkyd resin reacts with curing agent to build up the sufficiently high MW needed for good performance.

Another approach for high-solid alkyd resins is to synthesize the resin with a narrower MW distribution. It has been reported that by decreasing the MW distribution, the solids could be 2 to 10 % higher than an alkyd of the same composition prepared by the conventional method (with broader MW distribution).

Selection of solvents is also an important consideration in designing high-solid alkyd resins. Use of stronger solvents results in resin solutions with lower viscosities at lower solvent content. Hydrogen bonding between hydroxyl and ester groups has a significant effect on viscosity via a hydrogen bonded network; therefore, solvents that can block off hydrogen bonding are effective in viscosity reduction. Some examples of such solvents are lower alcohols and ketones.

Use of **reactive diluents** for viscosity reduction is another practical approach for high-solid alkyds. These are compounds with very low MW and low viscosity, with functional groups capable of reacting with alkyds and thus being incorporated in the cured film. Linseed oil is one such reactive diluent, but various other compounds such as the allyl acetal of pentaerythritol, allyl ether and acrylate ester compounds are currently used.

2.3.8 Waterbased alkyds

Waterbased binders are increasingly used in low VOC coatings, and like all other binders, demand for waterborne alkyds is continuously growing. Waterborne alkyd resins can be broadly categorized into two groups: water-reducible alkyds and alkyd emulsions.

2.3.8.1 Water-reducible alkyds

Water-reducible alkyds, in general, are prepared by formulating alkyds with an acid value in the range of 40 to 60 mg KOH/g. The free carboxylic acid groups are then partially or fully neutralized with a fugitive base such as ammonia or a volatile organic amine to provide enough polarity to make them water-reducible. Such systems typically require 5 to 20 % water-miscible co-solvents such as glycol ethers or alcohols. In initial attempts, they were prepared by halting the conventional polymerization of alkyd at a higher acid value; this often resulted in lower MW. The improved two-step process can produce higher MW polymers, which involves synthesis of a hydroxyl-rich alkyd by the conventional technique followed by reaction with phthalic anhydride or, preferably, trimellitic anhydride under milder conditions than direct esterification to give an acid functional polymer. Short to medium oil length alkyds are more common for this type of mixture. One of the important concerns with water-reducible alkyds is their poor hydrolytic stability on storage. A novel core shell type of polymer design has also been adopted to reduce their tendency for hydrolysis, in which acrylic modified alkyds are designed with carboxylic groups on the acrylic chain. Once a wet film is applied, water, solvent, and neutralizing amine evaporate and the film cross-links by autoxidation. Since there are a fairly large number of residual carboxylic acid groups left in the cross-linked binder, the water resistance, and particularly the alkali resistance, of the films is reduced.

2.3.8.2 Alkyd emulsions

Alkyd emulsions are among the major developments in alkyd resins in the past few decades. Water-reducible alkyds contain considerable amounts of co-solvents that contribute to VOCs in the final compositions, while alkyd emulsions are aqueous alkyd resins with little, if any, VOCs. They are prepared by emulsification of alkyd resins in water using emulsifiers (surfactants) and are normally supplied at 40 to 55 % solid content. They are generally prepared by a phase inversion technique in which water is added progressively to the molten resin containing the emulsifiers. Initially, a water-in-oil type of emulsion is formed that subsequently inverts to an oil-in-water type when a sufficient amount of water is added. This phase change is characterized by reduced particle size, homodispersity and good rheology of the alkyd emulsion. The particle size may range from 0.5 μm to 15 μm. The small particle size is desirable for good storage stability and better gloss. Important factors in the process are the phase inversion temperature, manufacturing controls, and engineering aspects of the process, such as the stirring method and impeller design, which govern the overall shear exerted during the emulsification process. In formulating alkyd emulsions, careful selection of type and amount of surfactants is very important to optimize their properties and performance. In order to obtain satisfactory water resistance and drying behavior, the content of emulsifiers should be kept as low as possible while maintaining good emulsion stability. Polymeric non-ionic surfactants are often the choice over normal anionic surfactants, especially when they contain autoxidizable reactivity (reactive emulsifiers). Alkyd emulsions are used in architectural coatings, wood coatings, and to some extent, corrosion protection coatings. Recently, there has been considerable interest in alkyd emulsions for direct-to-metal coatings.

2.3.9 Hyperbranched alkyd resins

One of the recent advancements and interests in alkyd resin technology is hyperbranched alkyd resins, which, due to their unique highly branched polymer architecture, have low viscosities at higher MWs. An important characteristic of these alkyds is rapid drying. Generally they are prepared by reacting hyperbranched polyester polyols with fatty acids. The main limitation of such alkyds, however, is higher cost, due to the need for unique, more expensive raw materials in their synthesis.

2.4 Saturated polyesters

As the name indicates, saturated polyesters are polymers with ester linkages in their backbone. They are the condensation products of polyols and polybasic acids. The early development of saturated polyesters traces back to preparation of **glyptal resins**, formed from glycerol and phthalic anhydride, which are also the foundation for development of alkyd resins, as mentioned earlier. Though in a strictly chemical sense, the term polyester can also be applied to alkyd resins, the essential difference is the presence of oil or fatty acid in an alkyd resin, while saturated polyesters are free of such compounds. Therefore, saturated polyesters are sometimes also termed **oil-free alkyds**. Due to the absence of unsaturated oil or fatty acids, saturated polyesters cannot air-dry via oxidative polymerization as do alkyds, so they need to be formulated in coatings with curing agents or cross-linkers. Based on the curative, they can be cured at ambient conditions or require baking. In general, compared to alkyds, the cured films of polyesters are superior in most performance properties such as color and gloss retention, water and chemical resistance, and overall durability.

2.4.1 Chemistry of polyester resins

Direct esterification is one of the most important routes for forming saturated polyesters, and involves condensation of polybasic acids and polyols with removal of water of the reaction. Another important reaction of this type is self-condensation of polyfunctional monomers having both hydroxyl and carboxylic acid group.

Transesterification between polyols (generally diols) and dialkyl esters of dicarboxylic acids (generally methyl esters) can also lead to polyesters. This is an important method for deriving powder coating resins with terephthalic acid and isophthalic acid. The generic reactions involved in direct esterification and transesterification were discussed in Section 2.3.1.

Ring opening polymerization of lactones (cyclic esters) is another interesting technique to derive polyesters. For instance, lactones are reacted with polyols (as an initiator) to derive a linear polyester (polylactone) by ring opening polymerization as shown in Figure 2.13. One interesting aspect of this technique is that the functionality of the final polymer is the same as that of the initiator polyol.

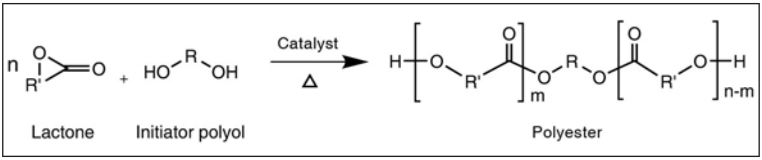


Figure 2.13: Representative scheme for ring opening polymerization

2.4.2 Formulation and raw material selection

Safe preparation of polyester resins from polyfunctional monomers ($F_n > 2$) without gelation requires careful optimization of average functionality and calculation of the degree of polymerization at the gel point (P_{gel}). *Wallace Carother* and *P.J. Flory* have made significant contributions in this area; however, a detailed discussion is outside the scope of this book.

A wide range of raw material is available to design polyesters with a broad spectrum of properties. In addition to the polyols listed in the section on alkyd resins (Section 2.3), other specialty diols are also used in polyester synthesis. Some important polyols are listed in Table 2.4.

Various polybasic acids are used in polyester synthesis, including aromatic acids as well as aliphatic acids. Some important acids used in polyester synthesis and their primary characteristics are shown in Table 2.5.

In addition to polybasic acids, some monobasic acids including lower MW synthetic branched fatty acids and monobasic aromatic acids are also used for controlling functionality and MW of polyesters.

Table 2.4: Important polyols for polyesters

Polyol	**F_n**	**Remarks**
Neopentyl glycol	2	Hardness, heat resistance, impact resistance, chemical resistance
TMPD	2	Good heat resistance, solubility, compatibility, low viscosity
1,6-hexanediol	2	Flexibility, impact resistance
CHDM	2	Reactivity, thermal stability, good balance between hardness and flexibility
BEPD	2	Low viscosity, better solubility and compatibility, exterior durability, hydrolysis resistance, corrosion resistance, hydrophobicity
HBPA	2	Excellent solvent and chemical resistance, durability, high expense
TMP and TME	3	Branching, hardness, reactivity, durability
Pentaerythritol	4	Branching, too much functionality to handle, hardness, durability

F_n = number average functionality; TMPD = 2,2,4-trimethyl-1,3-pentanediol; CHDM = cyclohexane dimethanol; BEPD = 2-butyl-2-ethyl-1,3-propanediol; HBPA = hydrogenated bisphenol A; TMP = trimethylol propane; TME = trimethylol ethane

Table 2.5: Important polybasic acids for polyesters

Polybasic acid	Remarks
Phthalic anhydride	Cost-effective, hardness, poor in exterior durability
Isophthalic acid	Good mechanical properties, chemical resistance
Terephthalic acid	Improved heat resistance, good mechanical properties, strong crystallizing tendency of polymer, hence solubility problem
TMA	Trifunctionality, useful for water-reducible polyesters and acid-functional polyesters for powder coatings
CHDA	Excellent flexibility – hardness balance, better corrosion resistance than linear diacids, good thermal resistance, excellent durability
HHPA, THPA	Better hydrolysis resistance, yellowing resistance (HHPA)
Linear diacids*	Flexibility, durability
Succinic acid	Sustainability

CHDA = cyclohexane dicarboxylic acid, HHPA = hexahydrophthalic anhydride; THPA = tetrahydrophthalic anhydride; TMA = trimellitic anhydride
** Adipic acid, azelaic acid, sebacic acid and related acids*

Some examples of such monobasic acids are benzoic acid, *p-tert*-butylbenzoic acid, hexahydrobenzoic acid, 2-ethylhexanoic acid and isononanoic acid.

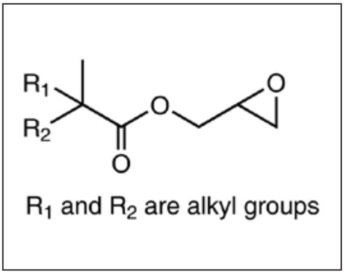


Figure 2.14: Glycidyl ester of versatic acid

Another interesting material often used in polyester resins is the glycidyl ester of versatic acid (Figure 2.14), a synthetic saturated monocarboxylic acid of highly branched C_{10} isomers. The highly branched alkyl group provides excellent wetting, exterior durability, hydrophobicity, flexibility and impact resistance, and acid etch resistance, and low viscosity.

2.4.3 High-solid resins

Like many other resins, high-solid polyesters are an increasingly important class of polyester resins due to the increasing regulatory pressure for reducing VOC emissions. Achieving the low-viscosity polyester resins required for high-solid coatings can be accomplished by considering many factors. Low number average MW and a narrow MW distribution are two important parameters required for high-solid polyester resins. To maintain the final properties of the coating, the lower MW must be compensated by a higher hydroxyl number and hence higher cross-link density. However, a high hydroxyl number generally results in higher resin viscosity due to the effect of intermolecular hydrogen bonding through hydroxyl groups. Therefore, to obtain lower viscosity by minimizing the associative effect of hydrogen bonding, hydrogen-bond acceptor solvents (such as ketones) are frequently used. Structural modifications that reduce hydrogen bonding interactions can also help in reducing the viscosity. The glass transition temperature, T_g, of the resin also controls the viscosity of the polyester solution at a given non-volatile content. Lowering of T_g can be achieved by using acyclic polyol and aliphatic diacids.

2.4.4 Water-reducible polyesters

As discussed in the section on water-reducible alkyd resins (Section 2.3.8), water-reducible polyesters can also be prepared by the classical approach of formulating an acid-rich resin (acid value 35 to 60 mg KOH/g), which upon neutralization with a tertiary amine, forms an anionic salt. Water is then added to produce reasonably stable dispersions of polyester chains swollen with water and solvent. The method for deriving water-reducible polyesters is very similar to that described for water-reducible alkyds (Section 2.3.8). Hydrolytic stability is a very important concern since ester groups are prone to hydrolysis. Steric shielding of the ester group is one of the approaches to increase hydrolytic stability. In addition, the choice of glycol also affects stability. Polyesters prepared from hydrophobic diols with low water solubility, such as 2-butyl-2-ethyl-1,3-propanediol, have better stability against hydrolysis. In another approach, use of use 2,2-dimethylolpropionic acid (DMPA) as one of the diol components is recommended. The carboxylic acid group of DMPA is located on a tertiary carbon and hence is highly hindered, which makes it possible to esterify the hydroxyl groups while leaving many of the acid groups unreacted and available for neutralization with amine.

2.4.5 Polyesters for powder coatings

Powder coatings are an important technology that offers 100 % solid products with practically zero volatile emissions. Polyester resins for powder coating are friable solids with a relatively high T_g (50 to 60 °C) to avoid sintering of particles during storage. They are commonly prepared from terephthalic acid and neopentyl glycol as the principal monomers, though other monomers are also used as required for functionality and balancing of T_g. Isophthalic acid-based polyesters are believed to give better exterior durability. Both hydroxyl and carboxyl functional polyesters are used in powder coatings. Hydroxyl functional polyesters, commonly cross-linked with blocked isocyanates, and carboxyl functional polyesters are cured with epoxy resins.

2.4.6 Curing of saturated polyester resins

In contrast to alkyd resins, which have unsaturated fatty acid structures capable of yielding a cross-linked network by air-drying via oxidative curing, polyesters need to be cured by a suitable external cross-linking agent to obtain the desired mechanical properties as well as durability and chemical resistance. Depending upon expected performance and application conditions, a range of curing agents is used, including amino resins, polyisocyanates and epoxy resins. Some important cross-linking reactions of polyester systems are shown in Figure 2.15 and Figure 2.16.

2.4.6.1 Amino resin cross-linkers

Amino resins are the most important curing agent for hydroxyl functional polyester resins to give baking finishes with adequate curing rate and very good mechanical and chemical resistance properties. Mainly butylated melamine and urea formaldehyde resins are used, up to 40 % by weight of the total binder, depending upon the characteristics of the polyester and final properties required. Acid catalysts are generally used to reduce baking temperature. The residual carboxylic acid group can also take part in the curing reaction.

2.4.6.2 Polyisocyanate cross-linkers

Polyisocyanates are used with hydroxyl functional polyesters for ambient-cure two-component systems giving rise to films with an excellent combination of mechanical properties, solvent resistance, adhesion, durability and optical properties. More details can be found in Section 2.11.

2.4.6.3 Epoxy resins

Epoxy resins are important curing agents for powder coatings based on acid functional polyester resins. Epoxy-polyester hybrid powder

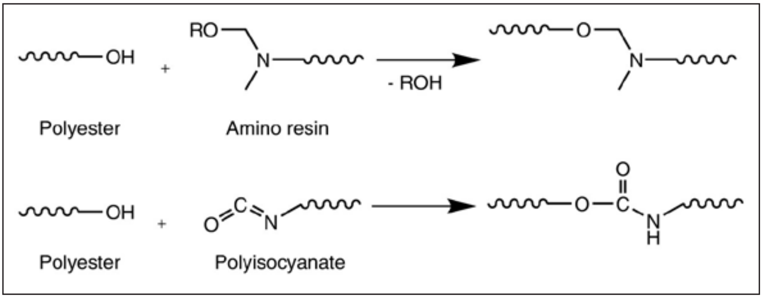


Figure 2.15: Reactions of hydroxyl functional polyesters

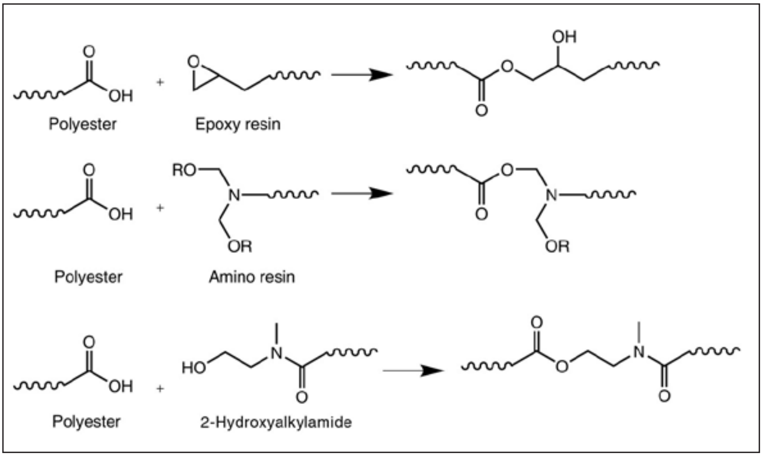


Figure 2.16: Reactions of carboxylic acid functional polyesters

coatings show excellent adhesion, hardness, toughness and chemical resistance. High MW solid epoxy resins are normally used for such coatings. In addition to conventional epoxy resins, triglycidyl isocyanurate is used as a cross-linker for powder coatings with improved durability. More details on epoxy resins can be found in Section 2.9.

In addition to these systems, polyesters modified with silicone are important binders for coatings with excellent weather resistance and mechanical properties coupled with improved heat resistance.

2.4.7 Applications in coatings

Saturated polyesters can be designed for all types of application techniques, including air sprays, airless sprays, electrostatic liquid sprays, electrostatic powder sprays, roller coatings, and curtain coatings. Such coatings are offered as conventional solventbased, high-solid, waterbased systems as well as powder coatings. Due to the broad latitude of raw material selection, they can be designed to meet requirements of different markets. In the automotive industry, they are used in primer surfacer, colored and metallic base coats, and clear coats. With proper selection and balance of various additives, durable films with excellent optical properties can be attained. Other important applications in industrial coatings include can coatings, coil coatings, furniture coatings, OEM coatings, and coatings for light fixtures.

2.5 Unsaturated polyester resins

Unsaturated polyester resins are generally linear low MW polyesters having unsaturation (reactive double bonds) within their backbone. They are supplied as a solution of polymerizable monomers (reactive diluents), most commonly in styrene.

2.5.1 Chemistry of unsaturated polyester resins

The chemistry involved in synthesis of unsaturated polyester resins is very similar to that in synthesis of saturated polyester resins, except that part of the dicarboxylic acid is replaced by diacids containing unsaturation, such as maleic anhydride and fumaric acid. In addition to this unsaturated acid, the predominant saturated acids used are phthalic anhydride, terephthalic acid and isophthalic acid. Phthalic anhydride is more economical, but isophthalic acid is preferred when better chemical resistance and mechanical properties are required. Aliphatic diacids such as adipic acid, azelaic acid and sebacic acid are also frequently used to modify resins requiring increased flexibility and toughness.

Low MW glycols such as ethylene glycol, propylene glycol, diethylene glycol and dipropylene glycol are more common polyols, but other diols such as neopentyl glycol may also be incorporated for superior properties. Monofunctional alcohols are also used as a chain stopper, towards the end of the reaction, to control acid or hydroxyl number.

Reactive diluent is a very important component of unsaturated polyester resins. It should act as a solvent for unsaturated polyester resins as well as copolymerize with unsaturated bonds in the polymer backbone. Styrene is the most commonly used diluent due to good solvency, low cost, low viscosity and good reactivity. Apart from styrene, other monomers such as vinyl toluene, methyl methacrylate and a-methyl styrene as well as some polyfunctional diluents such as 1,6-hexanediol diacrylate, diallyl phthalate, divinyl benzene, and trimethylolpropane triacrylate are used.

In unsaturated polyester resins, the amount of maleic anhydride in proportion to other diacids may range from 25 to 75 % on a molar basis, which influences the number of cross-linking sites and hence governs the properties of the final network. The unsaturated sites may be the maleate (*cis*-configuration) or fumarate (*trans*-configuration) groups in the backbone. During esterification, partial isomerization of maleic anhydride to fumaric acid takes place, and the extent of isomerization may reach 100 %, depending upon composition and reaction conditions. The influence of isomerization on final curing is vital, because copolymerization with styrene is favored with the *trans*-configured fumarate, while maleate gives more of the homopolymer of styrene.

Once unsaturated polyesters are synthesized, they are diluted in reactive diluents that are capable of polymerizing thermally. Therefore, care needs to be taken at this stage to keep the temperature as low as possible. As an additional precaution during thinning, as well as to have better stability on storage, a polymerization inhibitor such as *p-tert*-butylcatechol or hydroquinone are necessarily added to the monomers in the thinning tank before resin dissolution.

2.5.2 Curing aspects

Unsaturated polyester resins are low MW condensation polymers which are transformed to a cross-linked network via radical initiated polymerization. The double bonds in the backbone copolymerize with unsaturated monomer (reactive diluent) present in the system. During polymerization, relatively short low MW polyester chains are cross-linked by short bridges consisting of, on average, around two to three styrene units, forming a densely cross-linked polymer network (see Figure 2.17).

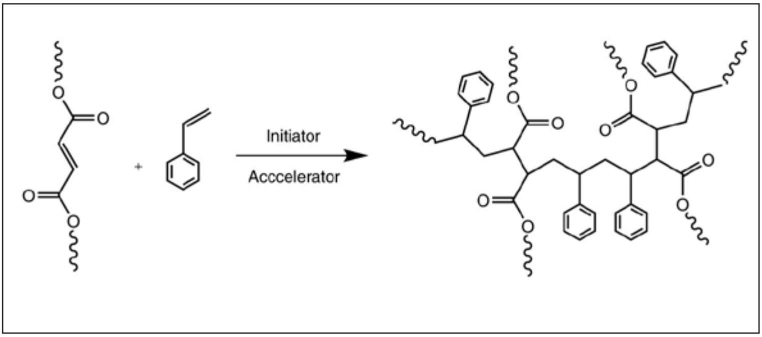


Figure 2.17: Curing reaction of unsaturated polyesters

Free-radical initiated copolymerization can be accomplished either by conventional initiation with organic peroxides or hydroperoxides or phytochemically by using a photoinitiator in UV light. A detailed discussion of UV cured systems is outside the scope of this section; therefore, only conventional initiation is discussed here. The conventional curing of unsaturated polyester resins can proceed either by thermal curing or under ambient conditions using redox system accelerators and promoters, in addition to initiators. The latter approach is more common in the coating industry as two-pack systems where initiator solution or paste is supplied separately, while accelerators and promoters are normally mixed with the unsaturated polyester.

Examples of some important initiators are ethyl methyl ketone peroxide, cyclohexanone peroxide, benzoyl peroxide and cumene peroxide. Accelerator is a reducing agent, such as cobalt octoate, which is added in very small quantity to catalyze decomposition of the initiator into free radicals. Aromatic amines such as dimethyl aniline or dimethyl *p*-toluidine are added to promote that reaction. The two components are combined prior to application, ensuring even distribution of initiator in the system. The dosage of initiator, accelerator, promoter and inhibitor will determine the **pot life**, the longest period of time during which mixture is still usable and can be applied.

Air inhibition of the curing reaction is one of the major limitations of unsaturated polyester systems. Polymerization is considerably inhibited by oxygen, which is added to the terminal radical of growing polystyrene chains by forming a stable peroxide radical. In most coating applications, the top surface is exposed to the air and will remain tacky while the layers below are cured. This is normally addressed by incorporating some insoluble semi-crystalline paraffin wax in the formulation to minimize the problem. Once the coating is applied, the low surface tension wax particles preferentially migrate to the surface and provide a barrier between the oxygen and polymerizing coating, thereby minimizing the difficulty of surface cure. It also reduces the rate of styrene loss from the coating. However, it has tendency to reduce the gloss of the surface, and therefore, for high gloss finishes, the surface needs to be polished after application.

In another approach, to minimize air inhibition, reactive oxygen species are added to the system, which preferentially consume oxygen before it can interfere with the curing reaction. Allyl ethers such as trimethylolpropane diallyl ether, pentaerythritol monoallyl ether and allyl glycidyl ether are normally used for this purpose.

2.5.3 Applications of unsaturated polyester resins

The more significant volume of unsaturated polyester resins are used in fiberglass reinforced plastics, but they also find some applications in coatings and lining materials. The important characteristics of unsaturated polyester systems in coatings are high hardness, high gloss, rapid setting, low volatile content (reactive diluent) and high build capacity. Their low flexibility and high volume shrinkage may result in poor adhesion in the absence of good surface preparation or suitable primers. They also have very good chemical resistance.

In coatings, one of the main applications of unsaturated polyester resins is in furniture and wood finishes. They are also used in gel coats for boats and bathroom fixtures. Another important area of application is in automotive fillers and putties. Unsaturated polyesters are also widely used in chemical resistant coatings and linings for chemical and petrochemical storage tanks.

2.6 Phenolic resins

Phenolic resins were among the first synthetic resins explored by the coating industry, initially used to modify properties of oil-based varnishes as a replacement for some natural hard resins. They are essentially solvent-soluble phenol-formaldehyde condensates with reactive methyllol groups. They are widely used as cross-linkers for thermosetting baking finishes, yielding films with excellent solvent and corrosion resistance properties coupled with favorable mechanical properties.

2.6.1 Raw materials for phenolic resins

Phenolic resins are prepared by condensation of phenolic compounds with aldehyde, commonly formaldehyde. Phenol was initially predominantly used to prepare phenolic resins, but subsequently, a greater variety of alkyl or aryl substituted phenols were explored to tailor the properties of resins by controlling functionality to meet diverse requirements of different coatings. An alkyl group substi-

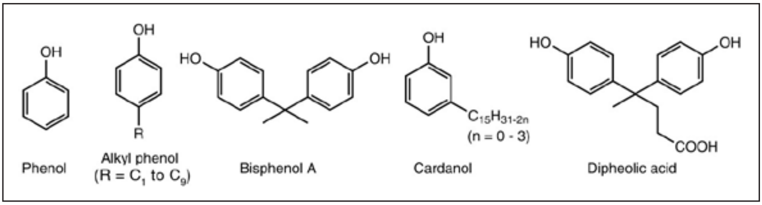


Figure 2.18: Examples of phenolic compounds

tuted at the **para** position increases color stability, and increasing the number of carbon atoms in the alkyl group improves oil and hydrocarbon solubility. Along with various petrochemical derived phenols, some phenolic compounds of plant origin, such as cashew nut shell liquid and its derivative cardanol, are also used widely. A few representative phenols are shown in Figure 2.18.

Formaldehyde is the most common aldehyde used for making phenolic resins. Formaldehyde, being a gas, is normally used as a 37 to 41 % aqueous solution (formalin) or as a solid in polymeric form (paraformaldehyde) that thermally decomposes to formaldehyde during reaction. For some special purposes, furfural or another complex aldehyde is also used.

2.6.2 Reaction chemistry

Formaldehyde reacts with phenol by electrophilic substitution at the 2-, 4- and 6-positions of phenol and will subsequently condense, forming a densely cross-linked network. This reaction can be catalyzed by acid as well as base catalysts. The nature of the product obtained is largely dependent on the type of phenol, the molar ratio of formaldehyde to phenol (f:p) and the catalyst used. Phenolic resins are mainly divided into two broad classes: resoles and novolacs.

2.6.2.1 Resoles

Resoles are produced by a base catalyzed reaction between phenols and formaldehyde with a molar excess of the formaldehyde (f:p > 1), see Figure 2.19. Methylolated phenol is more reactive than phenol; therefore, once the reaction starts, the reaction accelerates in a short time. A higher molar excess of formaldehyde increases the reaction rate but results in a low MW polymer, while lowering the f:p, though still keeping it >1, gives a higher MW product with a lower reaction rate. The methylol group can react at the **ortho** or **para** position of another phenol molecule, producing a methylene linkage and thus giving rise to a polymeric structure. Polymerization may also occur by reaction of the hydroxymethyl group of methylolated phenol with the methylol group of the other molecule to form a dimethylether linkage. Upon further heating, these ether linkages get converted to methylene linkages by liberating formaldehyde. Resoles, by virtue of having reactive methylol groups, are thermosetting resins that can self-cross-link upon heating or acid catalysis.

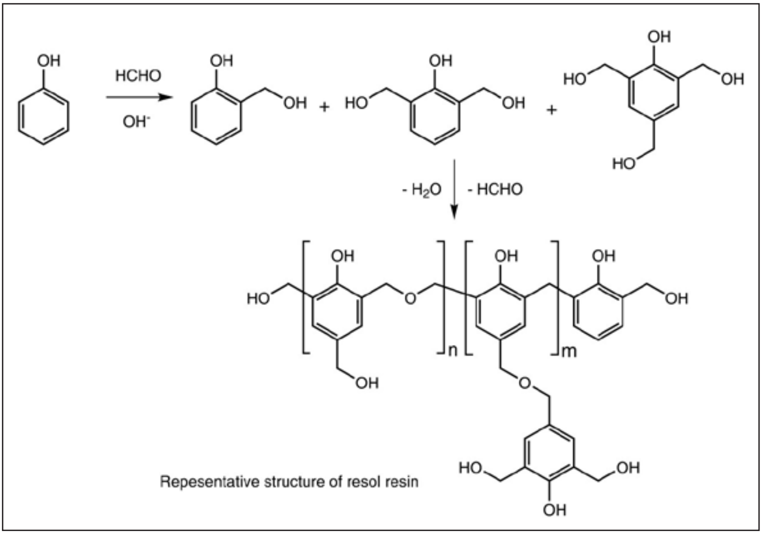


Figure 2.19: Synthesis of resole from phenol and formaldehyde

The classical resoles produced from phenol and formaldehyde are viscous brown syrups soluble in alcohol, which are not suitable as the sole film forming agents in coatings because of their poor flexibility. However, they are used as a curing agent for hydroxyl functional resins, such as alkyds and polyesters, imparting flexibility. The more useful products for the coating industry that are storage stable and compatible with other resins are produced by partial or full replacement of phenol with alkyl or aryl substituted phenols. In another approach, methylol functional resoles are etherified with aliphatic alcohols (Figure 2.20). The type of alcohol and level of etherification is varied to tailor reactivity, compatibility and solubility.

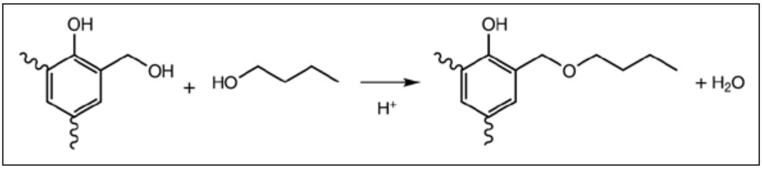


Figure 2.20: Etherification of resole with aliphatic alcohol

Resoles are used as cross-linkers for resins such as alkyds, epoxies, epoxy esters or polyesters. Such coatings find applications in drum and can linings, tank linings and pipe coatings. Phenolic resole or epoxy based baking systems, due to their very good chemical resistance at low film thickness, are popular as linings for food and beverage cans.

2.6.2.2 Novolacs

Novolacs are phenolic resins prepared under acid catalyzed conditions with a molar excess of phenol (f:p <1), see Figure 2.21. Acids such as oxalic acid, sulfuric acid, hydrochloric acid, formic acid, and aromatic sulfonic acids are used as catalysts. In contrast to resoles, here the methylolated phenol molecules are rapidly polymerized through methylene linkages rather than ethers. To control the reaction in larger scale production, normally formaldehyde is gradually added over time.

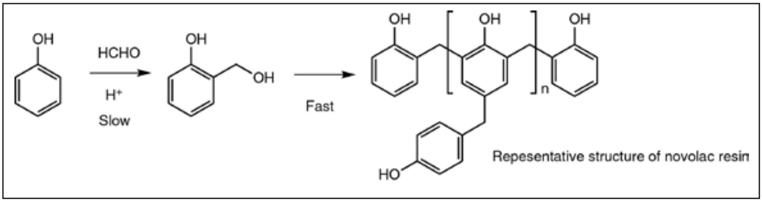


Figure 2.21: Chemistry of novolac resins

As novolac resins do not have any reactive methylol groups, they are thermoplastic in nature, but with further addition of aldehyde or resole, they are converted to a cross-linked insoluble polymer. Novolacs can be considered reactive resins with respect to their phenolic groups, which can be used to cure epoxy resins or be converted to glycidyl ethers to produce epoxy resins (Section 2.9.1). Novolacs prepared from unsubstituted phenol and formaldehyde are hard, brittle, amber colored products that are soluble in polar solvents and are not of much significance in the coating industry. However, more linear resins are formed by using substituted phenols, generally alkyl phenols, with reduced functionality of the phenolic monomer, which leads to a less branched structure. Novolacs useful in the coating industry are of the following types:

Alcohol-soluble non-heat-reactive types are low MW novolacs derived from phenol or cresols that are used in the preparation of novolac epoxy resins, epoxy curing agents, epoxy-phenolic systems, and powder coatings.

Oil-soluble non-heat-reactive novolac phenolic resins are produced from a substituted phenol such as *p*-phenylphenol, *p-tert*-butylphenol or *p*-nonylphenol with a lower f:p ratio. They are designed to be used with drying oil-based varnishes as hard components. Due to the availability of a larger variety of synthetic varnishes, the usage of such varnishes has been declining fast.

2.6.3 Modified phenolic resins

Phenolic resins of both types – novolacs and resoles – are frequently chemically modified to improve their mechanical properties and to make them more suitable for coating applications. **Rosin modified phenolics** have been widely used in oleoresinous varnishes and printing inks. They are prepared by reacting resole type phenolics (~10 to 20 % by weight) with rosin at high temperature (up to 270 °C). The phenolic and alcoholic hydroxyl groups of resoles react with unsaturated double bonds in rosin by what is known as chroman ring formation. The product is then esterified with polyhydric alcohols, such as glycerol or pentaerythritol, to reduce the acid number and build MW. Similarly, resoles from alkylated phenols are reacted to olefinic sites of drying oils or alkyds based on drying oils, and such products are useful in formulating spar varnishes and insulating varnishes.

Another important group of phenolic resins are those derived from cardanol, a substituted phenol obtained from a natural material, cashew nut shell liquid (CNSL). CNSL has a polyunsaturated C_{15} alkyl chain substituted at the m-position of phenol. The phenolic resins derived from cashew nut shell liquid have oxidative curing properties. Despite their dark color, they are very popular binders for anticorrosive air-drying primers.

In phenolic resins, the acidic phenol groups remain chemically unchanged even after chemical cross-linking, making their coatings sensitive to alkali. To obtain alkali-stable products, chemical modifications involving blocking of the phenolic hydroxyl, such as with acetyl chloride or allyl chloride, are used. Coatings produced from such resins have even greater chemical resistance and much reduced alkali sensitivity.

Diphenolic acids, a product from levulinic acid and phenol, are used to make water-dispersible phenolic resins with good storage stability after neutralization of their carboxylic acid groups with a fugitive base.

2.7 Amino resins

The term amino resins is used to describe a very important and versatile group of thermoset polymers derived from nitrogen-containing compounds, most typically, melamine and urea. Amino resins (also known as aminoplasts) are widely used in a number of non-coating thermoset applications. In coatings, they are used mainly as cross-linkers, and not as primary film forming resins. The introduction of amino cross-linking agents facilitated coating formulators in designing products with improved thermo-mechanical and resistance properties, because before their introduction, most coatings were physically drying or oxidative curing systems, with a few exceptions of thermosetting coatings based on phenoplasts. Amino resins helped overcome some inherent limitations of phenolic resins, such as high baking temperatures and discoloration, and therefore they emerged as very versatile cross-linkers for thermoset coatings.

Amino resins are thermosetting polymers that are produced from nitrogen-containing compounds with reactive amino or amido groups that can readily be converted to corresponding methylol compounds upon reaction with formaldehyde. Urea, melamine, benzoguanamine and glycoluril are among the important amino compounds used to derive aminoplasts suitable for surface coatings. Among these, the two most popular amino resins are urea-formaldehyde and melamine-formaldehyde. Amino resins are water-white, viscous materials that may contain added alcohols such as n-butanol, isobutanol, or isopropanol or sometimes their blends with aromatic hydrocarbons. Some water-soluble or water-reducible grades are also available that find application in waterborne coatings.

2.7.1 Chemistry of amino resins

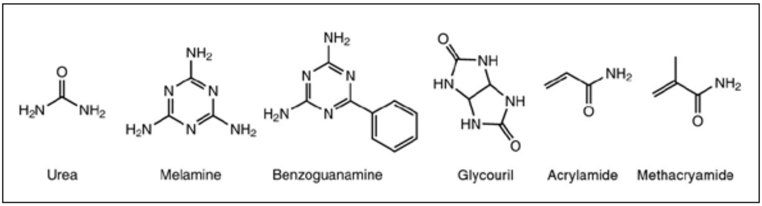


Figure 2.22: Amino compounds for amino resins

Some important compounds used in synthesis of amino resins are shown in Figure 2.22. Synthesis of amino resins for surface coatings typically involves two steps. In the first step, known as a **methylolation reaction** (Figure 2.23), the amino compound is reacted with formaldehyde to yield a methylolated intermediate. In the second step, known as an **alkylation/etherification reaction** (Figure 2.23), the methylolated intermediate is reacted with an alcohol to produce an alkyl ether of methylol groups. While methylol formation (step 1) is possible over the entire pH range, this reaction is generally carried out under basic conditions to obtain useful products.

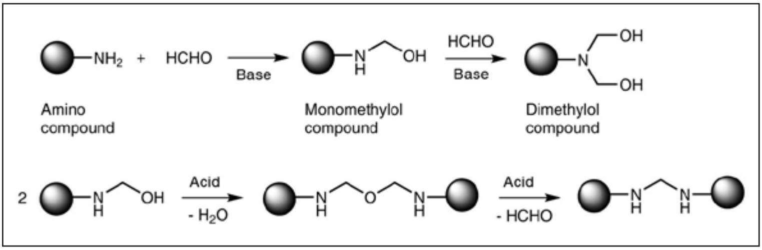


Figure 2.23: Schematic representation of methylolation reaction

Catalysis as well as type of amino compound have a significant influence on this stage; therefore, it is very important to mediate this stage for proper control of the molecular design of the final cross-linker. In the case of urea, under acidic conditions, polymerization of the methylol group is much faster than the methylolation reaction, which leads to insoluble products that are not suitable as cross-linking agents. Alkaline conditions favor methylol formation and provide improved stability against polymerization. Also important is the molar ratio of amino compound to formaldehyde. A molar excess of formaldehyde drives the reaction towards complete methylolation, while lower molar amounts of formaldehyde result in partially methylolated products. Melamine, with its six reactive sites, can yield a range of methylolated compounds depending upon the formaldehyde: melamine molar ratio.

The methylol products formed by the above reaction are partially or fully etherified with alcohol to confer compatibility with co-resins and improved storage stability. This reaction is carried out under acidic pH conditions. The condensation reaction of two methylol groups (polymerization) competes with an alkylation reaction, which can be controlled by a molar excess of alcohol. The processing conditions are quite different for methylated aminoplasts compared to butylated ones, because for methanol, being water soluble, it is not possible to remove water of the reaction easily, while it is in the case of butanol. Therefore, to achieve the desired level of alkylation, a large excess of methanol, up to 1.6 mole per mole of the methylol group, is used. Primary alcohols react more readily with methylol groups than secondary alcohols, while tertiary alcohols are non-

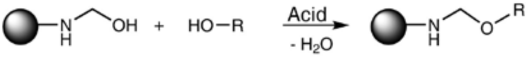


Figure 2.24: Alkylation reaction

reactive. Also, in general, reactivity of a primary alcohol decreases as the length of the aliphatic alcohol chain increases. The type of alcohol also influences viscosity of the resin for a given solid; for example, a butoxyl methyl melamine resin is less viscous than a corresponding methoxy methyl melamine resin.

2.7.2 Types of amino resins

A large variety of melamine resins are commercially available, with important variables being type of amino compound, molar ratio of formaldehyde to amino compound, degree of polymerization, type of alcohol used for etherification and degree of etherification.

Based on the type of amino compound, the aminoplasts used in coatings are classified as four main types: urea formaldehyde (UF), melamine formaldehyde (MF), benzoguanamine formaldehyde (BF) and glycouril formaldehyde (GF) resins. The majority of commercially used amino cross-linkers are MFs and UFs, with others used only for specialty applications. These resins vary in their characteristics as summarized below:

- Reactivity: UF > MF > BF > GF
- Adhesion: UF > GF > BF > MF
- Flexibility: GF > MF > BF > UF
- Resistance properties: GF > BF > MF > UF
- Exterior durability: GF > MF > UF > BF
- Cost: UF > MF > BF > GF

Commercially, each of these types of amino resin is available in different subtypes and degrees of alkylation. Based on alcohol type, the main grades are methylated, butylated, isobutylated and mixed ethers (using mixed alcohols). The type of alkylating agent (alcohol) significantly affects the properties of the final coatings; that is, longer chain alcohols tend to reduce curing rate and increase weight loss on curing but give better flow and leveling and stronger intercoat adhesion.

Depending upon the degree of alkylation and methylolation (Figure 2.25), the above four categories of aminoplasts may be further divided into three subtypes: highly alkylated aminoplasts (alkoxy being the main functional group), partially alkylated aminoplasts (with a considerable number of methylol groups) and high imino content aminoplasts (with relatively more secondary amine groups). For the coating industry, generally only GF is marketed in non-alkylated grades.

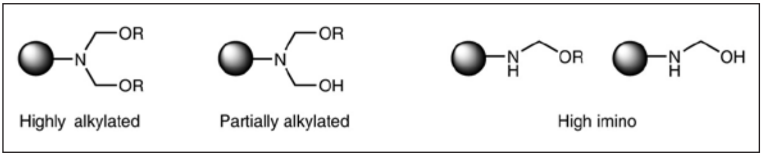


Figure 2.25: Representative structures of aminoplasts with different degrees of alkylation and methylolation

Highly alkylated aminoplasts have very low methylol and imino content with high monomer content. Due to their very low tendency for self-cross-linking, they improve the flexibility and toughness of cured films. They are also known for their excellent compatibility with coresins, low viscosity and excellent stability. A strong acid catalyst and higher curing temperatures are needed while using highly alkylated aminoplasts in coatings. Due to availability of more functional sites for cross-linking, they can produce a higher cross-linkage density.

The partially alkylated aminoplasts are characterized by a considerable number of methylol groups with a polymeric structure and lower monomer and imino contents. MW is an important factor in deciding compatibility of such cross-linkers with solvents and other resins, with higher polymeric aminoplasts having limited compatibility. Higher MW also results in higher viscosity. During curing of coatings, these types of aminoplasts undergo a noticeable degree of self-cross-linking. The cross-linking requires a weak acid catalyst and lower temperature compared to the highly alkylated version, but these aminoplasts suffer from poor storage stability.

High imino aminoplasts are characterized by a lower methylol content and high imino content but high levels of alkylation, an oligomeric structure and higher viscosity. These types of products are predominantly derived from melamine. They are highly reactive with some tendency for self-cross-linking. Curing them with a co-resin can also be carried out without a catalyst or with a weak catalyst. These types of amino cross-linkers release less formaldehyde than partially alkylated or conventional butylated versions. Partially alkylated high imino aminoplasts are available commercially that are even more reactive.

2.7.3 Use of aminoplasts in coatings

Amino resins, being thermosetting materials, can self-polymerize, but this results in a transparent but very hard and brittle polymer network that is not useful for coatings. Therefore, since their introduction, aminoplasts have been used as cross-linking agents for primary film forming resins such as polyesters, alkyds, epoxies, epoxy esters and acrylics. Aminoplasts are predominantly used with polymers having hydroxyl functionality (–OH), though other functionalities such as carboxylic acid (–COOH) and amide (–$CONH_2$) are also used. See Figure 2.26 for the possible reactive sites. The cross-linking reactions need different types of catalysis and curing temperatures. For example, for cross-linking various functional groups in acrylic resin with hexamethoxymethyl melamine at 150 °C, the general order of reactivity of functional groups in co-resins is –OH > –$CONH_2$ > –COOH in the presence of a strong acid catalyst, while in the absence of catalyst, it is –COOH >> –$CONH_2$ > –OH.

During the cross-linking process, the film forming reactions involved are mainly of two types: polymer-aminoplast cross-linking and aminoplast-aminoplast cross-linking. The reactions involved between aminoplast and polymer are represented schematically in

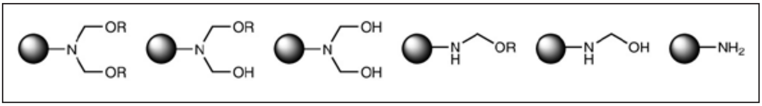


Figure 2.26: Possible reactive sites in aminoplasts

Figure 2.27. The competitive self-condensation reaction will also occur between aminoplast molecules; however, the extent of such reactions will significantly depend on degree of alkylation of the aminoplasts, among other factors.

Urea resins are more economical and faster curing than other aminoplasts, but the final cured films have poor water resistance. They find main applications in wood finishes and in paper coatings due to their faster curing and lower curing temperatures. Ambient cured systems are also designed by using UFs and an alkyd or polyester with higher levels of very strong acid catalysts. These types of systems are supplied in two packages, with a solution of catalyst in alcohol supplied separately, that need to be mixed just prior to the application. Due to their low cost, they are also used in general-purpose low-bake industrial finishes.

MFs are the most widely used amino cross-linkers in the coating industry due to good mechanical properties, good chemical resi-

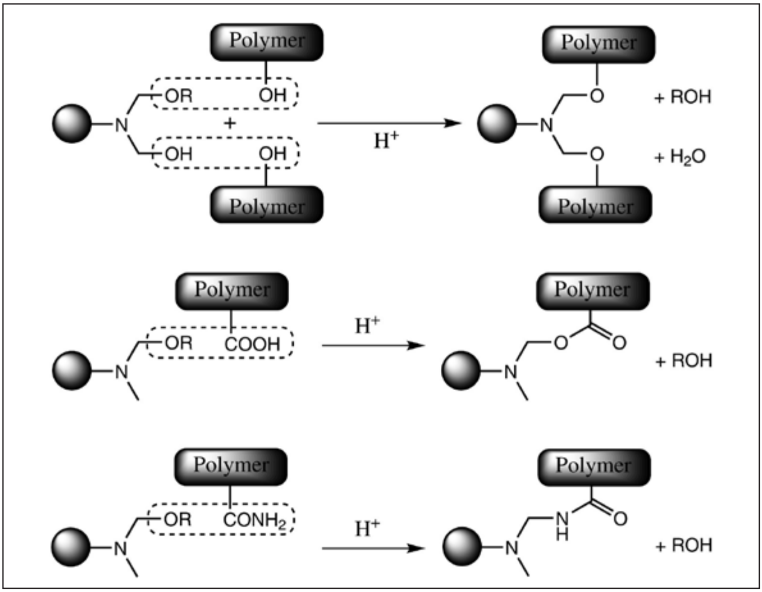


Figure 2.27: Representative reactions between aminoplasts and co-resin

stance, excellent durability and good gloss of their cured coatings. A higher cross-link density compared with the UFs can be obtained with MFs because of the use of hexa-functional melamine. Most of the classical MFs used are partially butylated or isobutylated polymeric products that undergo self-cross-linking in addition to cross-linking with co-resins. Depending on their composition, these types of cross-linkers may have very high viscosity and hence a higher solvent content. Therefore, with development of high-solid and waterborne polymeric systems, use of highly methylated MF cross-linkers has gained considerable attention. Though they require very strong acid catalysts and higher curing temperatures, their lower tendency for self-cross-linking make them suitable for designing coatings with very good flexibility and toughness. These cross-linkers have low viscosity and they are compatible with highly polar as well as waterbased resins, making them excellent candidates for high-solid and waterborne coating systems. Among the most commonly used such products are hexamethoxymethyl melamine resins, which have secured a special place in the coating industry. Partially methylated MFs have also been developed to improve the cure response, but they have a tendency for self-cross-linking. Highly alkylated mixed ether MFs are used to achieve a performance that is a compromise between the highly methylated and butylated products. Popular applications of MFs include automotive coatings, coil coatings, wood coatings and industrial finishes.

BF cross-linkers are used where a combination of film flexibility and hardness is required along with good resistance to corrosion, humidity and chemicals. Due to their high cost and poor exterior durability, their use is limited to specific applications where the above merits are of prime importance and exterior durability is not a concern, such as internal can linings, coil coatings (primers only) and electro-deposition primers.

Demand for high performance amino cross-linkers with low formaldehyde release and high solid content led to development of GF cross-linkers. Highly alkylated GFs are cross-linkers with good storage stability, excellent adhesion to metallic substrates, and anticorrosive properties coupled with a low formaldehyde release during curing. Important applications of GFs include high-solid, high performance coatings, automotive primers, coil coatings and coatings for appliances.

It should be noted that despite their widespread acceptance in the coating industry as a cross-linker of choice for many high performance coatings, aminoplast cross-linkers face many challenges. In the most developed countries, the trend is away from formaldehyde-based polymers due to the highly toxic nature of formaldehyde.

2.8 Acrylic resins

Acrylic resins, also known as acrylates or polyacrylates, are an important class of versatile resins used in a wide variety of architectural, industrial and specialty paints and coatings, sealants, adhesives, and elastomers. In general, their excellent resistance to sunlight exposure and water make them especially suitable for a number of end-use applications. Acrylic resins are commercially offered as solid powders or pellets, waterbased dispersions, and as solutions in organic solvents, including high-solid grades and photo-curable grades, and thus cater to a broad range of product technologies.

Typical acrylic resins are high MW polymers or copolymers of acrylate and/or methacrylate monomers prepared by radical-initiated chain-growth polymerization (see Figure 2.28). In addition to the (meth) acrylate monomers, other functional (meth)acrylate monomers as well as non-acrylate monomers (typically vinyl monomers) are frequently used in preparation of commercial acrylic copolymer resins to impart reactive functionality or special properties or for lower cost. Some examples of these monomers are shown in Figure 2.29.

The terms **pure acrylics** or **100 % acrylic resin** is frequently used to differentiate acrylic resins derived strictly from (meth)acrylate

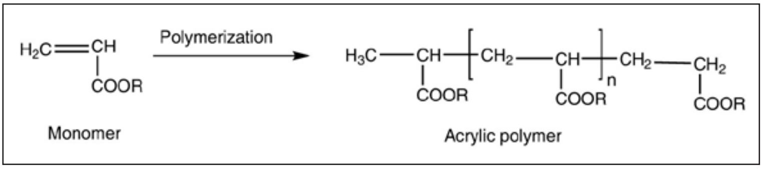


Figure 2.28: Polymerization reaction for acrylic resins

monomers from those derived from non-acrylate monomers in addition to (meth)acrylate monomers. The commercial availability of a large number of monomers makes it possible to prepare acrylic resins and copolymers with virtually unlimited possibilities. This allows manufacturers to customize these resins precisely to the requirements of the final product. For instance, using different combinations of monomers and processing conditions, acrylic resins with such a wide range of properties as fibers, plastics, coatings and elastomers can be prepared.

