Principles of Organic Coatings and Finishing

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By

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Preface

This textbook is written for college students as well as for scientists and engineers newly entering the field. After college students learn fundamental chemistry knowledge, they do not necessarily know how to use the knowledge in industrial practices. Senior college students need to have some basic knowledge of industrial practices to satisfy employment demands; while graduates have usually carried out profound study in a major field, they often have insufficient industrial background. This book provides the principles of organic coatings and finishing based on intellectual fundaments and general chemistry knowledge.

A coating film with a thickness of a few microns to 1mm can achieve the required performance both regarding decoration and protection, and so the use of coatings in industry is economic and efficient. In practice, organic coatings are applied on the surfaces of automobiles, machinery and equipment, marine applications (i.e., ships), furniture, buildings and so on.

However, books on the subject usually have great length and highly complex content, and they often seem to readers to be empty and abstract.

The present book answers this dilemma. Coating materials are presented from the perspective of chemical reactions and the mechanisms of film formation. These mechanisms are easily understood, and the content is accessible to readers. Many finishing processes are introduced with figures or flow charts. Moreover, examples and exercises are used to demonstrate how to adjust the performance of coating materials and coating films. All these help readers obtain a deep understanding of the principles underlying the techniques.

Coating performance is expressed in relation to the molecular structures, chemical bonds and intermolecular forces of the polymers used in coating formulations. For example, the presence of electron-donating groups in aromatic rings or abstractable H atoms causes polymers to have poor photochemical oxidization resistance. The incorporation of large amounts of chlorine atoms into natural rubber produces chlorinated rubber, and the intermolecular forces of rubber are greatly increased by chlorination, resulting in dense films with low permeability. A deep analysis of the molecular structures and chemical bonds of resins and compounds makes it easy for readers to learn the properties of coatings. Moreover, organic coatings composed of binders, pigments, solvents and additives are mixtures, and so this book also provides basic knowledge and skills in handling mixtures (i.e., polymer mixing by the controlling of their structures, materials dissolved in organic solvents, water dispersions of polymers, and solid particles in liquid systems).

The purposes of organic coatings and finishing are to obtain required coating films, and organic coatings and finishing are intertwined with each other. The demands of organic finishing frequently drive innovations in the field of organic coatings. For instance, minimal or non-sanding surfacers have been developed due to costly and labour-intensive sanding operations on painting production lines.

Some organic finishing techniques, such as electropainting, electrostatic spraying and coil coating, are the landmarks of modern industrial manufacturing. Specific coating materials have been developed for finishing techniques. Therefore, this book introduces organic coatings and finishing, although organic finishing is usually considered as a part of industrial manufacturing.

Coatings and their application began in ancient times and were present in the form of skills or crafts. Traditional tests of coatings often give only a "yes/no" judgment, and it is difficult to correlate such test results with science. The consistent control of flow properties is of the utmost importance throughout the manufacturing and application processes of organic coatings. Rheological techniques provide measurable technical means for assessing coatings by the use of rotational rheometer and dynamic mechanical analysis (DMA). Rheological tests, especially oscillatory ones, correlate mechanical properties with chemical transformations in the sample. This is used to investigate the interactions between paint components for academic discussion. What's more, rheological techniques are used to resolve practical problems, such as the sedimentation of pigments, the selection of coating additives, the selection of operation parameters, and the optimization of coating material formulation and the painting process.

For these reasons, references are collected and compiled to establish a rheology of coatings. This content is scattered through the sections "3, Rheology of coatings" in chapter 3; "2.2, Separation" and "2.3, Stabilization" in chapter 5; "6.2, Levelling and sagging" in chapter 7; and "6.3, Viscoelasticity of coating film" in chapter 8.

Now organic coatings and finishing are meeting new challenges: improved performance, newly required functions, lower VOC emissions, reduced energy consumption, the elimination of potential health hazards from organic coatings, etc. A deep understanding of the principles of organic coatings and finishing provides the basis for addressing these challenges.

For instance, the effects of monomer compositions on the performance of coating materials are systematically discussed to develop environment-friendly coatings (waterborne, powder, high solids and radiation curable coatings). The interactions between paint components are used to control the film formation processes for obtaining required functions. IR radiation drying and electric induction drying reduce energy consumption. LVLP and LVMP spray guns improve the transfer efficiency of air spray painting. Moreover, new techniques, such as the mini-emulsion polymer processing technique and cure-on-command technology, automatic spray painting, and new dry-filter booths, are also described. The descriptions of new innovations in organic coatings and finishing and in the rheology of coatings will be helpful even for established scientists and engineers in the field.

Teaching tips: the exercises in this book cover the basic requirements of students. Students need to spend time learning, mastering and using the knowledge and skills. Teachers should appropriately repeat content to help students acquire this knowledge. For instance, the "Fill in the blank" and "Explanation" exercises can be used to communicate and interact with students in class; and the "Answer" and "Calculation" exercises can be selected and used for students' after-class homework, depending on class hours.