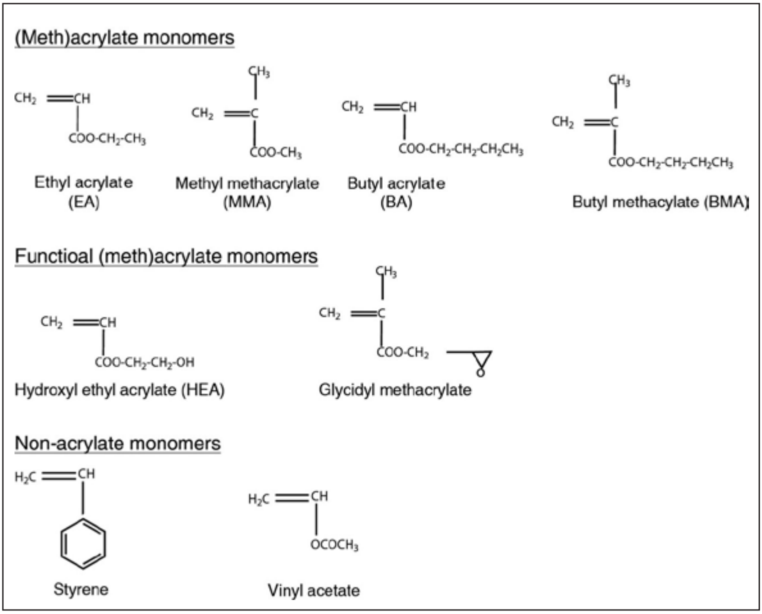


Figure 2.29: A few examples of monomers used in acrylic resins

2.8.1 Polymer composition and properties

Acrylic resins are generally prepared by radical initiated chain-growth polymerization. As mentioned earlier in this chapter, chain-growth polymerization allows for preparation of polymers with very high MWs, of the order of a few hundreds of thousands of grams/mole. Acrylic resins with such high MWs are generally capable of forming useful coatings under ambient conditions without the need for cross-linking. These resins, known as **thermoplastic acrylics**, are generally used in a wide range of architectural and specialty coatings. Resins prepared using one or more functional (meth)acrylate monomers will result in functionalized acrylic resins (Figure 2.30) that can be cross-linked through their pendant functional groups using appropriate cross-linkers. Such acrylic resins and coating systems are known as **thermosetting acrylics**. Thermosetting acrylics are widely used in high-end industrial coating applications such as automotive coatings and appliance coatings.

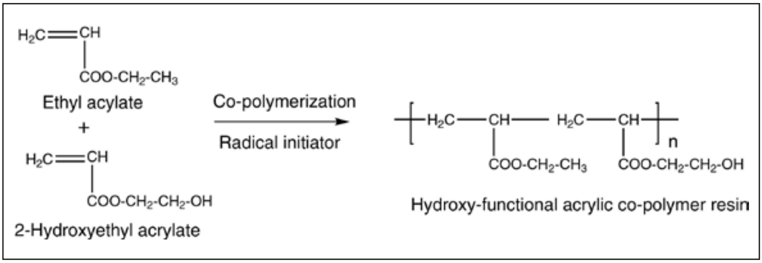


Figure 2.30. Hydroxyl functional thermosetting acrylic copolymer resin

The two most important features of any acrylic monomer are: (a) its parent structure and (b) the type of alcoholic chain forming the ester group. As mentioned before, there are two primary types of acrylate monomer families: acrylate monomers and methacrylate monomers (see Figure 2.31). By virtue of their chemical structures and reactivity, the film properties of resins obtained from these

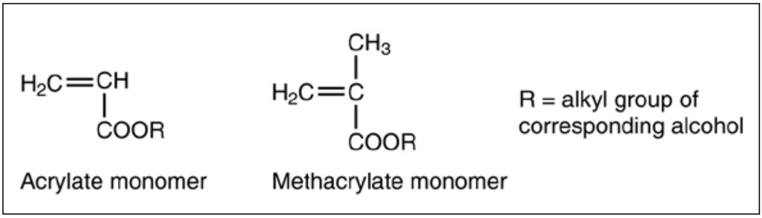


Figure 2.31: General structures of acrylates (acrylic acid esters) and methacrylates (methacrylic acid esters)

monomers are significantly different. In general, coatings based on methacrylate resins are much harder (have a higher T_g), less flexible and have better outdoor durability properties than their acrylic counterparts. Therefore, resins based on methacrylate monomers are used in applications requiring outstanding outdoor durability and chemical resistance.

The type of alcoholic part has a significant effect on thermo-mechanical properties, such as T_g, hardness, flexibility, impact resistance and adhesion of acrylic coatings. In general, as the number of carbon atoms in the alcoholic chain increases up to about 8, their film hardness, T_g, viscosity and solvent resistance decreases while their compatibility with a wide range of resins and solvents increases. This is because the dangling chain of the pendant alcohol on the polymer backbone increases the free volume of the cured film. The increase in free volume brings about all the changes in their physicochemical and thermo-mechanical properties. Branched chain alcohols have more significant impact compared to their linear counterparts due to steric effects. Figure 2.32 illustrates the effect of an increase in number of carbon atoms of the alcoholic chain of the acrylic monomers on the T_g of their polymers.

Table 2.6 shows T_g values of some selected acrylic and vinyl homopolymers expressed in °C. Note the effect of type of alcoholic chain as well as parent monomer structure on the T_g of homopolymers. The

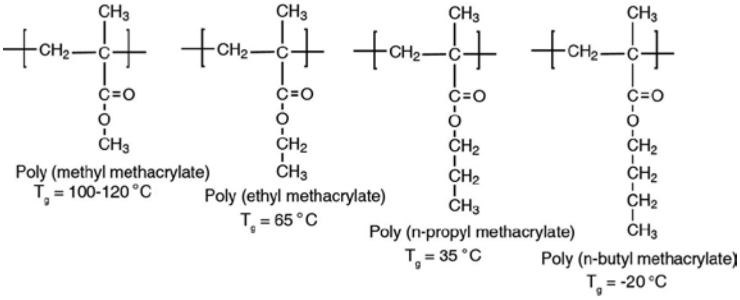


Figure 2.32: Effect of increasing chain length of alcoholic part on polymer properties

T_g of acrylic copolymer resins depends on the T_g values of individual constituent monomers and their proportion in the chain. A particularly useful means of estimating the T_g of a copolymer is that given by the **Fox equation**:

$$1/T_{g\,(\text{copolymer})} = (x_1/T_{g1})+(x_2/T_{g2})+(x_3/T_{g3})+\ldots+(x_n/T_{gn})$$

Where, x_1 is the weight fraction of the first monomer in the copolymer and T_{g1} is the homopolymer glass transition temperature of the first monomer. In this equation, T_g is the glass transition temperature expressed on the Kelvin scale.

Table 2.6: T_g of some selected acrylic and vinyl homopolymers

Homopolymer	T_g [°C]	Homopolymer	T_g [°C]
Poly(acrylic acid)	105	Poly(ethyl methacrylate)	65
Poly(methyl acrylate)	9	Poly(butyl methacrylate)	22
Poly(ethyl acrylate)	-24	Poly(2-hydroxyethyl acrylate)	-15
Poly(butyl acrylate)	-54	Poly(vinyl acetate)	32
Poly(2-ethylhexyl acrylate)	-70	Polyacrylonitrile	110
Poly(methyl methacrylate)	105	Polystyrene	100

The effect of T_g of acrylic resins on various film properties is depicted in Figure 2.33.

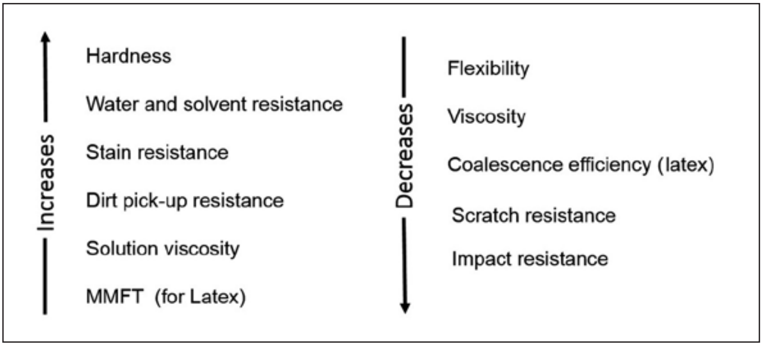


Figure 2.33: Effect of T_g of acrylic resins on various film properties of coatings

Thus, it follows that proper selection of the types and amounts of monomers is critical in deriving acrylic copolymer resins with the correct T_g, which in turn controls many physic-chemical properties of their coatings. Besides T_g considerations, monomer selection also takes into account such important properties of coatings as outdoor durability, film clarity, gloss, gloss retention, film formation capability and emulsion stability.

2.8.2 Acrylic resin types

As mentioned above, both thermoplastic and thermosetting type acrylic resins are commercially available for coatings, elastomers, sealants and adhesive applications. These resins are supplied in many different delivery forms such as powders or pellets, solutions in organic solvents and aqueous dispersions. These resin types are briefly described below.

2.8.2.1 Solution acrylic resins

The term **solution acrylics** refers to acrylic resins prepared by chain-growth polymerization using a solutionbased polymerization process. Here, acrylic monomers and initiators are slowly added to an organic solvent and polymerization is carried out at a predetermined temperature and inert atmosphere with efficient stirring. Both monomers and the polymer formed are miscible in the selected solvent. With the progress of polymerization, the solution viscosity will increase and heat transfer becomes difficult, limiting the solid content of the final solution. Both thermoplastic and thermosetting solution acrylics can be prepared by this technique.

Thermoplastic solution acrylics (TPAs)

TPAs are high MW acrylic copolymers supplied in organic solvents. These copolymers are typically prepared from monomers such as methyl methacrylate, styrene, or n-butyl acrylate. The selection of solvent is dictated by solubility of the resin, solution viscosity, evaporation rate, type of final coating for which it will be used, and cost. TPAs are generally used in systems that cure at ambient temperature without the need for cross-linkers. Therefore, such resins are designed with specified T_g so as to produce dried films with desired thermo-mechanical properties. For example, TPAs for use in automotive top coats must have a T_g over 70 °C. In general, film strength increases with MW of TPA resins, although above a MW of about 90,000, the change in properties with increasing MW is not substantial. Such TPAs are generally not supplied above a MW of about 100,000 because they tend to exhibit **cobwebbing** upon spraying rather than atomizing to small droplets.

One major limitation of TPAs is their high solution viscosity (due to their high MW), which necessitates use of a large amount of organic solvent in their coating formulations to be able to offer products at sprayable viscosity. This has two major consequences: (a) final coatings will have very high solvent content and may not be compliant to VOC related regulations and (b) due to the large amount of volatile solvent, such coatings will have low non-volatile content, resulting in lower dry-film thickness. This may require labor-intensive multi-coat applications to achieve the desired film thickness. Due to these reasons, solventbased TPA coatings are rapidly declining in their usage.

Thermosetting solution acrylic resins

Thermosetting acrylic resins contain reactive functional groups that can be used to obtain cross-linked films after application. These resins are prepared by a very similar process to that used for TPAs by using functional acrylic monomer as one of the co-monomers. Typical functional monomers used for such resins are 2-hydroxyethyl acrylate for –OH groups, acrylic or methacrylic acid for –COOH groups, and glycidyl methacrylate for epoxy group functionalization. Since these resins are used in coatings in conjunction with cross-linker, their MW and degree of cross-linking increases during the curing process. Therefore, these functional acrylic resins do not necessarily have to be of high MW. Such resins are therefore prepared with a low MW (and hence lower viscosity) and a specific functional group content. High functional group content resins after cross-linking generally yield coatings that are harder, are more resistant to water and solvents, and have greater film strength. The product data sheets often list information about their functional group content, non-volatile content, and type of solvent used to help formulators in selection of such resins.

2.8.2.2 Waterborne acrylic resin dispersions

As discussed above, there are many technical and environmental pollution related issues in using solventbased acrylics, especially solventbased TPAs. This has led to the development of waterborne acrylic resins and coating systems. Commercial waterborne acrylic resins are supplied as dispersions in water. Generally, a polymer dispersion is a two-phase system consisting of spherical polymer particles, usually less than 1 μm in diameter that are uniformly distributed (dispersed) in a continuous water phase. The particles in such dispersion are kept from agglomerating and becoming unstable by different stabilization mechanisms so as to provide long-term stability during their manufacture, storage, transportation and use. Aqueous polymer dispersions are usually milky liquids with a viscosity that varies from very low, like that of water, to high, like that of whipped cream. Unlike polymer solutions in organic solvents, the viscosity of polymer dispersions is not dependent on the MW of the polymer particles. This allows formulators to use very high MW acrylic resins without facing the challenges of VOCs or low solid content that are frequently encountered in solution systems. It is also important to note that most polymer dispersions are sensitive to such factors as temperature, pH and applied shear rate and can undergo destabilization, irreversibly separating into two phases – called **breaking** of the dispersion – if not properly formulated, handled and stored.

The commercially available acrylic dispersions are broadly of two types: acrylic latex and water-reducible acrylics.

Acrylic latexes are high MW acrylic (co)polymer particles dispersed in water. Synthetic latexes are prepared by a radical polymerization mechanism using an emulsion polymerization technique. The emulsion polymerization is carried out in water using monomer(s), surfactant (emulsifier) and water-soluble initiator. In a typical manufacturing process, an initiator and a separate emulsion of monomer(s) in water are slowly added to a reaction vessel containing water and emulsifier, at a predetermined rate. Polymerization of monomers occurs within tiny pockets formed by aggregation of emulsifier molecules, called **micelles**, resulting in formation of stabilized polymer particles. The mechanism of emulsion polymerization is very complex, and the composition, MW, properties, particle size and morphology, and stability of the latex formed are dependent on several factors, including types of monomers, emulsifiers, and initiators, rate of addition, stirring speed, pH and temperature. Latexes are typically supplied at 35 to 45 % non-volatile content with varying particle size range. Because the stability of the latex formed is dependent on pH, temperature and shear rate, care must be exercised in handling, storage and use of latex to avoid irreversible destabilization.

Commercial latexes are supplied both as thermoplastic and thermosetting types. Thermoplastic acrylic (and vinyl) latexes are very commonly used as binders for architectural paints and some specialty coatings. Such coatings are required to dry under ambient conditions without any chemical cross-linking and hence are designed to precise T_g and minimum film formation temperature.

Thermosetting acrylic latexes are prepared similarly to thermoplastics but using some additional functional acrylate monomers in their copolymer composition. For example, when 2-hydroxyethyl acrylate is used as a co-monomer, the resulting latex will be a hydroxyl functional acrylic latex. Functional group type and content can be varied by using different functional monomers and by varying copolymer composition. Thermosetting acrylics require appropriate cross-linkers, and their coatings are cured at temperatures dictated by the type of cross-linker. Thermosetting latexes are typically offered with such functional groups as hydroxyl, carboxylic acid, and epoxide, while many other types may be possible. Self-cross-linking acrylic resins are another type of thermosetting acrylic latex finding increasing interest. While the terminology is a bit confusing, self-cross-linking acrylic latexes are typically comprised of reactive functional groups (such as –OH, –COOH) and the added cross-linker. The cross-linking reaction is triggered at ambient temperature after water has evaporated from the wet film. An example of such a system is a stable carboxylic acid functional latex supplied with a polyaziridine type cross-linker, which after application will undergo a cross-linking reaction at ambient temperature over a period of a few days.

2.8.2.3 *Acrylic resins for high-solid coatings*

In general, high-solid resins are resin solutions in organic solvents that are required to be supplied at >70 % solid content at manageable viscosities. Since viscosity of resin solutions is very dependent on their MW, high-solid resins are designed with low MW. In order to obtain the desirable properties of coatings with these low MW resins, high functionality is required for cross-linking. Thus, typical high-solid resins have low MW and high functionality per unit weight. High-solid acrylic resins are prepared by using higher amounts of functional monomers (compared to conventional thermosetting acrylic resins), and MW is reduced by using a higher initiator concentration during solution polymerization. Thus, by controlling composition and MW, a wide range of high-solid acrylics is possible. High-solid hydroxyl functional acrylics are very widely used in high-solid two-component polyurethane coating formulations for applications such as automotive clear coats.

2.8.2.4 *Acrylic resins for powder coatings*

All the major ingredients, including resins, of powder coatings are solid powders. The ingredients are mixed and then homogenized in a heated extruder (a process called **melt kneading**). The extruded product is cooled, crushed and milled, sieved and classified. The resin must melt at a predetermined temperature to effect proper mixing and pigment dispersion. In the case of thermoset powder coatings, there should not be any cross-linking during this extrusion process or the product will be rendered useless. Thus, resins for power coatings must meet a number of critical specifications pertaining to their T_g, melting temperature, and functionality type and amount. Hydroxyl functional and carboxylic acid functional acrylic resins are very commonly used in commercial applications. These are prepared to predetermined T_g and functional group content by solution polymerization. The process solvent is then removed by distillation, polymer melt is discharged onto cooling conveyer belts and is then crushed to the desired particle size. Depending upon the type of functional groups and end-use requirements, different cross-linker types are used in the formulation.

2.8.2.5 Acrylic resins for radiation curable coatings

Radiation curable coatings are special types of systems that are cured by exposure of their wet films to high energy radiation such as UV light or an electron beam. The markets for such coatings, because of their rapid curing at ambient temperature, low energy requirement, and solvent-less composition, have been steadily growing and expanding in many new areas. The binder systems used for such coatings are currently dominated by those containing acrylate functional groups. Unlike the acrylic resins described above, the resins for radiation curable systems contain free acrylate groups with the unsaturated double bonds of acrylates still present. During the radiation curing process, cross-linking reactions occur through these free acrylate groups by radical polymerization, resulting in formation of a cross-linked network, as depicted in Figure 2.34.

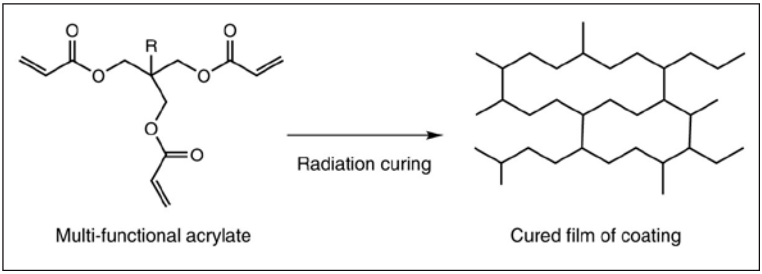


Figure 2.34: Typical structure of an acrylate functional system for radiation curable coatings

A typical resin for a radiation curable coating contains two or multifunctional acrylate oligomer(s) with MWs ranging from a few hundred to a few thousand grams per mole. These oligomers have a high viscosity depending upon their chemical makeup and MW. Low MW multifunctional acrylate compounds with very low viscosity are invariably added to the oligomers to reduce the viscosity of their formulations. A photoinitiator is also used in the formulation and produces free radicals upon exposure to radiation, which initiates the curing reaction. These low MW acrylates are reactive diluents (Figure 2.35), which both serve as solvents in reducing viscosity and become part of the cured film network by virtue of their reactive

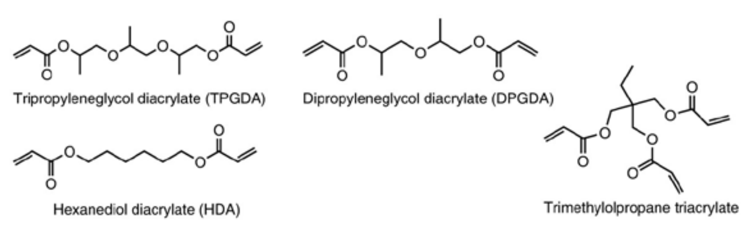


Figure 2.35: Some commonly used monomeric acrylates (reactive diluents)

acrylate functionality. Such systems thus do not require addition of solvents and hence can be supplied as 100 % solid systems.

Commercial acrylate oligomers are available that have a wide range of chemistries, functional group (acrylate) content, and viscosity. Among the most commonly used oligomers are difunctional polyester acrylates, epoxy acrylates, polyurethane acrylate and polyether acrylates. The chemical structures of oligomers control such properties as viscosity, reactivity, and thermo-mechanical properties of cured films. For example, epoxy esters produce much harder films compared to polyether acrylate of comparable

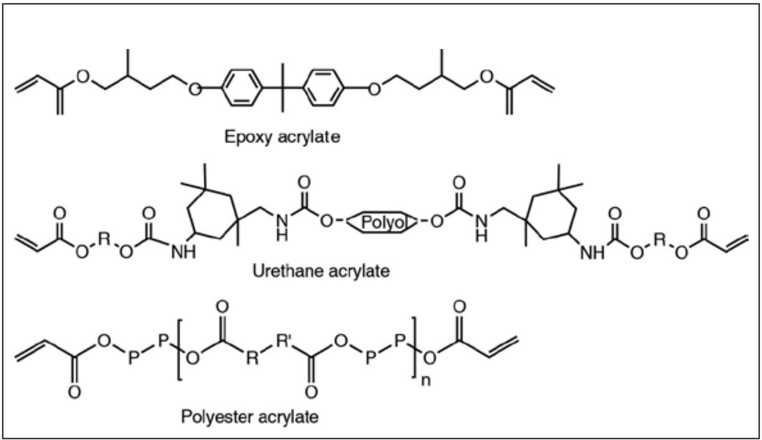
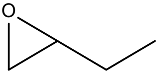


Figure 2.36: Some examples of acrylate oligomers used in radiation curable coatings

MW and acrylate content. Reactive diluents also play an important role in controlling viscosity of compositions, cure speed, and thermo-mechanical properties. Formulators of radiation curable coatings must select suitable combination of oligomers (Figure 2.36) and reactive diluents so as to attain desirable film properties for any given application.

2.9 Epoxy resins

Epoxy resins are a very important class of thermosetting synthetic polymers used in coatings, adhesives and composites. Epoxy resins are characterized by having three-membered epoxy (also called oxirane or epoxide) functional groups as reactive sites for cross-linking. A typical terminal epoxy group, as depicted below, is commonly known as a glycidyl group.



Glycidyl group

These resins have been commercially available for more than half a century and are used in a diverse range of applications such as coatings, plastics, adhesives, and construction chemicals due to their important characteristics, as listed below.

- Excellent adhesion to a wide range of substrates
- Chemical and water resistance
- Corrosion resistance
- High electrical resistance
- Better heat resistance than most general binders used in coatings
- Resistance to hydrolysis
- Excellent toughness, hardness and flexibility
- Ability to have properties varied or balanced through chemistry
- Wide latitude of curing agents and chemistries.

Besides these excellent characteristics, one major limitation associated with common classes of epoxy resins is their poor durability in exterior conditions. Nevertheless, epoxy resins have been the workhorse of high performance polymers for protective coatings where high corrosion and chemical resistance are important.

2.9.1 Types of epoxy resins

The majority of the commercially important epoxy resins are derived by reacting epichlorohydrin with various starting materials containing functional groups with an active hydrogen, such as a phenolic hydroxyl, hydroxyl, carboxylic acid, or amine. The initial reaction yields chlorohydrin, which upon subsequent dehydrochlorination yields a glycidyl group (Figure 2.37). Another class of epoxy resins and compounds are prepared by epoxidation of compounds containing carbon-carbon unsaturation using peracids or hydrogen peroxide. This chapter will briefly describe the major types of epoxy resins used in the coating industry.

2.9.1.1 Bisphenol A epoxy resins

Epoxy resins prepared from the reaction between bisphenol A (BPA) and epichlorohydrin are commercially the most important ones, covering around 80 to 85 % of the volume of epoxy resins used in the industry. Various BPA epoxy resins available on the market primarily differ in their MW, and can be categorized as:

- Low MW: mainly used in adhesives, composites and some high-solid or solvent-free coatings
- Medium MW: most commonly used in conventional two-component epoxy coatings
- High MW: predominantly used for epoxy esters, powder coatings, can coatings and electrophoretic coatings
- Very high MW (also known as phenoxy resins): commonly used for thermoplastic epoxy lacquers.

A reaction scheme for synthesis of the diglycidylether of bisphenol A (DGEBA) and higher MW epoxy resins is shown in Figure 2.37.

Epoxy resins with varying MW can be prepared by varying the molar ratio of epichlorohydrin to BPA. DGEBA is the lowest MW epoxy resin and is produced in high volumes. Pure DGEBA (average number of repeat units $n = 0$) tends to crystalize at room temperature (melting point 45 °C), and therefore, commercially important liquid epoxy resins are supplied with $n \approx 0.1$, which inhibits crystallization. The higher MW epoxy resins are more commonly prepared

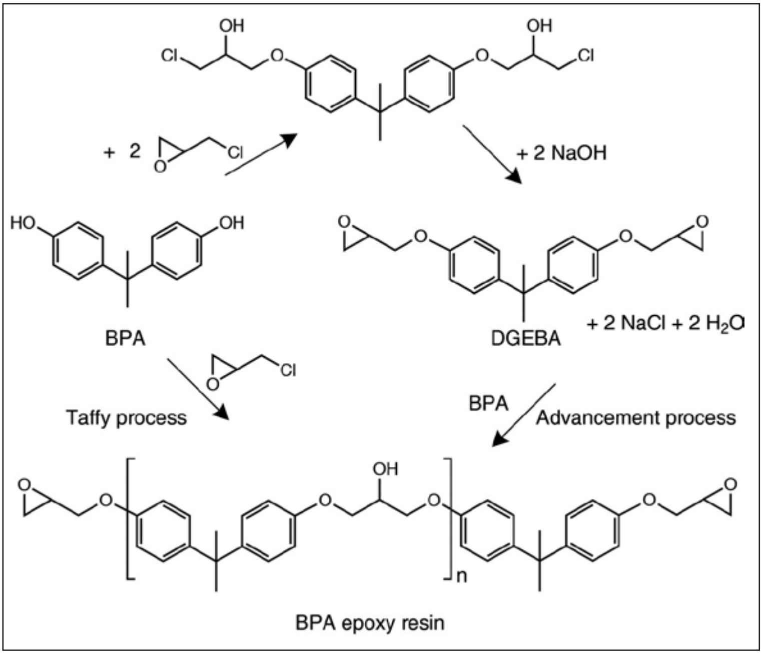


Figure 2.37: Synthesis of an epoxy resin

by reacting DGEBA with additional BPA by what is known as the **advancement process** (Figure 2.37).

Epoxy resins have two sets of functional groups – two terminal epoxy groups and hydroxyl groups on the polymeric backbone. These reactive functional groups are utilized in modification or cross-linking reactions of epoxy resins. The aromatic structure in the backbone contributes to rigidity and hardness along with very good chemical, thermal and electrical resistance. The aliphatic sequence with an ether linkage imparts flexibility and toughness. While the generic structure shown is linear, the actual resin may have some degree of branching arising from side reactions of epoxy and secondary hydroxyls, particularly in the higher MW grades. As the n value increases, the MW, epoxy equivalent weight, hydroxyl content and melting point of the resin increases. The typical commercial grades of BPA epoxy resins are shown in Table 2.7.

Table 2.7: Typical grades of BPA epoxy resins

Average number of repeat units (n)	Melting point [°C]	EEW*	Typical applications (coatings)
0.1	Liquid	182–192	Floor coatings, solventless and high-solid ambient cure two-component coatings
2	50–60	475–550	Conventional solvent-borne two-component coatings
4	80–100	860–930	Powder coatings, intermediate for epoxy ester resins
9	100–120	1600–1950	Epoxy-phenolic/amino baking system (can coatings)
12	120–150	2500–4000	Epoxy-phenolic/amino baking system (can coatings)

** Epoxide equivalent weight*

2.9.1.2 Bisphenol F epoxy resins

Another aromatic ether type of commercial epoxy resins, analogous to BPA epoxy resins, is based on bisphenol F. Such epoxy resins are known as bisphenol F epoxy resins (Figure 2.38).

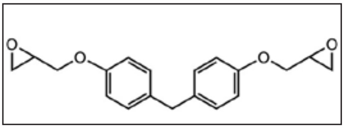


Figure 2.38: Bisphenol F resin

Compared to BPA, bisphenol F epoxy resins have lower viscosity, and their cross-linked films have higher T_g and heat distortion temperatures along with better solvent and chemical resistance. Due to these excellent properties coupled with low viscosity, bisphenol F epoxy resins are popular in very high-solid and solvent-free coating systems.

2.9.1.3 Epoxy novolac resins and high functionality epoxy resins

Being a glycidyl ether of a novolac type phenol formaldehyde resin, epoxy phenol novolac resins (Figure 2.39 (a)) are the polymeric multifunctional counterpart of bisphenol F resin. They are supplied as highly viscous through semisolid to solid resins. They are generally prepared by reacting epichlorohydrin with novolac type phenol formaldehyde resins.

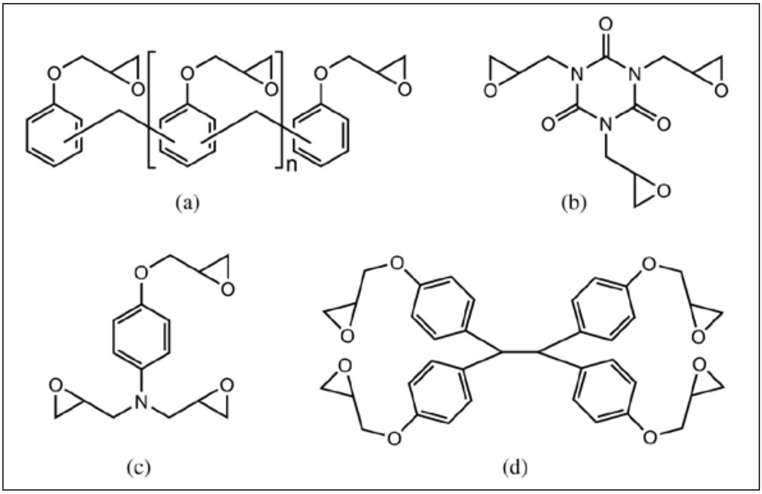


Figure 2.39: Some multifunctional epoxy resins: (a) epoxy phenol novolac, (b) triglycidyl isocyanurate, (c) aminophenol epoxy resin, (d) tetraphenolethane epoxy

The majority of commercial novolac epoxy resins are available with average functionality ranging from around 2.2 to 4, though higher functionality (up to ~6) is used when required. Unlike BPA epoxy resins, these resins do not have hydroxyl functionality. Due to higher functionality, they can produce films with a highly cross-linked matrix having high heat and solvent resistance and resistant to aggressive chemicals. With proper selection of cross-linking agent, these networks can even resist mineral acids such as H_2SO_4, HCl or HF.

Some examples of multifunctional epoxy resins other than epoxy phenol novolac resins are depicted in Figure 2.39 (b), (c) and (d). Triglycidylisocyanurate is a solid trifunctional epoxy cross-linker used in powder coatings, which provides a higher cross-link density and superior photochemical stability compared to BPA epoxy resins. The use of triglycidyl isocyanurate may present toxicity hazards.

2.9.1.4 Brominated BPA epoxy resins

Brominated BPA epoxy resins are analogues to BPA epoxy resins that are derived from tetrabromobisphenol A (Figure 2.40). These resins

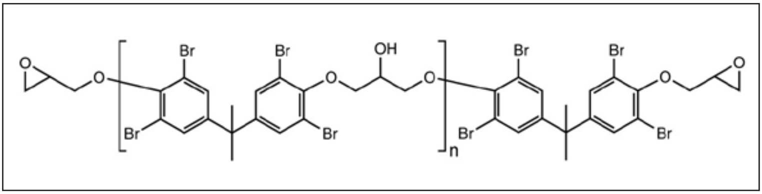


Figure 2.40: Brominated BPA epoxy resin

are supplied both as liquid and solid grades and are mainly used for fire retardant applications. They are copolymerized with BPA to derive various grades with varying bromine content (up to 48 %).

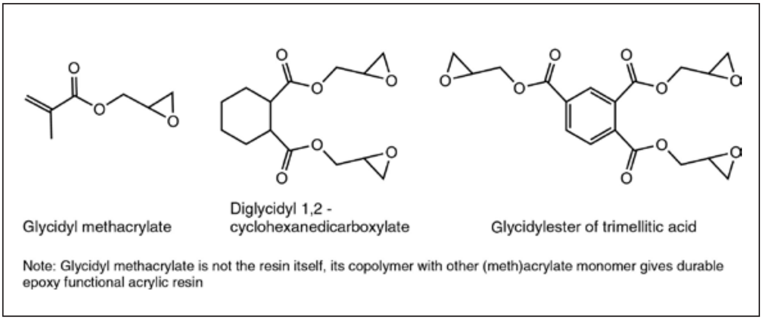
2.9.1.5 Cardanol-based epoxy resins

Most of the BPA-based epoxy resins are quite rigid and are based on petrochemicals. A quite different type of flexible epoxy resin is based on cardanol, derived from cashew nut shell liquid. Mono-, di- and multifunctional derivatives are possible. Mono- and difunctional low viscosity derivatives are used as modifiers and diluents, while complex di- and multifunctional epoxies are used in two-component ambient cure epoxy systems. They give the cross-linked matrix excellent flexibility, toughness and impact resistance. They possess very good water, chemical and corrosion resistance.

2.9.1.6 Light fast epoxy resins

Poor light fastness (exterior durability) of BPA type epoxy resins, due to the presence of aromatic ether linkages, limits their outdoor applications. Epoxy resins with improved weathering performance can be obtained by using aliphatic epoxy resins. One of the important epoxy resins in this class is the glycidyl ether of hydrogenated bisphenol A. These resins have lower viscosity, lower reactivity and higher cost compared to BPA epoxy resins.

Other types of aliphatic epoxy resins with glycidyl functionality are derived by copolymerization of glycidyl methacrylate with other acrylate monomers. A range of products is offered by varying the glycidyl methacrylate content, co-monomer composition and MW. These resins produce coatings with excellent exterior durability and acid etch resistance. They are reported to be widely used in



Note: Glycidyl methacrylate is not the resin itself, its copolymer with other (meth)acrylate monomer gives durable epoxy functional acrylic resin

Figure 2.41: Some examples of light fast epoxy resins

automotive clear coats. Some examples of technically important, durable glycidyl ester type epoxy resins are depicted in Figure 2.41.

2.9.1.7 Other epoxy resins and reactive diluents

Reactive diluents are low viscosity mono- or difunctional epoxies based on aliphatic alcohols, diols, alkylated phenols or carboxylic acid that are used to reduce the viscosity of standard epoxy resins and react with curatives during the curing process (Figure 2.42). They tend to reduce chemical resistance, heat resistance and hardness of the coatings. The difunctional diluents have fewer negative effects than monofunctional diluents. Higher vapor pressure (volatility) of some of the reactive diluents increases their toxicity, health risks and problems with skin irritancy.

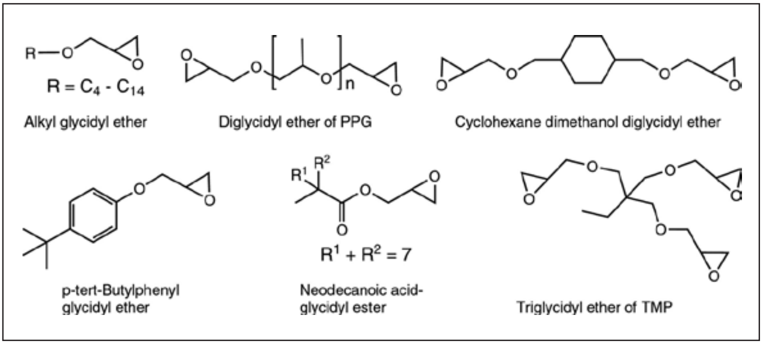


Figure 2.42: Examples of reactive diluents

Glycidyl ethers of polyalkylene glycols are low viscosity epoxy resins that are useful as reactive diluents for conventional BPA epoxy resins. Their aliphatic ether backbone structure improves flexibility, elongation and impact resistance. However, heat, solvent, water, chemical and corrosion resistance are reduced. They are therefore frequently employed as a modifier rather than the sole binder.

2.9.1.8 Resins with internal epoxy groups

This class of epoxide resins is completely different than the resins discussed so far. Internal epoxy groups (Figure 2.43) have very different reactivity compared to glycidyl epoxy groups. These epoxy resins are typically prepared by epoxidation of carbon double bonds (olefin type) using peracids or hydrogen peroxide. Epoxidized vegetable oils (mainly soybean oil and linseed oil) are important products of this class. Other important resins in this class are cycloaliphatic diepoxy compounds such as 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate. The internal epoxy groups have reduced reactivity towards nucleophiles but can easily undergo self-condensation induced by Lewis or Bronsted acids. Therefore they are frequently used in cationically cured thermal or photocured coating systems. They can also be used by cross-linking with polycarboxylic acids and anhydrides.

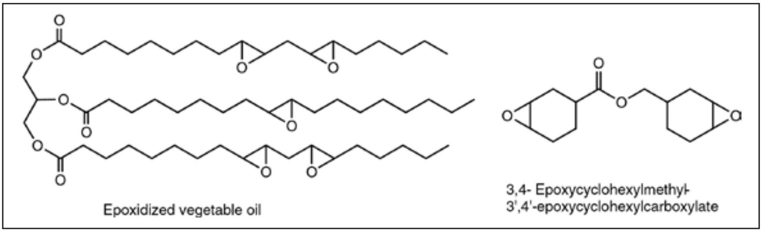


Figure 2.43: Examples of internal epoxy groups

2.9.2 Modified epoxy resins

Epoxy resins are often modified through their reactive oxirane groups as well as hydroxyl groups to design molecules meeting special requirements. Below are some important modifications.

2.9.2.1 Epoxy esters

A majority of the epoxy esters used in the coating industry are synthesized by reacting an epoxy resin with fatty acids from drying, semidrying or non-drying oils based on the end-use requirements for their properties. For epoxy ester resins suitable for air-drying (autoxidative curing), drying or semidrying oil fatty acids are used, while for stoving finishes, non-drying oil fatty acids are commonly used. The fatty acid content in epoxy esters may vary from 30 to 60 %. In synthesis of epoxy esters, the main chemical reactions involved are reaction of carboxylic acid groups of fatty acids with epoxy and hydroxyl groups of epoxy resins. The epoxy resin backbone contributes to adhesion and hardness along with water, chemical and corrosion resistance, while fatty acid modification provides necessary flexibility, flow and pigment wetting characteristics.

2.9.2.2 Epoxy acrylates

Another important class of modified epoxy resins, known as epoxy acrylates, are reaction products of a low MW epoxy resin and acrylic acid or methacrylic acid, which are used in radiation curable systems. The acrylate functionality is ~2, but higher functionality variants can also be prepared by using epoxy phenol novolac in place of BPA epoxy resin. Radiation curable formulations from these oligomers provide a better balance of properties and cost compared to some of the alternative polymer systems.

2.9.3 Curing agents for epoxy resins

Epoxy resins are thermosetting polymers, and the final properties of the polymer network are largely influenced by proper selection of the curing agent. Cross-linking of epoxy resins may be carried out through epoxide as well as hydroxyl groups. These reactions may be of the ambient curing or thermal curing type. The electron-deficient carbon atom of the oxirane ring is conducive to nucleophilic attack and therefore can react with a wide range of nucleophiles. The order of reactivity of most common nucleophiles used as curing agents is amine > phenol > carboxylic acid > alcohol. This chapter will briefly describe important classes of curing agents for epoxy resins.

2.9.3.1 Amine curing agents

Most frequently, for ambient curing systems, aliphatic or cycloaliphatic polyamines or amine functional polymeric or oligomeric derivatives are the curing agents of choice. Epoxy groups can react with primary and secondary amine groups, respectively forming secondary and tertiary amine groups. The reactivity depends on type of amine. The general order of reactivity of amines is primary > secondary >> tertiary and aliphatic > cycloaliphatic > aromatic. These reactions are catalyzed by water, alcohols, tertiary amines, and weak acids (such as phenols). The generalized curing reaction of a two-component epoxy-amine system is depicted in Figure 2.44.

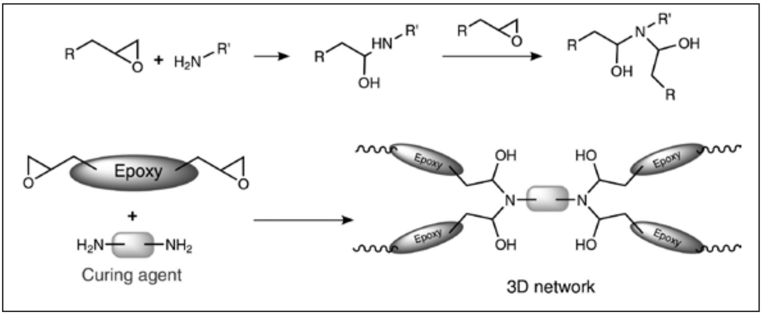
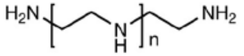


Figure 2.44: Representation of curing reaction of two-component epoxy-amine systems

Polyamines

The most common **aliphatic polyamines** belong to the homologous series of diethylene triamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA), which contain both primary and secondary amine groups.

Aliphatic polyamines (Figure 2.45) cure epoxy resins at a fast rate and produce a densely cross-linked network with very good chemi-



n = 0 to 4…. (DETA, TETA, TEPA, PEHA….)

Figure 2.45: Aliphatic polyamines

cal resistance. However, they suffer from such limitations as short pot life, poor flexibility, poor impact resistance, and more importantly, high volatility, toxicity and potential for skin sensitization. They also have the tendency to produce blushing (amine bloom) when used in high humidity and low temperature conditions.

Cycloaliphatic amines (Figure 2.46) are less volatile than aliphatic polyamines but are still considered skin sensitizing agents. Unless modified by acid accelerators such as salicylic acid, they require higher temperature for full curing. Other important cyclic curatives are N-aminoethylpiperazine and m-xylylenediamine; the latter has aliphatic amines attached to the aromatic ring and therefore gives the typical performance advantages of aromatic and cycloaliphatic amines.

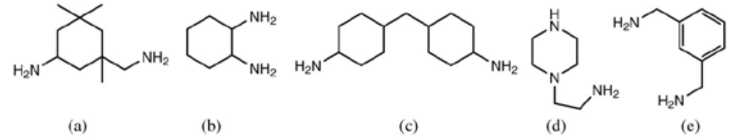


Figure 2.46: Cycloaliphatic amines: (a) isophorone diamine, (b) 1,2-diaminocyclohexane, (c) 4,4'-diaminodicyclohexylmethane, (d) N-aminoethylpiperazine, (e) m-xylylenediamine

Aromatic amines (Figure 2.47) are less reactive than aliphatic amines and require higher curing temperatures. They yield rigid networks with superior chemical and heat resistance, but their dark color limits their applications.

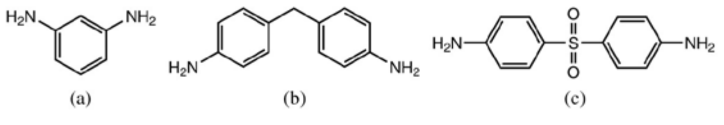


Figure 2.47: Aromatic amines: (a) m-phenylenediamine, (b) 4,4'-diaminodiphenylmethane, (c) 4,4'-diaminodiphenylsulfone

Polyoxyalkylene amines (polyglycol amines) are another important group of polyamine hardeners. Chemically they are amine terminated polyethers derived from polyethylene glycols or polypropylene glycols. Among their unique features are flexibility, longer pot life and lighter color.

In order to address the issues of volatility and toxicity associated with low MW aliphatic amines, different chemical modifications are adopted to derive amine cross-linkers with higher MW and hence lower volatility. Some commercially important derivatives are polyamine adducts, amine terminated polyamides, amidoamines, Mannich bases, and phenalkamines.

Polyamine adducts

Polyamine adducts (Figure 2.48) are the products (adducts) prepared by using excess equivalents of a polyamine (such as DETA and TETA) to a standard epoxy resin. Such amine-functional products have higher MW and lower volatility, making them good candidates for amine type curing agents. Their final film properties are similar to those obtained by polyamines, but they have a reduced tendency for blushing.

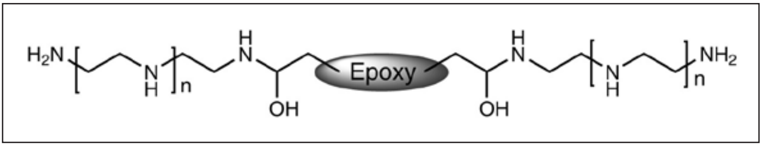


Figure 2.48: Polyamine adduct

Polyamides and amidoamides:

Amine functional polyamides are prepared by reacting dimer fatty acids with excess equivalents of polyamines. The products are effective epoxy curing agents, with both primary and secondary amines available for curing. Figure 2.49 shows a representative structure, though more than one dimer fatty acid segment is possible based on the ratio of reactants. The spacing between amine groups by a dimer fatty acid segment gives an open network with high flexibility and impact resistance but reduced resistance to chemicals and strong

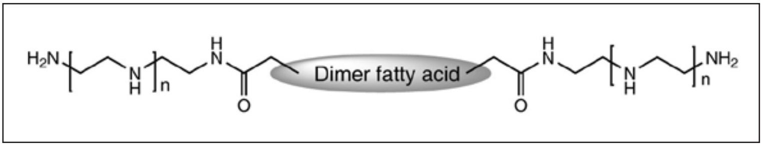


Figure 2.49: Representative structure of reactive polyamide resin

solvents. These agents provide better water and corrosion resistance along with improved wetting and adhesion. Their curing rate is slower but the tendency for blushing is much less.

Other curing agents analogous to polyamide are amidoamides, which are produced by reacting fatty acids with an excess of polyamines. They have lower viscosity than polyamides. Their cured film properties are closer to those of polyamide cured systems, but their lower cross-link density results in lower corrosion resistance.

Mannich bases and phenalkamines:

Mannich bases are derived by reaction of phenol, formaldehyde and an aliphatic or cycloaliphatic polyamine. These curing agents show enhanced reactivity due to the catalytic effect of phenolic hydroxyl. Phenalkamines are similar products using alkyl phenols (Figure 2.50). Cardanol-based phenalkamines are very popular products used in marine and protective coatings. These types of curing agents are known for their excellent low temperature curing (up to 0 °C) characteristics even in damp conditions. They exhibit better compatibility, excellent blush resistance and excellent chemical resistance along with good wetting, adhesion and surface tolerance properties.

Ketones can reversibly react with primary amines with the loss of water to give ketimines (Figure 2.51). They can be considered **blocked**

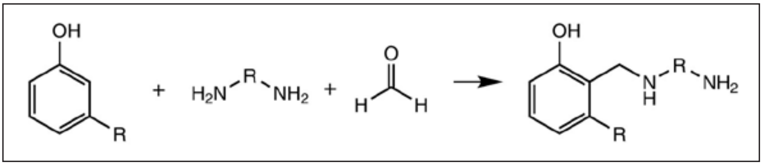


Figure 2.50: Representative structure of phenalkamine

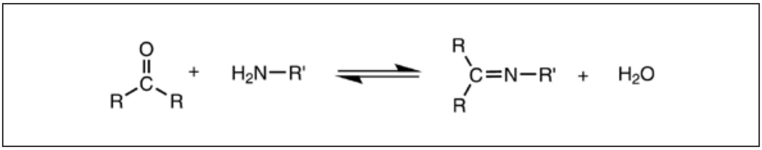


Figure 2.51: Ketimine chemistry

polyamines. Absorption of atmospheric moisture during and after application of the coating produces a ketone and a polyamine.

Dicyandiamine

Dicyandiamine is a crystalline solid (melting point 207 °C) that is incompatible with epoxy resin at room temperature. It is used as a cross-linker for epoxy powder coatings. However, the reaction of dicyandiamide with the epoxy group proceeds differently from the classical amines, as the primary adducts undergo different chemical rearrangements. They are frequently modified to improve solubility in epoxy resins (Figure 2.52).

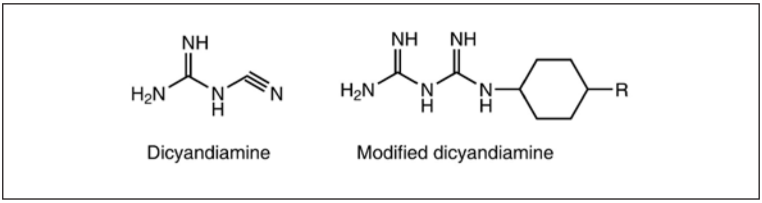


Figure 2.52: Dicyandiamine and modified dicyandiamine

2.9.3.2 Polymercaptans (polythiols)

The terminal mercaptan group of polythiols can react with epoxy groups under ambient conditions, especially when catalyzed by tertiary amines (Figure 2.53). Important characteristics of such cured films

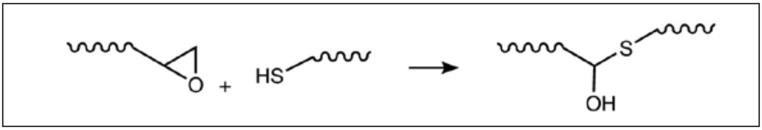


Figure 2.53: Curing of epoxy with thiol

include good flexibility and adhesion. They are not frequently used in coatings due to the strong sulfurous odor of thiols, but are more commonly used in adhesives, sealants and civil engineering applications.

2.9.3.3 Polyisocyanates

Secondary hydroxyl groups of the epoxy resin backbone may be reacted with polyisocyanates, aromatic as well as aliphatic, in two-component ambient curing systems that are commonly known as epoxy-urethane hybrid systems. This type of coating combines advantages of epoxy and polyurethane systems.

2.9.3.4 Carboxylic acids and anhydrides

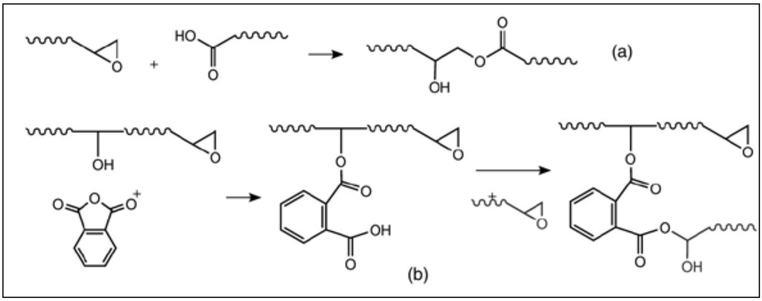


Figure 2.54: Curing of epoxy with (a) carboxylic acid and (b) anhydride

In the presence of amine catalysts, carboxylic acids react with epoxy groups, producing hydroxyl esters at elevated temperatures (Figure 2.54). This type of curing chemistry is used in epoxy-polyester hybrid powder coatings. Some examples of such polymers are carboxylic acid terminated polyesters or carboxylic acid functional acrylic resins. Self-cross-linking acrylic resins containing both (meth)acrylic acid and glycidyl methacrylate in the same copolymers, are also known.

Cyclic anhydrides of carboxylic acid are also used as cross-linkers for epoxy resins. Curing is initiated by reaction of a hydroxyl with an anhydride to yield a half ester and a carboxylic acid group. The newly formed carboxylic acid will in turn react with the epoxy to generate an ester and a new hydroxyl group. These complementary reactions result in a cross-linked network. Etherification reactions (side reactions) between epoxy-epoxy and epoxy-hydroxyl groups are also known to contribute to a cross-linked network. Examples of some typical cyclic anhydrides are pyromellitic anhydride, hexahydrophthalic anhydride, methyltetrahydrophthalic anhydride and ethylene glycol bis(anhydromellitate). These systems are more sensitive to alkali than amine cured epoxy systems.

2.9.3.5 Phenolic and amino resins

Both resole and novolac type phenolic resins are used to cure high MW epoxy resins to give a hard and tough film with very good chemical and corrosion resistance. Such systems are generally cured at high temperatures of about 150 to 200 °C. The phenolic hydroxyl groups in both resoles and novolacs can react with the glycidyl groups of epoxy resins; in the case of resoles, methylol groups contribute to cross-linking via self-condensation as well as by reaction with hydroxyl groups of epoxy resins (Figure 2.55). Such systems are very popular in coatings for food and beverage cans.

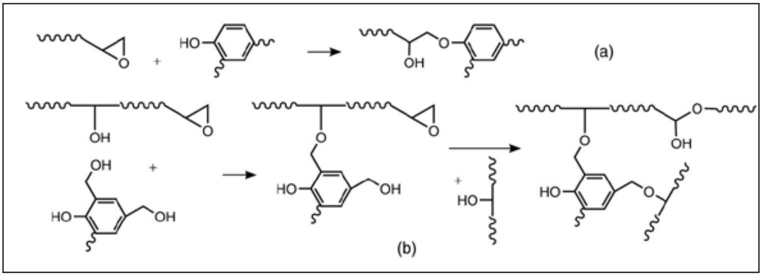


Figure 2.55: Curing of epoxy with (a) phenolic hydroxyl and (b) methylol groups of phenolic resins

In an analogous thermally cured system, high MW epoxy resins are cured by reaction of their hydroxyl groups with methylol or alkylated methylol groups of amino resins (Figure 2.56). Melamine formaldehyde and urea formaldehyde systems are most common. While chemical resistance of these systems is lower than those of phenolic cured systems, their lower curing temperature and better color compared to phenolic systems is taken advantage of when faster cure speed is important.

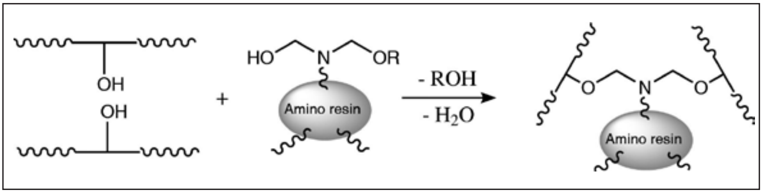


Figure 2.56: Schematic representation of curing of an epoxy with an amino resin

2.9.3.6 Self-cross-linking (epoxy homopolymerization)

In the presence of a suitable catalyst, epoxy groups can undergo self-polymerization to generate a polyether through either a cationic or anionic mechanism. Anionic polymerization occurs in the presence of tertiary amines (Lewis bases) such as tris(dimethylaminomethyl) phenol, benzyldimethylamine or imidazole derivatives, while cationic polymerization can occur in the presence of Lewis acids. Boron trifluoride (BF_3) or superacids such as triflic acid (F_3CSO_3H), hexafluoroantimonic acid ($HSbF_6$) or hexafluoroarsenic acid ($HAsF_6$) are frequently used for cationic polymerization of epoxy resins. **Photolatent superacids**, also known as **photoacid generators**, are frequently used in cationically cured UV epoxy resin curing systems.

2.9.4 Waterborne epoxy systems

Like other resins and coating systems, demand for waterborne epoxy resins has steadily increased over the past several decades. Waterborne epoxy resins and their coatings are commercially available. Waterborne epoxy resin systems can be broadly classified into the following categories, based on the techniques involved in their processing.

- Emulsified system
  - Type I: based on low MW liquid epoxy resin
  - Type II: based on medium to high MW solid epoxy resin
- Water-reducible system (self-emulsified system)
  - Neutralization of acid-rich resin
    - Carboxylic acid functional
    - Phosphate ester based
  - Neutralization of base-rich resinw

2.9.4.1 Emulsified system (type I)

Type I epoxy systems are aqueous emulsions of liquid epoxy resins (with epoxy equivalent weight ~200). In this type of waterborne epoxies, no external emulsifiers are used, but rather, curing agents (fatty polyamide type) serve as emulsifiers due to their amphiphilic nature. Liquid epoxy resin and curing agent are mixed in calculated quantities just prior to application and emulsified into water under high-shear conditions (stirring). Emulsion droplets, consisting of resin and cross-linker, are intimately mixed. After application, water evaporates and droplets coalesce to form a film with uniform morphology. Such systems have a shorter pot life (~2 h), and the films have high hardness, low flexibility and low impact resistance.

2.9.4.2 Emulsified systems (type II)

Type II waterborne epoxy systems are based on solid epoxy resins in the form of uniform aqueous dispersions containing co-solvents and stabilized by emulsifiers. These systems can be prepared by direct emulsification involving dispersion of epoxy resin (a solution in co-solvent) in water using an emulsifying agent (surfactant). These systems can also be prepared by an inversion process, in which water is added to a liquid resin to form first a water-in-oil emulsion that subsequently is inverted to an oil-in-water emulsion upon addition of a further quantity of water. The inversion technique is preferred, as it gives a more stable emulsion with a small particle size and narrow particle size distribution. Just prior to application, hardener is added and emulsified into the resin emulsion. The pot life is longer than type I due to the high epoxy equivalent weight and difficulty of hardener diffusion into the particles. After application, as dispersion particles coalesce, resin and hardeners interdiffuse and curing takes place. However, there is a greater tendency for such films to develop a heterogeneous morphology (due to improper diffusion of hardener) with epoxy-rich and amine-rich domains.

2.9.4.3 Water-reducible systems

In water-reducible waterborne epoxies, acidic or basic functionalities are introduced into an epoxy polymer, which upon respective

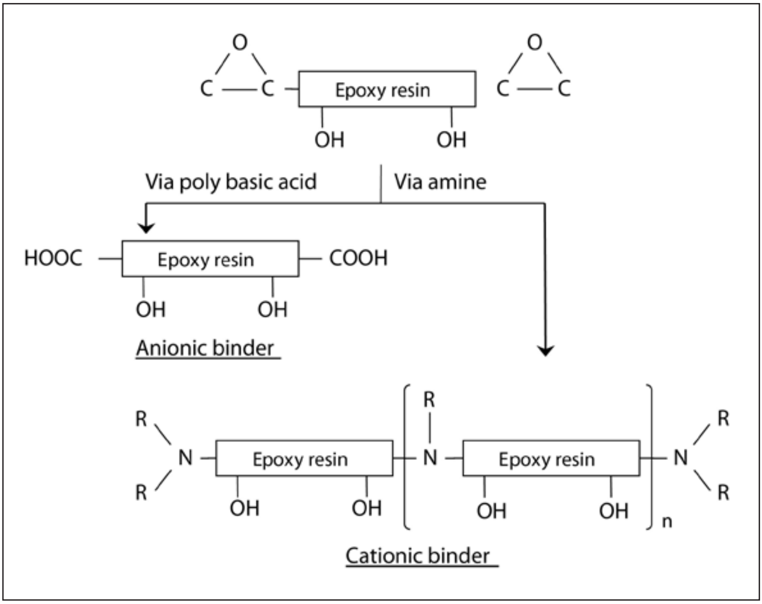


Figure 2.57: Important routes for water-reducible epoxy resin

neutralization with a fugitive base or acid, generates an ionic group that renders it water reducible (Figure 2.57).

Acid functionalized epoxy resins are generally prepared by esterification of epoxy resin with an excess of acid equivalents, or by grafting of acrylic copolymers containing methacrylic acid or acrylic acid onto the epoxy backbone. They are generally cured by an aminoplast at elevated temperature.

Base-rich epoxy resins are prepared by reaction of epoxy resins with an amine (preferably a secondary amine). These types of epoxies are commonly employed in **cathodic electrodeposition coating**, often cured by a blocked isocyanate and termed *thermal curing*.

2.10 Polyamides

Polyamides are polymers with amide linkages (–NH-CO–) in their backbone structures. A well-known example of this type of polymer is nylon, the condensation product of an aliphatic dicarboxylic acid with aliphatic diamines, which was originally developed for replacement of silk. Very high MW and poor solubility of nylon makes it unsuitable for coating applications. Polyamides suitable for coatings are produced from condensation of aliphatic diamines with dimerized fatty acids. Two types of commercial products are offered: (a) thermosetting (reactive) and (b) thermoplastic (non-reactive). The dibasic fatty acids commonly used to manufacture polyamides are prepared by dimerizing unsaturated C_{18} fatty acids from vegetable oils such as linseed, soybean, or tall oils. The polyamines commonly used are polyethylene polyamines of various chain lengths, such as diethylenetriamine, an example of a simple linear polyethylene polyamine used for making reactive polyamides, while diamines such as ethylenediamine are commonly used for thermoplastic polyamides.

2.10.1 Reactive polyamides

Reactive polyamide resins are typically prepared by condensation of dimerized fatty acid with excess equivalents of aliphatic diamines. Reactive liquid polyamide resins are designed primarily for use in two-component epoxy-polyamide coatings and adhesives. Generally, reactive polyamide resins are supplied as either very viscous liquids or viscous solutions in organic solvents. In reactive polyamides, monofunctional fatty acids are used with dimer fatty acids to control the MW as well as viscosity. During their synthesis, a cyclization reaction between an amide group and secondary amine nitrogen, separated by an ethylene linkage, forms imidazoline ring structures. By varying the imidazoline content, products with a wide range of solubility, compatibility and pot life can be prepared.

2.10.2 Non-reactive polyamide resins

Non-reactive polyamide (thermoplastic) resins are higher MW (up to 10,000 g/mol) condensation products of dimer fatty acids and diamines. Such resins are important binders for liquid inks. In the synthesis of these resins, both dibasic acid and diamine components are blended at medium temperatures and reacted until the water of reaction can be distilled off. They are solid umber colored products marketed in different grades that differ in their MW and softening points (typically 90 to 150 °C).

The grades with MW above 4000 g/mol are soluble in aromatic hydrocarbons and higher alcohols but alcohol/hydrocarbon blends are more commonly used. They are frequently used with nitrocellulose binders too. The lower MW grades (<4000 g/mol) have improved alcohol solubility and better compatibility with nitrocellulose. They are also compatible with such other binders used in printing inks as shellac, rosin, and maleic, phenolic and ketonic resins. The flexographic and gravure inks developed using these binders confer excellent adhesion to treated polyolefins, polystyrene and films coated with polyvinylidene chloride or similar difficult substrates. High gloss, heat sealability, fast solvent release and clean printing are among the important characteristics of these binders along with their good resistance to fats and greases. They are frequently used in overprint varnishes to provide scratch resistance. Other important uses for thermoplastic polyamides are as hot-melt adhesives and heat-seal coatings. They also find some applications in thermoplastic powder coatings. Polyamides manufactured from omega-aminoundecanoic acid are used in thermoplastic powder coatings suitable for fluidized-bed applications. Some products derived by reacting polyamide resins with alkyd resins are used as thixotropic agents for solventbased coatings.

2.10.3 Polyimides and polyamide-imides

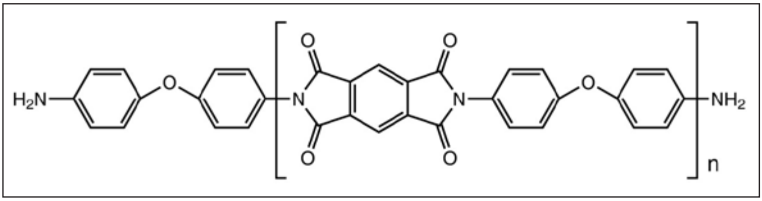


Figure 2.58: Polyimide resin

Polyimides (Figure 2.58) are typically prepared by reacting a tetracarboxylic acid anhydride such as pyromellitic dianhydride with aromatic diamines such as 4,4’-diaminodiphenylether. Heat resistance of greater than 250 °C during continuous exposure can be obtained using coatings based on such binders. Polyimides are thermoplastics that are difficult to dissolve and are therefore used as a binder in specialty coating applications such as in high temperature and high insulation coatings.

Another variant of such resins having both imide and amide linkages is prepared by the reaction of a low MW amine-capped polyamide with pyromellitic dianhydride. Such resins have been used to give good adhesion, hardness, and resistance properties to flexographic inks.

2.11 Polyurethanes

Polyurethanes are an increasingly important type of resins finding applications in virtually all types of coatings due to their versatility and excellent performance properties. Polyurethane resins are polymers containing urethane (–NH–CO–O–) linkages, usually made by reaction of compounds containing isocyanate groups (–NCO) and hydroxyl groups (–OH).

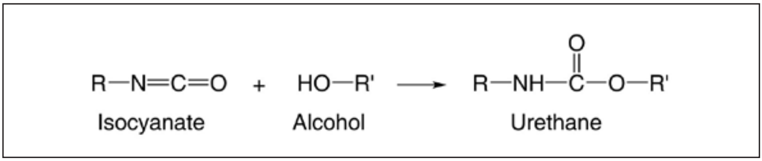


Figure 2.59: Urethane formation

The reaction between isocyanates and alcohols, also called the **urethane reaction**, can occur at room temperature without any catalyst. The presence of urethane linkages in polyurethane resins confers unique and desirable properties to their coatings, mainly because –NH–CO–O– is a strong linkage that is resistant to acids, bases and hydrolysis by water. One unique feature of polyurethane resins is their ability to strongly interact through formation of strong interchain hydrogen bonding between urethane linkages that provides stiffness and resilience to polyurethane coatings, unmatched by most other resin systems.

One of the most important considerations in polyurethane chemistry and technology is the high reactivity of isocyanate compounds with a wide range of active H-compounds (generally, compounds containing a H atom attached to an O or N atom), including moisture in the air or human skin. This poses serious challenges of health and toxicity hazards as well as safety, handling and storage issues for isocyanate compounds. However, the currently available technologies have made possible safe handling and use of isocyanate compounds for use in paints and coatings.

Reaction of isocyanates with different active H-compounds that form the fundamental basis for polyurethane coating systems are shown in Figure 2.60. The order of relative rates for these reactions is: $-NH_2 \gg -OH > H_2O > -COOH$. Many types of catalysts are available that are used to control these reactions. It should be noted that while urethanes are produced only from reaction of isocyanates with alcohols, other reactions are also effectively controlled and used in different polyurethane coating systems.

The most important components of polyurethane resins, therefore, are isocyanates and polyols (compounds containing two or more than two hydroxyl groups); nevertheless, other additives and modifiers, such as catalysts and solvents, are also used.

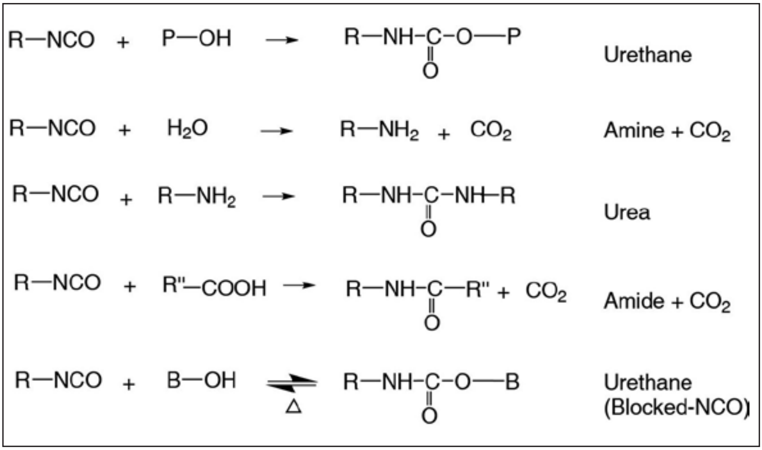


Figure 2.60: Reactions of isocyanates with active hydrogen compounds

2.11.1 Isocyanate compounds

Two types of isocyanate compounds, differing greatly in their reactivity, coating performance and cost, are (a) aromatic isocyanates and (b) aliphatic isocyanates. Aromatic isocyanates have much higher reactivity with active H-compounds than aliphatic isocyanates. Polyurethane coatings based on aromatic isocyanates suffer from poor resistance to sunlight exposure (poor UV resistance), poor gloss retention and significant discoloration and chalking tendency upon exterior exposure. Aliphatic isocyanates have excellent resistance to exterior exposure and discoloration and therefore are preferred candidates for polyurethane coatings designed for high performance exterior applications. However, their substantially high cost restricts their use in some applications.

Isocyanate compounds are supplied in both monomeric as well as polymeric forms. The monomeric isocyanates are generally low MW liquid difunctional materials and are used as primary building blocks. Due to their greater toxicity, they must be handled very carefully, and generally, free monomer content is restricted in the

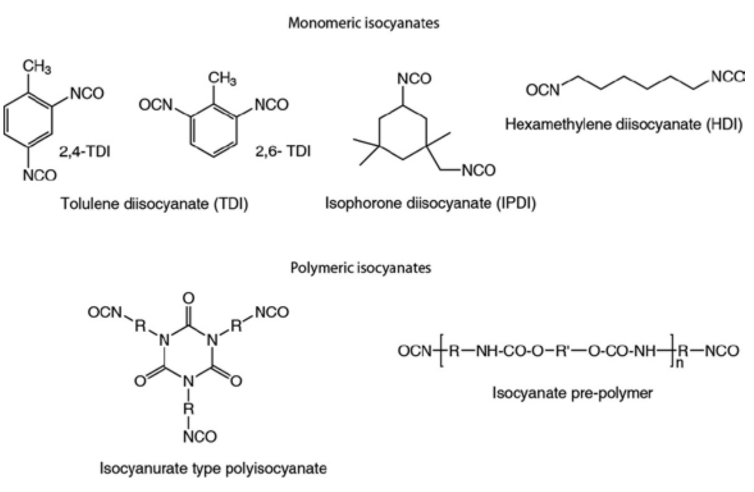


Figure 2.61: Typical isocyanate components used in polyurethane resins

final products. Figure 2.61 shows some examples of isocyanate compounds used for paint and coating applications.

2.11.2 Polyols

Polyols are materials with hydroxyl (–OH) groups. Polyols are very important components of polyurethane resins and control many mechanical, thermal and physical properties of their coatings, besides the overall cost. Like isocyanates, polyols for polyurethane resins include monomeric polyols and polymeric polyols (Figure 2.62).

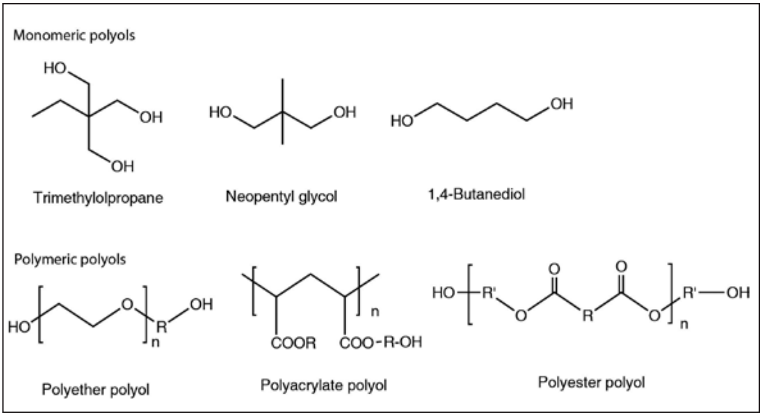


Figure 2.62: Typical polyols used in polyurethane resins

Polyols with primary –OH groups are more reactive with isocyanates compared to those with secondary –OH groups. Tertiary alcohols have extremely low reactivity and they practically do not react with isocyanates. Monomeric polyols, due to their low equivalent weights, produce more rigid urethane linkages per unit weight and thus tend to produce harder segments in the polyurethane chains. Therefore, such polyols are also known as **hard polyols**. Polymeric polyols, on the other hand, have –OH groups spaced farther apart, and hence will produce fewer urethane linkages producing softer segments, and hence are known as **soft polyols**. Polyurethane coatings with varying hardness, flexibility and degree of elongation can be formulated using a proper balance of soft and hard polyols.

2.11.3 Polyurethane resins and coating systems

Unlike most other resin systems, polyurethane resins, in most cases, are not supplied to coating formulators, but rather their components – polyols and isocyanates – are supplied. Coating formulations are made using these components, and in most cases, urethane linkages (polyurethane resins) are produced during the curing process. This offers a great deal of freedom to formulators to offer products with different compositions and curing chemistry.

2.11.3.1 Two-component polyurethane resin systems

Two-component (also called by such terms as 2K, plural component, two-can, and two-part) polyurethane coatings are among the most popular types, and such coatings are offered in two separate cans that are required to be mixed in specified proportion just prior to their use (Figure 2.63). Since polyols and isocyanates are reactive at ambient temperature, these two components are packed (in precisely calculated stoichiometric amounts) in two separate cans. Due to the

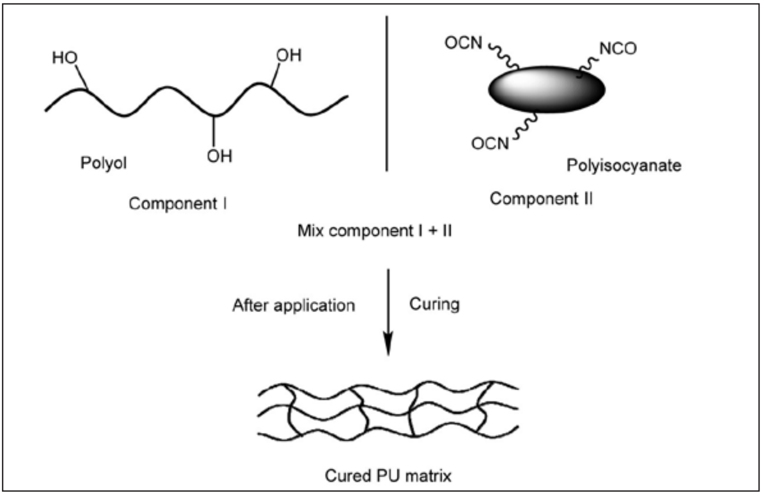


Figure 2.63: Schematic representation of two-component polyurethane resin system

high reactivity of isocyanate components and hence possible stability problems, all other coating components, such as pigments, solvents, additives and catalyst, are generally added to the polyol component.

Once the two components are mixed, the viscosity of the system will gradually increase due to an increase in MW and cross-linking as a result of formation of polyurethane. After reaching its pot life, the product can no longer be applied due to excessively high viscosity and/or cross-linking. Therefore, such products have to be formulated to a specified pot life. After application of the coating, the polyurethane formation reaction continues and results in a dry coating within a few hours. Properties of coatings such as hardness, flexibility, chemical resistance, pot life and cure time can be balanced by using the appropriate types of isocyanate and polyol components, solvents, additives, pigments and catalyst. Two-component-polyurethane coatings still have limited shelf-life due to the presence of the very reactive free isocyanate in one of the cans.

2.11.3.2 One-component polyurethane resin systems

Polyurethane resins and coatings are also offered as one-component (also called single-component, 1-part or 1K) systems. Such systems are typically comprised of polyurethane prepolymers with reactive functional groups. As a single-component system, the functional groups are kept from reacting with any internal or external agents to provide shelf stability. A number of different types of functionality and approaches are used to make resins that provide curing by a different mechanism.

Moisture-curable urethane resin

A moisture-curable urethane resin is simply a urethane prepolymer with free –NCO groups. Typically made from aromatic isocyanates, the free –NCO group of such a resin, when exposed to the environment after application, will react with ambient moisture and produce urea linkages between prepolymer chains, resulting in formation of the cured coating (Figure 2.64).

The type of isocyanate, MW and –NCO functionality are controlled to balance drying time and film properties. The drying time is signi-

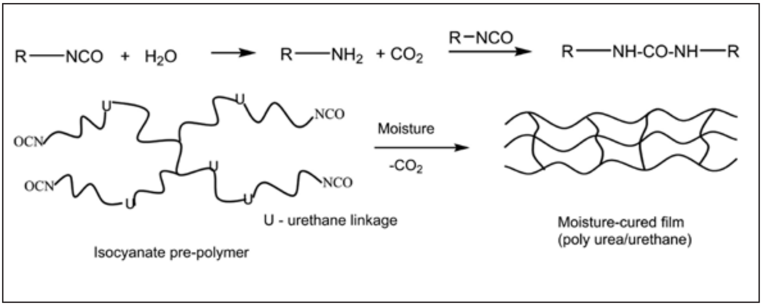


Figure 2.64: Schematic representation of curing of moisture-curable urethane system

ficantly dependent on the ambient moisture content, temperature and film thickness. Coatings applied at higher film thickness under high humidity frequently show a bubbling defect due to formation of CO_2 gas during curing that gets trapped in the film. Due to free –NCO content, such systems have limited shelf-life.

Blocked isocyanates

Blocked isocyanates are a type of urethane that are made from reaction of polyisocyanates with special active H-compounds that form thermally reversible urethane linkages. When heated above a certain characteristic temperature, called the deblocking temperature, blocked isocyanates undergo a reversible reaction with formation of free –NCO groups and an active H-compound. Some examples of such active H-compounds, known as **blocking agents**, and their deblocking temperatures are: caprolactam (~170 °C), methyl ethyl ketoxime (~150 °C) and 3,5-dimethylpyrazole (~125 °C). Blocked isocyanates prepared from a wide range of polyisocyanates and blocking agents, with a range of deblocking temperatures, are commercially available. Thermally curable one-component polyurethane coatings can be prepared by combining blocked isocyanates and polyols (along with other paint ingredients), and after application, require thermal curing above the deblocking temperature of the blocked isocyanate. Figure 2.65 depicts the composition and curing of a one-component blocked isocyanate system. During curing, free isocyanate groups are generated and

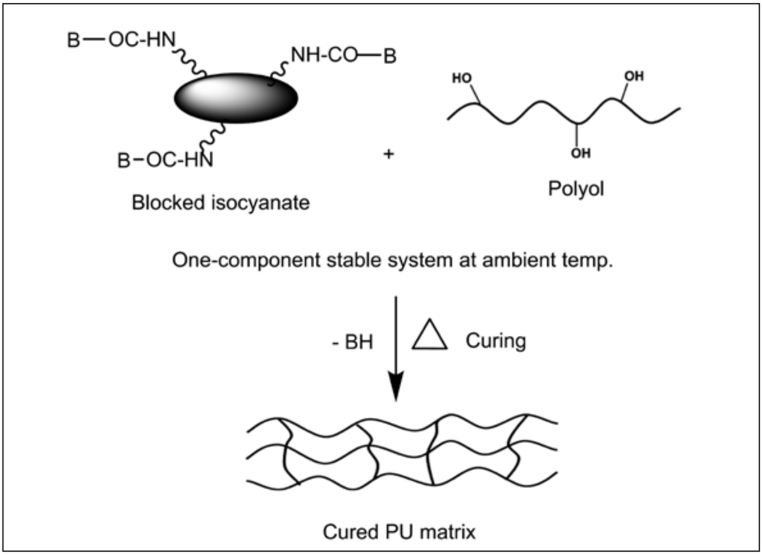


Figure 2.65: Schematic representation of one-component blocked isocyanate system

react with polyols to form a cross-linked urethane matrix. Due to the absence of free –NCO in the can, such systems have longer shelf-life, and do not require especially moisture-free pigments or solvents.

Air-drying one-component polyurethane resins

These resins are generally polyurethanes modified by drying-oil fatty acids. These types of resins are essentially urethane modified alkyd resins, and hence are also called **urethane alkyds** or **uralkyds**. Like alkyds, urethane alkyds dry by auto-oxidative polymerization, and their drying rate can be improved by use of conventional driers used for alkyds. A reaction scheme for preparation of a urethane alkyd is shown in Figure 2.66. Inclusion of urethane linkages in the alkyd resin structure brings about a number of beneficial properties in uralkyds. In general, uralkyds are faster drying and produce films with improved gloss and hardness. Thus, urethane alkyds are not true urethane resins but upgraded alkyds with remarkable performance benefits. However, due to the use of

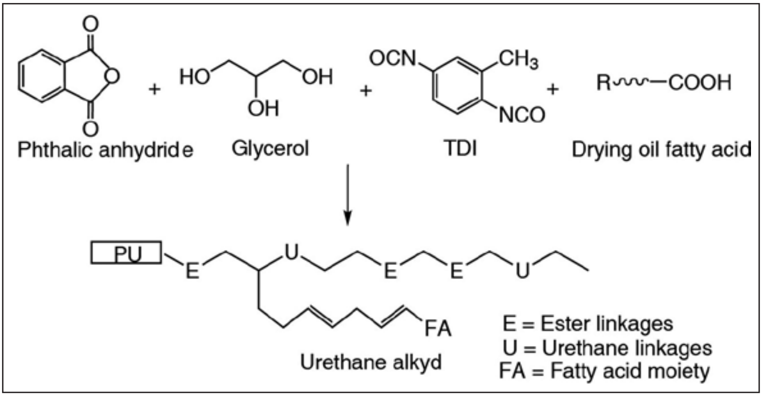


Figure 2.66: A simplified reaction scheme for synthesis of urethane alkyds

aromatic isocyanates, uralkyd based coatings have a tendency to discolor upon exposure. Uralkyds find applications as low-cost, fast-drying enamels, primers, wood coatings and many similar types of coatings.

Urethane (meth)acrylates

Urethane (meth)acrylates are another class of polyurethane resins mainly used in radiation curable systems. Urethane acrylates are oligomeric urethanes with (meth)acrylate functionality. They are used as components of radiation curable systems, in which coatings are applied and exposed to high energy radiation such as UV light or an electron beam. The free radicals generated during such exposure results in chain-growth polymerization through the (meth) acrylate functionality of urethane (meth)acrylates. Due to superior performance compared to many other (meth)acrylates, urethane (meth)acrylates find applications in many high-end radiation curable coating applications.

2.11.3.3 Waterborne polyurethanes

As discussed earlier, many polyurethane resin systems offered for coatings contain free –NCO groups, which are expected to react with appropriate cross-linkers during the curing reaction after application. Since isocyanates are reactive to water, until the 1990s, it was thought difficult to offer waterborne polyurethane resin systems. While isocyanate can react with water at ambient temperature, the rate of this reaction is much lower compared to that with polyols or polyamines. For instance, aromatic isocyanates react with water about 1000 times slower than with primary amines, and about 10 times slower than with primary alcohols. This differential reactivity of isocyanates with different active H-compounds is an important consideration in the success and commercialization of waterborne polyurethane resins.

Two-component waterborne polyurethane systems

Earlier we discussed two-component polyurethane systems for solventbased or high-solid systems. In general, any waterborne coating system requires resins and cross-linkers that are water dispersible. To confer water dispersibility, resins and cross-linkers are generally modified with a sufficient degree of hydrophilic groups or structures. When such modified materials are added to water under sufficient shear, they break down into discrete droplets or particles and are stabilized by the hydrophilic moieties. Thus, two-component waterborne polyurethane systems can be prepared using water-dispersible polyols (component I) and water-dispersible polyisocyanates (component II). See Figure 2.67 presents an example of the structure of water-dispersible polyisocyanates. Such components are commercially available. Component I is generally supplied as a polyol dispersion in water and component II (supplied free from water) is added to component I just prior to application.

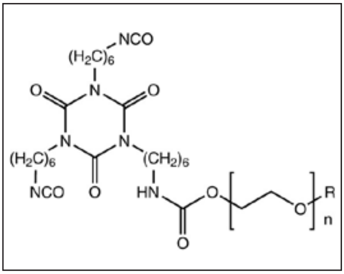


Figure 2.67: An example of water-dispersible polyisocyanates

Once the two components are mixed and the coating applied, the curing reaction begins. It is important to note that during curing, despite the presence of a large excess of water, the predominant curing reaction is between isocyanate and polyol compounds. This is mainly because of a significantly lower reaction rate of isocyanate with water compared to that with polyols. Nevertheless, a certain degree of reaction between isocyanate and water does take place, and the cured film always contains a distribution of urethane and urea linkages.

Two-component polyurethane systems have become very popular for many commercial applications, as they can offer products with low VOC content while maintaining high performance. Such polyurethane systems are increasingly used in industrial coating applications.

Polyurethane dispersions (PUDs)

PUDs are another commercially important type of waterborne polyurethane systems. Due to their versatility, stability, high performance, and low VOCs, PUDs are increasingly used as binders for a wide range of coatings and related products. Conventional PUDs are aqueous secondary dispersions of high MW polyurethanes with a typical particle diameter of 0.1 to 0.2 µm. Such polyurethane resins are offered as translucent dispersions with ~35 to 45 % by weight solids. After application, PUDs form films by evaporation of water (and other volatiles) followed by particle coalescence, similarly to latex.

Typical thermoplastic PUDs are prepared by reaction of polymeric diols with diisocyanate, monomeric diols or diamines, called **chain extenders**, and a diol-containing hydrophilic group. The high MW polymer chains of such polyurethane resins contain soft domains arising from polymeric polyols and hard domains from isocyanates, chain extenders and hydrophilic groups containing a diol. A commonly used **prepolymer process** for preparation of PUDs is shown in Figure 2.68. The first step in PUD synthesis by this process is preparation of a –NCO functional prepolymer, generally in the presence of a polar aprotic solvent such as N-methyl-2-pyrrolidone, followed by neutralization of the carboxylic acid group using a volatile amine. The product is then dispersed in water under high shear conditions and the prepolymer MW is further increased by **chain extension** using diamine compounds. The higher reactivity of –NCO groups towards amines compared to water is taken advantage of in preventing excessive formation of urea linkages over urethane linkages. Nevertheless, such products always contain a distribution of urethane and urea linkages and hence, more specifically, such dispersions are called polyurethane-urea dispersions. The current trend is to offer solvent-free (typically N-methyl-2-pyrrolidone-free) dispersions because of VOC concerns. PUDs find a number of applications in coatings for wood, plastics, leather, and many more products.

Cross-linkable PUDs contain reactive functional groups pendant to the backbone and/or at the chain ends, and can be cured using a variety of cross-linkers and curing conditions. The reactive functionalities may include, among others, a fatty acid moiety in air-drying PUDs, –OH functionality for cross-linking with melamine or isocyanate type cross-linkers, –COOH groups for curing with carbodiimide

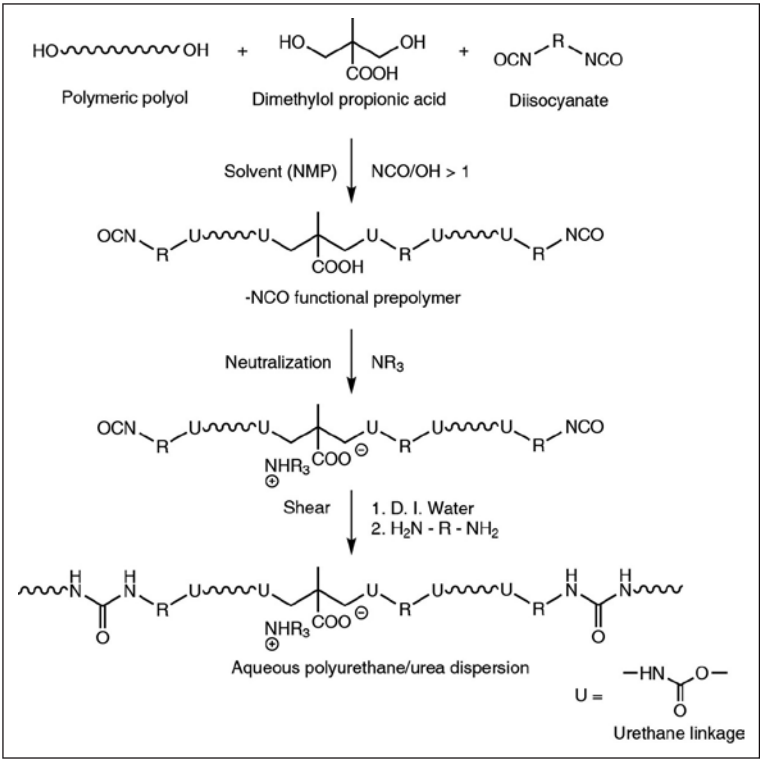


Figure 2.68: A simplified reaction scheme for preparation of an aqueous PUD using a prepolymer process

Table 2.8: Types of polyurethane coatings

Polyurethane system (ASTM designation)	**Composition**	**Cure mechanism**	**Technical platform**	**Free –NCO present**
One-component systems				
Air-drying (ASTM type I)	Drying oil–modified polyurethane + metal driers	Oxidative drying (air-drying)	SB WB	No
Moisture curable (ASTM type II)	–NCO functional polyurethane prepolymer + catalyst	Reaction of atmospheric moisture with –NCO	SB HS	Yes
Blocked Isocyanate (ASTM type III)	Blocked isocyanate + polyol	Thermal cure through reaction of deblocked iscyanate with polyol	SB HS PC WB	No
Radiation cure	Acrylate-functional polyurethane, reactive diluents, photoinitiators	UV-induced chain-growth polymerization	SFWB	No
Thermoplastic polyurethane (ASTM type VI)	High MW thermoplastic polyurethane resin dispersed in water (PUD)	Physical drying through particle coalescence	WB (PUD tech.)	No
Two-component systems				
Catalyzed polyurethane system (ASTM type IV)	Isocyanate prepolymer + catalyst or crosslinker or accelerator	Ambient temperature cure of –NCO with catalyst or accelerator	HS	Yes
Polyol/ polyisocyanate (ASTM type V)	Part I polyisocyanate Part II polyol catalyst	Ambient temperature cure by –NCO and –OH reaction; low bake <80°C with urea	WB SB HS	Yes

SB = solvent-borne, WB = waterborne, HS = high solid, PC = powder coating, SF = solvent-free or aziridine type cross-linkers, and (meth)acrylate functionality for UV-curing applications. In general, thermomechanical properties of cross-linked films of PUDs are much superior to those of thermoplastic films and hence find high-end industrial applications.

Table 2.8 summarizes different types of polyurethane coating systems, their compositions, curing mechanism and ASTM classification.

2.12 Silicone resins

Outstanding properties such as thermal stability, weathering resistance, low temperature flexibility, low surface tension, hydrophobicity and surface activity of silicone resins and their combinations with other resins made them a commercially important category of binders for high performance coatings.

Table 2.9: Typical monomers for silicones

Monomer	Functionality*	Effect in final structure of silicone	Symbol
SiX_4**	4	Forms special structure (branching)	Q (quad)
$RSiX_3$	3	Forms special structure (branching)	T (tri)
R_2SiX_2	2	Forms linear structure (chains)	D (di)
R_3SiX	1	Chain termination	M (mono)

R = methyl or phenyl, X = halogen (most commonly Cl)
** With respect to hydrolyzable groups*
*** Though used in silicones, it is not an organosiloxane*

2.12.1 Chemistry of silicone resins

In contrast to most organic polymers, in silicone resins (also called silicones or polysiloxanes), the backbone is made of silicon and oxygen, with organic groups substituted as side chains on this backbone. Thus, the skeleton of silicones is related to silica and silicates, but some of the oxygens are replaced by organic groups. The most common organic groups are alkyl (methyl to amyl), phenyl or even vinyl groups grafted onto the silicone backbone. Thus, silicone resins are placed at a hybrid position between inorganic and organic polymers.

Silicones are now most commonly manufactured using the *Müller-Rochow* synthesis. Finely ground elementary silicon is reacted with alkyl or aryl halides in the presence of cuprous catalyst to form mono-, bi- and trifunctional organohalosilanes. The individual components are then separated by fractional distillation for preparation of silicones. Some important organo-halosilanes are shown in Figure 2.69. The most widely used monomers are the methyl and phenyl substituted halosilanes, with hydrolyzable functionality ranging from 1 to 4.

Hydrolysis of chlorosilanes forms unstable silanols, which in turn can condense to form polysiloxanes with elimination of water. By varying the ratio of the M, D, T and Q (occasionally used) monomers, the molecular size and structure of the final polysiloxane can be designed to produce a wide range of products with varying MW and chemical structure. The "D" units are the main components producing linear chain polymers. The "M" units terminate chains and thus limit molecular growth, while "T" units cause molecules to branch. Along with linear structures, low MW cyclic structures are often formed to varying degrees. Based on this chemistry, a range of pure silicone resins and some modified silicones are produced for the coating industry. In the following sections, some important types of silicone resins used in surface coatings are discussed.

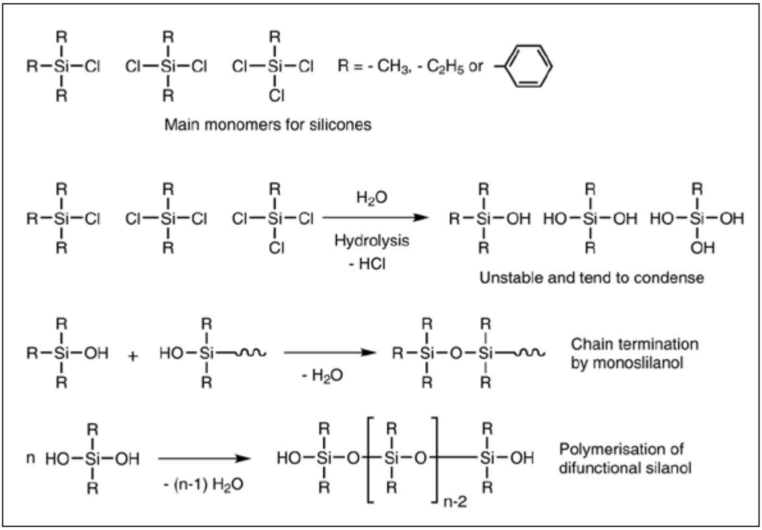


Figure 2.69: Chemistry of silicones

2.12.2 Pure silicone resins

The classical pure silicones are made from hydrolysis of $RSiX_3$, R_2SiX_2 and R_3SiX, where R, in most cases, is methyl, phenyl or a mixture of both. If only methyl substituted “D” units are used, with few “M” units as chain stoppers, extremely nonpolar polydimethylsiloxanes, commonly known as silicone oils (Figure 2.70), are obtained. Their viscosity is governed by the D:M ratio. They are chemically inert, non-film forming products. Nevertheless, due to their low surface energy, they are extensively used as wetting additives, flow modifiers and defoamers.

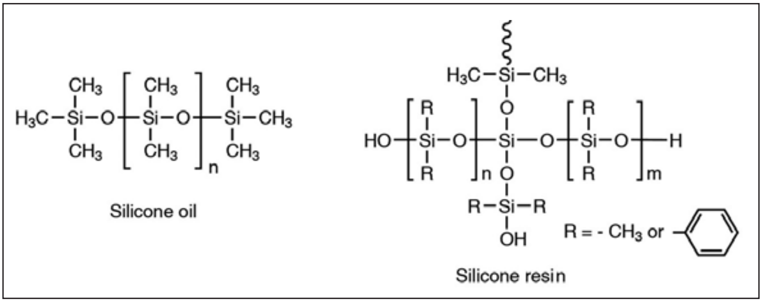


Figure 2.70: Schematic representative structure of silicone oil and silicone resin

Branched polysiloxanes are more useful as binders for coatings. The branching is introduced by the use of “T” units in the composition. The organic substitution may be methyl, phenyl or a mixture of both (Figure 2.70). Properties of the final resins are largely governed by the R:Si ratio (composition of M, D and T units), and methyl and phenyl content.

2.12.2.1 Types of pure silicone resin

Most silicone resins are copolymers of methyl and phenyl substituted monomers. Based on the type of organic substitution, the two main types of pure silicone resins are **high-methyl silicone resins** and ***high-phenyl silicone resins.***

High-methyl silicone resins are polymethylsiloxanes that have methyl groups as the predominant organic substitution and hence have the lowest carbon content. Pigmentation of these binders is difficult, and their incompatibility with other resins limits their use in blends with conventional organic binders. They are normally supplied as solutions in aromatic hydrocarbons (50 to 80 % solids). They are mainly used as binders for high temperature coatings, water repellents and co-binders for **breathable** and weather resistant exterior coatings.

High-phenyl silicone resins are a group of silicone resins with phenyl content greater than 20 %, with the rest being predominantly methyl and occasionally other alkyl groups. Silicones with only phenyl substitution do not have significance in coatings, as they produce brittle films. Phenyl groups increase their heat resistance and improve compatibility with co-binders. Some important properties of pure silicone resins are summarized in Table 2.10.

Table 2.10: Typical highlighting properties of high-methyl and high-phenyl silicone resins

High-methyl silicone	High-phenyl silicone
Faster curing	Better storage stability
UV stability	Higher heat stability
Good low temperature flexibility	Better oxidation resistance
Low weight loss during curing	Higher weight loss during curing
Chemical resistance	Thermoplasticity
Breathability of coating	Compatibility with co-resins

2.12.2.2 Curing

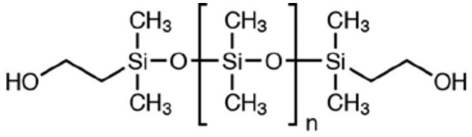
Curing reactions of silicone resins essentially involve continuation of the condensation reaction used during their preparation. They need a higher temperature of 225 to 250 °C or more for curing. By using an oil-soluble organometallic catalyst such as zinc octoate, the curing temperature can be reduced.

2.12.3 Blends of silicone resins

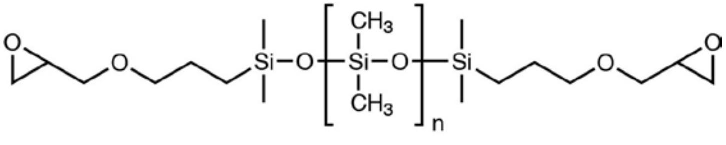
Classical silicone resins have limited compatibility with organic resins, but some specially designed high-phenyl content silicones have good compatibility with other organic film formers. In general, organic film formers contribute to quick-drying (dry to handle) characteristics, hardness and abrasion resistance, while silicones improve weatherability and heat resistance. Commonly used organic binders for blending with silicones are short and medium oil alkyds, polyesters, phenolics, UF-and MF-based baking finishes, low MW epoxies, and acrylics.

2.12.4 Modified silicone resins

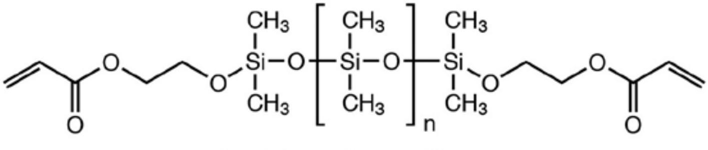
Conventional silicone resins have either alkoxy siloxane (–SiOR) or silanol (–SiOH) functional groups, which limits their application to certain specific curing chemistries. To expand their scope in coatings, modified silicone resins have been developed with functional groups suitable for conventional curing chemistries. For example, the –SiOH group of silicone resin, being acidic, does not react with isocyanate cross-linkers, and therefore it is modified with an alcoholic hydroxyl group (Si–CH_2–CH_2–OH) that can easily react with isocyanates. A few such representative examples of modified silicones are given in Figure 2.71.



Hydroxy functionalized silicone for curing with isocyanate



Epoxy functional epoxy, to be cured with polyamines/diamino silanes



Acrylate functional sillicone

Figure 2.71: Representative structure of some modified silicone resins

2.12.5 Silicone modified resins

Silicone modified resins differ from silicone resin blends in that they are chemically reacted with hydroxyl functional organic resins to obtain copolymerized products. Because of their high cost and long curing cycle at high temperatures, pure silicone resins have limited application in coatings. Copolymerizing with organic resins expands their usability in coatings by improving ease of curing and solvent resistance and providing a wider latitude of mechanical properties with considerable cost effectiveness. The silicone intermediates used for such modifications are low MW silicone resins having reactive silanol (–Si–OH) or alkoxysiloxane (–Si–OR) groups. These functional groups react with hydroxyl groups of organic polymers to form C–O–Si bonds. The most common organic polymers that are modified with silicones include alkyds, polyesters, acrylics and epoxies. Silicone modification may typically range from 25 % to 50 %, though higher levels up to 80 % are possible for designing special heat-resistant systems. The reaction is accomplished by heating the organic polymers and reactive silicone intermediate in the presence of a catalyst at about 140 °C. Two reactions are possible: the reaction of silanols with hydroxyls of the polymer or self-condensation of silanol groups. Excessive self-condensation may lead to gelation. Better control of the reaction is possible with an alkoxysilane functional group than a silanol group. The most commonly used catalysts for such reactions are organotitanates, such as tetraisopropyltitanate. Some representative structures of silicone intermediates and the reactions involved are shown in Figure 2.72.

2.12.6 Waterbased silicone resins

In keeping with the global trend, waterbased silicone resins are also commercially available for the coating industry. Some important commercial categories of waterbased silicone resins are primary emulsions, secondary emulsions, and waterborne silicone modified resins.