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CHAPTER 1

INTRODUCTION

1. What are coatings?

The concept of coatings most probably originates with the cover of animals' bodies, such as the skin. There is no general terminological specification defining the notion of coating and its types now.

An organic coating film is a layer of material with the primary aims of obtaining protective and decorative properties. The film is deemed relatively thin, whereas the object to which it is applied is massive in comparison. The object absorbs energy from outside impacts and reduces the effect of the impacts on the coating film.

Coating is a more general description of any material that may be applied as a thin continuous layer to a surface, while paint is used to colour surfaces and make them attractive. The terms "paint" and "organic coating" are often used interchangeably.

Coating may refer to a coating material, coating film or coating layer, or the application process of a coating material, depending on the context.

1.1. Components of coatings

Organic coatings generally consist of four components: a binder, pigments, solvents and additives. Solvents evaporate during film formation. The binder, pigments and additives are intended to be relatively permanent and serve specific functions in the final film.

(1) Vehicle

The vehicle, composed of the binder and a solvent or thinner or both, is the liquid portion of the paint in which a pigment is dispersed. The binders are mainly synthetic polymers (macromolecules) and vegetable oils. Vegetable oils are often used to prepare synthetic polymers.

The smallest precursors are *monomers*, low-molecular-weight (10 to over 100) chemicals that can react with each other to form chains. Short–chain systems are frequently viscous liquids, called *oligomers* or *prepolymers* (molecular weight of 100 to 10000), and longer chain systems are solids. The long chains entangle each other, which imparts strength and hardness to the material. The term "resin" is often used to indicate oligomers and polymers.

Most binders of coating systems that are composed of oligomers and a curing agent (crosslinker or hardener) undergo crosslinking to form longer chains during film formation.

The vehicle acts as the adhesive to glue pigment particles to the substrate and to each other. The binder forms a continuous polymeric phase in which all the other components may be incorporated. Thus, the degradation of polymers results in poor appearance and deteriorated function of the coating. Moreover, the binder composition largely determines the permeability, chemical resistance and ultraviolet (UV) resistance of the coating.

(2) Pigments

Pigments are rigorously defined as insoluble colorants as opposed to soluble colorants or dyes. The particle size of a pigment is often in the range of 0.2–10μm. There are subcategorizations for pigments

according to the function intended or performed: colorant pigments, anti-corrosive pigments and fillers. Many pigments perform several functions.

Colorant pigments, called colour pigments or coloured pigments, afford coatings aesthetic and decorative functions. Some of them act as colorants, such as red/yellow/black iron oxide, and others as whiteners, such as lithopone and titanium dioxide. Colour pigments impart colour and powers of concealment to a coating film.

The protective properties of a coating film are embodied in their resistance properties, such as resistance to water, solvents, acids, alkalis, UV light, etc. Some pigments provide anti-corrosion properties, such as zinc phosphate and aluminium flakes. Some pigments are used as preservatives against mildew or bacteria (e.g., barium metaborate), or UV stabilizers (e.g., lithopone and zinc sulphide).

Fillers (e.g., limestone and clay) increase the volume of a coating through the incorporation of low-cost materials, and they are often used to partially replace expensive colorant pigments.

(3) Additives

Additives are usually low-molecular-weight chemicals with very specific properties. The functions of different additives may be quite diverse. Their amounts are small, seldom more than 5%.

Colloidal stabilizers are used to improve pigment dispersion and the stability of coatings. They are surface-active agents, protective colloids, dispersants and wetting agents.

Cure additives are catalysts (e.g., acids and driers) that speed up the cure reaction.

Plasticizers are softeners used for high polymer formulations to ensure their workability (elasticity, extensibility and conformability).

UV stabilizers block the attack of UV light or heat on the polymer.

(4) Solvents

Polymers are either dissolved in solvents to become solutions or dispersed in diluents to become dispersions. Polymers exist in fine granular form in water dispersions. This makes it possible to apply the liquid coating in a thin, smooth, continuous film on a specific surface. Solvents control the film formation process, so then influence the appearance and gloss of the film.

The commonly used solvents are organic solvents, such as mineral spirits, xylene, butanol, butyl acetate, etc. However, organic solvents pollute the atmosphere, and some are toxic. There are strict restrictions on the types and amounts of organic solvents used in the paint industry.

(5) Interactions of components

Organic coatings are mixtures. The four components are not necessarily present in each coating formulation. Powder coatings contain no solvents. *Clearcoats* containing no pigment form glossy and transparent films that become the final interface with the environment. Paints are of pigmented liquid composition, and enamels are pigmented coatings often used as topcoats.

The interactions between the components (i.e., polymer-solvent and pigment-vehicle) and the influence of additives on the interactions are in this tome described. This will help not only to supplement readers' knowledge of handling mixtures, but also to provide a deep insight into the internal structures and evolutions of coating systems.

1.2. Functions of organic coatings

Organic coatings are mainly used for decoration and protection. Organic coatings can easily be formulated in a variety of colours, and their coating films can hide the original colours of the objects to be coated, being used to provide a pleasant appearance or create attractive surroundings.

Equipment and structures are often protected from the environment by a barrier between the substrate and the aggressive environment, such as marine or industrial environments. Organic coating technology is the main method of protecting steel and iron from corrosion. About 2/3 of the anti-corrosion cost of iron and steel is spent on organic coatings and organic finishing.

Organic films modify the chemical, mechanical, thermal, electronic and optical properties of substrates, resulting in increased functions and cost savings.

2. What is organic finishing?

Organic finishing is simply what is called painting or coating. The object to be coated may be referred to as the workpiece, part, product or substrate. The fundamental procedures of painting are surface preparation, coating application and the drying or curing of coatings.

(1) Surface preparation

Surface preparation can also be called surface pretreatment. Adhesion takes place at the coating-substrate interface, and any contaminants on a substrate surface will decrease adhesion. Surface pretreatment is accomplished prior to the painting operation.

The surfaces of metal parts have contaminants or gross soils, such as grease and mill scale. The contaminants are generally removed in industrial practice through two approaches: mechanical pretreatment or chemical pretreatment.

• Mechanical pretreatment (e.g., air blast cleaning, centrifugal blast cleaning) is performed by using a driving force to pretreat objects (such as ships and bridges, for example), but surface roughness cannot be easily controlled, and so the approach is not suitable for high-end coating (e.g., for car bodies). High-end coating employs chemical pretreatment.

• Chemical pretreatment is accomplished through the removal of organic soils (degreasing) and inorganic soils (derusting). Organic soils are removed by the use of either detergent solution or organic solvent, while inorganic soils are removed by acid pickling.

The term "chemical pretreatment" often refers to a combination of chemical cleaning and conversion coating. A conversion coating (e.g., phosphate film, SiO_2 film) is formed on the cleaned metal surface. Subsequent coatings will then be applied on the conversion coating that will have provided a surface suitable for organic coatings, enhancing adhesion.

(2) Coating application

Organic coatings can be applied by various methods, such as spraying, brushing, electrocoating and so on. The selection of painting methods depends mainly on (a) type of coatings; (b) application site; (c) size and geometry of parts; and (d) production capacity (large-scale, short run or single piece). Painting is often performed in a spray booth to handle overspray and volatiles.

(3) Drying or curing of coating film

After being deposited on surfaces, wet coating films change from a liquid or powder state to continuous solid films, and then they form permanent coating films as the result of physical transformation and /or chemical crosslinking.

The substrates to be coated can include metals, wood, plastics, concrete, etc. When parts made from different materials are coated, they can adopt the same coatings and application method, but they need different types of surface preparation.

Since few coatings can meet requirements for protective and decorative properties, a typical multi-coat system is often used. The multi-coat system consists of a primer, an intermediate coat and a

topcoat. Among them, the primer provides protection, for example, zinc rich primer protects steel from corrosion; intermediate coats are used to smooth the surface or increase the total film thickness; and topcoat contacts directly with the service surroundings, and provides such properties as colour, gloss and weather resistance.

The properties of a coating film depend strongly on the paint formulation, on the application procedures and on the precautions taken during the application of the layer.

3. Classification and Nomenclature for Coatings

Organic coatings have a long history and wide application, and so they have, perhaps unsurprisingly, picked up many methods of nomenclature and classification. They have traditionally been classified into solvent-borne coatings, waterborne coatings, powder coatings, high solid coatings and radiation curable coatings. Since all coatings contain binders, the classification and nomenclature of coatings are based on the resins used.

3.1. Main chemical reactions of polymers used in coatings

A preliminary understanding of the polymers used in coating formulations provides the basis for grasping the nomenclature of coatings. The important reactions associated with the polymers are described in brief.

(1) Synthesis reaction

(i) Esterification

The step-growth condensation of hydroxyl and carboxylic groups produces ester bonds (-OH + -COOH → -COO- + H_2O). Unsaturated polyester is synthesized by the use of an unsaturated dibasic acid (e.g. maleic anhydride). Both saturated polyester and unsaturated polyester are used in coatings.

Alkyd resins are oil-modified polyesters. Ester rosin (ester gum) is formed by the reaction of rosin containing carboxylic groups and polyols.

There are many hydroxyl groups in cellulose molecules, and the hydroxyl groups react with nitric acid (HNO_3) to produce nitrocellulose by esterification.

(ii) Condensation with formaldehyde

Phenols or cresols undergo a condensation reaction with formaldehyde to produce phenolic resins containing methylols ($-CH_2OH$). Amines react with formaldehyde to form amino resins containing methylols ($-NH_2 + HCHO = -NHCH_2OH$). These methylol-containing resins are esterified with alcohols (e.g., butanol) to form ether bonds ($-CH_2OC_4H_9$). This improves their compatibility with other resins and their solubility in organic solvents.