Primary emulsions are prepared by polymerization of low MW cyclic siloxanes in combination with branched silicone resins or often with multifunctional alkoxy silanes. All the components are

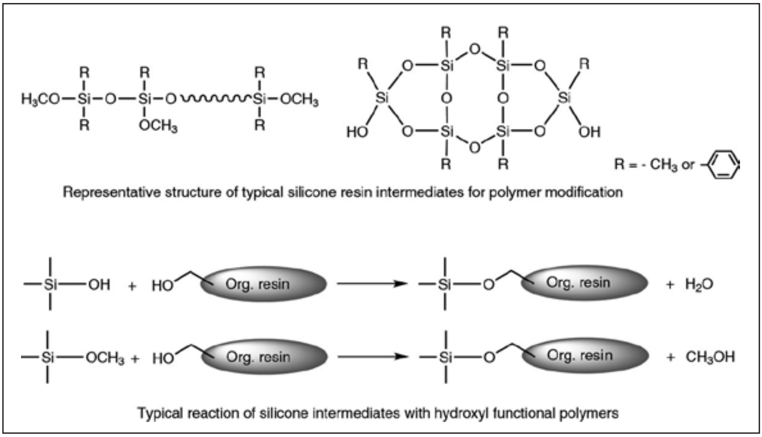


Figure 2.72: Chemistry of silicone modified resins

first emulsified using a suitable emulsifier to give a stable aqueous dispersion, followed by base catalyzed condensation of alkoxy silane groups. **Secondary emulsions** are of more significance in the coating industry. They are prepared by emulsifying solvent-based silicone resins as well as silicone modified resins in water with subsequent removal of solvent by distillation. Some residual amount of solvent (up to 10 %) is not removed to assist film formation through coalescence of dispersed resin particles. **Waterborne silicone modified resins** are prepared from silicone modified water-reducible acrylic or polyester resins, where ionic groups in acrylics or polyesters ensure water dispersibility of the final polymer.

2.12.7 Ethyl silicate

Ethyl silicate is a clear liquid derived by reacting silicone tetrachloride with ethanol. In the coating industry, it is useful as a binder in zinc-rich primers, one of the important layers in many protective coating systems. The partially hydrolyzed solution of ethyl silicate is one of the two components in the system, with the second being zinc dust. Upon application, it is completely hydrolyzed with atmospheric moisture and cures to a silica matrix with zinc particles embedded. During this curing process, silanol groups (–SiOH) also react with the metal substrate to form a covalent bond, which ensures exceptional adhesion of the zinc-rich primer to the metal.

2.13 Cellulosic binders

Chemically, cellulose is a natural polysaccharide with a high MW, linear structure having repeating anhydroglucose units. It is mainly amorphous but also has considerable crystallinity, making raw cellulose insoluble in organic solvents and water. Because of this insolubility, cellulose finds no applications in coatings in its unmodified form. To render solubility, it must be chemically modified to reduce hydrogen bonding between adjacent polymer chains. This can be accomplished by substituting some of the hydroxyl groups by bulky, less polar groups such as nitro (forming nitrocellulose) or alkyl groups (forming cellulose ethers). As the degree of substitution increases, solubility increases. Important cellulose ester binders are nitrocellulose, cellulose acetate and cellulose acetate butyrate.

2.13.1 Nitrocellulose

Nitrocellulose, also known as cellulose nitrate, was the workhorse thermoplastic binder to produce fast-drying lacquers for many decades. However, its very low solids (~20 %) at spraying viscosity was the main reason for the steep decline of its market share with inception of legislation pertaining to the reduction in VOC emissions.

Nitrocellulose is manufactured by nitration of cellulose by reacting it with a mixture of nitric acid and sulfuric acid in the presence of water. The degree of substitution is the important consideration of the product for its use in coatings. The degree of substitution is

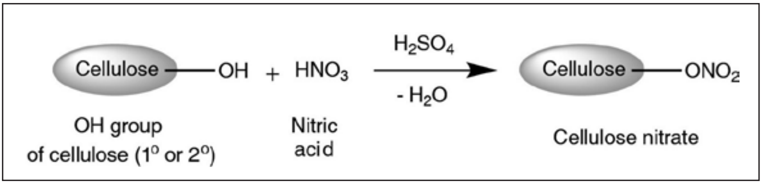


Figure 2.73: Synthesis of nitrocellulose

normally expressed as nitrogen content, and different grades are listed in Table 2.11. Nitration of approximately two hydroxyl groups per cellulose unit is useful for coating applications, while a higher level of substitution results in more unstable material that is used as an explosive (gun cotton). Even coating grade nitrocellulose has the tendency to ignite readily if allowed to dry out in finely divided form. Therefore, it is invariably supplied as alcohol wetted fibers (30 to 35 %) and requires special care during handling, storage and transportation. It must not be stored in dry form, and any source of heat, sparks or static electricity should be avoided. It is quite common practice to store it away from other raw materials.

Table 2.11: Grades of nitrocellulose for the coating industry

Grade	Nitrogen content	Degree of substitution	Solubility
A	10.7–11.3 %	1.89–2.05	Alcohol
AM	11.3–11.8 %	2.05–2.20	Esters, ketones and glycol ethers
E	11.8–12.2 %	2.20–2.35	Esters, ketones and glycol ethers

AM – partly soluble in alcohol
A and AM grades are obviously soluble in esters, ketones and glycol ethers, too.

A second important criterion for classification of nitrocellulose is its average MW, which is more conveniently expressed as the viscosity of its solutions. Based on this, it is classified as low viscosity, medium viscosity, and high viscosity grades.

Rapid drying is one of the most important characteristics of nitrocellulose-based coatings. Nitrocellulose alone produces hard and brittle films, and therefore, nitrocellulose-based coatings generally are formulated with plasticizers to improve flexibility and adhesion as well as compatibility with other resins. They are also blended with other polymers such as hard resins and non-drying alkyd resins, to name a couple. On the limiting side, nitrocellulose-based lacquers have generally poor resistance to chemicals and poor durability.

Use of nitrocellulose-based coatings has declined considerably in the United States and Europe because of their low solids at application viscosity and hence high VOC content. However, they are still used in parts of the world where environmental regulations are not very stringent.

2.13.2 Esters of cellulose

In order to find a safer non-flammable alternative to nitrocellulose, cellulose esters of lower organic acids have been developed and commercialized.

Cellulose acetate is prepared by reacting cellulose with acetic acid or acetic anhydride in the presence of a catalyst. Cellulose acetate has low flammability and better weathering resistance, but is of little interest as a binder for coatings due to its limited solubility and sensitivity to hydrolysis.

Cellulose acetate butyrate is an important cellulose ester derivative used in the coating industry. Chemically it is a mixed ester of cellulose with acetic and butyric acid. Residual hydroxyl groups and the ratio of butyrate to acetate groups are the main structural variations along with MW for various grades of cellulose acetate available on the market. Because of the bulky substituent (butyric acid), the regularity in the molecule decreases and spacing between cellulose chains increases, resulting in better solubility and improved compatibility with other binders and plasticizers. Bulky group substitution also renders flexibility and better moisture resistance. The residual hydroxyl groups of cellulose acetate butyrate resins can also react with other binders used in the composition. Cellulose acetate butyrate has seldom been used as sole binder, but rather is blended with other resins to balance the properties. It is used in clear and pigmented coatings for different substrates including metal, wood, paper and plastic. Some important applications of cellulose acetate butyrate are as an additive in automotive coatings and wood finishes, to increase solvent release and viscosity buildup, and for flow control, sag control, minimizing cratering and orange peel, and good hardness development. In automotive metallic basecoats, cellulose acetate butyrate assists in consistent orientation of metallic flakes as well as resistance to redissolving upon application of a subsequent coat. Cellulose acetate butyrate is also useful for better pigment dispersion in automotive coatings, providing consistent dispersion of multiple pigments (anti-floating). It also has good UV stability and is known to provide better intercoat adhesion. In wood coatings for furniture, cellulose acetate butyrate is used for its durability, non-yellowing properties, stain resistance, reduced picture framing and better optical properties, including gloss and distinctness of image. It also finds applications in advanced coil coatings and printing inks due to the properties listed above.

2.13.2.1 Ethyl cellulose

Ethyl cellulose is the only ether derivative of cellulose that is used as a main binder in which the hydroxyl groups of cellulose are etherified with ethanol. Based on the degree of substitution (~ 2.2 to 2.5) and MW, various grades are marketed. By increasing the degree of substitution, the solubility of ethyl cellulose in non-polar solvents increases. It has good alkali and water resistance. Like cellulose esters of organic acids, ethyl cellulose exhibits good durability. It is used in applications such as paper coatings, leather finishes, printing inks and wood finishes as well as some protective coatings.

2.14 Hydrocarbon resins (petroleum resins)

Hydrocarbon resins are primarily composed of cyclic, polycyclic or heterocyclic aliphatic and aromatic structures. Hydrocarbon resins are non-reactive thermoplastic binders, but have low MW compared to other conventional thermoplastic binders such as vinyl, acrylic, and cellulose esters. They are rarely used as sole binders in coatings, but rather as modifiers. In general, hydrocarbon resins have good solubility in non-polar solvents but are insoluble in polar solvents. Being composed of hydrocarbons and free of any reactive groups, their films are resistant to water and chemicals, making them useful as protective coatings, water proofing, hot-melt adhesives, floor coatings, and hot-melt road marking paints, to name a few applications. However, their sensitivity to solvents is a primary limitation. Hydrocarbon resins with a high level of unsaturation have a tendency for yellowing upon exposure to UV light and hence are generally required to be formulated with suitable antioxidants and light stabilizers.

2.14.1 Coumarone indene resins

Coumarone indene resins (Figure 2.74) are one important class of hydrocarbon resins. They are mixtures of homopolymers and copolymers of coumarone and indene. Coumarone and indene are obtained together in fractional distillation of coal-tar naphtha. They are polymerized through their unsaturation using either sulfuric acid or metal chloride catalysts. The products are low MW polymers varying from viscous liquids to hard and brittle solids (softening point 90 to 140 °C). They have good compatibility with many of the binders used in coatings and are often used as modifiers to improve gloss and drying time. Due to the absence of acidity, they are good hard binders for aluminum paints and provide good leafing stability. Some low viscosity grades are also used as plasticizers in epoxy coatings.

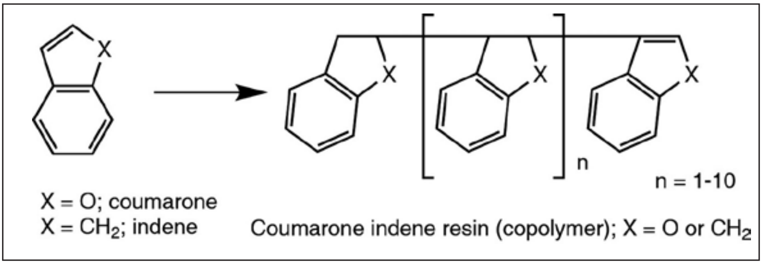


Figure 2.74: Schematic representation of coumarone indene resin

2.14.2 Petroleum oil derived hydrocarbon resins

Petroleum oil derived hydrocarbon resins are another important class of hydrocarbon resins worth mentioning. They are derived from unsaturated hydrocarbon monomers obtained from cracking of petroleum oil. Polymerization of these monomers results in a complex mixture of various low MW copolymers and homopolymers known as petroleum-based hydrocarbon resins. Based on monomer composition in the feedstock, various grades are available ranging from liquids to hard and brittle solids. Their performance characteristics are very similar to other hydrocarbon resins and they are useful modifiers for various conventional coating systems as well as low VOC, high-solid systems.

3 Pigments

3.1 Introduction

Chapter 2 described the vital function of polymers as film formers in paints and coatings. However, successful paint formulation needs to meet other properties such as color and opacity that the binder alone cannot provide. Pigments are one of the most important components of coatings.

Colorants are materials used to impart color, which may be either pigments or dyestuffs. Therefore, before entering into the discussion about pigments, they must be distinguished from dyestuffs. The essential difference between them is their solubility in the medium in which they are incorporated.

Pigments and dyes are defined in DIN 55943, ISO 4617 and ISO 4618. A dye is defined as a colorant that is soluble in the application medium. A pigment is defined as a substance that is insoluble in the application medium and is used as a colorant or on account of its corrosion inhibiting or magnetic properties. Because of their solubility, dyestuffs, when used in coatings, produce transparent films, which limits their use in particular types of coatings that require a high degree of opacity.

More generic to the paint industry, pigments can also be defined as organic or inorganic fine-particulate solids, substantially insoluble in paint vehicles, that are used to impart certain properties to paint such as color, opacity, corrosion inhibition, mechanical properties and durability.

Some pigments called lakes are dyes that are combined with fine, inert inorganic particles as a base or carrier, which in turn give insoluble colorant particles. On the other hand, organic pigments that do not contain an inorganic carrying base are known as toners. In

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Europe, the term toners is applied to insoluble metal salts of water-soluble acid or basic dyestuffs.

3.1.1 Functions of pigments

Most coatings are formulated to have two important functions: aesthetic and protective. Pigments are incorporated into coatings to contribute to both of these functions.

3.1.1.1 Aesthetic functions

Color and opacity, the important aesthetic attributes of paint, are given by incorporation of pigments. Pigments impart color by selective absorption of visible light, while opacity is obtained by scattering and/or absorption of visible light by pigment particles. Pigments may also affect texture-related appearance characteristics of coatings, such as gloss and sheen. Various special-effects coatings can also be formulated by special types of pigments discussed in Section 3.3.8.

3.1.1.2 Protective functions

Generally, for a given binder system, pigmented coatings provide better corrosion protection than clear systems. Depending upon particle size, shape and amounts used, the barrier properties of pigment coatings vary. Lamellar pigments such as aluminum flakes, mica, and micaceous iron oxide improve barrier properties of coatings. Also, certain active anticorrosive pigments intervene with electrochemical corrosion reactions in the corrosion process at the interface between a metallic substrate and coating film. UV radiation can cause degradation of the polymer matrix in the coating film. Certain pigments increase the durability of the coating system by absorbing UV light and thus protecting the film from degradation. With careful selection of pigments and their amounts, it is possible to increase the mechanical strength of coatings by reinforcement of the polymer matrix by harder pigment particles. Some pigments, like zinc oxide, may efficiently increase mold resistance of coating films.

3.1.1.3 Other functions

Pigments may also influence rheological properties, which play a vital role in storage and application of coatings. In addition, some pigments have specific functions such as mold resistance, antifouling properties, infrared light absorption or reflection, phosphorescence, conductivity, thermochromism or fire retardancy, which are important for certain coatings.

3.1.2 Nomenclature – the Colour Index system

In modern scientific and techno-commercial publications, pigments are frequently discussed using a universally accepted standard coding system known as the Colour Index, which was jointly developed by the Society of Dyers and Colourists in the United Kingdom and the Association of Textile Chemists and Colorists in the United States. The Colour Index identifies each colorant by giving the compound a unique Colour Index name and a Colour Index number. The five or six digit Colour Index number is allocated to a colorant according to its chemical constitution as described in Table 3.1.

Table 3.1: Colour Index (CI) constitution numbers

Chemical class	CI numbers	Chemical class	CI numbers
Nitrosol	100000–102999	Thiazole	490000–493999
Nitro	103000–109999	Indamine	494000–496999
Monoazo	110000–199999	Indophenol	497000–499999
Diazo	200000–299999	Azine	500000–509999
Stilbene	400000–407999	Oxazine	510000–519999
Diphenylmethane	410000–419999	Thiazine	520000–529999
Triarylmethane	420000–449999	Aminoketone	560000–569999
Xanthene	450000–459999	Anthraquinone	580000–729999
Acridine	460000–469999	Indigoid	730000–739999
Quinoline	470000–479999	Phthalocyanine	740000–749999
Methine	480000–489999	Inorganic pigments	770000–779999

The CI generic name is composed of:

- The application class of the colorant (for example, pigment, solvent dye, basic dye)
- The hue of the colorant (for example, yellow, blue, violet, red)
- The number (unique within the same group and shade designation)

The Colour Index, names for pigments and their abbreviations are shown in Table 3.2.

Table 3.2: Abbreviated Colour Index (CI) names for pigments

Abbreviation	CI name	Abbreviation	CI name
PB	Pigment Blue	PBk	Pigment Black
PBr	Pigment Brown	PG	Pigment Green
PM	Pigment Metal	PO	Pigment Orange
PV	Pigment Violet	PR	Pigment Red
PW	Pigment White	PY	Pigment Yellow

For example, phthalocyanine blue has the Colour Index name Pigment Blue 15 (CI PB 15) and the Colour Index number 74160.

For distinguishing pigments with the same chemical composition but a small difference in structure, such as the metal or acid used for salt formation, a subdivision has been made by addition of a digit to the CI name or CI number after a colon. This is also used to distinguish pigments in which crystal modifications yield products with the same chemical structure but significantly different properties.

3.1.3 Classification of pigments

Pigments may be classified on different bases, such as color, chemical nature (inorganic or organic) and process of manufacture (synthetic or natural). A few of such classifications are explained below.

3.1.3.1 Classification based on color

Based on color, pigments can be classified in the following categories:

- Achromatic pigments
  - White pigments: titanium dioxide, zinc oxide, antimony oxide
  - Black pigments: carbon black, iron oxide black

- Chromatic pigments (colored pigments)
  - Red pigments: iron oxide red, toluidine red, quinacridone red
  - Orange pigments: cadmium orange, pyrazolone orange
  - Yellow pigments: chrome yellow, benzimidazolone yellow
  - Green pigments: chromium oxide green, phthalocyanine green

  - Blue pigments: iron blue, ultramarine blue, phthalocyanine blue
  - Violet pigments: cobalt violet, dioxazine violet, quinacridone violet
  - Brown pigments: iron oxide brown, benzimidazolone brown

3.1.3.2 Classification based on chemical nature

Here, pigments are classified based on their chemical composition as follows:

- Inorganic pigments
  - Oxides: titanium dioxide, iron oxide red, nickel titanate yellow
  - Sulfides: zinc sulfide, cadmium sulfide
  - Chromates: chrome yellow, chrome orange, zinc chromate
  - Molybdates: molybdate orange, zinc molybdate
  - Phosphates: zinc phosphates, aluminum phosphate
  - Elements
    - Metallic: aluminum, copper, zinc
    - Non-metallic: carbon black
  - Coordination complex: iron blue
  - Others: ultramarine blue, bismuth vanadate, zinc metaborate

- Organic pigments
  - Azo pigments
    - Monoazo pigments: toluidine red, arylamide yellow, naphthol red
    - Diazo pigments: diarylide yellows, pyrazolone orange
    - Salt-type azo pigments (lakes): PR 53, PR 57
    - Azo condensation pigments: PY 93, PR 144
    - Azo complex pigments: PG 10, PO 59
    - Isoindolinone and isoindoline pigments: PY 109, PO 61

- Polycyclic pigments
    - Phthalocyanine pigments: phthalocyanine blue and green
    - Quinacridone pigments: PR 122, PV 19
    - Anthraquinone pigments: PY 108, PO 51, PB 60, PR 177
    - Perylene pigments: PR 123, PR 178, PV 29
    - Perinone pigments: PO 43, PR 194

- Diketopyrrolopyrrole pigments: PR 254, PO 73
- Thioindigo pigments: PR 88, PR 181
- Dioxazine pigments: PV 23
- Quinopthalone pigments: PY 138
- Triarylcarbonium pigments: PB 61, PB 19

3.2 Important properties of pigments

Not all colored insoluble products synthesized are commercial pigments. To qualify as a pigment, a product needs to demonstrate various characteristics that are not covered in the definition alone, but are important from an application standpoint. Some important properties and characteristics of pigments are briefly discussed below.

3.2.1 Optical properties

Most pigments that are part of any paint formulation are intended to provide visual effects – predominantly, color and opacity.

3.2.1.1 Color

Color can be described as a visual sensation that is produced from the stimulation of the retina of the human eye by light in the visible region of the electromagnetic spectrum. The cones of the retina, comprised of three groups of sensory cells, are responsible for perceiving color, while rods in the retina are stimulated in accordance with the intensity of the light. If all wavelengths of incident daylight are reflected from an object, it appears white, and if all are absorbed by the object, it appears black. This is what happens with white and black pigments, respectively. In the case of colored pigments, a selected part of the spectrum is removed by interaction of light with pigments, and the rest reaches the retina, where the cones register this change and the color is perceived according to the wavelength of the reflected portion of the visible light. For example, a blue pigment appears so because it reflects the shorter blue wavelengths of the incident white light and absorbs all of the other wavelengths.

Factors affecting color of a pigment:

Chemical purity: The selective absorption of visible light by a pigment is predominantly decided by its chemical structure; therefore, chemical purity is one of the important factors that produces consistent color.

Particle size: In general, below a certain optimum particle size, pigment particles are optically active through their entire mass, and absorption is no longer a function of particle size; thus, it remains constant with further decrease in size. Above this optimum particle size, the amount of light absorbed is proportional to the surface area of the particles, and therefore, by increasing the particle size above the limiting value, the total absorption of light decreases per unit mass of pigment. In general, smaller particles are brighter in color. Also, by decreasing the particle size, the shade of color is shifted towards medium wavelengths. For example, greener yellows or yellower reds can be obtained at smaller particle sizes.

Crystal structure: In certain cases, chemically identical pigments existing in different crystal forms (also known as polymorphisms) may exhibit a different hue. Pigments that clearly show the effect of polymorphism on hue are quinacridone pigment (Pigment Violet 19), phthalocyanine pigment (Pigment Blue 15) and lead chromates.

Color of pigments – definitions

Mass tone (mass color): According to ASTM, when viewed by reflected light, the color of a pigment-vehicle mixture of a thickness that completely obscures the background is known as mass tone or mass color.

Tint color (reduced color): The color produced by mixing a predominant amount of a white pigment (generally titanium dioxide) with a colored pigment is known as tint color or reduced color.

Pigment suppliers typically provide chips of mass tone and tint colors (with two or three different levels of reduction in their technical bulletins.

Evaluation

Visual method: The most basic method for evaluating color of a pigment is to visually examine the mass tone and tint color of the pigment under specific illumination and to compare it with a standard physical sample. This method has the limitation that color perception may vary from person to person or under different conditions, such as type of light source and angle of viewing.

Spectrophotometric method: To overcome the limitations of visual methods, a more scientific approach to color quantification has been developed. The International Commission on Illumination (Commission Internationale de l'Eclairage, or CIE) introduced the element of standardization of sources and observer. The CIE also introduced methodology to derive numbers that provide a measure of a color seen under a standard source of illumination by a standard observer. The CIE system has become the international standard for color measurement.

3.2.1.2 Opacity

Opacity of a pigment is its ability to impart **hiding power** to the coating film in which it has been incorporated. Pigments render opacity to the coating mainly by two mechanisms:

- Scattering of light
- Absorption of light

Except for black and some saturated deep-blue pigments that absorb most incident light, all other pigments render opacity predominantly by scattering of light, with very little contribution from absorption. White pigments, which do not absorb visible light, achieve opacity only by scattering of light. The scattering of light by pigment particles in the medium is a result of a combination of three phenomena – predominantly the refraction of light and to some extent reflection and diffraction of light at the interface between pigment particles and the medium (Figure 3.1).

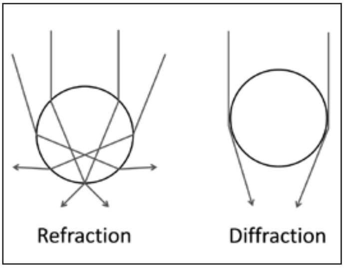


Figure 3.1: Schematic representation of refraction and diffraction of light by pigment particles

Important factors related to scattering power and hence the opa-

Table 3.3: Refractive index (RI) of some materials used in paint

Medium		**Pigments**		**Extenders (fillers)**	
Material	RI	Material	RI	Material	RI
Air	1.00	Titanium dioxide (anatase)	2.55	Talc	1.54
Water	1.33	Titanium dioxide (rutile)	2.76	Silica	1.55
Film formers	1.45–1.6	Zinc oxide	2.01	Calcium carbonate	1.58
		Zinc sulfide	2.37	Barite	1.64

city of a pigment are its refractive index and particle size. The larger the difference between the refractive index of pigment particles and that of the medium in which they are dispersed, the higher the opacity. Thus, the high opacity of titanium dioxide and transparency of extenders in a given coating binder can be explained if we take a look at the refractive indices of the materials listed in Table 3.3.

Another important factor affecting the scattering phenomenon is pigment particle size. The ability of pigment particles to scatter light increases as the particle size decreases, up to an optimum size (generally about 200 nm). Further decrease in pigment particle size results in decreased scattering (Figure 3.2). The hiding power is proportional to the scattering ability of a pigment; therefore, it follows the same trend and reaches a maximum at an optimum particle size, which is approximately half of the dominant wavelength of light. Ultimate dispersion of these optimum sized pigment particles is equally important to achieve maximum hiding power, because agglomerated particles will behave like a large particle. The refractive index is invariable

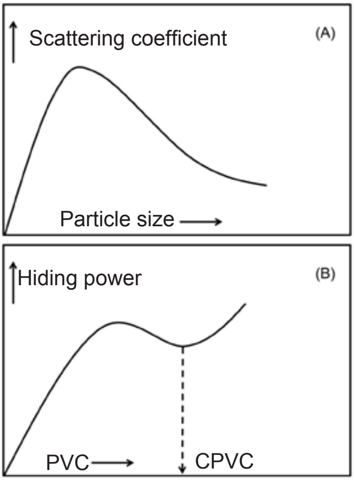


Figure 3.2: Factors affecting opacity: (A) effect of particle size on scattering (B) effect of PVC on hiding power

for a given compound; therefore, particle size control is an important tool for pigment manufacturers to control opacity. In addition to such physical properties, the amount of pigment in a dry film, commonly expressed as the pigment volume concentration (PVC), is another important factor governing the hiding power of the paint film. PVC is defined as:

$$\%\ \text{PVC} = \frac{100\ (\text{Volume of pigment}))}{(\text{Volume of pigment} + \text{Volume of medium})}$$

Evaluation

To evaluate the opacity of a pigment, it needs to be dispersed in a suitable vehicle at an appropriate concentration. Subsequently, films of various thicknesses are applied over a black and white substrate (known as a contrast or hiding power chart) and observed for color differences in the black and white portions. The hiding power (expressed in m^2/L) can be defined as the reciprocal of the minimum thickness (in mm) of the applied film at which the contrasting substrates cannot be distinguished by visual observation. Instead of applying films at different thicknesses, a coating can also be applied as a wedge-shaped film, and the minimum thickness at which obliteration is observed can be measured.

The visual method has been improved by the use of a photometric method to evaluate the hiding film thickness. In this definition, the hiding power is the reciprocal of the film thickness of a pigmented coating at which the **contrast ratio**, which is the ratio of the reflectance of a film on a black substrate to that of an identical film on a white substrate, is >0.98. Some photometric methods also use measurement of color difference over black and white portions, while others use measurement of the ratio of Y_S to Y_W, which are CIE tristimulus values respectively measured over a black portion and a white portion, as a parameter to evaluate hiding. Further information on evaluation of hiding power of pigmented coatings is found in methods DIN 55987, ASTM D 2805, ISO 6504-1 and ISO 6504-3.

3.2.1.3 Tinting strength and lightening power

The **tinting strength** of a colorant is its ability to impart color to a light scattering material by virtue of its absorption properties. Tinting strength corresponds to the effectiveness with which a unit quantity of a colorant changes the color of a material. Generally, tinting strength is expressed as the mass ratio in which the reference pigment (mass, m_R) can be replaced by the test pigment (mass, m_T) to give the same color quality in a white system. Tinting strength has an economic implication on paint formulation because the higher the tinting strength, the less pigment is required to achieve a standard depth of shade. Tinting strength of a colored pigment depends upon its light absorbing power, and therefore, factors such as chemical structure, purity and particle size largely govern tinting strength. In general, the smaller the particles, the higher will be their tinting strength. Generally, these factors are controlled during the pigment manufacturing process and not during paint manufacturing. The paint manufacturer can achieve maximum tinting strength from a given pigment by efficient dispersion of pigment particles.

The **lightening power** (the tinting strength of a white pigment, also referred as **reducing power**) is a measure of its ability to increase the reflectance of an absorbing black or colored medium by virtue of its scattering ability. Lightening power is the mass ratio at which the reference pigment can be replaced by the test pigment to give the same lightness in a colored system. Lightening power depends upon the scattering ability of the pigment particles, and therefore, important factors affecting lightening power are particle size and the refractive index of the pigment.

Evaluation

A test method for evaluation of tinting strength of colored pigments is briefly described here. A white reduction of the test pigment and another of the reference pigment are prepared by dispersing them separately in the same quantity of suitable solvent-free vehicle with an identical mass ratio of colored pigment to standard white pigment. Drawdowns are made of the test and reference tint pastes side by side on a paper chart. The color difference is then evaluated visually or photometrically by an instrument to compare the strengths. The lightening power can also be evaluated by a similar technique but using a test white pigment and reference white pigment with a standard absorbing pigment as described in standard procedures.

Detailed information on visual evaluation of tinting strength is found in ISO 787-16, and on photometric methods in ISO 787-24, ASTM D387 and DIN 55986 and DIN 55603. The methods to refer to for lightening power of white pigments are ISO 787-17, ASTM D 2745 and DIN 55982.

3.2.2 Physical properties

3.2.2.1 Solubility

Solubility is the most undesirable characteristic of a pigment. Although pigments by definition are insoluble, in practice, many pigments exhibit a minute level of solubility, leading to noticeable problems in the systems in which they are incorporated. Generally, organic pigments exhibit such a level of solubility in organic solvents, while inorganic pigments are completely insoluble in solvents. Molecular size, substituent groups, metal complex formation and intermolecular bonding are some of the important factors that affect solubility of organic pigments. Some of the predominant problems observed in coatings as a result of solubility of pigments in the solvent or vehicle are bleeding, blooming and recrystallization.

Bleeding: In coatings, a pigment is said to bleed if some portion of it, by virtue of its solubility, migrates from the film in which it is incorporated to the medium with which it is in contact, causing discoloration of the latter. For example, if a white coating is applied on a red coating, and if the red pigment is even slightly soluble, the white coating may be discolored to pink rather than white. Such pigments are said to bleed. Resistance of a pigment to this phenomenon is known as bleed resistance or overcoating fastness.

Blooming: In coatings, blooming refers to the migration of dissolved pigment particles from the inside of a paint film to the surface, where they are deposited as a layer of pigment crystals. As solubility increases with temperature, the phenomenon is more significant at elevated temperatures, such as in baking enamels. Even after wiping the deposit from the surface, a bloom may form again as a consequence of a pigment's solubility in the binder. The phenomenon continues until most of the pigment has crystallized either at the surface or in the film. Apart from temperature, the tendency of pigment to bloom is also the function of its concentration in the film.

Recrystallization: While milling the pigment in a vehicle, a portion of the pigment may get dissolved due to generation of the heat in the milling process. The resultant paint may meet the optical criteria of the final paint, appearing strong and bright, because the pigment is acting as a supersaturated solution of dye. However, over a period of time, the dissolved portion of the pigment starts to precipitate, causing loss in strength and brilliance. The problem is more evident as a noticeable shift in shade when organic pigments with significantly different colors and differential solubility are combined in a single composition. Recrystallization can be avoided by appropriate selection of pigments and temperature control during the milling process.

Along with solubility in solvents, the pigment should also be checked for water-soluble content. Water-soluble components are restricted to a few parts per million. Pigments prepared by precipitation or by calcination of metal salts tend to adsorb or retain traces of salts that are not always completely removed in the subsequent washing process. The presence of water-soluble matter in the paint film may impair performance of the coating. Water-soluble sulfates or chlorides in pigments used in corrosion inhibiting primers for metals can act as corrosion accelerators.

Evaluation

Tolerance to an individual solvent is tested by enclosing a certain amount of pigment powder in a piece of filter paper, which is then immersed in the organic solvent for a given amount of time. The extent of coloration of the test solvent indicates the solvent fastness of the pigment.

In another method for evaluating overcoating fastness, a uniform coating containing test pigment (generally a full shade) is overcoated with a uniform film of white paint to yield complete hiding. After complete drying, pigment migration from the base coat into the white topcoat and hence discoloration of the latter is determined visually or colorimetrically. The binder system for base coat and white top coat are generally selected based on the actual coating system in which the pigment is to be used. Further information on bleeding tests is in ISO 787-16 and ASTM D279.

The water-soluble matter can be determined by extraction of a known amount of pigment sample with water followed by filtration and evaporation of the filtrate to dryness in order to gravimetrically determine water-soluble.

3.2.2.2 Density

Density can be a useful pointer to such properties of a pigment when dispersed in paint as suspension and density of the paint itself. According to Stokes' law, a pigment particle will settle in paint at a rate proportional to the difference in the densities of the pigment and the medium. Therefore, paints with dense pigments exhibit quick settling during storage. The settling rate can be reduced by compensating for the high density by using a viscous medium and a pigment with low particle size.

A further use of density is in calculating important volume relationships while formulating the paint, such as PVC, which affects many important properties of coatings and volume solids in paint and is used to correlate dry film thickness and wet film thickness. The density of the pigment is primarily dependent on its chemical composition and to some extent on its crystal structure. Generally, inorganic pigments are denser than organic ones, with a few exceptions such as carbon black and iron blue pigment that have lower density than other inorganic pigments.

Evaluation

The density of a pigment may be determined by the pycnometer method at a standard temperature of 25 °C using kerosene as immersion liquid. The detailed procedure may be found in ISO 787-10 and ASTM D153.

Many pigments are tested disregarding air entrapment on the particle surfaces or in the voids between the particles. The mass (in g) of 1 cm^3 of the pigment after tamping in a tamping volumeter under prescribed conditions is referred to as its **apparent density**.

It depends on the true density, shape and size of the particle. Information on tamped volume determination is in ISO 787-11.

3.2.2.3 Particle size

Particle size and particle size distribution are very important characteristics of pigments because they influence various optical properties of the paint such as color (Section 3.2.1.1), hiding power/opacity (Section 3.2.1.2), tinting strength (Section 3.2.1.3) and gloss, as well as physical properties such as suspension of particles in the paint and rheology of the paint system. For high gloss in coatings, it is necessary for the surface to be as smooth as possible. Large pigment particles or aggregates may project to the surface, thereby diffusing light and reducing gloss. According to Stokes' law, settling velocity is directly proportional to the square of the radius of the particle. Thus, smaller particles can be suspended more efficiently in a paint system than larger particles.

Pigments are produced in form of finely divided powder particles that consist of primary particles, aggregates and agglomerates (Figure 3.3).

Primary particles are individual pigment particles that can be recognized by a suitable physical method such as optical or electron microscopy.

Aggregates are an association of primary particles that have grown together and are aligned side by side, where the total surface area is smaller than the sum of the surface areas of the primary particles.

Agglomerates are an association of primary particles aligned along the corners and edges, where the total surface area does not differ appreciably from the sum of the individual surface areas of the particles.

Agglomerates present in a suspension (for example, in pigment-binder systems) that can be disintegrated by weak shear forces are known as **flocculates**.

The ultimate size of the pigment particle (primary particle) is dependent on pigment manufacturing conditions. Paint manufacturers actually have no control over the ultimate particle size because the

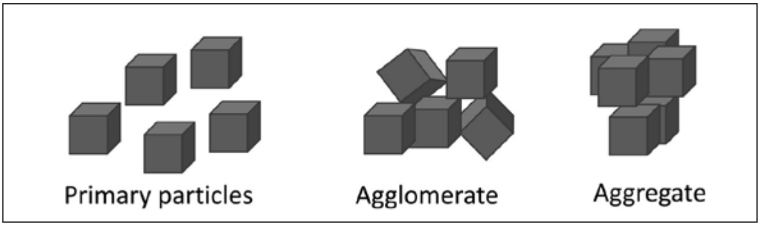


Figure 3.3: Primary particles, agglomerates and aggregates

shear forces involved in the paint milling process are not sufficient to break primary particles; only breaking of agglomerates takes place during the milling and dispersion process.

Evaluation

All particles in a given pigment are not identical in size; rather, they are a mixture of particles with different sizes. Therefore, pigments are generally evaluated for their mean particle size and particle size distribution by means of the following methods:

- Sieve analysis
- Accelerated sedimentation, such as centrifugal and ultra-centrifugal
- Light attenuation and scattering techniques, such as spectrophotometric techniques, light scattering techniques and laser diffraction
- Microscopy, such as using an optical microscope, electron microscope or transmission electron microscope
- Coulter counter
- Surface area measurement (using gas/liquid adsorption)

Each of the above methods has advantages and limitations, but sedimentation methods (using centrifuges) and diffraction techniques are frequently used for the determination of particle size of pigments.

Further details on particle size measurement and basic related terms are in ISO 9276, ASTM D 1366, DIN 53206-1, DIN 66141, DIN 66143, DIN 66144 and DIN 66145.

3.2.2.4 Particle shape

Pigments vary not only in size but also in particle shape. Although the inherent shape of pigment particles is determined from its crystal

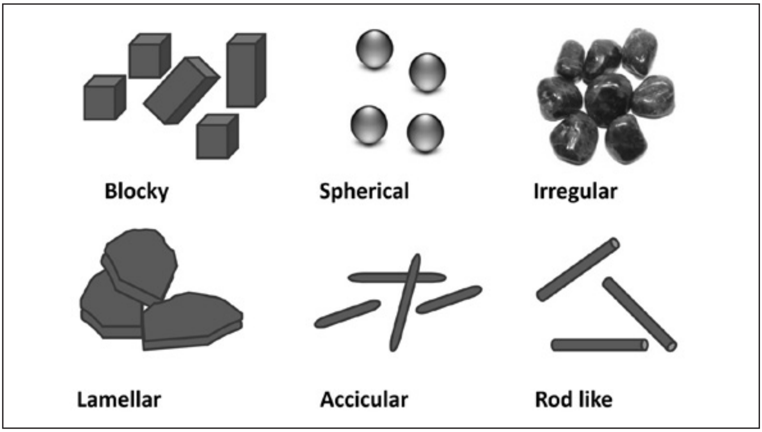


Figure 3.4: Shapes of primary pigment particles

form, it also depends to some extent on the method of synthesizing the pigment. In general, wet-ground pigments tend to have smoother and rounder edges than those produced by dry grinding. Micronized pigments also have smooth contours. The primary particles of pigments may be spherical, cubical, nodular (irregularly shaped), rod-like, acicular (needle-like) or lamellar (plate-like), as illustrated in Figure 3.4.

Particle shape of pigments also has an influence on such properties of paints as consistency, flow, brushability, settling and the mechanical properties of their films. Acicular pigments are several times longer than their smallest diameter. Needle or rod shapes have been found to exert a reinforcing action in paint films, similar to steel rods embedded in concrete. Acicular particles tend to settle in paint in a brush-heap structure, which is more readily re-dispersed than the compact layer formed by nodular, spherical or cubical particles. These relatively long acicular pigments may protrude through the surface of the film and thereby produce sufficient irregularity at the surface to reduce gloss. The surface roughness may be used to advantage in undercoats and intermediate coats by providing tooth for better adhesion of subsequent coatings. Lamellar pigments are extremely thin plates that reinforce the film. They tend to overlay one another in paint films, thereby making the film impermeable to the passage of moisture or gases. Nodular, spherical and cubical particles tend to have low oil absorption values, thus providing good flow properties to paint and providing the latitude to formulate paint with high PVC, while acicular, lamellar and rod-like particles have a tendency to increase the consistency of the paint due to their high oil absorption value. The abovementioned effects are not absolute, and should also be correlated with a pigment's other properties such as particle size and tendency to agglomerate. For example, even though primary particles of carbon black are spherical, they have a high oil absorption value because of their extremely low particle size, and frequently these spherical particles are transformed into chainlike structures.

Evaluation

The particle shape of a pigment can be observed through a light microscope. Nowadays, expensive but precise and more reliable techniques like electron microscopy are widely used to determine the particle shape of a pigment.

3.2.2.5 Texture of pigments (dispersibility)

The term texture generally is used to mean the feel – that is, the roughness or smoothness, and the softness or hardness experienced when a pigment is rubbed between the fingers. The more general meaning in the pigment and coating industry is the relative ease of dispersion of a pigment in a paint vehicle. The highest potential of pigments in coatings can be realized if their agglomerates are broken and dispersed as primary particles. In the paint manufacturing process, the pigment dispersion step is the most energy-intensive one, and hence ease of pigment dispersion is a desirable property of pigments.

Easily dispersing pigments are called **soft-textured pigments**, normally dispersing pigments are called **normal-textured pigments** and those that pose difficulty in dispersion are called **hard-textured pigments**. The pigment texture can be related to its packing and surface area, which are related to particle size and particle shape. Finer and more compacted pigments are more difficult to disperse than coarser and less densely aggregated ones.

Many pigments are surface treated by the manufacturers to enhance their ease of dispersion. Common types of surface treatment include adsorption of an organic or inorganic layer on the pigment surface to modify surface polarity and hence surface energy.

Evaluation

The ease of dispersion of pigments can be tested by dispersing a pigment in a given paint medium in an oscillatory shaking machine (for low viscosity medium) or automatic muller (for high viscosity medium). The time (in case of an oscillatory shaking machine) or the number of cycles at constant pressure (for an automatic muller) that are required to obtain a specified fineness of dispersion as indicated on a grindometer gauge may be used for rating the relative ease of dispersion. A change in tinting strength for identical composition and dispersion conditions may also be used as a criterion for testing relative ease of dispersion for colored pigments.

3.2.2.6 Oil absorption value

Oil absorption value has been used as an important specification for pigments and is very useful to coating formulators. Oil absorption value is defined as the minimum amount (in g) of linseed oil required to wet 100 gm of pigment to form a coherent paste.

To perform an oil absorption test, linseed oil is added dropwise to a weighed amount of pigment on a smooth glass plate while rubbing with a spatula until the mixture forms a coherent pasty mass. When the oil absorption test is completed, the surface of each pigment particle is wetted and saturated with oil to encapsulate pigment particle surfaces with a thin layer of oil. At the endpoint, there is just enough linseed oil to adsorb on the surface of all the pigment particles and to fill the interstices between closely packed particles. Thus, the oil absorption value for a pigment depends on surface area per unit mass, which is a function of the pigment’s particle size, shape, roughness and porosity. Pigments with small particle size have a large surface area per unit mass; hence, a larger amount of oil is absorbed on the surface. Similarly, pigments with acicular, lamellar and fibrous shaped particles have a high oil absorption value compared to spherical, blocky and nodular particles due to the larger surface area of the former types. Pigments with a highly porous structure such as diatomaceous silica also have a high oil absorption value due to the penetration of some oil into the pores. The oil absorption value is a mass-based evaluation, and therefore, pigment density also has a significant effect on the value. Denser pigments generally have lower oil absorption values than less dense pigments, provided that their particle size and shape are similar. Apart from these characteristics of pigments, other factors such as energy input during the test (time and vigor of rubbing), acid value of the oil (should be 3 ± 1 mg KOH/g), and moisture content of the pigment influence the oil absorption value.

Experience has shown that dispersion and the packing value obtained by linseed oil absorption are closely related to the critical PVC and pigment packing factor for the same pigment in paint and ink films.

The precision of oil absorption determinations by the spatula method is not high and may vary with operator, although with experience, deviations by a single operator can be reduced. Despite these deviations, the oil absorption value still remains very important to coating formulators, as it helps estimate binder demand for a given pigment in a coating formulation.

More details can be found in ISO 787-5, ASTM D 281 and ASTM D 1483.

3.2.3 Chemical and performance properties

3.2.3.1 Chemical purity

Most synthetic pigments produced by industry are pure chemical compounds, but natural inorganic pigments are processed minerals. The impurities in natural pigments may vary significantly from source to source. Even though physical appearance and some physical properties are similar, the presence of some chemical impurity may impair the performance of the final coatings. Such pigments must therefore be characterized for chemical purity before incorporation in a coating formulation.

3.2.3.2 Resistance to chemicals

One of the important characteristics of a pigment is its inertness to chemicals it may come in contact with. These chemicals may be paint ingredients or others that come in contact with the coating film. Resins, cross-linkers or certain additives may show reactivity toward a pigment, causing noticeable change in its performance. The chemicals that may come in contact with the coating film include water, soap or detergent in domestic situations, while in some industrial coatings, it may be strong acids or bases, acidic sulfide fumes or some oxidizing or reducing agents. This exposure may result in discoloration, fading or, in the worst cases, degradation of the pigment. Reactivity of pigments with paint ingredients may result in unacceptable viscosity increases or even gelation. For coatings that come in contact with food materials, it is essential that not only the coating but also the food is unaffected.

Evaluation

Chemical resistance tests are classified as short, medium or long-term resistance properties. Because of diverse and unique demands of coatings, limited published data is not reliable, and therefore it may be necessary to design special tests to reproduce conditions found in practice. Most test methods for chemical resistance of a pigment involve incorporation of the pigment in a coating prior to analysis, and seldom is the pigment analyzed as such. The test is carried out by keeping the coating surface in contact with the chemical for a predefined time and then examining for discoloration or staining.

3.2.3.3 Reactivity of pigments

Pigments such as white lead and zinc oxide react with free acids in paints and coatings to respectively form lead and zinc soaps of the acids. Titanium dioxide and many other extender pigments are non-reactive and do not form soaps. Lead and zinc soaps have low solubility in the vehicle and tend to increase the consistency of the paint. They also tend to prevent hard settling of pigment in the paint can during storage.

Pigments that have very small particle size, such as carbon black, iron blue, and certain organic pigments, may produce a physical or colloidal reaction in paint. The reaction results in an increase in consistency, which may become so great that an irreversible sol-gel transformation occurs and the paint becomes similar in texture to liver of human body. The phenomenon is referred to as livering, but the mechanism is not well understood. Apparently, pigment-vehicle complexes are formed that associate to produce a gel structure throughout the paint. In some cases, the pigment particles appear to form complexes with a near-gel fraction of the binder; in other cases, the pigment strongly adsorbs some of the solvent. Care must be taken to avoid livering because its irreversible character makes the paint almost impossible to apply satisfactorily.

3.2.3.4 Resistance to oxidative degradation

Oxidative polymerization of drying oil-based polymers is the most common mechanism of film formation. During the initial period of drying, the pigment is in a highly oxidizing environment due to the presence of free radicals, hydro-peroxides and activated catalysts. This environment becomes more severe with force-dried finishes that may be baked at elevated temperatures. The pigment should be inert to any of these reactions and should not exhibit a change of shade or crystal form.

3.2.3.5 Light fastness

Many pigmented coatings are required to retain their original color when they are exposed to daylight during their service life. Light fastness is a pigment's resistance to discoloration when exposed to daylight. Of the total radiation of daylight, UV is the most damaging portion, though it is not the only responsible factor. Light fastness is primarily governed by the chemistry of the molecule, though other factors that may influence light fastness are structure, defects, particle shape and size, and concentration of the pigment. The binder of the coating in which a pigment is incorporated also influences stability of the pigment to light. Therefore, the performance of a pigment varies considerably from one system to other, as the protection rendered by a binder varies considerably for different pigments. Other pigments may also influence light fastness when blends of pigments are used in coatings. For example, titanium dioxide promotes photo-degradation of some organic pigments, resulting in poor light fastness of tints in comparison to full shades of certain pigments. In general, most inorganic pigments are stable to light, while organic pigments vary considerably in their light fastness. Certain inorganic pigments, such as iron oxides, improve light fastness of compositions, as they are effective UV absorbers.

Evaluation

As light fastness is a system-related property, it cannot be evaluated for a pure pigment, but rather is evaluated for pigmented coatings. Although natural daylight would be ideal, the test is accelerated by using an intense source of light that corresponds as closely as possible to natural daylight. One common light source used is a xenon arc lamp. Specimens incorporated with the pigment being evaluated are exposed to the radiation in testing cabinets and observed for color fading. The evaluation of color change may be done by standard scales such as the ISO Grey Scale or the Blue Wool Scale. Discoloration may also be evaluated by CIE tristimulus values obtained by a spectrophotometric method.

Further information can be found in standard methods such as EN ISO 11341 or ASTM D 4303.

3.2.3.6 Weather fastness

When pigmented coatings are used in outdoor conditions, light is not the only factor affecting film degradation. A range of other factors such as heat, moisture, rain, fumes and other industrial gases are responsible, to more or less of an extent, for performance of the coating. **Weather fastness** is the ability of a pigment-binder system to tolerate the combined effect of daylight and other physicochemical factors of the outdoor environment. In the presence of light and other atmospheric factors, various photochemical processes take place, causing problems such as chalking, discoloration or loss of gloss. Weather fastness generally depends on chemical composition, structure, crystallography, particle size and shape of the pigment and on properties of the vehicle in which the pigment is incorporated.

Evaluation

While weather fastness may be evaluated by exposing the sample to actual outdoor conditions for a prolonged time, accelerated tests are more commonly used in industry. In an accelerated weathering test, the specimens are exposed to cycles of different atmospheric factors such as light, dark, water spray, temperature change and varying humidity in a specific test chamber, such as a weather-o-meter. Unlike light fastness, where only the degree of discoloration is measured, weather fastness involves more descriptive reporting. In addition to discoloration, defects such as degree of chalking and loss of gloss are reported. However, it should be noted that artificial accelerated test data may not represent actual outdoor conditions. Also, natural weathering tests have some limitations, as weather cannot be standardized.

Further information can be found in standard methods such as EN ISO 11341.

Thermal stability

Thermal stability of a pigment is its ability to withstand high temperature without any adverse effects such as discoloration, melting or deterioration. Pigments may be exposed to high temperatures during processing of the coating, thermal curing of the coating or during the service life of the coating. The thermal stability of a pigment should be higher than the highest temperature it may be exposed to during any of these stages. Most inorganic pigments have high thermal stability, while thermal stability of organic pigments may vary considerably. Most of the early classical organic pigments had poor to fair heat stability, but intense research in the field of organic pigments resulted in development of several high performance pigments with considerable improvement in thermal stability for applications where organic pigments were not suitable before. Major reasons for discoloration of pigments under high temperature conditions are their thermal decomposition, chemical interaction with the binder, dissolution in the application medium or crystal modification.

Evaluation

Thermal stability is also a system-related property. The system with a pigment under test is evaluated for color at a series of temperatures. The color difference between the test sample and a standard are than compared. The change in hue (or yellowing in the case of white pigments) is measured colorimetrically using a spectrophotometer and the CIE's CIELAB system. Thermal stability may be reported as the maximum temperature at which the color of a pigment remains unaffected or the maximum temperature at which a defined color change is observed.

Further information can be found in standard methods such as EN ISO 787-21, ASTM D 2485 or DIN 53774-5.