Para-substituted phenols (such as substituent tert-butyl or phenyl) react with formaldehyde to produce oil-soluble phenolic resins.

(2) Oxidative polymerization

Drying oils consist mainly of polyunsaturated fatty acids. The C-H bonds in allyl groups (methylene groups at the α-position of double bonds) are readily oxidized by atmospheric oxygen to form hydroperoxides (-OOH). The decomposition of a hydroperoxide generates two radicals that react with other diallyl groups to form new hydroperoxides. The mutual reactions of free radicals form ether bonds, peroxyl bonds and C–C bonds. Then the film is crosslinked.

Oleo-resinous resins are oil-modified resins (mainly alkyds, epoxy esters and uralkyds). However, oleo-resinous resins can be crosslinked with curing agents (e.g., amino resins) on baking.

(4) Condensation of amino resins

Amino resins containing functional groups (mainly -NHCH$_2$OR) are used as the crosslinkers of matrix resins (e.g., alkyd, polyester, acrylic resin). The crosslinking reaction proceeds on high temperature baking to release ROH. This is nucleophilic substitution. High nucleophilic activity reduces the reaction temperature.

$$-NHCH_2OR + polymer\text{-}OH \xrightarrow{\text{heating}} -NHCH_2O\text{-}polymer + ROH\uparrow$$
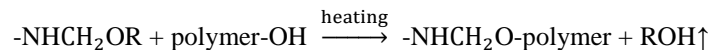
Networks are formed by the crosslinking, which imparts good mechanical properties and solvent resistance. Modifications with amino resins are widely used in baked coatings for high-end situations.

(5) Nucleophilic addition

(i) Isocyanate

Polyurethanes are mainly characterized by the reaction of polyols (-OH) and polyisocyanates (-NCO) to produce urethane linkage (-OH + -NCO → -NHCOO-). Polyurethanes have found wide applications in the paint industry, mainly, because they exhibit excellent abrasion resistance and solvent resistance due to the presence of hydrogen bonds formed between urethane groups.

(ii) Epoxy three-membered ring

Three-membered rings tend to react with nucleophilic reagents by ring-opening reactions. The most used epoxy groups can react with polyamines, polyacids and anhydride, etc.
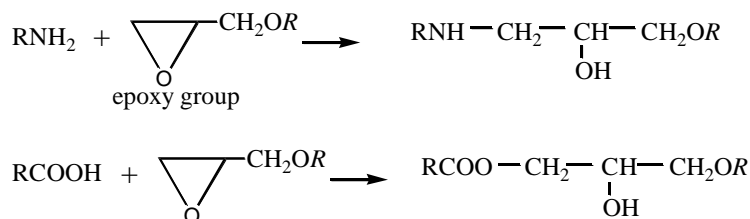
A 2K epoxy-amine reaction takes place at room temperature. The term '2K' refers to two-packages, that is, the two components are packed separately.
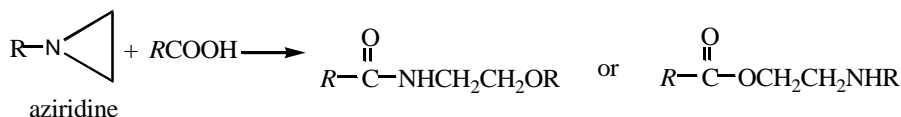
Carboxyl resins are often dispersed in waterborne coatings so as to be 2K coatings. They can be crosslinked by aziridine, and the systems have pot lives of 48–72h at room temperature. *Pot life* refers to the time from blending the paint with its hardener (curing agent) to the mixed paint starting to gel.

3.2. Classification and nomenclature for coatings

The binders used in coatings are classified into three groups: drying oils, natural resins and synthetic resins. Hydrophobic drying oils are a group of natural oils that can crosslink via air oxygenation and subsequent reaction.

Modified natural resins are chemically modified celluloses, rosins and natural rubbers, such as nitrocellulose and ester rosin. The quite hydrophobic chlorinated rubber is natural rubber that has been treated with chlorine to improve its resistance to chemicals, ozone and UV.

(1) Synthetic resin

Acrylic: A broadly varied group of systems made as copolymers of acrylic/methacrylic esters, and perhaps other monomers, to modify curability and solubility behaviour. Acrylic exhibits excellent UV resistance.

Alkyd: Oil-modified polyester, usually incorporating phthalic anhydride and glycerol, but

containing unsaturated fatty acids from vegetable oils.

Epoxy: The most used is bisphenol A epoxy resin. The crosslinkable resins react with added components to form networks with good strength and chemical resistance.

Fluorocarbon: A group derived from fluorocarbon monomers, perhaps copolymerized with others. Fluorocarbon resin exhibits good weather and chemical resistance, its excellent performance being due to very high C-F bond energy and high crystallinity.

Amino resins: Amino resins act as crosslinkers for other polymers to make hard coatings.

Polyester: A generic term characterizing polymers based on carboxylic acid (mainly) and alcohol group reactions to form the long chains (and perhaps crosslinks). Ester groups are hydrophilic, but the carbon/oxygen ratio determines how hydrophilic.

Silicone: Based on silane monomers, which are generally unreactive to chemicals, thermal stress and UV stresses. Silicone is somewhat hydrophilic. An important exception is that silicone is highly reactive to alkalis.

Urethane: Polyisocyanate reacts with polyols to make this polymer.

Vinyl: Based on vinyl acetate or vinyl chloride, usually with a co-monomer to yield curability or reduce the hydrophilicity of the acetate or the UV discolourability of the chloride.

(2) Market category

The paint and coatings industry is normally divided into three broad market categories: (a) architectural (decorative) coatings; (b) OEM/product (industrial) coatings; and (c) specialty (maintenance) coatings. OEM is short for original equipment manufacture.

(i) Architectural coatings

Architectural coatings, also called trade sales paints, are used as interior and exterior house paints, stains, and undercoats (i.e., primers and sealers). Their main requirements are fast drying, good adhesion to old paints and good appearance. Exterior paints need good outdoor durability.

Architectural coatings include paints, varnishes and lacquers. Varnish is a clear transparent hard protective film, and it has little or no colour and has no added pigment, as opposed to paints containing pigment. The term "lacquer" is used for a number of hard and potentially shiny finishes and often refers to quick-drying, solvent-borne varnishes or paints, such as nitrocellulose lacquers and acrylic lacquers.

(ii) Industrial coatings

Industrial coatings are formulated to specific customer specifications and applied to original, durable equipment within the confines of an established manufacturing process.

(iii) Specialty coatings

Specialty/maintenance coatings include paints and coatings that can withstand unusual exposure to high abrasion (wear), corrosion or temperature conditions, as well as prolonged exposure to either hazardous chemicals or water. They include coatings for automotive refinishing and traffic markings, as well as aerosol and high performance maintenance coatings.

4. Fundamental knowledge of polymers used in coatings

Polymers are macromolecules that are produced by small precursors (monomers) reacting with each other to obtain long chains. The London force (dispersion force) of a molecule, dominating in the intermolecular force, increases with increasing molecular weight. Polymers have very high intermolecular forces that exceed the strength of chemical bonds. When the polymer chains are

intertwined with each other, the solid exhibits substantial mechanical strength.

Thermoplastic polymers include linear and branched polymers. A linear polymer has a long chain, while a branched polymer is a linear polymer with branches. Thermoplastics are softened or melted on heating to thermoform, then after cooling they solidify again. They can be dissolved in suitable solvents.

Oligomers (prepolymers) are crosslinked on heating or UV irradiation to obtain thermosetting films with 3-D networks. Thermosetting materials can be swollen by solvents, but they do not dissolve in the solvents. Actually, the amount by which a polymer is swollen by a liquid depends on its crosslinking density. The more crosslinks present, the smaller is the amount of liquid swelling.

Thermoplastic polymer coatings form films by solvent evaporation. The film formation of thermosetting polymer coatings needs crosslinking. For convenience of expression, organic coatings are classified into four types according to film formation mechanisms: solvent evaporation, oxidative polymerization, condensation of thermosetting resins and coalescence of polymer particles. Powder coatings and waterborne coatings form films by the coalescence of polymer particles.

4.1. Glass transition of polymers

Thermoplastics are glassy plastics at low temperature. As the temperature rises, a certain temperature is reached at which the polymer changes from a glassy state to a rubbery state. The temperature at which this change takes place is called the glass transition temperature (T_g).
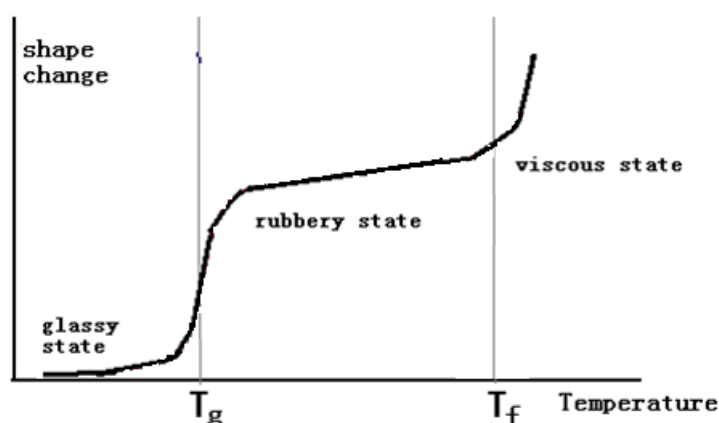
Thermoplastic polymer: Shape change with temperature

When heated above the T_g, the polymers pass successively through rubbery, gumlike and, finally, liquid states with no clear demarcation between the different phases. The latter two states are called the viscous state. Thermosetting polymers do not have viscous states.