3.2.4 Environmental and toxicological perspectives

For the pigment industry, environmental and toxicological considerations are primary concerns, as for any industry. Most coated articles come in contact with the human body; therefore, pigment manufacturers as well as paint manufacturers are responsible to protect not only the personnel involved in processing of pigments and the paints containing them but also the end user of the product. Therefore, the potential ecological and toxicological risks should be eliminated at the source. Pigment suppliers have a responsibility to provide complete information about their products' physiological, toxicological and ecological effects along with instructions for safe handling and waste disposal.

Compared to other chemicals, in general, pigments are less hazardous because of their low solubility, though many pigments have potential toxicological effects. Most organic pigments are considered to be safe, but certain inorganic pigments containing heavy metals such as chromium, lead, cadmium or antimony are being discontinued due to their toxicological effects. Another important risk associated with pigments is their dust. Therefore, precautions are needed to avoid creating dust during handling of pigments. While most organic pigments themselves do not exhibit potential hazards, manufacturing of such pigments involves several intermediates that require special care in waste disposal from manufacturing sites.

Toxicological considerations become extremely important for pigments used in coatings that come in contact with food or are to be applied to consumer goods or toys.

Two important publications that serve as starting points towards safer products are:

(1) **Safe Handling of Color Pigments** published by the Color Pigments Manufacturers Association, Inc. in 1993, which provides details of most of the hazards associated with pigments, legislation affecting pigments and details of the various agencies charged with the enforcement of such legislation in North America.

(2) **Safe Handling of Pigments**, published in Europe, with an emphasis on European legislation by the joint efforts of The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, the British Colour Makers Association, Verband der Mineralfarbenindustrie e.V. (VdMi, representing inorganic pigment manufacturers and many users in Germany), and Chambre Syndicale des Fabricants d'Emaux Pigments et Sels et Oxydes Metalliques (EPSOM, representing French pigment manufacturers).

There is other regional legislation that is outside the scope of this book.

3.3 Inorganic pigments

Inorganic pigments are naturally occurring or synthetically produced inorganic compounds having important pigmentary properties. Natural inorganic pigments have been used since prehistoric times. There are several minerals occurring in nature that possess pigmentary properties; they are mined, crushed, washed, finely ground and classified into different particle size ranges for their applications in industry. On the other hand, synthetic inorganic pigments are usually produced by processes such as precipitation from solution, fusion, calcination or partial combustion. Apart from their manufacturing route, inorganic pigments may be classified on the basis of their color or chemical nature. Chemical classification of inorganic pigments has been described in Section 3.1.3.2. For ease of description, here we will first discuss achromatic pigments – white and black – followed by various colored pigments according to their generic chemical classification.

3.3.1 White pigments

White pigments do not absorb visible light; rather, very fine particles of these pigments scatter the entire visible spectrum of light.

Therefore, the observer receives the whole spectrum of visible light and perceives a white color. Maximum light scattering is achieved when the difference between the refractive index of the pigment and the medium is maximum. White pigments have maximum market share of all the pigments used in the coating industry because they are used not only in white coatings but also in coatings with pastel colors. They are also used in combination with some transparent colored pigments when the white pigment contributes to opacity of the coating. White pigments used over the years in the coating industry include titanium dioxide, white lead, zinc oxide, zinc sulfide, lithopone and antimony oxide, of which only titanium dioxide and to some extent zinc oxide are used in modern coatings.

3.3.1.1 Titanium dioxide

Pigment White 6; formula: TiO_2

Titanium dioxide is the most important white pigment in today's coating industry considering its usage in almost all types of products. Its high refractive index (and hence opacity), the highest of the white pigments, and its excellent performance properties are the main reasons for its widespread use. More than half of the total titanium dioxide produced is consumed by the coating industry.

Titanium dioxide exists in three crystal forms, namely **rutile**, **anatase** and **brookite**, of which brookite has no commercial importance in the industry, while rutile and anatase are commercially produced. The rutile form is thermodynamically more stable than anatase; the latter is transformed to rutile above 700 °C. In each type of titanium oxide, the titanium atom in the lattice is surrounded octahedrally by six oxygen atoms, and each oxygen atom is surrounded by three titanium atoms, but they differ in the way the octahedra are linked through their corners and edges. The different crystal arrangements of anatase and rutile are shown in Figure 3.5. The more compact arrangement of the atoms in the rutile form is responsible for its higher refractive index (2.75) and correspondingly higher hiding power compared to the less compact anatase form with its lower refractive index (2.55). Therefore, rutile-type titanium oxide has the predominant market share over anatase. Another apparent difference is that the rutile titanium oxide is slightly yellower than

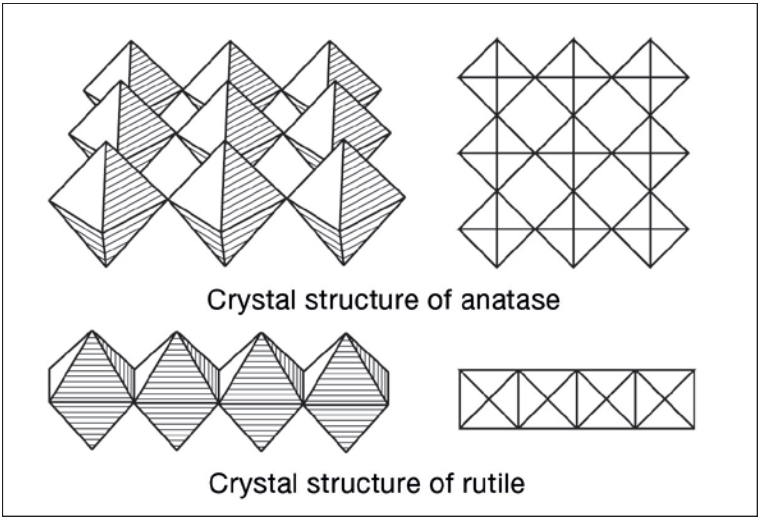


Figure 3.5: Crystal structure of anatase and rutil

anatase because it absorbs some visible light in the violet region of the spectrum. The density of rutile titanium oxide is 4.2 g/cm^3, while that of anatase is 3.9 g/cm^3.

Titanium dioxide is extremely stable at high temperatures (melting point 1800 °C). Titanium oxide pigments are chemically very stable. They are insoluble in all liquids with the exception of concentrated sulfuric acid and hydrofluoric acid (and only at 1000 °C). They are also resistant to hydrogen sulfide and other gases generally found in industrial atmospheres.

Titanium dioxide pigments are of commercial importance due to their excellent hiding power resulting from their high scattering power. As discussed in Section 3.2.1.2, hiding power is also dependent on particle size. The optimum particle size of titanium dioxide for highest hiding power and reducing strength is 20 to 300 nm. The typical primary particle shape of titanium dioxide pigments is nodular.

Despite having the highest hiding power and reducing power, one of the primary concerns with titanium dioxide pigments is their photochemical reactivity upon exterior exposure. Titanium dioxide is a strong absorber of UV radiation. When exposed to exterior conditions, UV irradiation of titanium dioxide excites electrons and leaves positively charged electron holes, which can move to the particle surface, where they react with surface hydroxyl groups and adsorbed oxygen to produce hydroxyl and hydroperoxyl radicals. These radicals cause degradation of binder at the pigment-binder interface that results in chalking. The anatase type has more tendency for chalking than rutile. To minimize the problem of chalking, the crystals are doped with elements such as zinc, aluminum or calcium. Also, surface treatment of titanium dioxide pigment particles by deposition of one or more oxides of silicon, aluminum, zinc or zirconium improves chalk resistance. Surface treatment also affects other properties such as dispersibility and gloss.

Titanium dioxide is manufactured by two processes, the sulfate process and the chloride process. In the sulfate process, ilmenite ore ($FeTiO_3$) is dissolved in concentrated sulfuric acid and insoluble impurities are removed by clarification, flocculation, sedimentation and filtration. The resulting solution is further purified by crystallization to remove ferrous sulfate from titanyl sulfate solution. The titanyl sulfate solution is then hydrolyzed to give hydrated titanium dioxide, which is calcined at about 900 to 1100 °C to give the titanium dioxide pigment. Both anatase and rutile-type titanium dioxide pigments are produced using this method.

In the chloride process, rutile ore is used as starting material. A finely ground mixture of ore and coke is reacted with chorine at 900 °C to yield titanium tetrachloride, along with chlorides of other metal impurities. Titanium tetrachloride is a liquid and is purified from other impurities by fractional distillation. Pure titanium tetrachloride vapor is then reacted with oxygen at 900 to 1400 °C to yield titanium dioxide and chorine, which is recycled. This method is used only for rutile grade titanium dioxide pigment. In both processes, the titanium dioxide so produced is subjected to subsequent product finishing by processes such as surface treatment, energy milling and size classification.

Titanium dioxide possesses many of the ideal properties required by a pigment for a coating, including excellent hiding power, very good brightness, a low oil absorption value, soft texture, high chemical resistance and excellent thermal stability. With this set of properties and the improved durability of modern surface-treated grades, titanium dioxide pigments have replaced most of the traditional white pigments used for coatings. Titanium dioxide pigments are widely used in both solvent-based and water-based exterior and interior paints for decorative as well as industrial segments. They are also used in printing inks.

3.3.1.2 Zinc oxide

Pigment White 4; formula: ZnO

This pigment is a fine brilliant white powder. Historically, it was used as a white pigment, but due to its low refractive index (2.01), it became uneconomical as a white opacifying pigment in comparison to titanium dioxide. It still finds some minor applications in coatings due to certain characteristics. Zinc oxide, being opaque to UV light, retards UV degradation of binders when used in exterior coatings. It is also a good fungistat, and therefore, when used in exterior house paint, it protects the coating from mildew. When used with oleoresinous binder, it has a tendency to produce zinc soaps, which improve hardness, abrasion resistance and moisture resistance. However, its reactivity with acidic media make it unsuitable for use in highly acidic binders. It is also used in anticorrosive coatings in combination with other active inhibitive pigments.

3.3.1.3 Zinc sulfide and lithopone

Pigment White 7; formula: ZnS

Pigment White 5; formula: $ZnS/BaSO_4$

Zinc sulfide (ZnS) is another historic pigment that is no longer used widely due to its low refractive index (2.37) compared to titanium dioxide. It has good whiteness with very good chemical resistance. One of the major limitations of this pigment is chalking when used in exterior applications. Lithopone is another such pigment with low refractive index (1.84). It is a coprecipitate of zinc sulfide with barium sulfate ($BaSO_4$). Lithopone as similar properties to zinc sulfide but less hiding power due to the barium sulfate.

3.3.1.4 Antimony oxide

Pigment White 11; formula: Sb_2O_3

This is another low refractive index (2.09) white pigment. It has good chalk resistance characteristics but its main functional application is in fire-retardant paints.

3.3.1.5 White lead pigments

Pigment White 1; formula: $2PbCO_3 \cdot Pb(OH)_2$

Despite its low refractive index (1.94), basic lead carbonate pigment was used in paint compositions for many years, but it is no longer used in the modern coating industry due to the toxicity of lead and the availability of more efficient titanium dioxide pigment with almost ten times more hiding power.

3.3.2 Black pigments

There are mainly three types of inorganic black pigments used in the coating industry, carbon black, iron oxide black and mixed-phase metal oxide pigments. Carbon black pigments dominate the volume of black pigments used in the coating industry, while the others are used in much smaller quantities. Iron oxide black and mixed-phase metal oxide pigments will be more suitably discussed in later chapters on other iron oxide pigments and high performance pigments, respectively. Therefore, in this chapter, only carbon black is discussed.

3.3.2.1 Carbon black

Pigment Black 7; formula: C

Carbon black pigments are pure elemental carbon produced by partial combustion or thermal decomposition of liquid or gaseous hydrocarbons such as natural gas, heavy oil or acetylene under controlled conditions. Different grades of carbon black pigments are produced possessing a range of properties that are governed by the type of hydrocarbon used and the manufacturing conditions. Important characteristics of carbon black pigments are particle size, surface area, surface chemistry, and structure, which influence important properties of these pigments, such as color, tinting strength, conductivity and texture.

Carbon black pigments are very fine, having a particle size ranging from 5 nm to 500 nm. Generally, the smaller the particles, the better the jetness (intensity of blackness) and tinting strength. On the other hand, finer particles have very large surface area and therefore absorb a high amount of polymer and build up high viscosity at very low pigment loading. Primary particles of carbon black pigments are spherical, but they aggregate in the form of clusters or chains. In the industry, the extent of this aggregation is called **structure**. A higher degree of structure results in higher viscosity and conductivity but provides a softer texture. Although all carbon black pigments are elemental carbon, they differ in their surface chemistry depending upon the manufacturing technique. As a result of oxidation at the surface during manufacturing, carbon black pigments have varying amounts of complexes containing chemisorbed polynuclear oxygen on their surface. The amount of these complexes is normally termed the percent volatiles (determined based on loss of mass at 950 °C in a closed platinum crucible). Higher volatile content increases dispersibility, jetness and gloss, while it lowers the conductivity. The oxygen complexes also reduce the pH of aqueous extracts of carbon black pigments.

Carbon black pigments are classified into six classes: lamp black, furnace black, thermal black, acetylene black, channel black and gas black. They all differ in their typical properties such as particle size, jetness, undertone and surface chemistry.

Lamp black is the oldest type of carbon black. In earlier days, it was produced from vegetable oil and hence is also called vegetable black, but in modern processes, it is produced from a high-boiling aromatic oil. Lamp black has a larger particle size and low jetness, but due to its bluer undertone, is frequently of choice as a tinting black to produce gray coatings, where it also has the advantage of low flooding and floating owing to the larger particle size. ***Furnace black*** is synthesized by partial combustion of hydrocarbon oil having a high aromatic content using a single flame in a closed furnace in the presence of insufficient oxygen. The process is highly efficient and has greater control of reactants. Furnace black has a finer particle size than other black pigments, except for channel black and gas black. This type of pigment is frequently oxidized in a subsequent step to improve its texture and jetness. **Thermal black** pigments are produced from thermal decomposition of natural gas, or occasionally hydrocarbon oil, in the absence of air. They have a large particle size and almost negligible volatile content. **Acetylene black** is produced by thermal decomposition of acetylene or acetylene mixed with light hydrocarbons. Once the reaction is started, it is maintained by exothermic decomposition of acetylene. This process is known to give products with higher conductivity. **Channel black** is produced by burning natural gas or methane in insufficient air where the flame impinges on a metal surface. The process gives a very low yield of carbon black, and hence channel black is more expensive than other carbon black pigments. Channel black has a very fine particle size, high volatile content, acidic pH, high structure, the highest jetness and the highest tinting strength. The **Degussa gas black process** is similar to the process used to form channel black, but coal tar oils instead of natural gas are used that give higher yields and production rates. Therefore, most of the channel black process has been replaced by the gas black process for high quality oxidized blacks.

Extremely high hiding power and tinting strength of carbon black pigments make them widely accepted black pigments in paints and printing inks. Carbon black pigments are relatively economical, but the prices are largely governed by particle size. Expensive, finer blacks are used in high quality coatings while coarser ones are preferred in low cost coatings. Carbon black is a strong absorber of UV light, which helps protect binders from degradation and hence is very useful in exterior coatings. Among the other important advantages of carbon black are excellent color stability, solvent resistance, acid resistance, alkali resistance and thermal stability. However, carbon black is difficult to disperse compared to other black pigments, although surface-treated, easily dispersible grades are available now. Carbon black pigments have a tendency to adsorb driers and other additives on their surfaces, requiring slightly higher dosages.

3.3.3 Colored inorganic pigments

This class of inorganic pigments differs from achromatic pigments (black and white) in that they selectively absorb part of the visible light spectrum, depending upon their chemical constitution and crystal structure, which produces different colors. Some of the characteristics of colored pigments are related to their chemical nature, and therefore, we will discuss different pigments according to chemical class rather than color.

3.3.3.1 Iron oxides

In the coating industry, iron oxide pigments are the second most widely consumed pigments after titanium dioxide pigments. They are available in different colors ranging from yellow, orange, red and brown to black. In general, iron oxide pigments are cost-effective pigments with excellent light and weather fastness. In addition to excellent hiding power, they have excellent chemical and solvent resistance. They are opaque to UV light, therefore protecting the binder from degradation. Therefore, iron oxide pigments are very popular in industry despite their dull colors. They occur naturally or are synthetically produced.

Natural iron oxide pigments

Natural iron oxide pigments are believed to have been used as colorants in cave paintings in prehistoric times. They are available in different shades and quality, depending on geographical location and the specific deposit. They occur naturally with other inorganic minerals such as clay or other metal oxides and therefore they vary significantly in their iron oxide content.

Hematite is found worldwide and has significant economic importance as a natural red iron oxide pigment. Generally, hematite has the highest Fe_2O_3 content among the natural iron oxide pigments. These pigments are frequently known on the basis of their origin, such as Spanish red or Persian Gulf red. Spanish Red has a brown undertone, while Persian Red pigments are brighter.

Goethite is a natural yellow oxide of iron also known as yellow ocher. These pigments are forms of hydrated ferric oxide having varying amounts of impurities, predominantly of silicates with some other oxides. Two well-known examples are French ocher and South African ocher, with hydrated ferric oxide content of about 20 and 55 %, respectively.

Umbers are natural brown oxide pigments with noticeable amount of manganese dioxide (5 to 20 %) in addition to Fe_2O_3 (45 to 70 %). Raw umbers have a greenish-brown to deep brown color, but calcined umber, also known as burnt umber, has a dark reddish-brown color.

Siennas are natural yellow iron oxide pigments with up to 50 % Fe_2O_3 and <1 % manganese dioxide, with varying clay content. They are calcined to give **burnt sienna**, which is brownish-red in color.

Natural iron oxide pigments have a dull color and low tinting strength, but they are used in inexpensive protective coatings, lime-based paints, primers, fillers and sometimes wood stains.

Micaceous iron oxide is a special type of natural iron oxide pigment having a black, brown or gray color. The name is a misnomer, as it does not contain any mica, but rather has a lamellar particle shape like mica. It is used in heavy-duty coatings to protect structural steelwork, where lamellar particles tend to orient themselves parallel to the substrate and reinforce the film as well as increase the barrier properties of the coatings to passage of oxygen and moisture. Also, due to its ability to absorb UV radiation, it protects the binder from degradation.

Synthetic iron oxide pigments

Synthetic iron oxide pigments are more popular because of their better color purity, consistent properties, and superior tinting strength compared to natural iron oxide pigments, which is a result of their higher chemical purity. They are available in red, yellow, brown and black colors.

Synthetic red iron oxide

Pigment Red 101; formula: Fe_2O_3

This is the largest class of synthetic iron oxide pigments. Synthetic red iron oxide pigment corresponds to the natural mineral hematite. It is prepared by mainly four processes:

- Precipitation process
- Calcination of iron sulfates (copperas process)
- Calcination of synthetic yellow iron oxide
- Calcination of synthetic black iron oxide

The properties of these pigments depend largely on their manufacturing process. The particle shape of red iron oxide produced by calcination of yellow iron oxide is acicular, while others are cuboid or spherical. Precipitation is especially suitable for producing soft pigments with a pure, bright hue. Most of the precipitation processes uses iron salts such as iron(II) sulfate or liquors from pickling of steel and iron along with scrap iron. Seeding in the precipitation and reaction conditions controls crystal growth and hence the properties of the pigment. These pigments are available in a wide range of hues from a yellowish to bluish undertone. Red iron oxide produced from calcination of yellow iron oxide has high tinting strength, but due to its acicular shape, it has higher oil demand, too. Generally, synthetic iron oxide red produces maximum scattering and hence hiding power, if the particle size is in the range of 0.1 to 1.0 µm. Pigments with particle size less than 0.1 µm are of commercial interest as **transparent iron oxides** in applications such as metallic automotive finishes.

Despite their dull color, red iron oxide pigments find applications in different architectural and industrial coatings due to their excellent thermal stability, weather fastness, solvent resistance, chemical resistance, cost effectiveness and high hiding power.

Synthetic yellow iron oxide

Pigment Yellow 42; formula: $Fe_2O_3 \cdot H_2O$ or $FeO(OH)$

Synthetic yellow iron oxides are dull yellow pigments with a low chroma value, but with better purity and tinting strength than their natural counterparts. They are commercially more important. They are synthesized mainly by the following processes:

- Direct precipitation using ferrous sulfate and alkali or ammonia
- The Penniman process using iron(II) sulfate, sodium hydroxide solution, and scrap iron

- The Laux process, involving reduction of aromatic nitro compounds using iron in the presence of aluminum chloride

Irrespective of the manufacturing process, they are all hydrated ferric oxide with an acicular particle shape. Longer crystals produce a greener and purer color. As a result, synthetic yellow oxides are sensitive to grinding; if overground, the shade becomes duller and redder. Another limitation of synthetic yellow iron oxide pigments is their poor heat stability. In contrast to red iron oxide, which is stable up to 1200 °C, yellow iron oxide stars to dehydrate above 150 °C, which shifts their hue to the redder side, and above 180 °C, they form red iron oxide. Despite their dull color and other limitations, these pigments are excellent choices for paints due to their low cost and overall good performance properties.

Synthetic black iron oxide

Pigment Black 11; formula: Fe_3O_4 or $Fe_2O_3 \cdot FeO$

Synthetic iron oxide black pigments correspond to the natural mineral magnetite. They are synthesized mainly by a direct precipitation process or the Laux process. They are far poorer in their depth of color and tinting strength than carbon black; therefore, they are not among the widely used iron oxide pigments. They still find some applications in the coating industry, as they are more readily dispersed compared to carbon black. They are used in gray paints where the tendency of carbon black pigments to float is intolerable. Their lower tinting strength is leveraged when used as tinters, particularly in bright and light gray shades. One of the limitations of black iron oxide is its poor heat stability. In an oxidizing environment, it changes to brown iron oxide at around 180 °C and to red iron oxide above 350 °C.

Synthetic brown iron oxide

Pigment Brown 6; formula: $xFe_2O_3 \cdot FeO$

Single-phase brown oxides of iron can be synthesized by controlled oxidation of black iron oxides. Different tones of brown can be prepared by controlling the oxidation process, and hence controlling the amount of Fe_2O_3 (red). Synthetic brown iron oxide is also synthesized by calcination of α-FeOOH with controlled quantities of manganese compounds. These pigments are not widely used in the coating industry, as similar brown shades may be derived by a combination of less expensive red and yellow iron oxide pigments.

3.3.3.2 Chromium oxide pigments

Chromium oxide green; Pigment Green 17; formula: Cr_2O_3

Hydrated chromium oxide green; Pigment Green 18; formula: $Cr_2O_3 \cdot 2H_2O$

Chromium oxide green pigments are chemically chromium(III) oxide; therefore, they should not be confused with chrome green, which contains hexavalent chromium. They are produced synthetically by reducing hexavalent dichromates in the presence of sulfur or carbon. They are also synthesized by thermal decomposition of ammonium dichromate. They are dull green pigments with an olive-green tint and varying undertones depending on particle size. Finer particles gives a yellowish hue, while larger ones give a bluish hue. They have very good hiding power and high UV absorption and light stability accompanied by excellent thermal stability, chemical resistance and solvent fastness. Because of their high hardness, they cause wearing of grinding media and paint grinding machines. One unique use of chromium oxide green is in camouflage coatings for military purposes, which is attributed to its infrared reflective properties.

Hydrated chromium oxide green is synthetically produced by calcination of dichromate with boric acid followed by hydrolysis of the calcined product. In contrast to chromium oxide green, hydrated chromium oxide green pigments are transparent and much brighter in color. They have very low particle size and very high oil absorption values. They also have good light fastness but poor heat stability and slightly less acid resistance than chromium oxide green. They are useful pigments for printing inks and metallic shades in automotive coatings where transparency is needed.

3.3.3.3 Iron blue

Pigment Blue 27; formula: $FeMFe(CN)_6 \cdot xH_2O$, M = K, Na or NH_4

Iron blue pigments are microcrystalline coordination compounds of Fe(II)Fe(III) cyano complexes. Conventionally, they were also known as Paris blue, Prussian blue, Berlin blue, Milori blue, Turnbull's blue, toning blue, and non-bronze blue. Iron blue pigments are some of the most economical inorganic blue pigments available on the market. They are produced by precipitation of complex iron(II) cyanides using iron(II) salts in aqueous solution to yield a white precipitate called Berlin white, which is subsequently oxidized to give the blue pigment.

Iron blue pigments are dark blue with high tinting strength and poor opacity, available in different undertones from reddish-blue to greenish-blue. They are the lightest of the common inorganic pigments with a density of 1.75 g/cm^3. Due to their extremely fine particle size, iron blue pigments are difficult to disperse and have a high oil absorption value. The light and weather fastness of iron blue pigment are acceptable in full color but considerably poor in tints. They are resistant to weak acids and oxidizing agents but sensitive to alkali and reducing environments. Upon exposure to alkali, they decompose to brown ferric hydroxide, which makes them unsuitable for water-based paints and lime colors. They are heat stable for a short time up to 170°C; extended heating beyond this temperature converts them to brown oxides. One of the important limitations of these pigments is that they are pyrophoric, which presents an explosion hazard. Iron blue pigments are combustible in powder form, ignition in air being possible above 140 °C.

Iron blue pigments are used to impart a pure black tone and high jetness in printing inks. They are used in paints with deep blue colors but seldom used in tints. Use of these pigments has been greatly reduced due to the availability of more durable copper phthalocyanine blue pigments.

3.3.3.4 Ultramarine blue

Pigment Blue 29; formula: approximately $Na_6Al_6Si_6O_{24}\cdot Na_2S_x$

This is the synthetic version of the first natural blue pigment used by humans, derived from grinding the mineral lapis lazuli. It is produced by calcining a mixture of china clay, feldspar, anhydrous sodium carbonate, sulfur, and reducing agents such as oil, pitch or coal at 800 °C. Chemically, the pigment is a sodium aluminum sulfosilicate with a zeolite-like crystal matrix. The warm blue color comes from incorporation of sodium and sulfur in the crystal matrix.

Depending upon manufacturing conditions, these pigments have a very clean and bright reddish-blue to greenish-blue hue. Generally, more sulfur shifts the hue to a redder blue. Particle size is also a factor controlling the optical properties of these pigments. Larger particles produce a deeper and redder blue with low tinting strength, while smaller particles give paler greenish-blues with higher tinting strength. With a very low refractive index (~1.5), these pigments are poor in hiding power; therefore, they are combined with white pigments to provide necessary hiding. Ultramarine blue has very good light fastness, heat stability, solvent fastness and alkali resistance, but is very sensitive to acids, which results in poor fastness in industrial environments. Non-toxicity is one of the important characteristics of these pigments for their use even in modern days. They are used in artist colors, toy enamels, decorative paints, transparent lacquers, flamboyant coatings and printing inks. Violet and pink ultramarines can also be manufactured by compositional variation. The violet and pink variants differ from the blue mainly in the oxidation state of the sulfur groups. Violet ultramarine can be prepared by heating a mid-range blue grade with ammonium chloride at ~240 °C in the presence of air. Treating the violet with hydrogen chloride gas at 140 °C gives the pink derivative.

3.3.3.5 Chromate pigments

This group of pigments includes chemically pure lead chromate or mixed-phase crystals of lead chromate with lead sulfate or lead molybdate. These pigments are available in a range of colors from a light greenish-yellow through orange and red. The color is dependent on the crystalline form of the pigment and the proportion of mixed crystals. Generally, they are not a physical mixture of crystals; rather, they are actually solutions of one solid in another. Green chromate pigment is also formed by combining yellow chromate pigments with iron blue pigment. Three crystal forms are possible:

- Orthorhombic – greenish-yellow (unstable)
- Monoclinic – reddish-yellow (stable)
- Tetragonal – orange (unstable)

Chrome yellow

Lead chromate; Pigment Yellow 34; formula: $xPbCrO_4 \cdot yPbSO_4$

Chrome yellow pigments are bright yellow with high chroma values. They are predominantly lead chromates, but some variants have a mixed crystal phase with lead sulfate. Important chrome yellow pigments are:

Primrose chrome: This is a pale, greenish-yellow pigment with a metastable orthorhombic crystal structure containing a solid solution of lead chromate and lead sulfate. The crystals are normally stabilized by additives. Due to a less-stable crystal form, they have poorer fastness properties compared to other monoclinic chrome pigments.

Lemon chrome: This is a greenish-yellow pigment (slightly redder than primrose) with a monoclinic crystal structure, which is more stable compared to other crystal forms. The undertone is dependent on the lead sulfate content – the more sulfate, the greener the shade.

Middle chrome: This is a reddish-yellow pigment precipitated as pure lead chromate in the monoclinic crystal structure.

Lead chromate pigments are heavy (density 5.5 to 6 g/cm^3) with very good opacity due to their higher refractive index (2.3 to 2.65). They are soft-textured pigments with low oil absorption values and have satisfactory light fastness as well as moderately good heat stability. They are insoluble in solvents and water, but soluble in acids and alkali. Lead chromate pigments are sensitive to sulfide fumes and therefore tend to discolor in industrial environments. These limitations can be improved by encapsulation of the pigment particles with inert metal oxides such as silica or alumina.

Despite these merits and their cost-effectiveness, toxicity concerns associated with the presence of both lead and chromium(IV) is one of the important demerits of these pigments, which cans restrict their usage.

Chrome orange

Pigment Orange 21; formula: $xPbCrO_4 \cdot yPbO$

Chemically, this is basic lead chromate with a tetragonal crystal structure. This pigment is available in orange to red shades. The proportion of lead hydroxide in the composition and to some extent the particle size affect the shade, but the crystal structure plays a more important role. This pigment is no longer of technical importance.

Molybdate red and molybdate orange:

Scarlet chrome; Pigment Red 104; formula: $xPbCrO_4 \cdot yPbMoO_4 \cdot zPbSO_4$

Chemically, these are mixed-phase crystals of lead chromate, lead sulfate and lead molybdate stabilized in a tetragonal crystal structure. The color ranges from orange to scarlet red. The shade is normally controlled by particle size. Smaller particles produce a more yellowish, stronger pigment with higher opacity, while larger particles have a bluer tone and less opacity. These soft-textured pigments have good opacity, low oil absorption value, good durability, solvent fastness and heat stability but moderate alkali resistance. They are also encapsulated with inert oxide layers to improve their properties. These pigments also are subject to legislative pressure or restricted use due to toxicity associated with lead and chromium(IV).

Chrome green and fast chrome green

Chrome green; Pigment Green 15

Fast chrome green; Pigment Green 48

Chrome green is a coprecipitate or dry blend of chrome yellow and iron blue, while fast chrome green is a combination of chrome yellow and phthalocyanine blue or phthalocyanine green. These pigments have the strengths and weaknesses of their constituent pigments. They have the additional limitation of differential wetting characteristics of the constituent pigments, which leads to the problem of flooding and floating in the coatings they are incorporated in. These pigments are also experiencing pressure to reduce their usage due to the environmental issues associated with chromium(VI) and lead, which has resulted in a decrease in their usage in coatings.

3.3.3.6 *Cadmium pigments*

Cadmium yellow; Pigment Yellow 37; formula: CdS

Cadmium yellow; Pigment Yelllow 35; formula: $CdS \cdot ZnS$

Cadmium orange; Pigment Orange 20; formula: $CdS \cdot CdSe$

Cadmium red, Pigment Red 108; formula: $CdS \cdot CdSe$

The term cadmium pigments refers to the pure sulfides and sulfoselenides as well as zinc-containing sulfides of cadmium. These pigments are offered in broad color ranges from yellows (pale primrose to golden yellow) to reds (light orange through deep orange to light red, crimson and maroon). Cadmium yellow is composed of cadmium sulfide or its mixtures with zinc sulfide, while cadmium red is cadmium sulfoselenide, a mixture of cadmium sulfide and cadmium selenide. Some cadmium pigments are also offered as lithopones, which contain barium sulfate coprecipitated with pigment.

Cadmium pigments have good hiding power, soft texture, and good light fastness and thermal stability. They are resistant to alkali, but are decomposed by acids. Despite these merits, their use is declining because they are relatively expensive, and in most applications, they are prohibited due to environmental problems associated with cadmium.

3.3.4 *High performance inorganic pigments*

In this chapter, we briefly discuss some classes of inorganic pigments relatively recently developed to meet increasing demands for performance and regulatory compliance not generally met by classical inorganic pigments. Another aspect of the development of high performance inorganic pigments is the need for developing more ecofriendly products.

3.3.4.1 *Bismuth vanadate pigments*

Pigment Yellow 184; formula: $BiVO_4$ or mixed crystals of $4BiVO_4 \cdot 3Bi_2MoO_6$

Bismuth vanadate pigments are inorganic yellow pigments that have gained significant commercial importance over the last two decades due to the decline in use of lead chromates and cadmium pigments because of environmental and human health concerns. They are available in bright greenish-yellow to reddish-yellow hues and the color resembles that of lead chromate and cadmium yellow. They have higher chroma than yellow iron oxide and nickel titanate yellow. These pigments possess high hiding power, high tinting strength, a low oil absorption value (27 g/100 g pigment) and a soft texture. Some of the other important characteristics of these pigments include excellent bleed resistance, chemical resistance, heat resistance and very good weather fastness. Early grades of these pigments exhibited reversible photochromism, but in modern grades with inorganic stabilizers, this problem has been resolved. Environmental benefits and excellent performance make these pigments useful for high quality applications such as automotive OEM and refinishes, coil coatings, industrial coatings, powder coatings and architectural coatings.

3.3.4.2 Cerium pigments

Cerium sulfide light orange; Pigment Orange 78; formula: $Ce_2S_3 \cdot LaS_3$

Cerium sulfide orange; Pigment Orange 75; formula: Ce_2S_3

Cerium sulfide red; Pigment Red 265; formula: Ce_2S_3

Cerium sulfide burgundy; Pigment Red 275; formula: Ce_2S_3

These pigments are among the truly high performance pigments that possess good thermal stability, light fastness, opacity and dispersibility while being environmentally benign and nontoxic. Cerium sesquisulfide exists in three allotropic forms: the α-Ce_2S_3 phase is exactly stoichiometric and stable up to 900 °C in non-oxidizing atmospheres, but is of very little commercial interest because of its brownish-black shade. The β-Ce_2S_3 phase is an oxysulfide with a minor amount of oxygen substituted for sulfide atoms in the crystal. It is burgundy in color and its exact color depends on the oxygen content. The lower the oxygen content, the lighter the tint. The γ-Ce_2S_3 phase is dark red in color and is isomorphous with $Ce_{3-X}S_{4,}$ where x is a cationic vacancy that accommodates other cations such as non-cerium lanthanide or alkaline earth cations. By varying the amount and type of the dopant cation in γ-cerium sulfide, a wide range of colors can be produced, from dark red to orange.

These are thermally stable, soft-texture pigments that exhibit high hiding power, excellent thermal stability and bleed resistance. They have excellent light fastness and weather fastness because they strongly absorb UV light without any photocatalytic effect.

Though initially developed for the plastic industry, various grades have also been developed for paints and coatings used as industrial coatings, automotive refinishes and OEM coatings, high-end architectural coatings, coil coatings and printing inks.

3.3.4.3 Complex inorganic color pigments

Complex inorganic color pigments represent the largest family of high performance pigments, and were formerly known as mixed-phase metal oxide pigments or ceramic pigments. Chemically, these pigments are synthetic crystalline metal oxides with structures resembling naturally occurring minerals. They are termed complex because they contain two or more different metals that give a wide range of colors to this class of pigments. Of these metal ions, transition metals are responsible for producing color, while other metal ions are colorless and balance the charge of the crystal lattice. Depending on the oxygen-to-metal ratio, complex inorganic color pigments acquire different crystal structures, such as rutile, anatase, spinel, hematite and corundum. Some important generic properties of these pigments include excellent solvent fastness, heat stability, light fastness, good chemical stability and good opacity. These pigments are very inert and are regarded as physiologically and environmentally harmless. They absorb UV light without decomposition or any photocatalytic effect, making them good UV absorbers.

The three main groups of commercial complex inorganic color pigments are titanates, which use a titanium dioxide base, aluminates, which use an aluminum oxide base, and chromites and ferrites, which have chromium and/or iron oxide bases. Some important complex inorganic color pigments are listed in Table 3.4.

Certain chromite type complex inorganic color pigments are suitable for use in camouflage paints and in low heat buildup paints due to their specific infrared reflectance properties. Due to their non-toxic

Table 3.4: **Complex inorganic color pigments**

Pigment (CI name)	Metal composition	Color	Crystal structure
Titanate pigments			
Pigment Yellow 53	Ni, Sb, Ti	Lemon yellow	Rutile
Pigment Brown 24	Cr, Sb, Ti	Yellow-orange	Rutile
Pigment Green 50	Co, Ti	Bluish-green	Spinel
Aluminate pigments			
Pigment Blue 28	Co, Al	Blue	Spinel
Pigment Blue 36	Co, Cr, Al	Blue-green to teal green	Spinel
Chromite and ferrite pigments			
Pigment Black 28	Cu, Cr	Black	Spinel
Pigment Black 29	Co, Fe	Black	Spinel
Pigment Black 30	Fe, Ni, Cr	Black	Spinel
Pigment Yellow 119	Zn, Fe	Tan	Spinel
Pigment Brown 33	Zn, Cr, Fe	Brown	Spinel
Pigment Green 26	Co, Cr	Yellowish-green	Spinel

nature, many are used as alternatives to chromate and lead-based pigments. Due to these performance properties, complex inorganic color pigments are used in high-end applications such as automotive coatings, coil coatings and some specialty industrial coatings.

3.3.5 Metallic pigments

Fine particles of malleable metals in elemental form are also used as pigments in coatings for aesthetic as well as protective purposes. They are generally platelet-shaped particles, but some are spherical.

3.3.5.1 Aluminum pigments

Pigment Metal 1; formula: Al

Aluminum pigments are the most often used metallic pigment in surface coatings. They are prepared from high purity aluminum metal by ball milling fine aluminum powder in the presence of a hydrocarbon solvent and grinding aids such as stearic acid and then formed into platelet-shaped particles. They are normally supplied as pastes in hydrocarbon solvents and occasionally in powder form.

There are two main types of aluminum pigments commercially available:

- Leafing type
- Non-leafing type

These types primarily differ in their optical effects due to different orientations in coating films. Their orientation is mainly controlled by adsorption of surface-active agents (typically stearic or oleic acids) on the surface of the platelets.

Due to the adsorbed layer of stearic acid, **leafing type** aluminum platelets float on the surface of the paint film and align themselves parallel to the surface during the paint's drying process. This gives the appearance of a mirror-like continuous film of metal. As the film dries, it forms overlapping layers of aluminum platelets that provide an excellent aesthetic effect and an effective barrier to moisture and corrosive species as well as reflection of heat and UV light.

On the other hand, **non-leafing type** aluminum pigments, which are generally stabilized by oleic acid, are wetted well by binder due to their non-polar surface, and hence they do not float on paint film, but rather get distributed more evenly in the film. Dried films appear as though tiny mirrors are embedded at different angular orientations, resulting in a sparkling visual effect. These pigments are used to produce a desirable aesthetic metallic effect in automotive coatings and printing inks. The orientation of leafing and non-leafing type aluminum pigments in paint film is illustrated in Figure 3.6.

These pigments are available in a wide range of particle sizes and aspect ratios to produce different aesthetic effects. Aluminum pig-

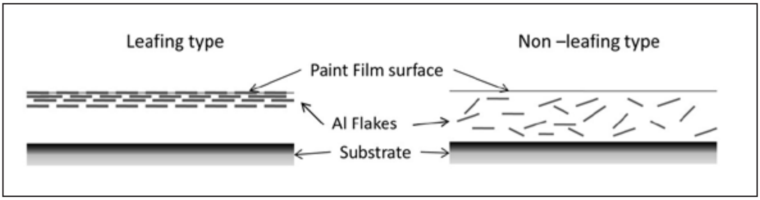


Figure 3.6: Schematic representation of orientation of leafing and non-leafing aluminum particles in paint film

ments are sensitive to acids and moisture, which results in deleafing, loss of sheen and hydrogen gas evolution.

3.3.5.2 Zinc pigments

Pigment Metal 6; formula: Zn

These are the second most important metallic pigments used in coating industry. They are supplied as fine gray powders with primarily spherical particles. Typical characteristics of these pigments include a very low oil absorption value, high density (~7 g/ml), and high UV absorption. They are mainly used in anticorrosive coatings in formulations of zinc-rich sacrificial primer, providing cathodic protection to steel substrates due to the higher electronegativity of Zn compared to Fe.

3.3.5.3 Bronze pigments

Pigment Metal 2; formula: $xCu \cdot yZn$

These pigments are platelet particles of copper-based alloys, frequently referred to as bronze pigments, even though brass (a copper-zinc alloy) is typically used. The composition ranges from pure copper flake (100 % Cu) to brass with 30 % zinc content. Depending upon composition, the color ranges from coppery red through reddish-gold to gold and greenish-gold. They are offered in different particle sizes in leafing and non-leafing versions. They have limited application in paints.

3.3.6 Anticorrosive pigments

Apart from optical properties such as color and hiding, certain pigments are used in protective coatings to increase their corrosion resistance properties. The anticorrosive pigments used in conjunction with suitable binder in protective coatings systems play a major role in protection of metals from corrosion.

Based on their mode of action to prevent corrosion, anticorrosive pigments may be classified in the following types:

Active pigments (inhibitive pigments): These are anticorrosive pigments with chemical and/or electrochemical action. When water penetrates the coating film, these pigments release soluble passivating ions that help in corrosion protection by promoting the formation of a protective layer at the metal surface, or by polarizing or inhibiting either or both of the two electrochemical reactions of the corrosion process, known as the cathodic and anodic reactions. Another mechanism of action of active pigments is neutralization of corrosive substances such as sulfates, acids and chlorides. Solubility and reactivity are the critical parameters of active pigments.

Barrier pigments: These act by reinforcing the paint film and reducing its permeability to corrosive agents. Generally, they are chemically inert pigments with a platelet-like or lamellar particle shape. This allows them to form a wall of flat particles stacked within a paint film, and therefore, water and electrolytes must take an extended indirect route through the paint film to the substrate, as described in Figure 3.7, thus increasing the barrier properties of the coating film.

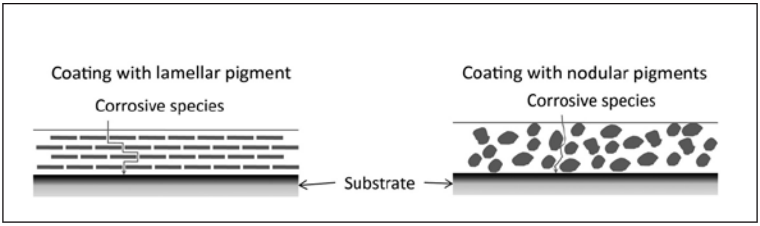


Figure 3.7: Demonstration of the barrier effect when using lamellar pigments

Sacrificial pigments: These are a special type of active pigments that act by cathodic protection when applied to ferrous substrates. They are metallic pigments that are higher in the electromotive series of metals than the metal substrate to be protected. Under corrosive conditions, sacrificial pigments, being more reactive than the substrate, act as the anode of an electrochemical corrosion cell, drawing attack on themselves and protecting the substrate metal. Therefore, this mechanism is also term cathodic protection. The coating must be formulated to yield good electrical contact between substrate metal and sacrificial pigment particles.

Some commercially important barrier pigments are micaceous iron oxide (Section 3.3.3.1) and aluminum flakes (Section 3.3.5.1). The only sacrificial pigment of commercial importance is zinc dust (Section 3.3.5.2).

3.3.6.1 Lead pigments

Red lead

Pigment Red 105; formula: Pb_3O_4

Red lead pigments are one of the oldest and most popular types of anticorrosive pigments, mainly used for primers for metals. They are indirect inhibitors and require reaction with a selected resin system. When used in linseed oil or other oleoresinous binders, they react with acidic groups in the resin and form lead soap, which has an inhibitory effect. They are no longer used in the coating industry due to the toxicity associated with lead.

Basic lead silicochromate

Basic lead silicochromate is composed of basic lead chromate and basic lead silicate firmly bound to a silica core. It was used in coatings for metal protection in structural steel, and finer grades were used in electrocoat paints. Because these pigments contain both lead and hexavalent chromium, due to toxicity and human health reasons, they have lost their commercial importance.

3.3.6.2 Chromate pigments

Chromate pigments have been used for long time as corrosion inhibitive pigments. The anticorrosive action of chromates is derived from the presence of a certain amount of water-soluble chromates. Soluble chromate ions are inhibitive, and chromate passivating ions are among the most efficient passivators known. They are effective both in cathodic and anodic areas. Anticorrosive properties of chromate pigments depend on their content of water-soluble chromate ions, their neutralizing and pH stabilizing effect, and their dispersibility, particle size and particle shape. Some important chromate pigments are as follows.

Zinc potassium chromate (zinc yellow)

This pigment contributes to anticorrosive properties through chromate ions as well as by a neutralizing effect through zinc ions.

Because of their yellow color, they are generally limited to use as primers. As they are versatile and highly efficient, zinc chromates are effective inhibitors even at relatively low pigment levels. As a result, they used to hold a major share of the anticorrosive pigment market for years, but due to toxicity associated with hexavalent chromium and related regulations, their commercial importance is declining.

Zinc tetroxychromate (basic zinc chromate)

This is mainly used to manufacture wash primers based on poly(vinyl butyral) resin, which is popularly used on aluminum or galvanized iron. Their main purpose is passivating the surface and improving adhesion of subsequent coatings. They are applied at very low solids to give a very thin film. Due to toxicity of hexavalent chromium, these primers are being replaced by new-generation thin films, typically sol-gel-derived organic-inorganic hybrid systems.

Strontium chromate

This yellow anticorrosive pigment is among the most expensive chromate-based pigments. It is mainly used to protect aluminum from corrosion. Epoxy primers containing strontium chromate are well-accepted in the aircraft industry. They are effective at low pigment levels and are also used in some coil coating applications.

3.3.6.3 Phosphate pigments

Phosphate pigments are widely explored as anticorrosive replacements for toxic lead and chromate-based pigments. Being white, they are more versatile than chromates. This large group of pigments may be classified in the following two subgroups.

Zinc-based phosphates: examples include zinc phosphate, aluminum zinc phosphate, zinc molybdenum phosphate, aluminum-zinc hydroxyphosphate, zinc hydroxymolybdate phosphate, basic zinc phosphate, zinc silicophosphate and zinc aluminum polyphosphate.

Zinc-free phosphates: examples include aluminum phosphate, dihydrogen aluminum triphosphate, strontium aluminum polyphosphate and calcium aluminum polyphosphate silicate.

Zinc phosphate

Due to their low solubility and reactivity, these pigments are widely used in different binder systems such as alkyd, epoxy and epoxy esters. Zinc phosphate provides corrosion protection through multiple effects, such as by phosphate ion donation, by creation of a protective film on the anode and by an inhibitive action when used with oleoresinous binders. Typically, coatings based on these pigments are reported to exhibit poor performance in salt spray or other accelerated tests, while they are found effective in real-world performance. Their typical loading levels are 10 to 30 % in maintenance coatings. Zinc phosphate pigments are often modified by an organic surface treatment to the pigment or by blending with other inorganic inhibitors.

Aluminum triphosphate

This is the second most important type of phosphate anticorrosive pigment. Passivation is normally accomplished through the ability of triphosphate ions to chelate iron ions. Additional passivation is through phosphate ions produced by de-polymerization of triphosphate ions. These pigments are also modified with silicates to control their solubility.

3.3.6.4 Phosphite pigments

These pigments contribute anticorrosive properties through anodic passivation through phosphite ions. The most important phosphite pigment used in the coating industry is zinc hydroxyl phosphite, with the theoretical formula $[2\ Zn(OH)_2 \cdot ZnHPO_3] \cdot xZnO$, where $x = 0$ to 17.

3.3.6.5 Borates

Alkalinity of borates is one of the important attributes of their inhibitive properties. They may also form calcium or barium soaps, depending on the pigment, with acidic functional groups in the resin. Borates act as anodic passivators, forming a protective film on metallic substrates.

Barium metaborate ($BaO \cdot B_2O_3 \cdot H_2O$)

Barium metaborate is the most important borate pigment. Its color is white. Due to high solubility, pure barium metaborate is not suitable as a pigment; therefore, to control its reactivity and solubility, it is frequently coated with silica.

Calcium borosilicate

Calcium borosilicate is a complex composite of calcium silicate available commercially in grades differing in borate content and oil absorption value. Its anticorrosive properties are derived from the alkalinity of the pigment as well as anodic and cathodic passivation.

3.3.6.6 Molybdate pigments

Molybdate-based pigments inhibit corrosion by passivating the anodic sites by formation of a protective layer on the substrate through molybdate ions. Pure molybdate-based pigments have limited commercial importance due to their high cost. Therefore, they are combined with phosphate pigments or are coated onto inorganic fillers like calcium carbonate and zinc oxide. Some important molybdate pigments include zinc molybdate, calcium zinc molybdate, zinc phosphate molybdate and calcium zinc phosphate molybdate.

3.3.7 Extenders

Extender pigments, also referred to as **fillers, supplemental pigments** or **functional filler**, are fine white powders of low refractive index (<1.7), which are substantially insoluble in the vehicle, reasonably chemically inert, and commonly but not always inexpensive. In addition to their traditional use for reducing cost (and thus why they are also called fillers, though this terminology is not appropriate with modern extenders), modern-day extenders are also used to modify and/or improve certain characteristics and the performance of coatings.

While the principal function of most extenders is to occupy volume in the coating film at lower cost, careful selection of type and quantity of fillers also modifies some of the key properties of coatings such as rheology (flow properties), antisettling properties, gloss control (sheen or matte finish) and mechanical strength of the coating (reinforcement) at relatively low cost. Due to their low refractive indices, closer to those of binders, they themselves do not contribute much to opacity of coatings, but they tend to enhance opacity by providing spacing between true pigments (which increases light scattering). In coating formulations, they are frequently used to control PVC, which in turn controls many paint properties such as opacity, gloss, porosity and permeability. They are extensively used in high-PVC formulations such as putties, filling compounds, primers, primer surfacers and undercoats.

Extenders are generally produced by grinding natural minerals, and in some cases, are synthetically produced by a precipitation process. In general, fillers are coarser than white pigments and available in grades varying from coarse (up to 250 µm) through fine (10 to 50 µm) to ultrafine (<5 µm). They also vary in their particle shapes and hence modify various properties of coatings that are influenced by shape of the dispersed particles, as discussed in Section 3.2.2.4. Fillers commonly used in the coating industry may be classified into the following groups: carbonates, silica, sulfates, and silicates.