The T_g value determines whether the polymer is in a glassy state or a rubbery state. A sharp change in the physical properties of a polymer occurs around its T_g, properties such as the compactness, mechanical properties, electrical performance, thermal behaviour, etc. In dried or cured coating films, the polymer is in a glassy state. The T_g value of a particular polymer mainly depends on its molecular weight, molecular structure and diluent concentration.

(1) Molecular weight

Crosslinking increases the molecular weights of polymers. The increase of T_g with increasing molecular weight is well described by the Fox-Flory equation:

$$T_g = T_{g\infty} - \frac{A}{\bar{M}_n}$$

where $T_{g\infty}$ is the T_g of a polymer with infinite molecular weight; A is a constant; and $\bar{M}_n$ is the

number-average molecular weight. Usually the T_g becomes constant when a polymer has more than 1000 to 2000 repeating units (i.e., $\bar{M}_n > 25000$–75000).

The mechanical strength of a film increases with increasing molecular weight, but its viscosity accordingly increases. When a thermoplastic resin is used to prepare liquid coatings, its molecular weight should be sufficiently high to attain mechanical strength, but its viscosity should be as low as possible for convenience of application. In order to obtain a suitable application viscosity (spraying, brushing, etc.), a great amount of solvents is added to the solution with solvent content of up to 70–80 vol%.

For thermosetting coatings, prepolymers are first prepared, and the prepolymer solution generally has a solvent content of about 50 vol% at the same application viscosity. After application, the prepolymers need be crosslinked. The most important coatings are thermosetting systems, such as combinations of amino-hydroxyl resins, isocyanate-hydroxyl resins and epoxy-amines, as well as alkyd and epoxy ester using oxidative drying.

(2) Molecular structure

The bonds of polymer backbones can rotate. The rotation along a polymer chain results in the chain presenting as a random coil.

Subtle differences in monomer structure produce significant differences in polymer properties. For example, polymethylmethacrylate (PMMA) has a T_g of 115 ℃, whereas polymethacrylate (PMA) has a T_g of 14 ℃, because the methyl group of PMMA increases steric hindrance to rotation, resulting in its high T_g.
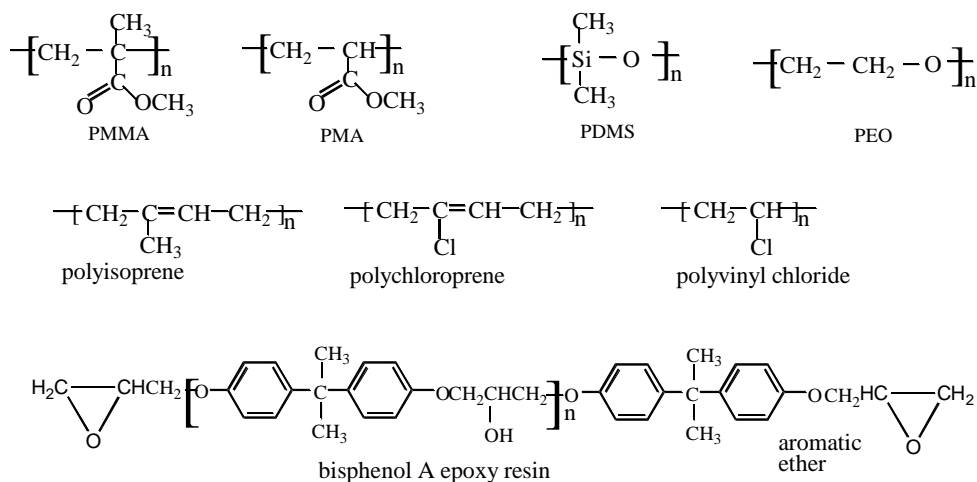
Ether bonds rotate easily. Polydimethylsiloxane (PDMS) with silicon-oxygen ether bonds (Si-O-Si) has a T_g of –127 ℃ (146K), and the T_g of polyoxyethylene (PEO) is in the range of 158–233K.

Double bonds cannot rotate, but a single bond adjacent to a double bond rotates more easily, and so polymers containing double bonds are more flexible. Thus, polyisoprene and polychloroprene are used as rubber materials whose T_g values are far lower than room temperature, but polyvinyl chloride, with a T_g of 78 ℃ is a plastic.

The introduction of relatively stiff chemical groups (such as benzene rings) interferes with the flowing process and hence increases T_g. Although the molecular weights of novolac (thermoplastic phenolic resins) and bisphenol A epoxy resin are in the range of the thousands, they are hard brittle solids. The incorporation of long nonreactive side groups to a polymer backbone keeps the chains away from one another, reducing the T_g value.

If a polymer with some desirable properties has too high a T_g, it can be copolymerized with another monomer with a T_g below the temperature of intended use, and the T_g of the copolymer is controlled

by adjusting the monomer composition. This is demonstrated by examples in chapter 2.

(3) Solution concentration

The T_g of a polymer solution falls between the melting point of its solvent and the T_g of the polymer. Further addition of liquid diluents and solvents decreases the T_g of the polymer solution. Smaller plasticizer molecules embed themselves between polymer chains, allowing them to move past one another even at lower temperatures, and hence to decrease the T_g.

The application viscosity of solvent-borne coatings is in the range of 0.05–1Pa s, and the viscosity of a through drying film exceeds 10^7Pa s.

After solvent-borne coatings are applied, the T_g and viscosity increase with solvent release. For applied medium oil length alkyd coating films, the T_g of the wet film gradually approaches room temperature, and the film has very high viscosity. Consequently, it is difficult for the paintbrush to move on the film surface; that is, the film has poor brushing performance. This drying is called *lacquer drying* and is caused by the high T_g of the coating film. Lacquer drying does not exhibit any real degree of crosslinking.

4.2. Resin structure and film performance

Resin structures affect the performance of coating films. Some typical modes are summarized here.

(1) Photochemical oxidation

Polymers containing aromatic ether or aromatic amine units are inclined to be photochemically oxidized when exposed to the elements, exhibiting poor colour retention and poor gloss retention. Bisphenol A epoxy resin and aromatic polyurethane are examples.

(2) Abstractable H atom

Since abstractable H atoms in resins are inclined to be oxidized by photolysis and radicals, polymers containing no abstractable H atoms, such as PDMS resins, have excellent weather resistance.

PMMA has better weather resistance than PMA due to the absence of abstractable tertiary H atoms on the PMMA backbone. Since the β-H atoms of polyols are abstractable, neopentyl glycol polyester has good weather resistance.

$$CH_3$$
$$HOH_2C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}-CH_2OH$$
Neopentyl glycol

$-(CH_2-\mathbf{CH})_n$
$\quad\quad\;\; OH$
polyvinyl alcohol

$-(CH_2-\mathbf{CH})_n$
$\quad\quad\;\; COOR$
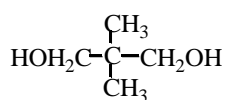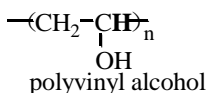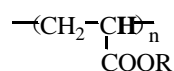
Abstractable **H** atom in bold font

For polyvinyl alcohol, the stronger induced effect is caused by the high electronegativity of oxygen directly connected with the carbon atom. Consequently, the tertiary H atoms in polyvinyl alcohol are more abstractable than those in PMA. Partially hydrolysed polyvinyl acetate can form graft chains at the abstractable H atoms to obtain graft copolymers that are used as a protective colloid. Similarly, chlorinated copolymers have poor photolysis resistance due to the presence of the tertiary H atoms of chlorine atoms.

(3) Corrosion resistance

Oxygen absorption corrosion of metals produces OH^- ions, and ester bonds are easily broken by the presence of strong alkalis. Ether bonds have better alkali resistance than ester bonds. Since bisphenol A epoxy-amine systems have no ester bonds, they show excellent corrosion resistance.

(4) Intermolecular force

Chlorinated polymers, such as chlorinated rubber, often have high chlorine content (often above 60%). Since the atomic weight of chlorine (35.5) is far higher than that of C (12) and H (1), the high chlorine content results in very high intermolecular forces such that the chlorinated polymers form

dense films with low permeability.

The hydrogen bond is one type of intermolecular force. The urethane linkages (-NHCOO-) in polyurethane coating films form a great amount of hydrogen bonds, which imparts excellent solvent resistance and abrasive resistance.

(5) Gloss

Molecules containing unsaturated bonds have high gloss, and the gloss of a conjugated system is higher. Alkyd coatings containing conjugated bonds of aromatic rings have higher gloss than drying oil coatings. Unsaturated polyester coatings containing styrene units exhibit high gloss.

4.3. Drying and crosslinking

For a coating film cured at room temperature, at the beginning of the cure, the T_g of the film is much lower than room temperature, the functional groups can move freely in the film and crosslinking reactions proceed smoothly.

Both solvent evaporation and crosslinking lead to an increase in T_g. As the T_g of the film approaches room temperature, the cure rate decreases sharply due to the restricted movement of crosslinking groups. Crosslinking reactions completely stop only when the T_g of the film reaches the room temperature plus 50 ℃. Thus, a film cured at room temperature may need several weeks to reach the required performance.

The drying of coatings is different from curing (crosslinking). Drying refers to the solvents in a coating film being released completely, while curing is the formation of networks in a film by chemical reactions.

A crosslinked film cannot be dissolved in solvents, but it can absorb solvents to swell. Therefore, lower crosslink density leads to lower resistance toward solvents and other chemicals. The extent of swelling is used to express the degree of crosslinking. The prepolymers used in thermosetting coatings often have functionality of three or higher to produce heavily crosslinked films.

The crosslinking of coating films can be investigated by standard methods such as dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), xylene testing and the pendulum hardness test.

5. Application and development of coatings

Coatings may be divided into three groups: (a) metallic layers; (b) non-metallic inorganic layers such as conversion layers, anodized layers, some ceramic chemical vapour deposition and physical vapour deposition layers and enamel layers; and (c) organic coatings.