3.3.7.1 Carbonates

Calcium carbonate ($CaCO_3$)

Calcium carbonate is one of the most widely used fillers in the coating industry. Natural calcium carbonate is obtained by grinding of chalk (whiting), limestone, calcite and marble. Except for chalk, the other forms are crystalline. Synthetic calcium carbonate, often referred as **precipitated calcium carbonate**, is often produced by passing carbon dioxide through purified slaked lime, and sometimes produced as the byproduct of other industrial processes. Due to the better control over the precipitation process, as compared to mechanical grinding of natural minerals, synthetic grades are available in much finer and more uniform particle sizes with higher purity.

The widespread use of calcium carbonate is attributed to its all-round properties – high brightness, low oil absorption, good flow, economic availability, good weather resistance and versatility of use with a variety of pigments. Calcium carbonate is an important extender used in water-based architectural paints, primers, anticorrosive paints, undercoats, putties and fillers. Very fine grade precipitated calcium carbonate is used to control flooding and floating of colored pigments in many formulations.

Dolomite ($CaCO_3 \cdot MgCO_3$)

During natural deposition of carbonates, when magnesium salts are present, a mixture of magnesium and calcium carbonates are precipitated, which is known as dolomite. Dolomite contains about 40 to 45 % $MgCO_3$ and 55 to 60 % $CaCO_3$. Its properties are close to those of natural calcium carbonate, except that it is slightly denser and less bright and less sensitive to acid than calcium carbonate.

3.3.7.2 Silica (SiO_2)

Both natural and synthetic silica are used as extenders in the coating industry. Naturally occurring silica exists as three types:

- Crystalline silica (the mineral quartz)
- Amorphous silica (cryptocrystalline; the mineral tripoli)
- Diatomaceous silica, also known as diatomaceous earth (kieselgur)

Most of the natural silica used in coating industry has a SiO_2 content higher than 95 %, and up to 99 % in some cases. Some of the important features of these relatively cheap extenders include high hardness, chemical inertness, durability and a low oil absorption value (the exception is diatomaceous silica). Crystalline and amorphous silica are used in compositions such as wood fillers for their abrasiveness; in road marking paints and floor coatings to improve abrasion resistance; in exterior flat house paints for sheen uniformity, burnishing resistance and durability; and in primers and undercoats to improve intercoat adhesion.

Diatomaceous silica is a very lightweight, fluffy hydrous silica. Diatomaceous silica, found in natural deposits, consists of the skeletons of various species of diatoms, which are minute marine plants that died millions of years ago. Their structure is very open and they present a large ratio of surface area to weight (and thus have a high oil absorption value). They are used to increase the consistency of coatings and as low-cost flatting agents.

Synthetic silica types are used in coatings less as filler than as thixotropic, antisettling and matting additives. The different types include pyrogenic silica, precipitated silica and silica aerogels and hydrogels. They consist of coagulated amorphous spherical particles of very fine particle size (5 to 50 nm). Precipitated synthetic silica is coarser than most other grades and is predominantly used as a flatting agent.

3.3.7.3 Sulfates

Among the large group of sulfates, barium sulfate ($BaSO_4$) is the predominant filler in coatings. Two types of barium sulfate are used in coatings: natural (barite) and synthetic (blanc fixe). Barite, a naturally occurring crystalline mineral, is the source for natural barium sulfate extender, which is often contaminated with color-producing impurities that are chemically bleached to get brighter grades. Blanc fixe (precipitated $BaSO_4$) is a very fine (0.5 to 4 μm) heavy powder comprised of $BaSO_4$ crystals having a rhombic structure. Due to high chemical purity, it is brighter than barite.

High density, high chemical inertness, low oil absorption value, and stability to light and heat are some of the most important features of this extender. With the highest refractive index (1.64) of the fillers, it exhibits a weak pigmentary property that is synergistic to opacifying pigments. Due to its low oil absorption value, high loading compositions are possible without affecting consistency; therefore, it is used in fillers and stoppers. It is used in industrial primers that require good filling power and fineness of particle size along with good sanding properties and hold-out. High density of these extenders is an important consideration, as they are prone to quick settling. For coatings requiring high gloss, blanc fixe with a very low particle size and narrow distribution (30 to 60 nm) is frequently recommended, though it is more expensive than general grades.

3.3.7.4 Silicates

Among the different chemical classes, this group of extenders has the most variety, with a wide range of properties and crystal forms. Following silicate extenders are important for the coating industry:

Magnesium silicate (talc, asbestine, French chalk); ($3MgO\cdot 4SiO_2\cdot H_2O$)

This category covers a number of minerals with varying chemical composition based on magnesia and silica. They frequently have calcium and aluminum as impurities. Depending upon source, they are either plate-like or acicular particles. Asbestine, an exception, is fibrous. Some of the beneficial properties of talc for use in coatings include good brightness, chemical inertness, good suspension properties, ability to provide mechanical reinforcement to paint films, brushability and good enamel hold-out. Talc is a hydrophobic and soft mineral that promotes sandability of fillers and primers as well as providing good intercoat adhesion. Talc is also used to impart a flatting effect and is suitable for semi-gloss and satin industrial enamels. One of the limitations of talc is that when used in exterior conditions, it chalks readily.

Aluminum silicate (clay, kaolin) ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

Kaolin or clay is a natural fine-grained, well-crystallized hydrous aluminum silicate mineral. Depending upon impurities, it is available in very white to grayish-white grades. The primary particles of clay are of lamellar shape, which contributes to good brushability and reinforcement of films. Due to its high oil absorption value and particle shape, it is also used as a cheap flatting agent. Clay imparts thixotropy to paints and improves suspension of other pigments. It is frequently useful as an extender along with white pigments. It is hydrophilic and widely used in water-based latex paints, but excessive usage can decrease the scrub resistance of films. Poor weathering resistance and poor flow properties are some of the important limitations of its use as an extender. Some of the other uses of clay as an extender include in primers and fillers. Finer grade clay is used in electrophoretic primers.

Calcination of clay at high temperature (1000 °C) causes an irreversible loss of chemically combined hydroxyl groups from the clay crystal structure, causing an interparticle sintering of kaolin platelets and giving rise to irregular-shaped particles with a microporous structure. The major use of calcined clay is as an opacifying extender in interior matte latex paints. High hiding power is obtained by the inability of paint binders to completely fill the pores of the microporous particles, leaving air in the pores, which contributes to light scattering.

Mica (aluminum potassium silicate – $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$)

Table 3.5: Important properties of extenders

Extender	Oil absorption value [g/100 g]	Particle shape	Density [g/ml]	Refractive index
Natural calcium carbonate	14–25	Nodular	2.7	1.5–1.66
Dolomite	15–25	Nodular	2.75–2.9	1.62
Precipitated calcium carbonate	28–60	Acicular, nodular	2.7	1.59
Crystalline silica	15–30	Nodular	2.5–2.7	1.49–1.55
Amorphous silica	25–30	Nodular	2.5–2.65	1.54–1.55
Diatomaceous silica	120–180	Nodular, rods, discs	2.0–2.3	1.42–1.48
Pyrogenic silica	~280	Spherical	2.2	1.45
Talc	30–50	Acicular, lamellar	2.7–2.8	1.54–1.59
Kaolin, clay	32–55	Lamellar	2.3–2.6	1.56
Mica	56–74	Lamellar	2.8	1.58–1.61
Barite	9–15	Nodular	4–4.5	1.64
Blanc fixe	14–20	Nodular	4.3–4.5	1.64

Mica is an orthosilicate of aluminum and potassium obtained from the natural mineral **muscovite**. The lamellar-shaped particles of mica have a grayish pearlescent appearance. Mica is a chemically inert extender with good weathering resistance and electrical insulating properties. In coating films, the platelet-shaped particles tend to orient parallel to the substrate and increase the barrier properties of films. They also provide mechanical reinforcement to polymeric matrices, leading to tougher films. Incorporation of mica also increases washability while helping in reducing chalking, checking and cracking of coatings. It is used in anticorrosive coatings, primers, fillers and exterior latex paints. Some of the limitations of mica include poor color, poor dispersibility and high price.

3.3.8 Special effect pigments

This is an interesting class of pigments that are capable of producing special color or visual effects when used in coatings. Special effect pigments are of two types: pearl luster and **interference pigments**. They are based on natural or synthetic materials that exhibit outstanding qualities of luster, brilliance, and iridescent color effects. Interference and pearlescent pigments cause color shifts that depend on the angle of view. The effect mimics pearls or fish scales, which consist of alternating transparent optically thin layers of $CaCO_3$ and protein that have different refractive indices. These natural pearlescent pigments have been used for centuries in the form of natural pearl essence, which is isolated as a silky lustrous suspension from fish scales. They are very expensive because of the extensive extraction process and very low yield. They are generally used exclusively for expensive cosmetic applications.

Synthetic special effect pigments are either single-crystal platelets (substrate-free pigments) with high refractive index or platelets of low refractive index coated with an optically thin layer of material with a high refractive index (called **coated substrate pigments**). The optical effect produced by these pigments is attributed to their platelet shape as well as the reflection and refraction of light at the pigment-binder interface and, in the case of the latter type, at the phase boundaries within the particle itself.

Substrate-free effect pigments include basic lead carbonate ($Pb(OH)_2 \cdot 2PbCO_3$), bismuth oxychloride (BiOCl), micaceous iron oxide (α-Fe_2O_3) and titanium dioxide flakes (TiO_2). All of them have a settling tendency due to their high density. Basic lead carbonate flakes are not used these days due to their low chemical stability and toxicity. Bismuth oxichoride has limited light stability that can be improved by cerium doping. Its dull, dark brown color is the limitation for micaceous iron oxide, but the color can be shifted to a more attractive reddish-brown by incorporating certain dopants. Titanium oxide flakes are very brittle and therefore not suitable for applications where high mechanical stresses are exerted.

Coated substrate pigments are the dominant class of special-effect pigments in recent commercial applications. Based on the type of substrate being coated, this class of special-effect pigments can be categorized into three groups – mica-based pigments, silica flake pigments and alumina flake pigments. A schematic representation of the interference effect of such pigments is illustrated in Figure 3.8.

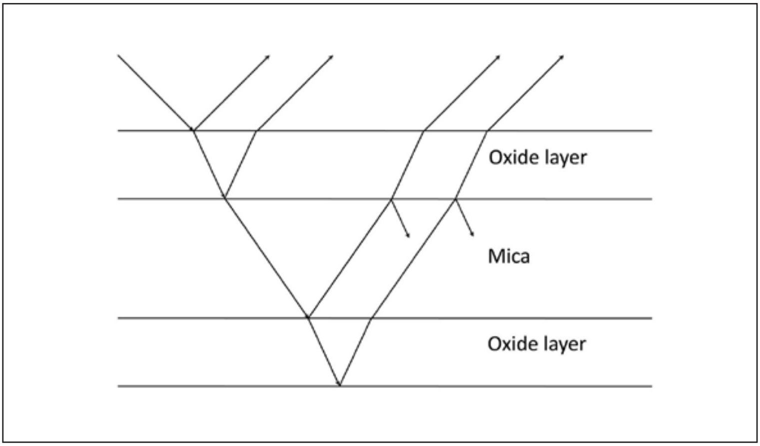


Figure 3.8: Schematic presentation of interference by pearlescent pigments

Among these groups, mica-based effect pigments are the largest. Mica acts as a support for deposition of optically thin layers of coatings with a high refractive index, such as titanium dioxide, iron oxide or multiple layers of these. Thus, the pigment particle behaves like two titanium dioxide platelets held together by mica. The interference color produced depends on the thickness of the oxide layer on the substrate. Also, when mica is coated with colored oxides such as Fe_2O_3, more intensely colored pigments are obtained.

Mica, being a natural product, does not have absolutely uniform surfaces on its platelets, which limits the amount of luster produced by these pigments. In order to produce stronger interference, silica flake pigments have been developed. The main advantages offered by synthetic silica flakes over the use of natural mica include uniform controlled thickness, no impurities and lower refractive index (1.46) than mica (1.58). High quality, thin hexagonal monocrystalline Al_2O_3 flakes are also used as a substrate for interference pigments.

In contrast to normal pigments, where colors are subtractive, interference pigments lead to additive color mixing. Also, particle size plays a vital role in the effect produced – smaller particles give a satin effect, while coarser ones produce a sparkle effect. In actual coating formulations, transparent pigments are used with interference pigments, which produces a variety of two-color effects.

The latest category of special-effect pigments is **diffractive pigments**, in which interference is produced by diffraction technology. These pigments are produced by vacuum deposition on specially patterned surfaces.

3.4 Organic pigments

Organic pigments are a vast class offering a large number of pigments with varying hues and chroma. Organic pigments gained importance in the coating industry due to restrictions on some inorganic pigments containing heavy metals as well as due to their high color purity and tinctorial strength compared to most inorganic pigments. Some important pigmentary properties of organic and inorganic pigments are compared in Table 3.6.

Organic pigments are synthesized from different petrochemical intermediates; therefore, thousands of molecules are possible due to wide latitude in selection of petrochemicals, but only a few hundred are commercially produced that have balanced price and performance. Discussing all the pigments individually is outside the scope of this book; therefore, selected important organic pigment families are briefly discussed here.

Table 3.6: Important properties of extenders

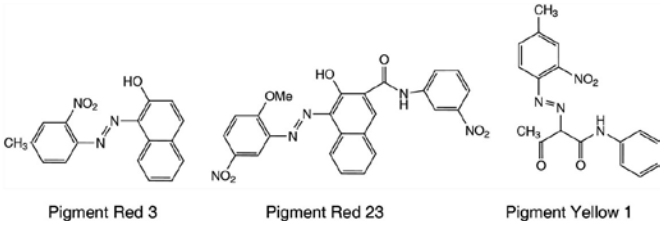
Property	Organic pigment	Inorganic pigment
Color	Bright	Dull (mostly)
Light and weather fastness	Varies	Usually excellent
Tinting strength	High	Varies
Opacity	Usually lower	Usually higher
Solvent fastness	Extremely varies	Excellent
Particle size	Usually smaller	Usually larger than organic
Ease of dispersion	Varies	Much easier than organic
Thermal stability	Varies	Usually higher than organic
Surface type	Hydrophobic	Generally hydrophilic

3.4.1 Azo pigments

Azo pigments are the most common organic pigments and cover a large volume of the commercially available organic pigments. They are compounds having an azo group (–N=N–) in their structure as the chromophore (color producing group). Azo pigments are synthesized by the standard sequence of diazonium salt formation from an aromatic amine and subsequent reaction with a wide choice of coupling components that allow the possibility of a wide range of products in this class. Normally they produce a range of yellow, red and orange pigments with a few browns and violets. Azo pigments are further divided into the following groups.

3.4.1.1 Monoazo pigments

Monoazo pigments are obtained by coupling a diazonium salt of a substituted aromatic amine with a suitable coupling agent. Acetoacetic arylides are used as coupling agents to yield a range of yellow pigments generically known as arylamide yellow, while b-naphthol is used for orange and red pigments generically known as b-naphthol red. Another important group of pigments, an extension of the b-naphthol red pigments, use arylides of 2-hydroxy-3-naphthoic acid as coupling agents and are known as naphthol AS pigments. Most monoazo pigments have poor heat stability along with poor solvent and migration resistance that limit their applications. They are used extensively in alkyd-based architectural coatings, in emulsion paints and in printing inks. Typical examples are Pigment Yellow 1, 3, 73, 74 and 98, Pigment Orange 5, Pigment Red 3, 4 and 6 and Pigment Red 2, 12, 23 and 112. Some examples are shown in Figure 3.9.



Pigment Red 3 Pigment Red 23 Pigment Yellow 1

Figure 3.9. Examples of monoazo pigments

3.4.1.2 *Diazo pigments*

This group of pigments has improved fastness to heat, solvents and light compared to monoazo pigments due to molecular enlargement. They are produced by the coupling of substituted aromatic diamines as diazonium salts with acetoacetic arylides or pyrazolones as coupling components to give diarylide yellows and pyrazolone oranges, respectively. In another approach, diazotized aromatic amines are coupled with bisacetoacetic arylides. A range of light fastness properties are obtained, from poor to good, depending upon substitution on the aromatic diamine and coupling compounds. Some important diarylide yellow pigments include Pigment Yellow 12, 13, 14, 15, 55, 63, 83, 106, 126 and 174 while important pyrazolone oranges and reds are Pigment Orange 13 and 34 and Pigment Red 38. Examples are shown in Figure 3.10.

3.4.1.3 *Salt-type azo pigments*

In Europe, salt-type azo pigments are known as **toners**, while in the rest of the world, they are known as **lakes**. These pigments are formed by precipitating a monazo compound (dyestuff) that contains sulfonic and/or carboxylic acid groups with suitable metal ions such as sodium, calcium, barium or strontium. The acid groups may be carried by aromatic amines or coupling agents. Some important coupling components are 2-naphthol, 2-hydroxy-3-naphthoic acid and

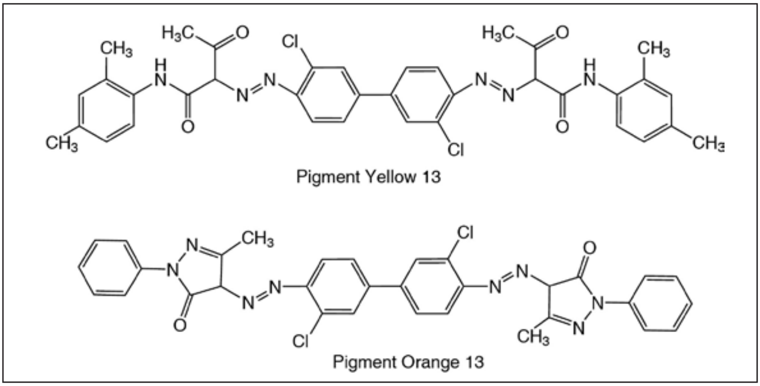


Figure 3.10: Examples of diazo pigments

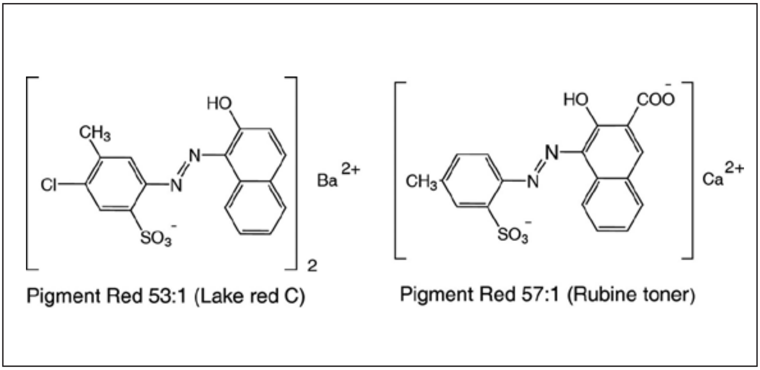


Figure 3.11: Examples of salt-type azo pigments

2-hydroxy-3-naphthoic acid. The shade of the pigment depends on chemical composition as well as the salt used for precipitation. These pigments have improved solvent and migration resistance, but their salt structure makes them vulnerable in terms of chemical resistance. They are economical pigments with high tinting strength and therefore are widely used in printing inks. Some important examples of such pigments (Figure 3.11) include Pigment Yellow 61 and 62 and Pigment Red 49, 48, 52, 53 and 57.

3.4.1.4 Azo complex pigments

This small yet unique class of azo pigments offers azo coordination complexes with chelating metals such as nickel, cobalt or iron(II). They have good light, weather and solvent fastness properties. They offer greenish to reddish-yellow and yellowish-orange colors. They are used in industrial and automotive paints as well as printing inks. Some common examples are Pigment Green 10 (Figure 3.12), Pigment Yellow 150 and Pigment Orange 59.

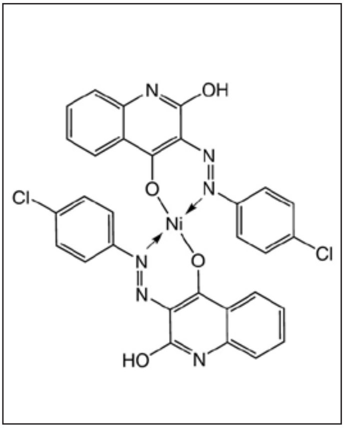


Figure 3.12: Pigment Green 10 (nickel azo yellow)

3.4.1.5 *Azo condensation pigments*

Azo condensation pigments are among the high performance organic pigments used in the industry. These pigments can be visualized as the condensation of two carboxylic monoazo components with one aromatic diamine through formation of an amide (–CONH–) bridge. Their high MW as well as the presence of amide groups leads to improved solvent fastness, migration resistance, good heat stability and light fastness properties. They have reasonably good tinting strength and excellent chemical stability but are relatively expensive. They are used in high grade industrial coatings and specialty printing inks. The products cover the range of colors from yellow through orange and bluish-red to brown. Some common pigments in this class are Pigment Yellow 93, 94, 128 and 166 and Pigment Red 144 and 166. The example of Pigment Yellow 128 is shown in Figure 3.13.

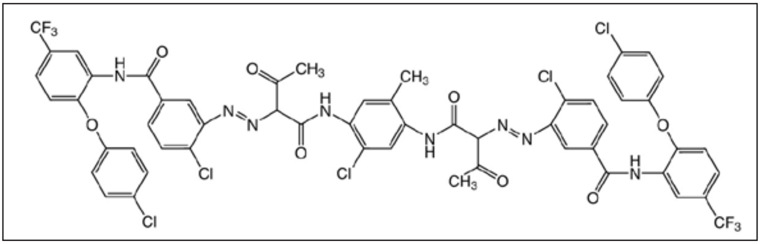


Figure 3.13: Pigment Yellow 128

3.4.1.6 *Isoindolinone and isoindoline pigments*

Although these heterocyclic azomethine-based high performance organic pigments have comparatively good light and weather fastness and solvent and migration resistance, very few of them are commercially available as pigments. They produce greenish to reddish-yellow hues and are used in high grade coatings and inks. Some widely known examples are Pigment Yellow 10 (Figure 3.14), 110 and 139.

3.4.2 *Polycyclic pigments (non-azo pigments)*

These are pigments with condensed aromatic or heterocyclic ring systems. Chemically, there are several subclasses in the category.

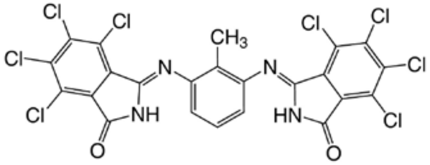


Figure 3.14: Pigment Yellow 109

Most of them have good light and weather fastness combined with good solvent and migration resistance.

3.4.2.1 *Phthalocyanine pigments*

After azo pigments, the second most important class of pigments in terms of usage is copper phthalocyanine and its derivatives because of their excellent overall performance properties combined with good economy. They are ideal pigments, having high color strength, excellent thermal stability, good light fastness and excellent solvent fastness. They cover the blue and green range of the color spectrum.

Phthalocyanine blue pigments are polymorphic, existing in at least five crystal forms, but commercially important crystal forms include the reddish-blue α-form, the greenish-blue β-form, and the occasionally used intense reddish-blue ε-modification. Phthalocyanine green pigments with a bluish to yellowish undertone are produced by introduction of chlorine or bromine atoms into the phthalocyanine molecule. Crude phthalocyanine blue pigment is normally in the β-form, with coarse particles. To produce commercially useful fine particles of different crystal modifications, different finishing technologies are used. The unstabilized α-form reverts to the β-modification under action of heat or aromatic solvents; therefore, it is modified by partial chlorination or certain additives to form stabilized grades. Due to very small particle size, phthalocyanine pigments have a tendency to flocculate, so flocculation-stable grades are prepared by special surface treatment. Different types of phthalocyanine pigments are Pigment Blue 15 (unstabilized α), Pigment

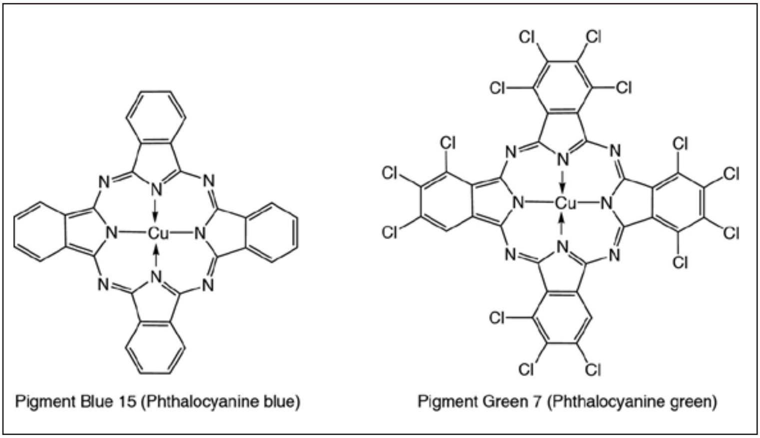


Figure 3.15: Phthalocyanine pigments

Blue 15:1 (stabilized α), Pigment Blue 15:2 (non-flocculating stabilized α), Pigment Blue 15:3 (β), Pigment Blue 15:4 (non-flocculating β), Pigment Blue 15:6 (ε) and Pigment Green 7 and 36. Examples are shown in Figure 3.15.

3.4.2.2 Quinacridone pigments

These are high performance organic red and violet pigments. Despite their high price, due to their outstanding light and weather fastness and solvent and migration resistance, they are used in high grade industrial coatings, automotive finishes, and special printing inks. Pigment Violet 19 (Figure 3.16) is the basic unsubstituted quinacridone molecule, which can exist in five crystal forms, but only two crystal forms are commercially important, β and γ, which give violets and reds respectively. Depending on type of substitution and crystal form, different quinacridone pigments with orange, maroon, scarlet, magenta and violet colors are available on the market. Some examples are Pigment Red 122, 192, 202, 207 and 209.

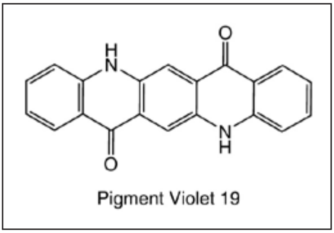


Figure 3.16: Pigment Violet 19

3.4.2.3 *Anthraquinone pigments*

Anthraquinone pigments are members of the pigment family originating from vat dyes, which are structurally or synthetically derived from the anthraquinone molecule. The basic anthraquinone molecule is normally too small to give good pigmentary properties, and therefore, molecular enlargement is done via different reactions to yield commercial grade products with good pigmentary properties. They are divided into four groups – anthrapyrimidine pigments, flavanthrone pigments, pyranthrone pigments and anthanthrone pigments. They offer a wide range of colors including red, orange, yellow, blue and violet. Even though these pigments are expensive due to their multistage synthesis, they are used in industrial coatings, automotive finishes and specialty coatings due to their excellent light and weather fastness, chemical resistance, solvent fastness and migration resistance. Some examples of this group of pigments are Pigment Red 168, 177 and 216, Pigment Orange 51, Pigment Yellow 24 and 108, Pigment Blue 60 and Pigment Violet 31. Figure 3.17 shows the structure of Pigment Red 177.

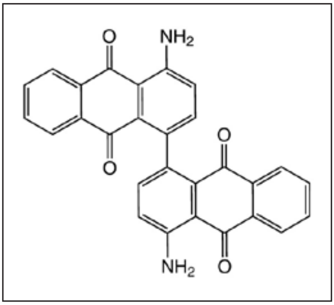
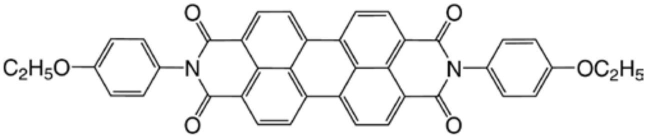


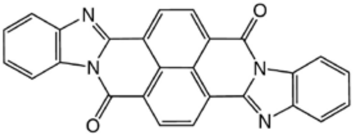
Figure 3.17: Pigment Red 177

3.4.2.4 *Perylene and perinone pigments*

Perylene and perinone pigments (Figure 3.18) are a class of high performance organic pigments. Perylene pigments are diimides of perylenetetracarboxylic acid while perinone pigments are produced by condensation of naphthalenetetracarboxylic acid with aromatic diamines. They originated from vat dyes. Perylene pigments exist in a wide range of hues, providing red, bordeaux, violet, brown and black shades, while perinone pigments exhibit color in the range from orange to bordeaux. These pigments exhibit excellent light fastness, exterior durability and high heat resistance because of their chemical structure. Therefore, they are used in high quality industrial paints, automotive coatings and powder coatings. Some



Pigment Red 123 (Pyrelene pigment)



Pigment Orange 43 (Perinone pigment)

Figure 3.18: Examples of perylene and perinone pigments

examples of commercially available perylene pigments are Pigment Red 123, 149, 178, 179 and 190, Pigment Violet 29 and Pigment Black 31, while examples of perinone pigments are Pigment Orange 43 and Pigment Red 194.

3.4.2.5 Thioindigo pigments

These pigments also originated from the vat dye route. They have very little practical significance in the coating industry. Only chlorinated and methylated thioindigo derivatives have any noticeable commercial presence as pigments. They provide a range of colors from red-violet and maroon to brown shades based on the type and position of the substituents. They offer good light and solvent fastness with moderate heat stability (200 °C). Some important examples are Pigment Red 88 (Figure 3.19) and 181.

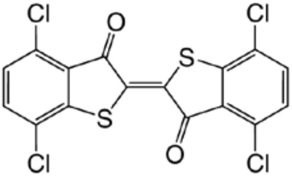


Figure 3.19: Pigment Red 88

3.4.2.6 *Dioxazine pigments*

Dioxazine pigments are a small but important class of high performance organic pigments derived from triphenodioxazine. They are extremely light fast and weather fast pigments with good to excellent solvent and migration resistance. They are used both in coatings and printing inks. They offer a unique, clean violet hue that cannot be achieved by blending other pigments. Apart from producing violet shades, they are used to tint white paint to clean up the slight yellowish tone of rutile to produce brilliant white paints. Similarly, they are also used in minute quantities to modify the undertone of phthalocyanine blue and carbon black. Important examples are Pigment Violet 23 (Figure 3.21) and 37.

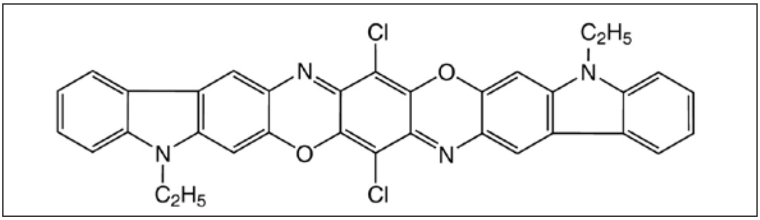


Figure 3.20: Pigment Violet 23

3.4.2.7 *Diketopyrrolopyrrole pigments*

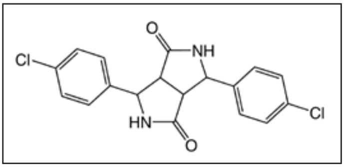


Figure 3.21: Pigment Red 254

This is relatively newly developed group of high performance organic pigments. They offer a range of medium orange to bluish-red hues. These pigments gained importance in high grade industrial coatings, especially automotive finishes, because of their bright shade, good opacity, excellent heat stability and resistance to solvents along with excellent light and weather fastness properties. Important examples include Pigment Red 254 (Figure 3.21), 255 and 264 and Pigment Orange 73 and 81.

4 Solvents

4.1 Introduction

According to DIN EN 971-1, solvents are defined as liquids comprising one or more components that are volatile under the specified drying conditions and capable of dissolving binders purely physically without any chemical reactions.

Most resins used as binders for solventbased or high-solid coatings are solids or viscous liquids that need to be diluted to lower viscosity for easy processing into paint, ease of applicability of the paint and better film formation thereafter due to evaporation. Thus, even though solvents are not an integral part of dry coating films, they are important components of paints and coatings.

Apart from their primary role of providing lower viscosity for proper application, solvents also play a significant role in paint processing as well as in controlling final film properties. Solvents reduce the viscosity and, in most cases, the surface tension of the binder, which assists the wetting process at the pigment dispersion stage of paint manufacturing. Once the films are applied, solvents also assist in better flow and leveling, which improves appearance and gloss of coatings. In some reactive systems, solvents such as alcohols and ketones may influence the kinetics of certain crosslinking reactions and pot life (in two-component systems). In metallic paints, use of solvent combinations plays a vital role in orientation of the metal flakes, which controls the final appearance of films.

In contrast to the solvents described above, a **reactive solvent** is defined as a solvent that undergoes a chemical reaction with a binder during film formation and becomes an integral part of the dry

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film. These types of solvents are important due to their reduced or no emissions, making them useful in low-VOC coatings.

Solvents are frequently classified based on their relative solvency. **Prime solvents** (also known as **true solvents** or **active solvents**) are solvents capable, by themselves, of dissolving a resin. For example, aliphatic hydrocarbons are true solvents for long oil alkyds and esters are true solvents for nitrocellulose. **Latent solvents** are not true solvents for a resin, but they enhance the solvency of a true solvent. For example, alcohols are latent solvents for nitrocellulose. **Diluents** or **extenders** for solvents are volatile liquids that cannot dissolve a resin by themselves but are frequently used in combination with true solvents to balance the overall evaporation rate of a coating and/or reduce the overall cost of the coating. For example, aromatic hydrocarbons are diluents for nitrocellulose lacquers.

Thinner is the term generally used in the coating industry to describe an optimized combination of the abovementioned types of solvents, which is added to coatings just before application to reduce the viscosity of the coating in order to assist better application.

In general, solvents to be used for coatings should have the following desirable properties:

- Dissolve the binder completely
- Clear and colorless appearance
- Volatile enough to leave the film completely without leaving residue
- Inert to other ingredients of the paint
- Minimum odor or pleasant odor
- Consistent physical properties as per specifications
- Low toxicity
- Low cost

4.2 Theory of solvency

In the early phase of coating technology, due to the small number of binders, empirical selection of solvents had been adopted with the general rule of like dissolves like. But after around 1930, when a more diverse variety of synthetic binders was introduced, selection of solvents based on this rule became more difficult. As a result, more scientific approaches were developed to understand resin dissolution, resin processing and selection of solvents for optimum performance.

A dry resin is a polymeric mass of macromolecular chains entangled and held together by secondary intermolecular attraction forces between adjacent polymeric chains. The dissolution of a polymer or a resin in a solvent is governed by the magnitude of the intermolecular forces that exist between the molecules of the polymer and the molecules of the solvent. If polymer-polymer interactions are stronger than polymer-solvent interactions, no dissolution will occur. However, if polymer-solvent interactions are stronger, solvent molecules will tend to displace polymer chains away from each other. As the process continues, additional solvent molecules penetrate between the polymer chains, forcing them further apart. As a result, the solvated polymer chains get disentangled into individual chains. This process is referred to as dissolution of polymer in a solvent. The forces of interaction operating between the polymer chains are of the following types.

London dispersion forces, which arise from mutual induction of atomic dipoles due to the electromagnetic field between the nucleus and electrons of the atom, leading to attraction between molecules. In the case of non-polar molecules, these are the only intermolecular forces that exist.

Dipole-dipole forces, which are the forces of attraction between molecules with a finite, permanent overall dipole moment.

Dipole-induced dipole forces, which arise from the interaction between a permanent dipole and another dipole induced by its proximity to the permanent dipole.

Hydrogen bonding forces, which arise by attraction between an active hydrogen atom and electron deficient sites. Such forces can be intermolecular or intramolecular. For example, molecules having hydroxyl or amino groups act as hydrogen donors and functional groups such as esters and ketones act as hydrogen acceptors.

4.2.1 Solubility parameters

As described in the previous chapter, intermolecular interactions between solvent molecules are very important in determining the strength of the solvent in dissolving a polymer. The concept of a solubility parameter was introduced by Hildebrand for its application to mixtures of non-polar liquids. The concept was derived from considerations of cohesive energy density, which is the ratio of the energy required to vaporize 1 cm^3 of liquid to its molar volume. The square root of the cohesive energy density is designated the solubility parameter δ.

Equation 4.1 $$\delta=\sqrt{(\Delta E_v/V_m)}$$

where ΔE_v = heat of vaporization, V_m = molar volume of solvent

Solvents with similar values of δ have comparable intermolecular forces and hence they are expected to be miscible in all proportions. On the other hand, if δ values for two solvents are significantly different, it is unlikely that they will be miscible.

The above concept was restricted to non-polar solvents and hence was of little use in modern paint technology, where polymers and solvents with a wide range of polarity from non-polar to highly polar are used. Subsequently, Burrell recognized the potential of the solubility parameter concept and carried out work on solubility based on the swelling of polymers, which resulted in introduction of another parameter based on degree of hydrogen bonding by a solvent. He proposed a system in which solvents were classified, based on their hydrogen bonding capacity, into three categories: poorly, moderately, and strongly hydrogen bonding types. The resulting ranges of solubility parameters in these three groups of solvents permitted fairly good predictions of solubility based on which parameter can predict whether a solvent mixture will dissolve a resin. Plotting the solubility parameter against hydrogen bonding indices gives a solubility map, in which solvents are represented as single spots while polymers are contours.

The above theory proposed by Burrell was also moderately successful in prediction of solubility characteristics of resins in solvent mixtures. Therefore, one of the most widely used systems, especially in the paint industry, is the three dimensional Hansen solubility parameter system. Hansen divided the cohesive energy density into three components, related to dispersion forces, dipole forces and hydrogen bonding forces. The Hildebrand solubility parameter δ is related to these components by the following Equation 4.2.

Equation 4.2:

$$\delta^2 = \delta_d^{\,2} + \delta_p^{\,2} + \delta_h^{\,2}$$

Where δ_d, δ_p and δ_h, are the solubility parameters corresponding to the non-polar (dispersion) contribution, polar contribution and hydrogen bond contribution respectively. Values of the Hansen solubility parameter δ for some common solvents as well as their δ_d, δ_p and δ_h values are shown in Table 4.1. In the Hansen system, solvents are represented as a single spot in the three dimensional model, while polymers are represented by a volume. Solvents that have their spot within this volume dissolve the polymer, while solvents lying outside the volume will not. For mixed solvents, a weighted average of the three partial solubility parameters can be calculated.

Table 4.1: Three dimensional solubility parameters of some common solvents (in units of MPa$^{1/2}$)

Solvent	δ **(total)**	δ **d (non-polar)**	δ **p (polar)**	δ **h (hydrogen bonding)**
n-Dodecane	16.0	16.0	0.0	0.0
Toluene	18.2	18.0	1.4	2.0
o-Xylene	18.4	17.6	1.0	3.1
n-Butanol	23.1	15.9	5.7	15.7
Isopropyl alcohol	23.5	15.8	6.1	16.4
Methyl ethyl ketone	18.9	15.9	9.0	5.1
Methyl isobutyl ketone	17.5	15.3	6.1	4.1
n-Butyl acetate	17.4	15.8	3.7	6.3
Ethyl acetate	18.6	15.8	5.3	7.2
2-Butoxyethanol	20.8	15.9	4.5	12.7
1-Methyl-2-pyrrolidone	23.0	18.0	12.3	7.2

4.3 *Important characteristics of solvents*

Some important physical and chemical characteristics of solvents from the standpoint of their use in paints and coatings are discussed below.

4.3.1 *Solvency*

Dissolving a resin to yield a solution with viscosity suitable for application is one of the primary roles of solvents in paints and coatings. Therefore, solvency is the foremost performance requirement of a solvent. The solvency or solvent power is the efficiency with which a solvent can reduce the intermolecular forces between polymer molecules and separate them to solvate them in the solvent. One of the methods of presenting the solvency of a solvent (or solvent mixture) is by a viscosity profile of a solution of resins. The data are normally represented by a plot of viscosity of resin solutions in a given solvent (or solvent mixture) against the percent resin solids at a constant temperature. In coating formulations, the normal aim is to have as little solvent as possible while achieving a viscosity sufficiently low for efficient application. Even though the Hansen three dimensional approach based on solubility parameters is a more scientific way to understand the solvency of solvents, some empirical test methods have traditionally been used as a quick tool to rate solvency.

The **Kauri-butanol** value, used to rate solvency of hydrocarbon solvents, is defined in ASTM Method D 1133 as the volume in milliliters of the hydrocarbon solvent at 25 °C that is required to produce a defined degree of turbidity when titrated into a specified quantity of a standard clear solution of kauri resin in n-butyl alcohol. Kauri-butanol values range from approximately 20 for the weakest hydrocarbon solvents to more than 100 for stronger aromatic solvents. The test is limited to hydrocarbon solvents and is not applicable to oxygenated solvents. As Kauri resin (a natural resin) is no longer easily available, the test has not maintained its acceptance in the industry. **Aniline point** (or mixed aniline point), another measure of solvency of hydrocarbon solvents, is more accepted. The aniline point is defined as the minimum temperature at which equal volumes of aniline and a solvent sample become completely soluble. The strongest solvent exhibits the lowest aniline point, while the weakest one exhibits the highest. To avoid measurement below 0 °C, a mixed aniline point is measured in which the solvent being tested is blended with an equal volume of n-heptane.

The **toluene dilution ratio** is used for rating solvency of oxygenated solvents. This test method involves the determination of the volume ratio of toluene to active solvent required to cause precipitation in a standard solution of nitrocellulose. Toluene dilution ratios vary from approximately 6 for very strong solvents to approximately 1.5 for weak solvents.

All these empirical test methods for arbitrary rating of solvency have the common limitation that they compare the ability of a solvent to keep in solution one solute, namely kauri resin, aniline and nitrocellulose for Kauri-butanol value, aniline point and toluene dilution ratio, respectively.

4.3.2 Evaporation rate

While the solvency of solvents is important in dissolving resins and controlling paint viscosity for ease of application, their evaporation rate is equally important, as a solvent must leave the coating film by evaporation at a controlled rate in order to give a uniform and defect-free dry film. Selection of solvents is important in controlling gloss, appearance and a number of coating defects that are related to evaporation rate of solvent during application and film formation.

As a solvent begins to evaporate, the viscosity of the wet film increases and its ability to flow spontaneously decreases. For good film formation, therefore, the solvent must evaporate at a controlled rate such that good flow and leveling occurs before the wet film becomes excessively high in viscosity. Fast evaporating solvents help in reducing sagging of coatings on vertical surfaces and require shorter flash-off time and tack-free time, but may present difficulty in flow-out to form films without defects, such as orange peel or brush marks. If solvent evaporates very rapidly from a wet film, its viscosity will rapidly rise and there will not be sufficient time to flow and level, resulting in non-uniform film formation that results in poor gloss and appearance. Furthermore, use of very fast evaporating solvents, such as acetone, may result in sudden cooling of the surface upon solvent evaporation, resulting in condensation of atmospheric moisture and its subsequent diffusion into the wet film. This causes **blushing**, a defect characterized by undesirable white opalescence, especially in environments of high humidity.

Slow evaporating solvents, on the other hand, provide better flow and leveling properties, but the coating may sag on vertical surfaces and solvents may be trapped in the film during curing, which may result in longer tack-free time. In extreme conditions, solvents trapped in the film may cause **blistering**, a serious defect in which vapors of trapped solvent put sufficient pressure on the film to cause formation of a blister and subsequent breakage of the film. Because of conflicting advantages and disadvantages of both fast and slow evaporating solvents, in most coatings, formulators often use a blend of solvents with different evaporation rates to balance the requirements of the film formation process and performance of coatings.

Evaporation of solvents from a wet film takes place in essentially two stages: initially, the solvent loss is primarily dependent on the volatility (related to vapor pressure) of the solvent, and at the later stage, as film formation proceeds, solvent loss by evaporation become increasingly difficult and essentially becomes diffusion controlled, a slow process. This latter stage may be dominant when as much as 20 % of the solvent is retained in the film.

In general, among the important factors affecting evaporation rate of a solvent from a wet film are vapor pressure of the solvent, temperature, the air flow rate at the surface, and the wet film thickness.

Measurement of evaporation rates is done very simply by a gravimetric method. Shell developed an automatic evaporometer described in ASTM D 3539. Two methods are commonly used: evaporation from a thin film of the liquid, or evaporation from filter paper, using equal volumes of liquids in each case. The filter paper method is preferred. The evaporation time of a given amount of solvent is determined experimentally under identical conditions and compared with that of butyl acetate or diethyl ether. The relative evaporation rate is defined as:

$$E\ (\text{butyl acetate}) = t_{90}\ (\text{butyl acetate}) \,/\, t_{90}\ (\text{test solvent})$$

$$E\ (\text{diethyl ether}) = t\ (\text{test solvent}) \,/\, t\ (\text{diethyl ether})$$

Where t_{90} = the time when 90 % of the test solvent or butyl acetate evaporates in a given type of equipment under the test conditions and t = evaporation time of the test solvent or diethyl ether in seconds.

The results relative to diethyl ether = 1 are termed **evaporation number** (EN), which is more commonly used in Europe. On the basis of these numbers, solvents are classified into four categories: high volatility (EN < 10), medium volatility (EN 10 to 35), low volatility (EN 35 to 50) and very low volatility (EN > 50). In the United States, the volatility of a solvent is normally evaluated relative to butyl acetate = 1, and is classified as Class 1 (rapid evaporation, $E > 3.0$), Class 2 (moderate evaporation, $0.8 < E < 3.0$) and Class 3 (slow evaporation, $E < 0.8$).

4.3.3 Other performance properties

Although solvency and evaporation rate are the most important properties, there are other properties that are important in specific circumstances. Some of them are briefly discussed here.

4.3.3.1 Moisture content

The presence of any appreciable amount of moisture in solvents used in a two-component polyurethane system can react with isocyanate crosslinkers and thus impair crosslinking efficiency. Therefore, moisture content is one of the important properties of solvents such as ketones and esters, which are used in two-component polyurethane coatings. Moisture content is normally determined by the Karl-Fischer titration method.

4.3.3.2 Aromatic content

Aliphatic hydrocarbon solvents frequently contain a certain amount of aromatic hydrocarbons. Since aromatic content can have a significant effect on the solid-viscosity relationship, and may impart undesirable odor, it is customary to determine and specify the aromatic content of aliphatic hydrocarbon solvents, generally expressed as percent by mass.

4.3.4 Physical properties

4.3.4.1 Surface tension

Surface tension of liquid paint is an important characteristic that influences a number of properties of the final coating. A liquid can wet a surface only when its surface tension is lower than the surface free energy of the surface. Solvents play a very important role in controlling the surface tension of the vehicle as well as the final paint. Lower surface tension of the vehicle facilitates such desirable processes as wetting of pigment agglomerates during dispersion, wetting of the substrate during paint application and flow and leveling during paint application and film formation. It should be noted that surface tension of liquid coating is also controlled by using appropriate additives. Surface tension of the solvent is frequently measured by the du Nouy ring method or drop weight method.

4.3.4.2 Boiling point and distillation range

The temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure is known as its boiling point. This is a characteristic property of pure solvents and is often used in specifications for solvents. When a solvent consists of a mixture of components, such as most hydrocarbon solvents, boiling occurs over a range of temperatures known as the boiling range or distillation range, which is also listed in solvent specifications. Distillation range also gives an indication of solvent purity; the purer the compound, the narrower the distillation range. With reference to their boiling properties, solvents are divided into low boilers (boiling range <100 °C), middle boilers (boiling range 100 to 150 °C) and high boilers (boiling range >150 °C).

4.3.4.3 Flash point

Flash point is one important indicator of the relative flammability hazard of solvents and solvent-containing products; therefore, this is a very important specification for solvents and paints. The flash point of a liquid may be defined as the lowest temperature at which the liquid, in contact with air, is ignited by a spark or flame under specified conditions. The Abel method (Institute of Petroleum Test Method 170), the Pensky-Martens closed-cup method (ASTM D 93), the Tag open-cup method (ASTM D 1310), the Tag closed-cup method (ASTM D 56), the Setaflash closed-cup method (ASTM D 3278), and ISO 3679 and ISO 3680 are some of the test methods used to determine flash point of a system; each method requires specific protocols and equipment. For compliance with regulations related to transportation and storage, the flash point must be determined by a specified method.

Flash point is roughly inversely proportional to volatility. When there are mixtures of miscible solvents, which is true for most coatings, in most cases the flash point can be assumed to be that of the solvent with the lowest flash point, provided that a substantial proportion of that component is present, such as 5 % or more.

4.3.4.4 Density and specific gravity

Density, a fundamental physical property, is an important consideration, as it can have a major effect on cost. In most cases, solvents are sold on a weight basis, but coatings are sold on a volume basis. In addition, the solvent is generally the lightest ingredient of the coating; therefore, density of the solvent is important with respect to the cost of the coating. Density is the mass of a unit volume of a material at a specified temperature, which is expressed in units such as grams per milliliter, grams per cubic centimeter or pounds per gallon. Specific gravity is the ratio of the mass of a unit volume of a material at a stated temperature to the mass of the same volume of gas-free distilled water at that temperature. A hydrometer is the quickest method used for measuring density of a solvent and a pycnometer is used for measuring specific gravity of the solvent. Specific gravity is a unitless quantity.

4.3.4.5 Color

Most solvents are clear and colorless. If a solvent exhibits some color, it may be an indication of the presence of impurities or contamination that might have occurred during storage and distribution. Therefore, color is often an important specification requirement to judge the quality of the solvent.

4.3.4.6 Refractive index

Refractive index is a characteristic property of solvents and is very sensitive to the composition of solvent blends. Therefore, it is use-

Table 4.2: Properties of some important representative solvents

Solvent	BP [°C]	ST [dyne/cm]	Density [g/ml] at 20 °C	ER	FP [°C]
Hydrocarbon solvents					
Mineral spirits (low aromatic)	182–190	26	0.79	200	63
Solvesso 100	155–181	29	0.88	40–45	41
Xylenes	137–142	27.9–29.6	0.87	17	28
Toluene	110–111	27.7	0.87	6.1	7
Dipentene	174–181	26	0.86		50
Alcohols and glycol ethers					
Isopropanol	82	23	0.79	11	12
n-Butanol	117.7	24.2*	0.81	33	34
2-Ethylhexanol	182-186	28.7	0.83	1210	73
2-Butoxy ethanol	169–172	26.6	0.90	136	62
1-Propoxy-2-propanol	149	25.4*	0.88	60.5	48.3
Esters and glycol ether esters					
Ethyl acetate	76–78	23.9	0.90	3	–4
Butyl acetate	124–129	25.1	0.88	12.1	27
PGMEAc	140–150	26.4	0.97	30.2	46
Ketones					
Acetone	56	25.2	0.79	2	–18
Methyl ethyl ketone				2.7	
Methyl isobutyl ketone	114–117	23.6	0.80	7.6	16
Isophorone	215	31.6	0.92	330	88

*BP = boiling point or range; ST = surface tension at 20 °C, * at 25 °C; ER = relative evaporation rate (diethyl ether = 1); FP = flash point by closed cup; PGMEAc: propylene glycol monomethyl ether acetate (Note: Properties are selected from different resources without claiming to be complete and accurate)* ful for checking purity and uniformity of solvent blends. Refractive index is mainly determined by the hydrocarbon backbone of a substance. In a homologous series, the refractive index increases with increasing length of the carbon chain, and decreases with increasing branching. The presence of cycloaliphatic and aromatic structures increases the refractive index of solvents.

4.3.4.7 Electrical resistivity

Electrical resistivity is a critical parameter of coatings, particularly those that are applied by an electrostatic spray or bell applicator, as it influences the transfer efficiency and coating appearance. Therefore, the electrical resistivity of paint must be properly adjusted and is mainly accomplished by selection of appropriate solvents. Nonpolar solvents, such as hydrocarbons, have high electrical resistivity (low conductivity), while polar solvents such as water, ketones, alcohols, glycol ethers, and esters generally have low electrical resistivity (high conductivity). Test methods that may be referred to for determination of electrical resistivity of solvents are ASTM D 5682-95 and ISO 15091:2012. Electrical resistivity is generally expressed in units like kiloohms (KΩ) or megaohms (MΩ).

4.3.4.8 Purity and composition

Gas chromatography is a commonly used analytical technique for the analysis of purity and composition of solvents that is very sensitive, rapid and simple to execute. It gives both qualitative and quantitative information from very small sample sizes of only a few microliters.

4.4 Classification of solvents used in the coating industry

A variety of the organic solvents used in coatings can be broadly classified by their chemical type into the following three categories:

Hydrocarbon solvents, which are organic compounds comprised of molecules consisting only of hydrogen and carbon atoms.

Oxygenated solvents, which are organic compounds comprised of molecules consisting of hydrogen, carbon and oxygen atoms.

Other solvents, which include organic compounds consisting of hydrogen, carbon, and atoms other than oxygen (such as chlorine or nitrogen). They also include inorganic compounds such as water or supercritical carbon dioxide.

4.4.1 Hydrocarbon solvents

The majority of hydrocarbon solvents are derived from fractional distillation of petroleum oil, with a few exceptions that are sourced from vegetable origin. Hydrocarbon solvents tend to be mixtures of organic compounds rather than pure chemicals, and they may vary in composition depending on source of the crude oil. Properties of hydrocarbon solvents are governed by two factors: their MW and type of hydrocarbon. Hydrocarbon solvents are non-polar and are less effective as active solvents for high MW synthetic resins with greater polarity. However, they are often used as diluents or latent solvents for such resins. They are used as true solvents for some of the non-polar or less polar binders such as drying oils, varnishes, alkyds, asphalt, rosin and petroleum resins. Hydrocarbon solvents are sub-classified into the four categories described below.

4.4.1.1 Aliphatic hydrocarbons

Aliphatic hydrocarbons, also termed naphtha, gasoline, or paraffin hydrocarbons, are chemically very stable saturated organic molecules that are generally mixtures of straight chain (normal paraffin) and branched chain (isoparaffin) hydrocarbons, with a minute quantity of cycloparaffins. Very weak solvency, low odor, low specific gravity and low cost are some of the unique characteristics of aliphatic solvents. Aliphatic hydrocarbons are subdivided, according to their boiling point range, into special boiling point hydrocarbons (DIN 51 631), mineral spirits (DIN 51 632), and petroleum ether (DIN 51 630). Special boiling point hydrocarbons are used in quick-drying paints and dip coatings, and have a flash point less than 2 °C. Mineral spirits are the predominantly used aliphatic hydrocarbon solvent in the paint industry for such binders as drying oils and long oil alkyd resins. Varnish makers' and painters' naphtha (bp 100 to 150 °C) is used mainly as a diluent.

4.4.1.2 Cycloaliphatic hydrocarbons

Cycloaliphatic hydrocarbons are also referred as cycloparaffins or naphthenes. Most of their properties such as solvency, odor, and specific gravity are intermediate between those of aliphatic and aromatic hydrocarbon solvents. The use of cycloaliphatic solvents is less common in paint and coatings than that of paraffin hydrocarbons.

4.4.1.3 Terpene hydrocarbons

Terpene solvents are of plant origin, obtained from pine trees and to some extent as a by-product of the citrus industry. The important solvents in this group are turpentine, dipentene, and pine oil, which are mixtures of C_{10} unsaturated hydrocarbon compounds. They are the oldest type of solvents used in the coating industry. Terpene solvents have a volatility comparable to that of mineral spirits, but they are losing their commercial significance in the recent years due to their higher cost compared comparable petroleum based hydrocarbon solvents. d-Limonene is a terpene hydrocarbon solvent obtained from by-products of the citrus industry. Their greater solvency compared to aliphatic hydrocarbons, narrower range of solvency and evaporation rate, and stronger odor are some typical characteristics of these solvents. They were mainly used in combination with mineral spirits in coatings based on oxidatively crosslinking oil and alkyd resins to improve flow and leveling, and hence gloss.

4.4.1.4 Aromatic hydrocarbons

Compared to aliphatic solvents, aromatic hydrocarbons (Figure 4.1) have higher solvency for almost all types of resins. Aromatic hydrocarbons are also used as diluents for coatings based on nitrocellulose, cellulose esters, and ethers in combination with active solvents, such as esters and ketones. Aromatic solvents that are commonly used in the coating industry are toluene, mixed xylene (xylol) and two types of high-flash aromatic naphthas. Aromatic naphthas are primarily higher-substituted alkylbenzenes, including tri- and tetramethylbenzene, isopropylbenzene (cumene), methylethylbenzene and diethylbenzene. There are two grades of aromatic naphthas, one with a flash point higher than 38 °C and predominantly C9 aromatics, and another with a flash point higher than 60 °C and

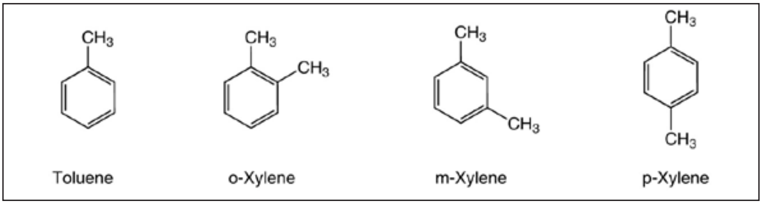

Figure 4.1: Examples of aromatic hydrocarbon solvents

C10 aromatics. Styrene and vinyl toluene are also aromatic hydrocarbons that act simultaneously as solvents and reactive diluents for chemical crosslinking with unsaturated polyester resins and in UV-cured coatings.

4.4.2 Oxygenated solvents

Oxygenated solvents are a very important group of solvents for the coating industry due to their strong solvency and wide range of availability. Unlike hydrocarbon solvents, oxygenated solvents are synthetically produced and hence are generally more expensive than hydrocarbons. Most oxygenated solvents are pure, single-component chemical products; therefore, they have very narrow boiling ranges relative to hydrocarbons, as narrow as 1 °C. Due to their much stronger solvency, they are used as active solvents for most synthetic resins. Some important types of oxygenated solvents are briefly discussed in the following chapters.

4.4.2.1 Alcohols

Because of their hydroxyl groups, alcohols (Figure 4.2) differ from hydrocarbons by having a higher polarity and a stronger tendency for hydrogen bonding. The mass ratio between the non-polar hydrocarbon chain and the hydroxyl group governs the solvency of alcohols. Lower alcohols are good solvents for polar resins such as shellac, amino resins and phenolic resins, but they are poor solvents for non-polar binders such as oils or oil modified alkyds. Polarity also affects water solubility of alcohols; lower alcohols, up to propanol, are water soluble, while higher ones are partially soluble, with progressively decreasing water solubility with increase in number

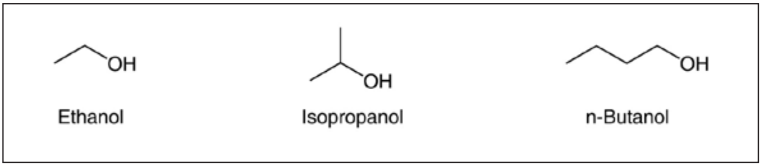

Figure 4.2: Examples of alcohol solvents

of carbon atoms in the molecule. Higher alcohols are mainly used as diluents in combination with esters. Higher alcohols can also be used to improve the storage stability of baking enamels formulated with etherified crosslinking resins.

4.4.2.2 Ketones

Ketones (Figure 4.3), compounds having a carbonyl group bonded to two carbon atoms or alkyl groups in the molecule, are highly polar solvents with outstanding solvency. They have the ability to form strong hydrogen bonds with polar resins containing active hydrogen atoms. Acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, cyclohexanone and isophorone are typical examples of solvents of this class. They are versatile solvents with powerful solvency for a wide range of synthetic binders and act as an active solvent in most cases. Ketones have a wide range of evaporation rates, from very fast evaporating acetone or methyl ethyl ketone, to moderately fast evaporating methyl isobutyl ketone, to slow evaporating isophorone. They have a strong, characteristic odor. The polarity of ketones is highest for lower ketones and progressively decreases from the lower to higher ketones. Acetone is completely miscible with water, while other ketones have varying degrees of water solubility depending upon the size of the alkyl group. The lower ketones are good solvents for polar resins, while the higher ketones are good solvents for non-polar polymers and copolymers. Due to their high solvency and hence viscosity reduction capability, they are frequently used in high-solid coatings. Although they are relatively chemically stable, their use should be avoided in systems containing free amine groups (such as amine hardeners in two-component epoxy coating systems), as they have a tendency to react with primary amines during storage.

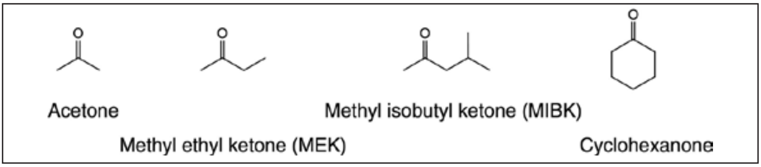

Figure 4.3: Examples of ketone solvents

4.4.2.3 Esters

Esters (Figure 4.4) are also an important type of active solvent used in the coating industry. Esters are similar to ketones in terms of their polarity and hydrogen bonding capability, but they are less polar than corresponding alcohols and their solvency is slightly weaker than ketones of similar volatility. Esters often have a characteristic fruity odor. Esters used as solvents are generally alkyl acetates and propionates and glycol ether acetates. Esters have extremely good solvency for a wide variety of polar resins. With increasing carbon chain length in the alcohol and acid, the solvency for polar products decreases, but increases for less polar products. The solvents of this class cover a wide range of volatility, depending on the number of carbon atoms in the alcohol component, which is generally methyl through hexyl. Glycol ether acetates are generally slow evaporating and are used in coatings as **retarder solvents** to increase **open time** and improve flow and leveling properties.

4.4.2.4 Glycol ethers

Glycol ethers (Figure 4.5) are ether alcohols, having both ether and alcohol functionality, that feature high polarity and a marked tendency to form hydrogen bonds. They are excellent solvents for a broad range of polar and semi-polar binders. Commercially impor-

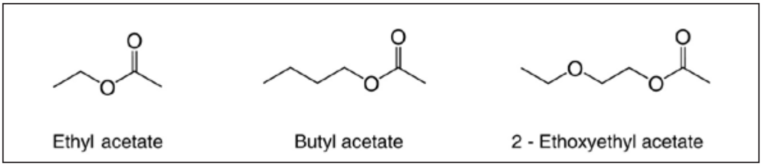

Figure 4.4: Examples of ester solvents

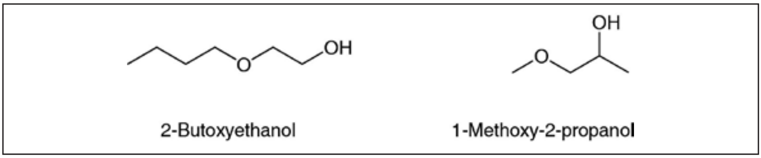

Figure 4.5: Examples of glycol ether solvents

tant glycol ethers are ethers of ethylene glycol, diethylene glycol and propylene glycol. Glycol ethers have strong solvency, slow evaporation rate, complete water miscibility, high flash point, and mild odor. Due to their water miscibility, they are very important as cosolvents in waterbased coatings.

4.4.2.5 Other oxygenated solvents

Among the important oxygenated solvents that are not covered above are furan solvents and organic carbonates. Furan solvents of commercial interest include furfuryl alcohol, tetrahydrofuran, and tetrahydrofurfuryl alcohol. They are characterized by strong solvency for some synthetic polymers. Tetrahydrofuran has an evaporation rate between that of acetone and methyl ethyl ketone. Organic carbonate solvents include ethylene and propylene carbonates, diethyl carbonate and dimethyl carbonate, which are good solvents for many polymers.

4.4.3 Other solvents

4.4.3.1 Chlorinated hydrocarbons

Chlorinated hydrocarbons have higher solvency than corresponding hydrocarbons for most resins and polymers used in coatings. They are miscible with many other types of organic solvents, but are insoluble in water. Non-flammability and high specific gravity are unique characteristics of this class of solvents. In recent years, their use in coatings has been almost negligible due to environmental and health reasons, but solvents such as dichoromethane were long used in paint removers due to their very strong solvency and fast evaporation rate. Chlorinated hydrocarbons have also been used in metal pretreatment for degreasing purposes.

4.4.3.2 N-methyl-2-pyrrolidone

N-methyl-2-pyrrolidone (Figure 4.6) is a cyclic amide with very strong solvency, high specific gravity, high flash point and low order of toxicity. It is completely water soluble and reported to be biodegradable. In the coating industry, N-methyl-2-pyrrolidone, an aprotic polar solvent, is especially used as a solvent in polyurethane dispersions and as an active solvent for urethane lacquers. It is also used in paint strippers, printing inks and occasionally as a coalescing agent in latex systems.

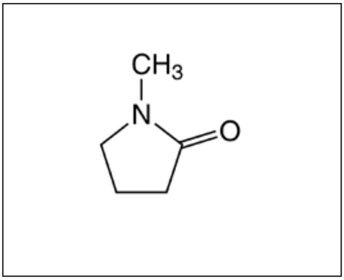

Figure 4.6: N-methylpyrrolidone

4.5 Toxicity and occupational health

It is evident that many solvents present considerable health hazards and hence have been subject to restriction through regulation. Even when using solvents of low toxicity, their odor may be undesirable in both the working environment and in the area around manufacturing facilities. The common modes of entry of these volatile substances in the body are inhalation, skin contact and ingestion. The toxic effects of solvents depend on the amount of solvent and the exposure time, based on which degree of toxicity is represented, as follows.

Acute toxicity represents the acute damage that may occur under short-term exposure to high solvent doses, which can be particularly important in cases of accidental ingestion or spills.

Chronic toxicity represents the chronic damage and sensitization that may occur as a result of the absorption of smaller amounts over a longer period of time. Chronic effects are more dangerous since they are often not detected early enough and may lead to health risks such as cancer.

The risk to human health can be minimized by proper personal safety precautions and the use of protective clothing and equipment, such as gloves, goggles, organic vapor masks, or even complete air-fed suits with visors for spray application in enclosed areas that are also ventilated to prevent build-up of vapor.

Lethal dosage values (LD_{50} based on oral administration to rats) of solvents are used to represent their toxicities. Lethal concentration values (LC_{50}) are also being used because, in most cases, solvent poisoning is caused by inhalation of solvent vapor.

Most solvents have a characteristic odor, which may be undesirable in many cases. Human perceptibility and sensitivity to the odor of solvent vapors depends on habituation, which varies from person to person, and therefore, it is impossible to give objective rules for determining when an odor becomes objectionable. As a practical perceptive approach, odor intensity is subdivided into four levels – **imperceptible, weakly perceptible, moderately perceptible** and **highly perceptible**. The **odor threshold** is the vapor concentration in a cubic meter of air (in ppm) that is just perceptible.

To eliminate the hazards associated with inhalation, limits of solvent vapor in air have been developed separately by different countries. In Germany, **the maximum allowable concentration** (Maximale Arbeitsplatzkonzentration) or MAK value was used, which is the maximum concentration of a substance in the atmosphere at the workplace that is generally not injurious to the health of the employees and is not regarded as intolerable by the latter, even after repeated and long-term exposure. After the new German Ordinance on Hazardous Substances („Gefahrstoffverordnung/ GefStoffV) came into force in 2005, the maximum workplace concentration of a substance in the air has been reassessed. The new concept regulates the occupational health limit value (Arbeitsplatzgrenzwert (AWG)) and the biological limit value (biologischer Grenzwert (BGW)).

In the United States, the equivalent of the MAK value is the threshold limit value (TLV), which is the concentration of a substance in the air to which virtually all workers can be exposed daily without any harmful effects. This value is subdivided into

TLV-TWA (time-weighted average concentration), TLV-STEL (short-term exposure limit) and TLV-C (ceiling limit).

4.6 Environmental aspects

Being a volatile component of coatings, all solvents inevitably evaporate into the atmosphere. The presence of organic compounds in the atmosphere can lead to serious problems related to air pollution. These solvents have been termed VOCs. When emitted from paints and accumulated in the troposphere, VOCs can react with oxygen in presence of nitrogen oxides and sunlight to generate smog and ozone. Ground-level ozone and smog cause a variety of health problems even at very low levels. They may cause permanent lung damage after long-term exposure. They can also damage plants and ecosystems. Smog can cause eye irritation and respiratory problems in humans and animals, and can be harmful to crops and trees. Therefore, many countries have enforced legislation to reduce emissions of both VOCs and nitrogen oxides. VOC regulations have been a major driver for development of many of the present coating technologies, such as waterborne, high-solid and UV-curable technologies.

The EU “Paint Directive” 2004/42/EC defines a VOC as an organic compound having an initial boiling point lower than or equal to 250 C at the atmospheric pressure of 101.3 kPa. In the EU, the VOC is calculated by the following formula, and is expressed as mass per unit volume:

Equation 4.3: $$\mathrm{VOC} = (M_{\mathrm{Volatile}} - M_{\mathrm{Exempt}}) / V_{\mathrm{Coating}}$$

Where M_{Volatile} = mass of volatiles, M_{Exempt} = mass of exempt volatiles and V_{Coating} = volume of volatiles

In the United States, as per the Environmental Protection Agency (EPA), a VOC is defined as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.”

It should be noted that unlike in the EU, the US EPA uses photochemical reactivity of organic compounds as a criterion to identify an organic solvent as a VOC. The US EPA has released a list of exempt solvents that have negligible photochemical reactivity. Methyl acetate, acetone, tert-butyl acetate, dimethyl carbonate and propylene carbonate are some examples of exempt solvents important for the coating industry. Per the US EPA, VOC concentration is calculated according to the following formula and expressed as mass per unit volume:

Equation 4.4: $$\mathrm{VOC} = (M_{\mathrm{Volatile}} - M_{\mathrm{Exempt}}) / (V_{\mathrm{Coating}} - V_{\mathrm{Exempt}})$$

Where V_{Exempt} = volume of exempt volatiles

Although this mass-based approach to calculate VOC concentration has been used for years, in 2008, the US EPA published new VOC emission standards for 36 aerosol coating categories. In this approach VOC contents are based on ozone formation potential of individual formulation components rather than the conventionally used mass-based approach. To express the ozone formation potential, each VOC is assigned a maximum incremental reactivity (MIR) value that indicates the compound's potential to generate ground-level ozone (its photochemical reactivity) in terms of grams of ozone formation per gram of solvent. The higher the value, the greater the potential for producing ground-level ozone. This provides more practical differentiation of the environmental impact of various compounds. In the earlier mass-based regulation, a low density, high activity solvent was more beneficial to paint formulators. In MIR-based calculations, the MIR value of each component is used to calculate grams of ozone formation potential per gram of product, often referred to as product weighted MIR, expressed in grams of ozone per gram of product. MIR values of different solvents have been documented by the US EPA.

The procedures specified by the US EPA for testing paint products for compliance with VOC limits are described in Federal Reference Method 24, which employs several ASTM test standards. VOC values for waterborne or solventborne coatings are calculated by the following formula:

Equation 4.5:

$$\text{VOC}=\frac{(\text{wt\% of volatiles} - \text{wt\% of water} - \text{wt\% of exempt solvent})(\text{density of coating})}{100\text{-Volume \% of water-Volume \% of exempt solvents}}$$

It is common to dilute paint during application; therefore, regulatory limitations are based on VOC content of coatings as applied. Experimental measurement of VOCs is not easy because the amount of VOCs released depends on several parameters under which the coating is applied and cured, such as time, temperature, film thickness and air flow over the surface. Most of the test methods for VOCs give results with some degree of deviation. Measurement of VOCs in waterborne coatings is even more complex due to the limitations of water content analysis.

5 Additives

5.1 Introduction

Resins or binders, pigments and extenders, and solvents are the major components of coatings by mass, which expectedly govern the major properties of these coatings. However, most coating compositions also contain components called additives. Additives may directly influence the coating properties or may modify the properties of the major ingredients.

Anything in a coating formulation that is not a resin, pigment or solvent may be considered an additive. Due to their vast variety and differing chemical compositions and mechanisms of action, it is difficult to provide a clear definition for additives, though they have been described according to DIN 55 945 A1 as follows: “An additive is a substance added to a coating material in small quantities in order to impart specific properties to the coating material itself or the coating films produced from it.” We can compare the role of additives in coatings to that of spices in food, in which a small amount of a specific spice may have profound influence on flavor.

Some of the important generic considerations and remarks for using additives are:

- Some additives are very product specific, so that they are effective only in certain systems while completely ineffective in others.
- The use of additives frequently leads to some undesirable side effects; therefore, the best policy is to use the minimum number of additives in the minimum amounts needed to achieve desired properties. The idea is to avoid a spiral formulation, meaning that use of one additive generates side effects that lead to the need to add another type of additive to resolve them, which may result in another side effect.

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- The effects of additives can be so dramatic that careful selection of additives and their usage levels are extremely important, together with a good understanding of the potential interactions with other ingredients.
- Because most additives are used in small quantities, extreme care must be taken in their calculation, weighing and addition.

Additives are much too diversified to be classified according to their chemical nature. Therefore, even though many additives are multifunctional, most suitably, they can be classified according to their functions. The most common types of coating additives will be described in this chapter according to their functional role in coatings.

5.2 Wetting and dispersing agents

Wetting and dispersing agents are additives that aid the incorporation of pigments and extenders in the paint. Pigments are an integral part of the paint that govern different aesthetic, performance and functional properties of the coating, as described in Section 3.1.1. For maximum effectiveness of pigments in imparting these properties, their homogeneous distribution in the vehicle is of prime importance. Uniform dispersion of pigment is necessary to achieve important properties in paints such as high gloss, high opacity, good color development, color uniformity, rheology of the paint, and storage stability and to minimize defects such as settling, floating, flooding, syneresis and flocculation. In order to understand the role of wetting and dispersing agents, it will be helpful to briefly review the pigment dispersion process.

5.2.1 Pigment dispersion process

The process of dispersing pigment particles in a vehicle involves a combination of three distinct phenomena called wetting, grinding and dispersion.

5.2.1.1 Wetting

The pigment used in the coating is supplied in the form of agglomerates (Section 3.2.2.3). The process of wetting involves displacement of air and moisture from the surface of the pigment by the vehicle, followed by penetration of the vehicle in the spaces between the pigment particles. Wetting additives are surface-active agents that enhance the process of wetting by reducing the interfacial tension between pigment particle and resin solution.

5.2.1.2 Grinding

Grinding involves the mechanical separation of agglomerates into primary particles, which is accomplished by providing mechanical energy through different types of grinding equipment, called grinding mills. Properly wetted particles are more easily disrupted into primary particles compared to agglomerates; therefore, wetting agents help grinding indirectly.

5.2.1.3 Dispersion

In the absence of repulsive forces, freshly disrupted pigment particles would recombine (flocculate) in response to continuous collisions between them due to Brownian movement and attractive forces, such as London van der Waals forces, between them. The flocculation of pigment particles leads to gloss reduction, loss of opacity, poor color development, inconsistent color, and defects such as settling, syneresis, flooding and floating, leading to poor paint performance. The process of dispersion stabilizes the particles by establishing enough repulsive forces between the separated particles to prevent them from flocculating. The stabilization is induced by using dispersing agents, which operate by a mechanism of charge stabilization or steric stabilization.

In **charge stabilization** (electrostatic stabilization), an anionic or cationic dispersing agent is adsorbed onto the pigment surface and forms an electrical double layer around the

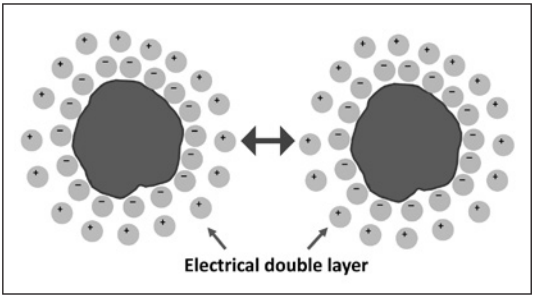


Figure 5.1: Dispersion of pigment particles by charge stabilization

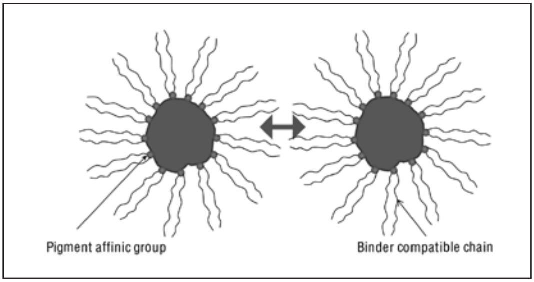


Figure 5.2: Dispersion of pigment particles by steric stabilization

pigment particles (Figure 5.1). The tendency to flocculate is reduced by electrostatic repulsion between pigment particles, as they all carry the same charge, and the dispersion is stabilized. Charge stabilization is an especially useful mechanism in waterbased systems. The dispersing agent must be ionic in nature to establish this mechanism.

In **steric stabilization** (entropic stabilization), the repulsion between particles is achieved by steric hindrance arising from the adsorbed layer of dispersing agent (Figure 5.2). The pigment affinic group, also known as the anchoring segment, of the dispersing agent is selectively adsorbed on the pigment surface, while the rest of the segment of the dispersing agent, consisting of long resin-compatible chains, are solvated and protrude into the binder phase. As pigment particles approach each other, these adsorbed polymeric chains intermingle, and in so doing, they lose a degree of freedom, causing a reduction in entropy, which is unfavorable and provides the necessary hindrance to prevent further attraction. Steric stabilization is an important mechanism applicable in both solventbased and aqueous systems. The effectiveness of this type of stabilization is dependent on the thickness of the adsorbed layer, the structure of the adsorbed layer and whether there is enough coverage of the pigment surface by the dispersing agent (adsorption density).

5.2.2 Chemical composition of wetting and dispersing agents

All wetting and dispersing agents are chemically surface-active agents with a characteristic amphiphilic structure comprised of

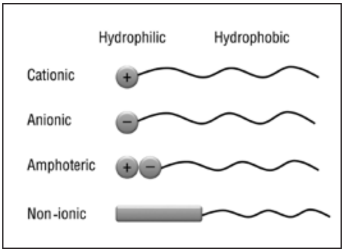


Figure 5.3: Schematic representation of different types of surfactants

one or more hydrophobic (lipophilic) groups along with one or more hydrophilic (lipophobic) groups in the same surfactant molecule. Due to this structure, they tend to adsorb at the interface, which results in decreased interfacial tension. This is the key property of surfactants determining their action as wetting and dispersing agents. Surface-active compounds may be schematically represented by a tail-head model, as shown in Figure 5.3. The tail symbolizes the hydrophobic group and the head the hydrophilic group.

Surfactants are classified according to the chemical structure of their hydrophilic groups as:

- Ionic surfactants
  - Anionic surfactants
  - Cationic surfactants
  - Amphoteric surfactants
- Non-ionic surfactants

In **anionic surfactants**, the hydrophobic segments are connected to anionic groups that are neutralized with cations such as sodium, potassium, ammonium, or amine ions. Some important examples of these surfactants are sulfates, sulfonates, phosphates and carboxylates (soaps). They are widely used as wetting and dispersing agents.

Cationic surfactants, having a hydrophobic group attached to the cationic group, are less common as wetting or dispersing agents for coatings compared to anionic surfactants. Derivatives of fatty amines, with hydrophobic residues in the form of cations, are an important example of this group.

Amphoteric surfactants have both anionic and cationic groups in the same molecule, and the pH value of the solution determines the predominant electrical charge on the surfactant. Examples of this class are aminocarboxylic acids and betaines.

Non-ionic surfactants are amphiphilic compounds that cannot dissociate into ions in aqueous solutions. Common examples include alkyl polyglycol ethers and alkylaryl polyglycol ethers.

5.2.3 Flooding and floating

Flooding and floating (Figure 5.4) is a defect that occurs in paint systems containing a combination of pigments that differ significantly in their wetting characteristics and particle sizes. It occurs after application in the wet film and is caused by segregation of the different types of pigments. This segregation is strongly influenced by flocculation of similar pigment particles. When this non-uniform pigment distribution is vertical, it is termed **floating**, which appears in the form of Bénard cells or streaks; on other hand, horizontal separation is termed **flooding**, which appears as a uniform change in color of the film while it is wet and can only be evidenced by a rub-out test. In this test, after a short drying period, part of the wet paint film is rubbed with the finger until almost dry; a color difference between the rubbed section and the rest of the film indicates flooding. The separation is caused due to differential mobility of different types of pigment particles under the influence of local eddies in the drying film. Flooding and floating can be avoided either by controlled flocculation of various pigments using an additive, or by using polymeric dispersants. Once different pigment particles are associated with each other by controlled flocculation, they no longer have a chance of segregation. Polymeric dispersants control flooding and floating by influencing pigment mobility through a

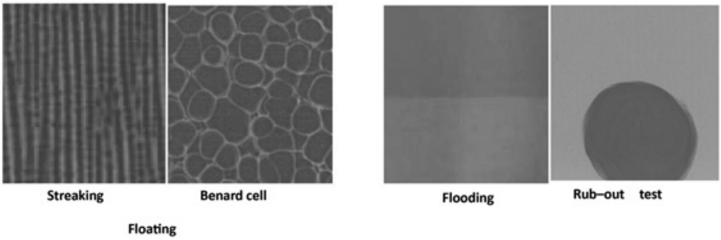


Figure 5.4: Flooding and floating

strong interaction between an adsorbed dispersant molecule and surrounding resin molecules, as opposed to flocculation, and therefore is the preferred route for high-gloss top coats.

5.2.4 Polymeric dispersing agents

Most inorganic pigments have surfaces sufficiently polar to have strong adsorption of dispersing agents. On the other hand, many organic pigments and carbon blacks have less polar surfaces, which leads to difficulty in having sufficient coverage of the surface by adsorption of the dispersing agent. In addition, they are very small in particle size compared to inorganic pigments and therefore have a very large specific surface area. As a result, they are not adequately stabilized by conventional dispersing agents. The requirement for brighter and more attractive colors in modern coatings has led to increasing use of organic pigments. Therefore, new and more effective types of dispersants have been developed, known as polymeric **dispersants** or **hyperdispersants**, which are gaining importance. Compared to conventional dispersants, polymeric dispersants characteristically have much higher MW

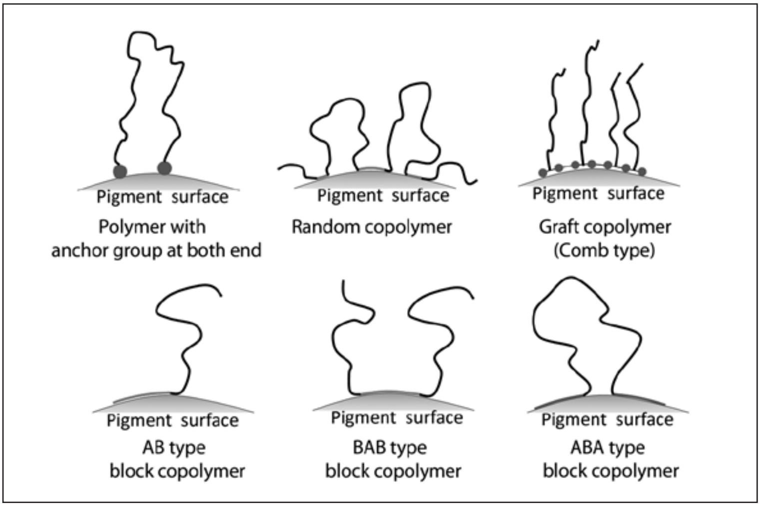


Figure 5.5: Schematic representation of different types of polymeric dispersants

and many pigment affinic groups with a specific structure conducive for easy adsorption onto pigment surfaces, which gives durable adsorption. Polymeric dispersants consist of functional copolymers that provide effective stabilization of pigment particles against flocculation by good steric hindrance, resulting from the loops and tails of the high MW polymer chains. For the most efficient steric stabilization, it is essential to have a polymer chain that is uncoiled and protrudes from the pigment surface as far as possible. Therefore, the polymeric dispersant must have good compatibility with the binder present in the system. The copolymer structure of hyperdispersants may be of different types (Figure 5.5), according to the distribution of monomers in the polymer chain, such as a statistical copolymer (random copolymer), block copolymer or graft copolymer. Typical dosage levels of polymeric dispersant are higher than those of classical low MW dispersants and are normally calculated based on surface area or oil absorption values of the pigments. They are not restricted to organic pigments, as they are equally effective in inorganic pigments too.

5.2.5 Deflocculating agents and controlled flocculating agents

The classical deflocculating additive has a typical structure with one or more closely spaced pigment affinic groups and a number of resin-like chain structures extending in the vehicle, as described in Figure 5.2. Such additives are low MW polymers that can be adsorbed strongly on the pigment surface and provide sufficient steric stabilization to give a deflocculated condition and hence more Newtonian flow. This type of additive is very important for high-gloss top coats and efficient utilization of expensive colored pigments.

Generally the phenomenon of flocculation is considered negative in coatings; however, controlled flocculation may be desirable in certain systems where gloss is not important. In the **normal flocculation** state, the pigment particles make direct contact with one another, while in the **controlled flocculation** state, no direct pigment-pigment contact occurs, as the additive molecules are always between the pigment particles.

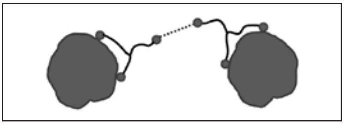


Figure 5.6: Schematic representation of controlled flocculation

In **controlled flocculating additives**, the pigment affinic groups are distributed in a special fashion over the molecule, rather than being confined to a small region therefore, they can function as bridges between various pigment particles (Figure 5.6). As a result, the controlled flocculation state forms a three-dimensional network structure, which is beneficial for thixotropic flow behavior in the coating and leads to less settling – which if it occurs, is less serious – along with reduced flooding and floating because different pigments are bound together in the flocculates, and consequently cannot separate to cause flooding or floating.

5.3 Rheology additives

5.3.1 Rheology and its role in coatings

Rheology is the science of deformation and flow behavior of materials under the influence of parameters such as shear rate and time. Liquids with viscosity not dependent on shear rate are termed **Newtonian liquids** while **non-Newtonian liquids** exhibit changes in viscosity depending on shear rate. Most paints exhibit non-Newtonian flow, which is desirable. Important types of non-Newtonian flows are **pseudoplastic flow behavior** (shear thinning), **thixotropic flow behavior** (time-dependent shear thinning,) and **dilatant flow behavior** (shear thickening). Pseudoplastic or thixotropic flow is often desirable in coatings because:

- Viscosity is fairly high at low shear rates, which avoids sedimentation of pigments and provides good anti-sag properties once the paint is applied on vertical surfaces.
- Viscosity is low at high shear rates, which allows better handling and easy application of coatings.

The rheology of a coating system is mainly influenced by the binder (chemistry and MW), solvents (type, content and solvency of resin), pigmentation level and additives such as wetting and dispersing agents that have an indirect effect on rheology. Therefore, it is important to control the rheology to achieve certain desired characteristics. Additives used for modifying rheological properties of coatings are known as thickeners or rheology modifiers. Apart from storage, processing, and application performance, the role of thickeners is also important to adjust the desired rheological characteristics of the mill base to ensure maximum use of the supplied energy during the dispersing stage. They are important additives for both solventbased coatings and aqueous coatings.

5.3.2 Thickeners for solventbased coatings

A wide range of rheology modifier additives is commercially available for solventborne coatings. Some important classes are discussed in the following chapters.

5.3.2.1 Organoclays

Organoclays are the most widely used inorganic thickeners in the paint and coating industry. They are derived by modification of naturally occurring laminar silicates (clays) such as hectorite and bentonite. They have replaceable cations (Na^+, Ca^+ or Li^+) on the surface of the crystal that are replaced, through an ion exchange reaction, by organic quaternary ammonium cations such as $[\text{dimethyldioctadecylammonium}]^+$ or $[\text{dimethylbenzyloctadecylammonium}]^+$. Occasionally a blend of quaternary amines is used to tailor the properties of the product.

Organoclays are supplied as a fine powder having agglomerated stacks of platelets. They must be added to the paint during the dispersing stage. Before addition, adequate wetting, deagglomeration

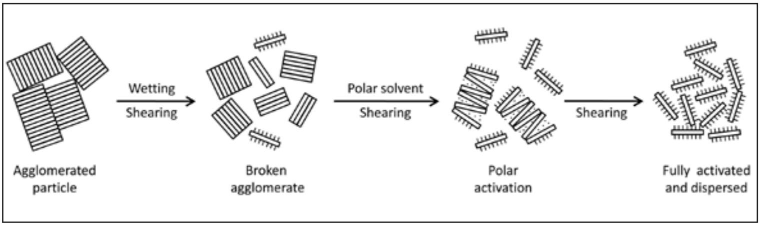


Figure 5.7: Process of gelation of organoclays

and activation should be accomplished in an appropriate solvent. Under the strong shear force and in the presence of a polar solvent such as alcohol, propylene carbonate or water as an activator, the stacks break up into individual platelets with simultaneous solvation of the organic cations on the planar surfaces. The three-dimensional gel structure developed via hydrogen bonding through the hydroxyl groups at the edges of the organoclay platelets results in thickening of the paint (Figure 5.7). The structure is reversible; it breaks down easily under low-shear forces and can be regenerated when the shear force is removed. This process explains the mechanism for development of thixotropic consistency by organoclays.

Rapid recovery of viscosity, which is useful for sag control, good pigment suspension at low dosage level, and temperature insensitivity are the key advantages of organoclays. Some of the limitations associated with organoclays are reduced gloss and flow at excessive dosage and possible reduction in corrosion resistance due to presence of bromides or chloride ions as impurities.

5.3.2.2 Fumed silica

Very finely divided fumed silica (pyrogenic silica) is another important inorganic thickener used in the coating industry that

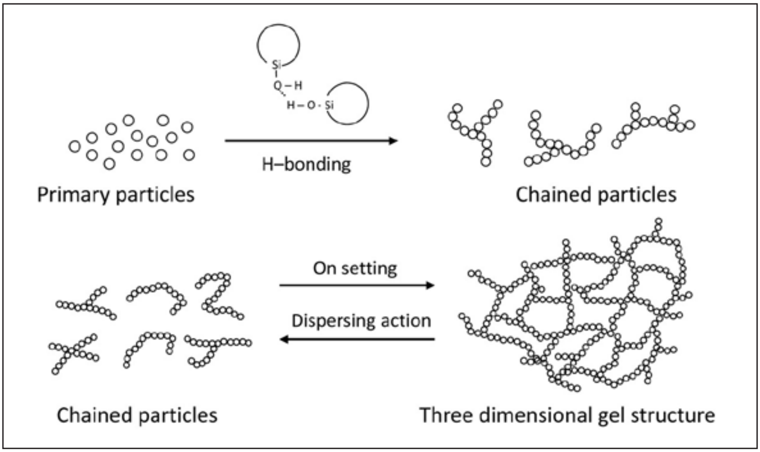


Figure 5.8: Development of thixotropy by fumed silica

possesses surface hydroxyl groups (silanols) capable of forming a three-dimensional structure via hydrogen bonding to yield increased viscosity. Depending on the system, the thickening effect is determined mainly by the grade and concentration of the pyrogenic silica, system pH, polarity of the medium, degree of dispersion, and presence of other additives.

The hydrogen bonds are relatively weak and get disrupted as soon as light shear forces are applied, with a consequent viscosity reduction. The three-dimensional silica chain structure reforms upon removal of shear force and thus produces thixotropic consistency in the system (Figure 5.8). The effect is more pronounced in systems without or with low hydrogen bonding capability (such as hydrocarbons) than in a system capable of hydrogen bond formation (such as water, an alcohol or an amine).

5.3.2.3 Metal soaps

Metal soaps such as aluminum stearate have been used as thickening agents for a long time in systems rich in hydrocarbon solvents such as alkyd-based systems. As a result of intermolecular hydrogen bonding, they behave as high MW compounds and consequently increase the viscosity, but under the effect of shear force, the hydrogen bonds break and viscosity is reduced. For incorporation in paints, they must be swollen in hydrocarbon solvent under gentle heating and should be added at the grinding stage. One of the limitations of this type of thickener is a plasticizing effect in the final coating, which reduces the hardness.

5.3.2.4 Overbased sulfonates

Another class of thickeners for solventborne coatings is the overbased calcium sulfonates. They contain acicular microcrystals (0.5 to 3 μm) of calcium carbonate associated with the long chain sulfonate by adsorption through the sulfonate group. The non-polar hydrocarbon chains (typically C12 to C30) form intermolecular bonds through weak van der Waals forces, producing a stable microstructure that causes an increase in viscosity suitable for anti-settling and anti-sagging properties. The gel structure achieved by them is strongly shear thinning.

The main advantages of these thickeners are their ease of incorporation, temperature stability, effectiveness, good sag resistance and very little effect on gloss. On the other hand, due to their high alkalinity, they cannot be used in acid catalyzed systems. They make the product more water sensitive.

5.3.2.5 Organic thickeners

Though inorganic thickeners are efficient thickeners for solventbased coatings, their major limitation is that they must be incorporated at the grinding stage of paint manufacturing. It is quite often necessary to optimize the rheological properties of solventborne coating materials during the let-down stage, and organic thickeners are important in such instances due to their versatility. Quite often, they give better appearance, gloss, and flow compared to inorganic thickeners.

Hydrogenated castor oilbased thickeners

One of the important classes of organic thickeners used in solvent-based coatings is based on hydrogenated castor oil and its modified amide, ether, and ester derivatives. The hydrogenated castor oil thickener molecule, due to its three-dimensional structure and hydroxyl functionality, can form hydrogen bonds to another thickener molecule or with the solvent. This type of intermolecular association leads to formation of a network by intermolecular association, resulting in increased viscosity. In addition to hydrogen bonds, thixotropy also develops as a result of molecular chain entanglements. Under the influence of shear force, the entangled molecules or hydrogen bonds are disrupted, causing a reduction in viscosity. Hydrogenated castor oilbased thickeners are available in the form of a powder or paste, which has to be dispersed and activated in the coating system to achieve the full thickening effect. This is achieved under the influence of shear forces and heat. Best effectiveness from these thickeners is achieved when they are partially dissolved in the coating system. Depending upon the chemical modification, the activation temperature ranges from 35 to 70 °C. Along with their advantages of thixotropic consistency and good flow properties, their main limitations are heat sensitivity, solvent dependence and tendency for seeding.

Polyamides

Polyamide thickening agents are available in a variety of chemical compositions depending on combinations of different carboxyls and amines as high MW waxy polymers with terminal amide groups. Their thickening effect in coatings is partly achieved by micelle formation resulting from their hydrophilic and hydrophobic ends, and partly by their association with pigment particles and chain entanglement. Hydrogen bond formation through amide groups also plays a role. A combination of such phenomena typically results in the shear-thinning flow of the coating. Stability and versatility are important merits of such thickeners. They may impair intercoat adhesion in certain systems.

Polyolefins

Waxes based on polyolefin chemistry are also used as anti-settling and sag control agents in high-solid coatings. They are supplied as fine powders or as pastes in solvent. They must be activated by a combination of heat and shear. During this process of activation, their coiled crystalline matrix becomes extended into a straight chain configuration, resulting in chain entanglement and hence increased viscosity.

Liquid thixotropes

This type of thickener is based on modified ureas dissolved in N-methylpyrrolidone, which are insoluble in common coating solvents. Upon careful incorporation into coating systems, the controlled precipitation of additive forms very fine, needle-like microcrystals. The crystals form a three-dimensional lattice structure via hydrogen bonding, which results in thixotropic behavior of the system.

Thixotropic alkyds

Alkyd resins chemically modified with polyamide resins are often used as thixotropic agents for air-drying non-drip paints and high-solid alkyd-based paints. Polyamide modified alkyds form a highly viscous mass that becomes reversibly free-flowing when shear force is applied. The mechanism for developing thixotropy is based on hydrogen bonding along the polymer structure.

5.3.3 Thickeners for waterbased coatings

Due to environmental concerns, waterborne coatings are becoming increasingly popular. The binders used for aqueous coatings, such as latex, are stabilized polymer particles in water; therefore, their rheological properties are independent of MW and more complex than simple resin solutions. Thus it is much more necessary to use a proper rheology modifier in aqueous coatings to provide a good balance of properties like storage viscosity, application viscosity, anti-settling properties, spatter resistance and flow and leveling. Also, latex is shear sensitive and therefore cannot be used at the grinding stage, meaning grinding must be done in the presence of a suitable thickener to provide enough consistency for efficient grinding. Thickeners for waterbased coatings can be categorized into two classes based on the mechanism of thickening: waterphase thickeners and associative thickeners.

Waterphase thickeners thicken the aqueous phase of the system due to dissolved polymer. Cellulose derivatives are most commonly used, but starch derivatives and acrylic thickeners are other groups in this class. The advantage of these thickeners is that they operate independently of the system, and hence rheological behavior of the paint is comparatively predictable.

Associative thickeners increase the viscosity of the paint by interacting with other paint ingredients through bridging of particles (surface to surface) or interaction of adsorbed layers. The interactions are assumed to be through hydrophobic forces. The operative mechanism is illustrated in Figure 5.9. Important groups in this class are associative acrylic thickeners, associative cellulose ethers and hydrophobically modified ethoxylated urethanes (HEUR).

5.3.3.1 Acrylic thickeners

Acrylic thickeners, also known as **alkali-swellable emulsions**, are used to a limited extent in cheap interior wall paints. They are acids containing acrylic copolymers supplied in liquid form as an emulsion. The main limitation of these thickeners is that the thickening action is a function of the pH of the paint system and therefore the viscosity varies with pH of the system.

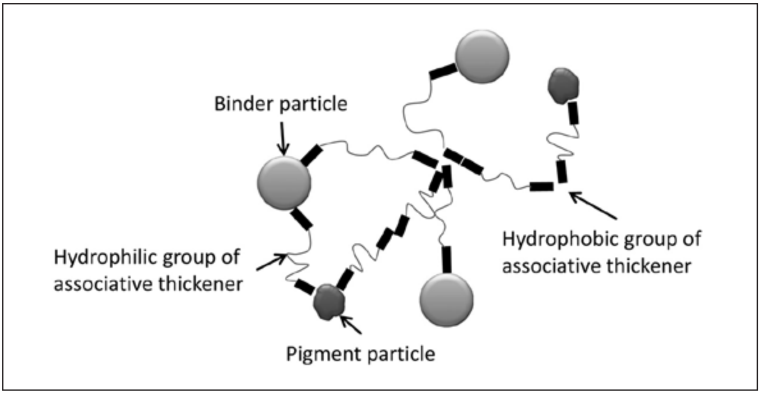


Figure 5.9: Operative mechanism of associative thickeners

5.3.3.2 Cellulosic thickeners

Cellulosic thickeners are among the most commonly used thickeners for decorative latex-based paints. They are produced by chemical modifications of cellulose such as carboxymethylation or etherification. The most widely used derivatives are hydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxyethyl cellulose, methylhydroxypropyl cellulose, and sodium carboxymethyl cellulose. The important characteristics that control the properties of different grades of individual derivatives are degree of polymerization, degree of substitution and molar substitution.

Though cellulosic thickeners may be added at various stages of paint production, it is more advisable to add them at the premix stage (grinding step). Addition of thickeners at the grinding step helps in dispersion of pigments and extenders by providing high viscosity and hence better de-agglomeration. They are sold in powder form and have a tendency to agglomerate during the solvating process; therefore, it is important that the particles are well dispersed throughout the aqueous phase before going into solution. Temperature and pH also affect the hydration process.

There is no best cellulosic thickener for all types of waterbased paints; rather, experimental study is needed to select the best suitable thickener for a given system because various performance parameters of the thickener vary with type of substitution. Cellulosics are the most common thickeners for semi-gloss and flat aqueous paint systems but are quite often unsuitable for glossy aqueous paints.

5.3.3.3 Associative cellulosic thickeners

Associative cellulose ethers are primarily used in the paint industry to increase spatter resistance and coverage of paint. They are generally derived from hydroxyethyl cellulose and ethylhydroxyethyl cellulose by modifying them with hydrophobic groups (alkyls or alkyl aryls). The concentration of hydrophobic groups is normally kept low (<2 %). The hydrophobic groups are able to interact with other paint components and thus provide associative characteristics. They achieve thickening via both aqueous-phase thickening and associative thickening. Therefore, they exhibit a certain degree of dependence on other components of paints such as binders, pigments, extenders and surfactants, but the dependence is not as strong as in the case of other types of associative thickeners.

5.3.3.4 Associative acrylic thickeners

Associative acrylic thickeners are also known as hydrophobically modified alkali-swellable emulsions (HASE). Chemically, they are copolymers composed of three blocks:

- Hydrophilic monomers such as acrylic acid, methacrylic acid or maleic anhydride
- Hydrophobic monomers such as butyl acrylates or methyl methacrylates
- Associative monomers with long alkyl chains such as alkyl vinyl ethers.

Like alkali-swellable emulsion thickeners, they are supplied as emulsions and are only active in a narrow pH range of 8 to 10, outside of which their viscosity decreases.

5.3.3.5 Hydrophobically modified ethoxylated urethanes

Hydrophobically modified ethoxylated urethane thickeners, also known as polyurethane thickeners, are a more recent type of associative thickeners that are more popular for premium quality paints with low pigment volume concentration, which require excellent flow and leveling, and better spatter resistance and coverage. Alkyd-like rheology, hydrophobic properties, and enzyme resistance are some of the other merits of these thickeners. They are composed of hydrophilic polymers such as polyethylene glycol connected through urethane linkages and terminal hydrophobic groups such as oleyl, stearyl, dodecylphenyl, and nonylphenyl. The composition of the hydrophobic segment is very important for the rheological characteristics because the associative characteristics are derived from the adsorption behavior of these groups. Linear or comb-like structures are more common for polyurethane thickeners. Sag resistance and compatibility with glycol-containing pigment concentrates are the main limitations of hydrophobically modified ethoxylated urethane thickeners.

5.4 Flow and leveling agents

The term flow and leveling in coatings is associated with smoothening of a coating film after application and during curing that leads to evenness of the coating surface. Though flow and leveling has no influence on a coating's performance properties, it plays a vital role in aesthetics. The term **leveling** can be defined as the ability of a liquid coating to form a level surface even though an uneven surface or surface defects result during or after application. **Flow and leveling agents** are the additives used in a paint formulation to enhance a film's flow and leveling to eliminate surface defects such as brush marks, orange peel and craters.

Important factors influencing flow and leveling of coatings include viscosity, surface tension and wet film thickness. Due to surface tension, the liquid film tends to minimize its surface area, which drives flow, reduces unevenness and creates an even surface (because an uneven film has greater surface area than a smooth film). Viscous resistance is the obvious factor countering the leveling influence of surface tension. Thus, lower viscosity after application of the wet coating promotes better flow and leveling but it will also lead to the problem of sagging. Generally, a more Newtonian rheology is desirable for better leveling. Deflocculated and well-dispersed systems provide more Newtonian flow, and therefore, good wetting and dispersing agents have a side effect of being leveling agents.

5.4.1 Solvents

As discussed before, low viscosity of the film is an important factor for better flow and leveling. With progressive evaporation of the solvents, the viscosity of the coating film increases rapidly. Therefore, slowly evaporating, active solvents are good leveling agents that allow sufficient time for the liquid film to level out any unevenness. Among the slow evaporating solvents, the choice is largely dependent on the binder system. Typical solvents are hydrocarbons such as alkylbenzenes, high boiling paraffinics, terpene solvents, esters such as lactates and esters of glycol ethers, ketones such as methyl amyl ketone, and glycol ethers such as 2-butoxyethanol.

5.4.2 Polymeric leveling agents

Polymeric leveling additives function through their tailor-made incompatibility in the paint film. During film formation, due to incompatibility, their molecules migrate to the interface. Unlike silicones, polymeric additives do not reduce the surface tension of the bulk of the paint film; rather, they reduce the local surface-tension gradient and thus create a physically uniform and flat surface. An important advantage of polymeric leveling additives over silicones or fluorosurfactants is that they do not cause any intercoat adhesion problem.

5.4.2.1 Polyacrylates

Polyacrylate leveling additives are homopolymers or copolymers of acrylates with alkyl, polyester or polyether modifications. They are normally supplied as solvent-free materials or as solutions. The performance of these additives is tailored through variations in their chemical composition (polarity and type of monomers) and MW, because their solubility and compatibility in coatings are dependent on these factors. Linear acrylic polymers are more incompatible than branched ones and those with higher MW are more incompatible than those with lower MW. Polyacrylate leveling additives for waterborne applications are also designed with incorporation of polar groups such as carboxylic acid groups or polyethylene glycol. An excessive dosage of polymeric leveling agents with high incompatibility tends to produce haziness in films.

5.4.2.2 Cellulose acetobutyrate

Cellulose acetobutyrate with high levels of butyric acid and medium MW is used as a leveling agent. It is typically used in wood coatings and automotive coatings. The low MW modifications are recommended for unsaturated polyester resins and UV-curable varnishes.

5.4.2.3 Other polymers

Some other polymers such as aromatic and aliphatic hydrocarbon resins, high MW alkylated amino resins, polyvinyl ethers and polyvinyl butyrals are utilized for the purpose of enhancing leveling. They are not marketed as leveling agents but are used in specialty products.

5.4.3 Silicones

Unmodified low MW silicones (dimethylpolysiloxanes) are used as leveling and surface flow additives. Some modified silicones are also used as surface-flow control agents. Such chemical modifications may be either in the backbone of silicones, by replacing some of the methyl groups with alkyl or aryl groups, or via grafting on side chains, such as polyethylene glycol. Many important properties of silicones such as compatibility, surface-tension reduction, heat stability, slip, and mobility in the paint film can be adjusted through such modifications. They work on the principle of migrating to the surface and eliminating local surface-tension differences resulting from solvent evaporation. Often silicone flow additives perform additional functions such as substrate wetting, slip improvement and providing anti-cratering effects. Silicones may reduce surface tension to a great extent, and therefore, overdosing may easily lead to side effects, such as poor wetting by subsequent coats and poor intercoat adhesion and foam stabilization.

5.4.4 Fluorosurfactants

Fluorosurfactants are anionic, cationic, or non-ionic surface-active materials having perfluorinated alkyl groups in their molecules. They strongly reduce surface tension and diminish the surface-tension gradient at the coating surface. They are more often used as anti-crater agents. The dosage of this type of flow additives should be just enough to achieve the desired effects, because they have side effects such as foam stabilization and poor intercoat adhesion when overdosed.

5.5 Defoaming and anti-foaming additives

Foam is a gas, usually air, that has been dispersed and stabilized in a liquid. Air may get incorporated in coatings during manufacturing (such as by agitation) or during application (such as by spraying or brushing). Foam may also be produced when paint is applied on porous substrates such as wood or mineral surfaces as a result of displacement of air from the pores by the liquid. Foam occurs more commonly in waterbased coatings. Coating formulations contain surface-active agents for various reasons, such as emulsifying agents in waterbased binders, wetting and dispersing agents, and substrate wetting agents. These surfactants may stabilize air in the form of foams.

Foam is always undesirable in coatings at any stage. Foam in the mill base during the pigment grinding stage acts as a cushion and hence reduces the stress transformation to pigment agglomerates that is necessary to break them apart. Foam may also create difficulty in filling cans with the correct amount of coating. Foam generated during the application process may lead to defects in films such as pinholes, craters or cissing. Apart from optical defects, foaming – even microfoam – may reduce the performance and protective properties of the coatings.

5.5.1 Foam formation and film stabilization

Generally, pure liquids do not foam, but coatings, being multicomponent systems, may produce foam. When air is introduced into a liquid coating, bubbles are formed, which rise through the liquid to the surface. Upon reaching the surface, liquid from the bubble wall starts to drain under gravitational force and it becomes thinner. If the liquid is pure, the bubble will burst as soon as it reaches the surface and no stable foam is formed. If the liquid contains surfactants, a stable foam can be formed. The stabilization of foam results from two effects across the foam lamella: the **electrostatic repulsion effect** and the **Marangoni effect.**

5.5.1.1 Electrostatic repulsion effect

Surfactants tend to concentrate in the lamella at a gas-liquid interface. With the drainage of the lamella, the inner and outer interfaces come closer together, and the electrostatic repulsion caused by the ionic groups of the surfactant prevents further drainage, so foam stabilization occurs.

5.5.1.2 Marangoni effect (Gibbs elasticity)

The foam lamella is elastic in nature due to the Marangoni effect, which is a mass transfer phenomenon resulting from a surface-tension gradient between two fluids. As the lamella is stretched, the concentration of the surfactant is reduced at the interface, producing a higher surface tension, which results in pulling the lamella back together by movement of the liquid from the area of low surface tension. This additional foam stabilization effect is known as **Gibbs elasticity.**

5.5.2 Defoamers and anti-foam

The terms defoamer and anti-foam are often used interchangeably, but they are not the same. A defoamer destroys an existing stabilized foam at the air interface. On the other hand, an anti-foam prevents the formation of a stable foam. However, it is difficult to distinguish between their mechanisms, and quite often, commercial products generally perform both tasks. We will use the term defoamer in subsequent discussion.

5.5.2.1 Requirements for defoamers

An effective defoamer must counteract the foam stabilization mechanism. Defoamers are low surface-tension liquids that have a controlled insolubility or incompatibility in the system to be defoamed, along with positive penetration and a positive spreading coefficient. When they enter the foam lamella and spread across the interface, the stabilizing surfactant molecules are displaced, resulting in lower cohesive strength of the lamella, which leads to rupture and collapse of the foam. The effect of such liquid defoamers can be boosted by adding finely dispersed hydrophobic particles, which help in destabilization by reducing the cohesive forces.

5.5.2.2 Composition of defoamers

Defoamers are mainly composed of active compounds, spreading agents and carriers. Spreading agents are surfactants that help in reducing the surface tension, while carriers are the solvents used to compound the other ingredients.

Defoamers for waterbased coatings

The main groups of defoamers for waterbased coatings are: mineral oilbased defoamers, silicone defoamers and fluorinated defoamers.

Mineral oilbased defoamers are composed of ~85 % carrier oil (aliphatic or aromatic mineral oil), ~10 % hydrophobic particles, with the remainder an emulsifier and other ingredients such as metal stearate and fatty acid derivatives. They are used in flat and semi-gloss emulsion paints but are not suitable for higher quality aqueous industrial coatings due to possible surface defects and gloss reduction.

Silicone defoamers are composed mainly of hydrophobic silicone oil (polydimethylsiloxanes). Pure silicone oil is effective, but overdose often leads to surface defects. Therefore, polyether modified polysiloxanes have been preferably used to give effective defoaming with negligible effect on appearance of the films. MW and side chain modifications are important considerations in their selection. For ease of incorporation, they are often supplied as emulsions. They may also contain hydrophobic silica to make them more effective. Possible adverse effects are poor intercoat adhesion or craters.

As a recent innovation, some fluorinated compounds and silicones with perfluorinated organic modifications, also known as fluorosilicone defoamers, are also used as defoamers. They are known for their very low surface tension and strong defoaming behavior.

Defoamers for solventbased coatings

Solventbased paints have significantly lower surface tension than aqueous paints. Mineral oils are not useful as defoamers for such paints, and therefore, silicone defoamers are widely used. Pure polydimethylsiloxanes with MW 10,000 to 100,000 can be used as defoamers. Their compatibility is an important consideration, as they can cause surface defects such as cratering. Their compatibility is controlled by using organically modified polysiloxanes such as those with polyether side chains.

5.6 Additives for surface modification

Mechanical properties such as hardness, scratch resistance and mar resistance of the coating surface as well as the surface slip are mainly defined by the binder of the system; use of additives makes it possible to control such surface characteristics independently from the coating binder.

The gloss of the coating is one of the important optical surface properties that is dependent on the resin system, pigment particles and extenders. Apart from these parameters, gloss can also be controlled by additives called **matting agents.**

5.6.1 Slip and mar additives

Slip is a term used to describe the smoothness, feel and slipability of a coating surface. It may also be related to the friction or lubricating aspect (feel) of the coating surface. Mar resistance is the ability of the coating to withstand mechanical abuse, such as abrasion. In many practical circumstances, an additive that provides better slip to the coating is also likely to give better mar resistance, improved scratch and scrub resistance, reduced metal and black heel marking and better anti-blocking properties. These additives modify the surface rather than bulk of the coating to impart such properties; therefore, such additives should migrate to the surface for effectiveness. Waxes and silicone-based oils are the most common materials used to improve slip and mar resistance.

Pure polydimethylsiloxane (low MW) or modified polysiloxanes are widely used as slip and mar additives in both solventborne and waterborne systems. Most are surface active and hence migrate to the surface and reduce surface irregularities, giving a much smoother film. The organic modifications in the additive molecule are oriented inside the coating film, while the polysiloxane units orient outside the paint surface. The presence of such a thin film of the silicone reduces sliding friction, which results in better feel and improved mar resistance. Similarly to other silicone additives discussed, their overdosing may result in many film defects and possible recoating problems.

The waxes used as slip additives are incompatible with the binder and hence migrate to the surface of the film, where they improve the lubricity and feel of the coating. The waxes that are most commonly used in modern coatings are synthetic waxes such as polyethylene, polypropylene, Fischer-Tropsch waxes, or ethylene vinyl acetate waxes. For easy incorporation in coatings, waxes are supplied as fine dispersions in a carrier such as water or organic solvents, as well as micronized waxes in fine powder form. Waxes with different degrees of hardness, melting points and polarities are used in these preparations in order to meet the various requirements of different applications. Normal dosage levels for wax-based slip additives are higher (1 to 3 %) than silicones.

5.6.2 Matting agents

In many applications, satin or low-gloss finishes are preferred over high-gloss finishes for reasons such as having an elegant and luxurious appearance, hiding imperfections of a large surface area or even safety reasons, such as on the dashboards of cars. Reduction in gloss can be achieved by increasing PVC or by introducing incompatibility into the binder. These approaches are not suitable in some formulations where certain mechanical properties or film clarity

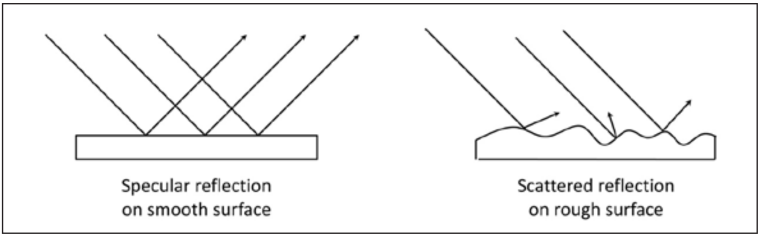


Figure 5.10: Reflection of light on smooth and rough surface

are important. Matting agents are additives that allow better control of gloss without impairing other properties of the coating. Some of the commonly used such additives are silica, polymethyl ureas and waxes.

Synthetic amorphous silica (precipitated and fumed) is the most widely used matting agent in the coating industry. These types of silica are of very low particle size and are often surface-treated to improve compatibility with all major resin systems. They generate micro-roughness into the surface of the coating film, which results in diffused scattering of the incident light and hence matting. However, they tend to increase viscosity of the systems. The refractive index of silica is very close to that of common binders; therefore, they can be used as a matting agent in clear finishes without any haziness. They are very effective and are used at levels of up to 3 % by weight in paint. Natural silica such as diatomaceous silica is also used occasionally together with extenders to produce a matte finish.

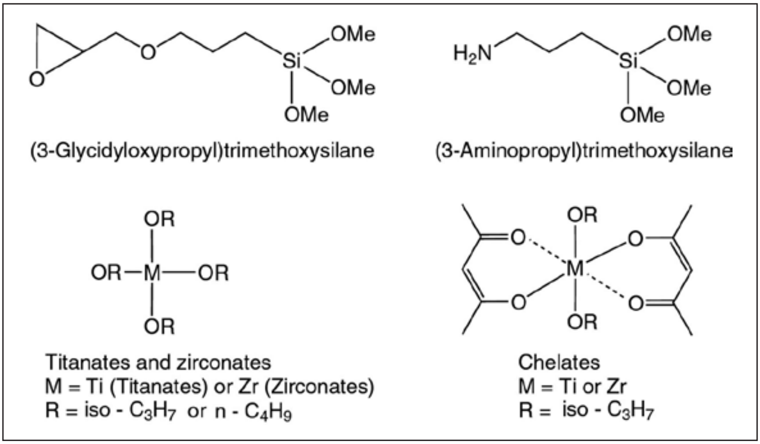
Organic matting agents such as micronized polymethylurea resins and polyethylene and polytetrafluoroethylene modified polyethylene waxes are used in coatings. They are incorporated in coatings by hot precipitation or as a dispersion. Like silica, they produce matting by migrating to the surface and producing micro-roughness. This affects how light is reflected from the surface (Figure 5.10).

5.7 Adhesion promoters

Adhesion is a key property of coatings and can influence many other mechanical and performance properties. Adhesion can be defined as the resistance of the coating film to mechanical separation from the substrate. While the nature of the binder is the primary factor influencing adhesion, it can be improved by the use of additives called **adhesion promoters.** Characteristics of the substrate are also very important factors governing adhesion.

Adhesion of a coating film to the substrate can be improved by mechanical surface treatments such as sanding or grit blasting, as well as other surface treatments such as chemical etching, flame treatment, plasma treatment or conversion coatings. In circumstances where these methods are not possible, improvements in adhesion must be achieved through careful selection of components in the paint formulation and using adhesion promoters.

Adhesion is a complex phenomenon involving physically and chemically induced intermolecular interactions at the coating-substrate interface. Almost all adhesion promoters work through a common mechanism associated with their unique molecular structure, which essentially contains two different functional groups, one of which can react with the substrate and the other with the polymer matrix of the coating film. This results in a chemical bridge between the two through strong covalent bonds, which improves the adhesive strength.



(3-Glycidyloxypropyl)trimethoxysilane

(3-Aminopropyl)trimethoxysilane

Titanates and zirconates
M = Ti (Titanates) or Zr (Zirconates)
R = iso - C_3H_7 or n - C_4H_9

Chelates
M = Ti or Zr
R = iso - C_3H_7

Figure 5.11: Examples of adhesion promoters

Because of a wide variety of coating systems and various types of substrates, it is impossible to have a single additive that may be used universally in all systems. Typical classes of commercially available adhesion promoters are organofunctional silanes, titanates, zirconates, zircoaluminates, alkyl phosphate esters, amides, imines and metal organic complexes. Some examples are shown in Figure 5.11. They all have their own merits and demerits. Silanes, titanates and zirconates are available with a wide range of organic modifications and have excellent solubility in organic solvents, but they are sensitive to water to varying degrees. Zircoaluminates, alkyl phosphate esters and metal organic complexes are less water sensitive but have limited solubility in organic solvents. The choice of the most suitable adhesion promoter, therefore, will depend on the type of polymer and substrate in question.

5.8 Additives for film formation

For thermoplastic binders, film formation occurs merely through evaporation of the volatile solvent or water. In the case of thermosetting binders, the extent of chemical cross-linking is an important factor influencing their mechanical and performance properties. Catalytically active additives are used in such systems to accelerate cross-linking reactions. In the subsequent chapters, some commonly used catalysts for thermosetting coatings are briefly discussed.

5.8.1 Driers

Some thermosetting binders, such as resins based on drying oil modified resins, like alkyds and epoxy esters, are cured by a cross-linking reaction that is triggered by the diradical and atmospheric oxygen; this is commonly known as oxidative or autoxidative curing. The first step in the cross-linking reaction is oxygen uptake by the film and autoxidation of an active methylene group of an unsaturated fatty acid by oxygen to form hydroperoxide. Subsequent steps in the autoxidation process involve hydroperoxide decomposition to a free radical, which in turn initiates the curing reaction (polymerization). The autoxidation process proceeds at a very slow rate that is practically not acceptable; therefore, catalysts are used to speed up drying of such systems.

Driers, also referred as **siccatives**, are compounds used to catalyze the autoxidation process in drying or semidrying oil based resins at ambient or elevated temperatures. They are typically organometallic compounds, most commonly metal soaps of long chain monocarboxylic acids, supplied in a suitable solvent (carrier). These metal soaps are synthesized from a variety of metals and acids. Although the metal, being the active part of the compound, effects the drying reaction, the monocarboxylic acid component confers solubility and compatibility of the drier in solvents and resin.

The first driers were based on fatty acids or rosin, which were subsequently replaced by naphthenic acid, a material obtained from crude petroleum. Due to scarcity of naphthenic acid, in modern driers it has been replaced by branched chain synthetic acids such as 2-ethylhexanoic acid and neodecanoic acid.

Driers are supplied commercially as solutions in hydrocarbon solvents such as white spirit and a low amount of alcohols to improve stability against precipitation. Driers are generally specified by their metal content in the supplied form.

Based on their catalytic effects, driers can be classified into two groups: active driers (primary) and auxiliary driers. **Active driers** are soaps of metals that have more than one oxidation state and therefore act as redox catalysts. They promote the uptake of oxygen and decomposition of hydroperoxides, which leads to cross-linking of resins that produce tack-free films. They are also known as surface or top driers. Another group of metals with a single oxidation state have a weak catalytic effect when used alone but are effective in combination with active driers. Some that promote the polymerization reaction for curing of resins are termed **through-driers**, while others that enhance the effect of redox catalysts are known as **auxiliary driers**. Certain driers are ineffective at ambient conditions but they are catalytically active at elevated temperatures. Common examples of active driers (redox type) are cobalt, manganese, cerium, vanadium and iron, while examples of through-driers are lead, zirconium, lanthanum, neodymium, aluminum, bismuth, barium and strontium. Some widely used auxiliary driers are calcium, lithium, potassium and zinc. Some pure organic compounds are also known to act as driers. Such driers function by their interaction with carboxyl and hydroxyl groups on the alkyd, producing coordination linkages. In effect, they act as through-driers and are also called coordination driers. Generally they are used along with a primary drier, such as cobalt, to give optimum drying performance, provided that the resin has sufficient acid and hydroxyl groups.

Cobalt is the most important and most widely used active drier metal that acts as a surface drier. If used alone or excessively, it may cause surface wrinkling and poor through-drying. In recent days, use of cobalt is becoming questionable due to its possible toxicological effects. Other cobalt-free alternatives are available on the market. They include coordination complexes of metals such as iron, acting as an effective substitute for conventional cobalt-based driers. Manganese and vanadium are other alternatives to cobalt. Manganese is an effective active drier, but it is not suitable for white paints, as it can cause considerable discoloration.

Iron and cerium driers effectively catalyze polymerization and through-drying at elevated temperatures and therefore are used in baking enamels. Iron driers have the limitation of dark color, and hence cerium based driers are often preferred where color retention is important.

Lead was used for years as a very effective through-drier, but for ecological and toxicity reasons, is rarely used in recent years. Zirconium driers are by far the most widely accepted replacements for lead. They improve through-drying mainly by the formation of coordination bonds with hydroxyl and carboxylic acid groups of the resin, and also by increasing the catalytic effect of primary driers.

Zinc driers have the capability to keep the film open, thus permitting curing of the film through the entire thickness and preventing surface wrinkling. Zinc driers are also used as effective wetting and pigment dispersing agents. Calcium driers are very useful and effective when used along with cobalt and zirconium to promote drying under adverse weather conditions, such as low temperatures and high humidity.

A combination of primary and auxiliary driers is often used to achieve optimum curing with the minimum drier dose. Some optimized combinations are sold as mixed driers. Most driers are added in the let-down stage of paint manufacturing, except for auxiliary driers such as zinc and calcium that are generally added to the mill base due to their effectiveness as wetting and dispersing agents.

5.8.2 Curing catalysts

The performance properties of thermosetting coatings, which rely on a chemical reaction between different functional groups to give a cross-linked polymer network, are dependent on the extent of the cross-linking reaction and hence the cross-link density. Similarly to other organic chemistry reactions, cross-linking reactions may be significantly accelerated at higher temperatures or by the use of a catalyst. Apart from decreasing the reaction time and temperature of curing, some catalysts may also be helpful in selectively catalyzing required chemical cross-linking reactions and minimizing undesirable competing side reactions. Catalysts for a wide range of thermosetting resin systems are commercially available, but this chapter will cover examples of catalysts important for some commonly used cross-linking systems.

5.8.2.1 Catalysts for polyurethane coatings

Polyurethane coatings, one of the most important coating systems among the modern high performance coatings, are two-component systems based on polyols and isocyanates. Curing occurs

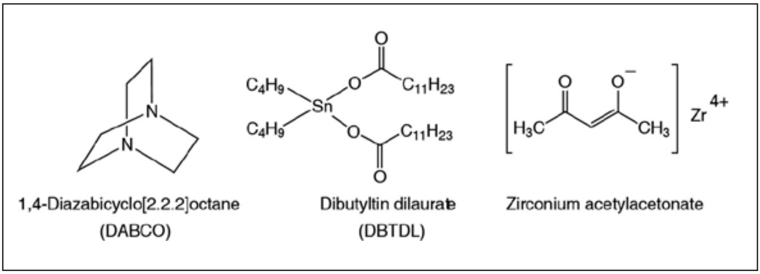


Figure 5.12: Catalysts for polyurethane

at ambient temperature. Aliphatic polyisocyanate-based systems react more slowly than aromatic ones, and therefore, they need to be catalyzed. The catalysts used for polyurethane systems can be broadly categorized as **tertiary amines** and **metal catalysts**. Some of the important ones are described below, with examples shown in Figure 5.12.

While dibutyltin dilaurate has been the most commonly used catalyst over the years, it is being replaced by safer alternatives such as bismuth and zinc carboxylates. Zirconium-based catalysts are preferred in waterbased two-component systems because of their better selectivity for isocyanate-hydroxyl reactions over isocyanate-water reactions.

5.8.2.2 Catalysts for epoxy system

Epoxy resin cross-linked with an amine functional resin is also an important coating system used in high-performance applications. Catalysts used for such systems have been either acidic compounds bearing phenolic hydroxyl groups or a tertiary amine. One of the most commonly used catalysts for two-component epoxy systems is tris(dimethylamino)phenol (Figure 5.13).

Epoxy/carboxy/acid anhydride systems are also important in OEM clear coats and powder coatings. Catalysts such as tertiary amines, amidines and imidazoles, 1,4-diazabicyclooctane and some alkaline metal-based catalysts such as zinc-based catalysts are commonly used.

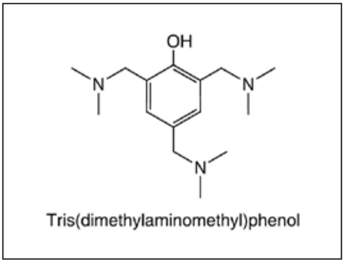
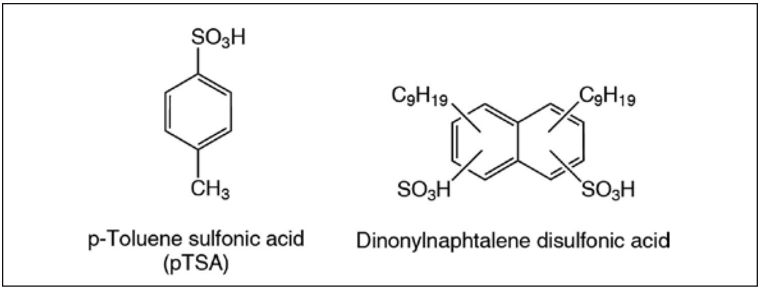


Figure 5.13: Example of catalyst for two-component epoxy system

5.8.2.3 Acid catalysts for baking systems

One-component baking types of coatings in which resins such as alkyd, polyester, hydroxyl functional acrylic or epoxy esters are cross-linked with amino resins are typically catalyzed by acid catalysts. Strong acid catalysts such as sulfonic acid and phos-



p-Toluene sulfonic acid (pTSA)

Dinonylnaphtalene disulfonic acid

Figure 5.14: Acid catalysts for amino-cured backing systems

phoric acid are generally used. Even though less reactive hexamethoxymethyl melamine resins are used in coatings, the curing rate can be accelerated significantly by use of a strong acid catalyst. Different types of acid catalysts varying in their acid strength are commercially available. The type and amount of catalyst is determined by the curing conditions of the coating, such as specific stoving temperature and time. High acid strength and high addition levels negatively impact their storage stability. The storage stability of coatings with a strong acid may be improved by blocking the acid group with amines to form a salt. At higher temperature curing, the amine evaporates and acid is released, triggering its catalytic effect. Some important examples of such a catalyst are shown in Figure 5.14.

5.8.3 Photoinitiators

UV curing is an environmentally friendly coating technology in which binder is cured on exposure to UV radiation via either free-radical copolymerization or cationic polymerization. The vehicles of UV-cured coatings contain oligomeric resins and reactive diluents. The main resin types for such coatings are radically polymerizable unsaturated polyesters and acrylates or methacrylate terminated oligomers of polyepoxides, polyesters, polyurethanes and polyethers, as well as epoxies and vinyl ethers that are cured cationically. The UV-curing process invariably requires generation of free radicals or cations that initiate polymerization and

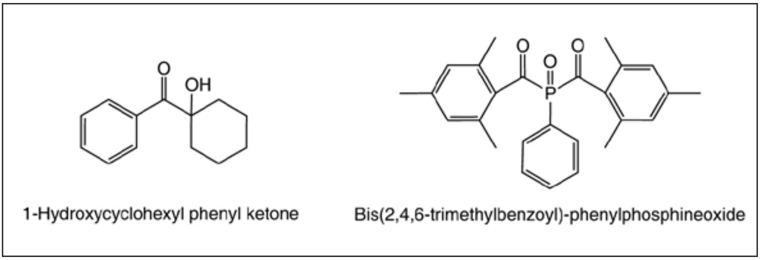


Figure 5.15: Type I free-radical photoinitiators

curing reactions. **Photoinitiators**, also known as **UV initiators**, are compounds capable of absorbing UV radiation and generating active species such as free radicals or cations. Therefore, they are the essential additives in any UV-curable coating composition. Photoinitiators are classified into two major classes; photoinitiators for radical polymerization and photoinitiators for ionic polymerization.

Free-radical photoinitiators are further divided into two types:

- Those that undergo intramolecular bond cleavage, known as homolytic fragmentation type or Type I photoinitiators (α-cleavage type). Examples are benzoin ethers, substituted acetophenone derivatives, acyloxime esters, benzil ketals, and cyclic benzoin and benzils. Representative examples are shown in Figure 5.15.
- Those that undergo intermolecular H-abstraction from an H-donor, known as H-abstraction type or Type II photoinitiators (non-fragmentation type). Tertiary amines with abstractable a-H atoms have been shown to be particularly effective as synergists (H-donors). Type II photoinitiators include benzophenone, Michler's ketone,

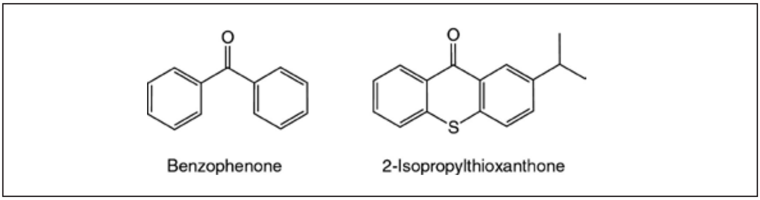


Figure 5.16: Type II free-radical photoinitiators

thioxanthones, benzils and quinines. Representative examples are shown in Figure 5.16.

5.8.4 Coalescing agents

Latex-type binders account for a large volume of waterbased coatings. Film formation in a latex paint involves the coalescence or fusion of discrete polymer particles of high MW polymers. When the film is applied, the polymer particles are pushed against each other under the capillary forces generated due to progressive evaporation of water. This results in coalescence at the particle boundaries, with interdiffusion of polymer chain across the boundaries (Figure 5.17).

For this phenomenon to occur successfully, the molecules within the polymer particles must have sufficient mobility to facilitate

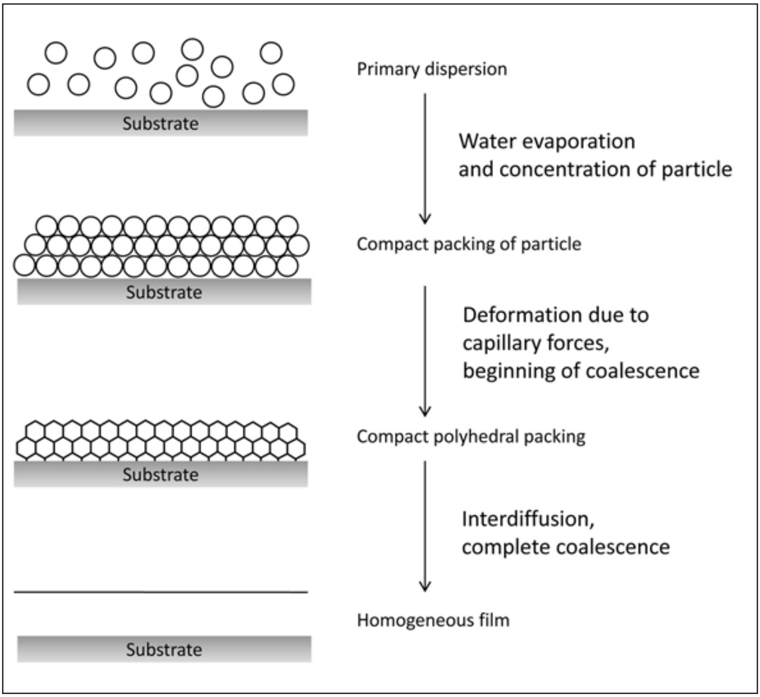


Figure 5.17: Film formation in latex (coalescence)

coalescence and allow the formation of a coninuous, integral film. This is most successful if the polymer has a sufficiently low T_g. The resulting films in such cases will be too soft to meet some of the resistance properties required by paint films. In order to address this problem, the T_g of a latex polymer can be reduced temporarily by the incorporation of high boiling solvents, known as coalescing agents, that will eventually evaporate, leaving a hard film due to the high T_g of the original latex polymer. Thus, coalescing agents are additives that are added to provide temporary plasticization of the latex particles, which is necessary for efficient coalescence and hence film formation.

For each latex, there is a characteristic limiting temperature above which the polymer particles are soft enough to coalescence completely under the influence of capillary forces. This temperature is known as the minimum film-forming temperature. The coalescing agents help in lowering of this temperature for a given latex and facilitate coalescence and the film formation process of latex paints, even at temperatures lower than the **minimum film-forming temperature** (MFFT) of the latex.

A typical coalescing agent is an organic solvent that exhibits most of the following characteristics:

- Migrates into and swells the polymer particle
- Has no effect on the stability of latex
- Has minimum solubility in water so that it preferentially dissolves in the polymer
- Evaporates quickly after film formation
- Has low odor.

Glycols, glycol ethers and their acetates, and ester alcohols have been widely used as coalescing solvents. Many of the coalescing agents are VOCs; the recent trend is to use non-VOC type coalescing agents. One of the most commonly used coalescing agents is

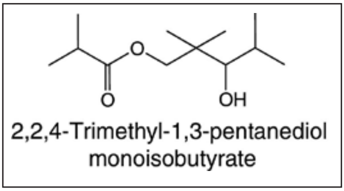


Figure 5.18: Example of coalescing agent

from the class of ester alcohols (Figure 5.18). In addition to facilitating film formation, coalescing agents can also influence other characteristics of coatings such as flow and leveling, wet-edge time and rheology.

5.9 Anti-skinning agents

Skinning is the formation of a film on the surface of a liquid coating containing oxidatively curing binder as a result of its reaction with the oxygen in the headspace in a can. It is particularly noticeable in partially filled cans. Skinning is an undesirable phenomenon because it results in material losses, delayed painting process due to time-consuming skin removal, and poor appearance of the film due to residual small skin particles. To prevent skin formation during production and storage in the can, anti-skinning agents are added, which are a type of inhibitor (antioxidant) that temporarily prevent or retard oxidative curing. As their effect is opposite to that of driers, they must fulfill two important requirements:

- They must retard oxidative curing in the paint container
- They must not retard oxidative curing of the coating film when applied.

5.9.1 Types of anti-skinning agents

Two important classes of anti-skinning agents used in the coating industry are phenols and oximes (Figure 5.19).

5.9.1.1 Phenols

Sterically hindered phenol derivatives are commonly used as anti-skinning agents because of their powerful antioxidant action, causing considerable loss-of-dry. Typical examples are butylated hydroxytoluene (BHT), and o-isopropyl phenol (Figure 5.19). They act as anti-skinning agents by scavenging free radicals and thereby terminating the polymerization reaction. Due to their considerable anti-oxidant effect, they must be added in low amounts, 0.05 to 0.2 % by mass of the paint, in order to avoid impairing the oxidative drying of the film. Another limitation of additives of this type is that they may cause yellowing of the film.

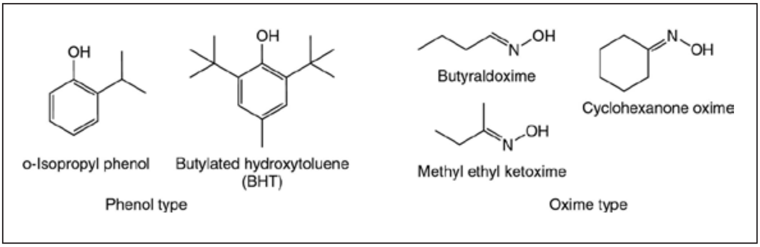


Figure 5.19: Anti-skinning agents

5.9.1.2 Oximes

Oximes are widely used as anti-skinning agents, but they are mild antioxidants. Their main contribution to antioxidant properties comes through their ability to form labile chelates with metal ions of driers, making them temporarily inactive. Complex formation is reversible, so that in actual drying conditions, the complexes are cleaved and the drier becomes active again. They are volatile and leave the film during the drying process; therefore, their use is not as critical as that of phenols with respect to the loss-of-dry problem. Typical loading levels are 0.05 to 0.3 % of the total mass of the paint. Methyl ethyl ketoxime is probably the most widely used anti-skinning agent, but butyraldoxime and cyclohexanone oxime also find use when low odor is required. Methyl ethyl ketoxime was classified as a carcinogen by the European Union in 2001, and therefore its use is restricted.

5.10 Light stabilizers

Coatings for exterior applications, such as automotive coatings, are subjected to severe weathering, causing degradation of coating binders. The primary damaging components of weather are light (especially UV radiation) and oxygen, though other factors such as moisture, fluctuations in temperature and acid rain also influence damage to some degree. UV radiation has sufficiently high energy to cause photooxidative degradation of some polymers as well as fading of several pigments. Photooxidative scission of long, tough polymer chains occurs via radical generation, and formation and decomposition of peroxides transforms them into small fragments. The result of this degradation is chalking, embrittlement, cracking, delamination, flaking, loss of gloss and drift in color.

The resistance of a coating to weathering is mainly driven by type of binder and presence of pigments in the film. Not all pigments are good UV absorbers, nor is every coating pigmented (such as automotive clear coats). Therefore, certain additives known as **light stabilizers** are often added to exterior coatings to improve performance of the coating in exterior conditions. It is possible to stabilize polymers against photodegradation in two ways:

- Prevention of radical formation by competitive UV absorption (filtration of UV) from added **UV absorbers**
- Trapping of the generated radicals before they are involved in polymer degradation reactions by using **radical scavengers**.

5.10.1 UV absorbers

UV absorbers (Figure 5.20) are organic compounds that absorb harmful UV light and dissipate the absorbed energy as harmless thermal energy. Important classes of UV absorbers are 2-hydroxybenzophenones, benzotriazoles, hydroxyphenyl-s-triazines, and oxalanilides. Some other compounds such as hydroxyphenylpyrimidines, salicylic acid derivatives and cyano acrylates are also useful.

The key to effectiveness of these compounds is intramolecular hydrogen bonding and their tautomeric characteristics upon absorption of UV radiation. UV absorbers should have good solubility, compatibility with the binder and thermal stability. They should selectively absorb UV light in competition with the binder to protect it from degradation. Their protective effect increases with an increase in their concentration, inherent absorption and film thickness. Thus, they pro-

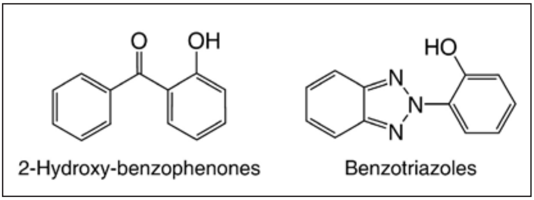


Figure 5.20: UV absorbers

tect the substrate and deeper layers of coating, but as such, there is no protection at the surface of the coating.

5.10.2 Radical scavengers

UV absorbers do not protect the surface of coatings, and therefore, they are often supplemented by another type of light stabilizers called radical scavengers. In contrast to UV absorbers, radical scavengers act at the coating's surface as well as in bulk, and act only when free radicals are generated. They are based on sterically hindered amines, most commonly known as **hindered amine light stabilizers (HALS).** All the technically important hindered amine light stabilizers have the 2,2,6,6-tetramethylpiperidine group as their basic structure.

Even the small amount of UV light that is not absorbed by a UV absorber will generate free radicals capable of starting the degradation process. Hindered amine light stabilizers scavenge these radicals to protect the polymer from degradation. In the process, under the influence of light and oxygen, these light stabilizers form a nitroxy radical as an active agent, which reacts with polymer radicals to produce an amino ether. The generated aminoether in turn consumes the peroxy radical to regenerate nitroxy radical. As all the active radicals, including peroxy radicals, are transformed to non-free radical compounds, the degradation reaction is terminated. A simplified scheme showing the mode of action of hindered amine light stabilizers is shown in Figure 5.21.

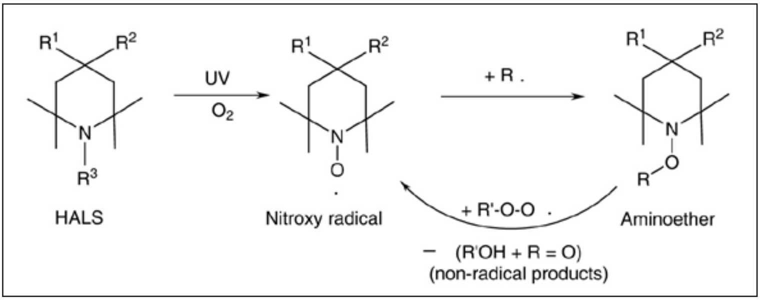


Figure 5.21: Mode of action of hindered amine light stabilizers

1,2-Benzisothiazolin-3-one (BIT)

2-Methyl-4-isothiazolin-3-one (MIT)

Figure 5.22: In-can preservatives

Typically hindered amine light stabilizers are used up to 3 % by mass of coating, depending on other formulation parameters such as type of binder and pigments. A combination of UV absorbers and hindered amine light stabilizers are often used in demanding applications due to their synergistic effect.

5.11 Biocides

Biocides are compounds that, even at low concentration, inhibit the growth of microorganisms. Many coatings are susceptible to attack, both in-can and as dry films, by microorganisms such as bacteria, fungi and algae. Addition of biocides such as fungicides, bactericides and algaecides are necessary to eliminate problems caused by microbiological attack. Based on their purpose of action, biocides fall into two broad categories: in-can preservatives and dry-film preservatives.

5.11.1 In-can preservatives

In general, in-can preservation is a much bigger problem for waterborne paint compared to solventbased paints. In solventbased coatings, the organic solvents are not conducive to growth of microorganisms. Microbial growth in liquid paint may often result in problems such as gassing, obnoxious odor, staining, pH drift and viscosity drop in paints containing cellulosic thickeners. Bacteria and fungi are the major reasons for such in-can problems. An in-can preservative should have high water solubility and stability over a wide range of pH values. Once the film is dry, it should degrade or evaporate from the film without any side effect on film performance.

Some cost-effective broad spectrum in-can preservatives include isothiazolinone derivatives (Figure 5.22) such as benzisothiazolinone, methylisothiazolinone and 5-chloroisothiazolinone. They are effective against bacteria, fungi and yeasts. Formaldehyde-releasing compounds such as o-hydroxymethyl compounds (hemiformals), 1,3-oxazolidines and N-hydroxymethyl chloracetamide are also effective in-can preservatives that can be used alone or in combination with other biocides. Alkyl and halogen substituted phenolic compounds such as sodium salts of o-phenylphenol have also been used as effective preservatives. Owing to their potential physiological harmfulness, their use has been restricted.

5.11.2 Dry-film preservatives

Dry films are also subject to microbiological attack by fungi and algae, which impairs the aesthetic appearance of the film by discoloration or patching. In certain situations, this also affects film integrity and hence performance of the coatings. Dry-film preservatives are aimed at preventing the growth of bacteria, fungi, and algae on the paint film surface. As opposed to in-can preservatives, the solubility in water and volatility of dry film preservatives should be as low as possible in order to prevent leaching from the film and to ensure long-term film protection.

Some important examples of dry film preservatives include benzimidazoles such as carbendazim, octylisothiazolinone, carbamates and dithiocarbamates such as thiram, zinc pyrithione and chlorothalonil. Representative examples are shown in Figure 5.23. As with in-can preservatives, the optimum use levels should be determined by experiments.

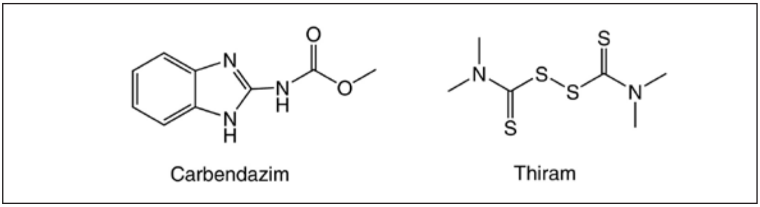


Figure 5.23: Dry film preservatives

5.12 Corrosion inhibitors

Protecting metallic substrates against corrosion is one of the prime functions of most coatings. Corrosion resistant coatings are typically formulated using anticorrosive pigments and suitable binders with the optimum formulation parameters. In addition, organic compounds known as **corrosion inhibitors** are often added at low levels, and can effectively reduce the corrosion rate of a metal or slow down the individual corrosion reactions.

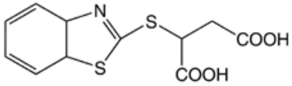
Various organic compounds are useful as corrosion inhibitors, such as acetylene derivatives, heterocyclic compounds containing nitrogen, sulfur and/or oxygen, long-chain aldehydes and ketones, amines, carboxylic acids and their derivatives, thiourea derivatives and thiophosphates.

Based on their function, the corrosion inhibitors used in the coating industry are classified into two categories:

- Flash-rust inhibitors (temporary corrosion protection)
- Inhibitors for long-term protection

5.12.1 Flash-rust inhibitors

Flash rusting is the phenomenon of formation of small brown rust spots that appear very soon after application of waterbased systems directly to steel. The problem is more prominent when the steel surface is active (for example, after blasting) and the pH is <7. To combat this problem, flash-rust inhibitors are added to waterbased coatings. They should have good water solubility. Flat surfaces are relatively easy to protect, while weld areas are considered difficult. Flash-rust inhibition at a weld area can be achieved by a combination of different products. Flash-rust inhibitors are typically based on ammonium and sodium nitrites, benzoates, metaborates and phosphates, occasionally in combination with materials such as morpholine and amino methyl propanol. Some other organic salts are also used, such as amine salts of 2-mercaptobenzothiazolyl succinic acid and calcium or barium salts of linear alkyl naphthalene sulfonic acids. Typically they are used at levels of 0.1 to 1.0 % of the total mass of paint. They also help in preventing in-can corrosion upon storage of aqueous paint.



2-Mercaptobenzothiazolyl-succinic acid

Figure 5.24: Example of a corrosion inhibitor

5.11.2 Inhibitors for long-term protection

Inhibitors for long-term protection are substances with low water solubility. The commercially available products are either used as a replacement for traditional anticorrosive pigments as the sole inhibitor or in combination with pigments to synergistically enhance anodic protection. Their use in coatings is expected to increase with rapid development of waterbased anticorrosive paints, in which some of the traditional anticorrosive pigments have limitations of compatibility and lower efficiency. Their usage level is higher than that of flash-rust inhibitors but markedly lower than anticorrosive pigments.

Typical examples of commercially used inhibitors are amine/zirconium complexes of toluylpropionic acid, zinc salts of 5-nitroisophthalic acid, zinc salts of cyanuric acid, zinc and magnesium salts of dodecylnaphthalenesulfonic acid and 2-mercaptobenzothiazolyl-succinic acid (Figure 5.24), and metal salts of aminocarboxylates.

5.13 Freeze-thaw stabilizers

Waterbased coatings have the inherent problem of the high freezing point of water. When some waterbased systems are exposed to subzero temperatures, water will freeze, causing destabilization of the paint. To resolve the problem, anti-freezing agents are added to depress the freezing point of the water in paints, and are commonly known as freeze-thaw stabilizers. Glycols are particularly effective for this purpose, and ethylene and propylene glycols have been widely used for years, though glycol ethers have also been successfully used. Coalescing solvents also decrease the freezing point of water and act as freeze-thaw stabilizers in addition to aiding coalescence.

5.14 Moisture scavengers

Certain coating systems such as polyurethane or coatings containing metallic pigments such as aluminum or zinc are very sensitive to moisture. Moisture can get into the coatings by a variety of routes, such as by being dissolved in solvents or absorbed onto the surface of pigments and extenders. To avoid the potential problems due to moisture, generally, properly dried and moisture-free raw materials must be used. Despite this, it is always advisable to use moisture scavengers to remove any residual traces of water or to take care of any possible ingress of moisture during and after manufacturing of paint.

In polyurethane systems, isocyanate curatives are reactive to moisture. The reaction between isocyanate and water produces carbon dioxide and an amine, which will cause gassing in the can or an increase in viscosity, which ultimately leads to gelation. To overcome this problem, aluminum silicate-based molecular sieves and finely divided silica gel are used to react with water. Some other options such as monomeric isocyanates, oxazolidines and triethyl orthoformate have also been used for this purpose. In coating systems containing finely divided metallic zinc and aluminum pigments, these metals react with water to produce hydrogen gas. Moisture scavengers such as molecular sieves and silica gels are used to prevent the problem.

5.15 Additives to modify conductivity

Electrostatic spraying, one of the important coating application techniques, relies on an electric charge on atomized droplets of the paint for higher transfer efficiency. The charged droplets are attracted to the surface of the target object, which has been grounded. Too high an electrical resistance of the liquid paint material would result in poor application and low transfer efficiency. The resistance of a liquid paint, therefore, should be adjusted for better electrostatic spray application of coatings. A resistivity between 10^4 and $10^7\ \Omega\ m^{-1}$ is suitable for good transfer efficiency. While resistivity is normally adjusted using proper solvent combinations, quite often it is supplemented by small quantities of quaternary ammonium salts for an improved effect. Care must be taken to decide the correct level, because too high a conductivity will result in charge leakage at the gun, a reduced electrostatic field and lowered transfer efficiency.

Another area where such additives are needed to improve conductivity is for imparting antistatic properties. Antistatic additives may be added to hydrocarbon solvents to improve conductivity and hence avoid any electrostatic buildup and risk of spark and fire hazard during transfer, storage and transportation.

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V. Mannari, C.J. Patel: Understanding Raw Materials

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