Compared with the other two types of layers, organic finishing is the simplest method by which to modify materials. Organic coatings can be applied to the surfaces of various materials by manual methods, or spray painting, or automatic painting for mass production. The film performance is controlled by coating formulation and finishing technology. The large-scale application of organic coatings in industrial production is economic and efficient. The term "coatings" in this book refers to organic coatings.

The paint and coatings industry is a mature industry. The competitive environment provides the drive needed to develop coatings that utilize less expensive raw materials. The paint and coatings sold into the higher value OEM/product and specialty market categories are more likely to utilize new technologies that will improve quality and performance.

Solvent-borne coatings involve a high content of volatile organic compounds (VOCs). VOCs not only waste large amounts of organic solvents, but also generate hazes and atmospheric ozone that are harmful for both environments and living organisms. Paint manufacturers have exerted great efforts to switch from using solvent-borne coatings to environment-friendly coatings.

Coatings should be environment-friendly, energy-saving and economical, that is, the impact on the ecological environment should be reduced and CO_2 emissions lowered, and coatings with better levels of performance should be obtained at lower cost. Moreover, demand for demonstrable improvements, such as in appearance, resistance against corrosion and wear, and weatherability (durability), has been one of the major driving forces behind the development of new coating formulations.

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Exercises

1. Explain

Pot life; clearcoat; VOC; lacquer drying

2. Answer the question

(1) What do organic coatings consist of? What are the fundamental procedures of organic finishing ?

(2) Explain the influence of the molecular weight, molecular structure and solution concentration of a polymer on the T_g value of the polymer and the film performance.

CHAPTER 2

POLYMERS USED IN COATINGS

Both the appearance and mechanical properties exhibited by a dry coating film rely on the chemical composition of the polymeric binder and on the associated curing process. The structure and reactivity associated with the important polymers are discussed below, with emphasis on basic chemical reactions and recent innovations.

Polymers (e.g. polyester, polyurethane, epoxy, alkyd, acrylic resins) are used as binders in solvent-borne coatings, waterborne coatings, high solid coatings, powder coatings and radiation cured coatings. For convenience of expression, they are classified into four types according to film formation mechanism: solvent evaporation, oxidative polymerization, condensation of thermosetting resins, and coalescence of polymer particles. Powder coatings and waterborne coatings form films by the coalescence of polymer particles.

1. Film formation by solvent evaporation

Solvent-evaporation coatings use thermoplastic resins and often contain a large amount of organic solvents. They are often applied by spraying because of fast drying and a high solvent-evaporation rate.

For typical solvent-evaporation coatings, cellulose derivative-based coatings that can withstand sanding and polishing are used as high quality wood coatings; halogenated polymers (chlorinated polymers and fluororesins), having low water permeability, are used in anti-corrosive formulations; and thermoplastic acrylic paints have high decorative value and weather resistance.

1.1. Cellulose derivatives

Cellulose is insoluble in water and organic solvents, but its derivatives can be dissolved in organic solvents. Nitrocellulose is the most widely used in the coating industry. Cotton is often used to prepare cellulose derivatives, in which case the nitrocellulose may also be called nitro-cotton.

Cellulose is a polysaccharide consisting of a linear chain with several hundred to thousands of β-(1.4) linked glucose units. Every glucose unit along a cellulose molecule, expressed as $[C_6H_7O_2(OH)_3]$, has three hydroxyl groups: one primary and two secondary hydroxyl groups.
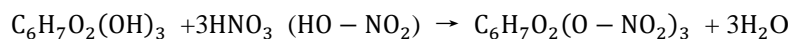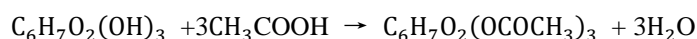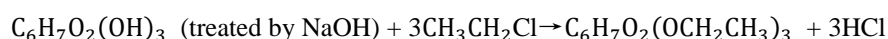
$$C_6H_7O_2(OH)_3 + 3HNO_3 \ (HO-NO_2) \ \rightarrow \ C_6H_7O_2(O-NO_2)_3 + 3H_2O$$
$$\textbf{\textit{Nitrocellulose}}$$
$$C_6H_7O_2(OH)_3 + 3CH_3COOH \ \rightarrow \ C_6H_7O_2(OCOCH_3)_3 + 3H_2O$$
$$\textbf{\textit{Cellulose acetate}}$$
$$C_6H_7O_2(OH)_3 \ (\text{treated by NaOH}) + 3CH_3CH_2Cl \rightarrow C_6H_7O_2(OCH_2CH_3)_3 + 3HCl$$
$$\textbf{\textit{Ethyl cellulose}}$$
$$C_6H_7O_2(OH)_3 \ (\text{treated by NaOH}) + 3HOCH_2CH_2Cl \rightarrow C_6H_7O_2(OCH_2CH_2Cl)_3 + 3HCl$$
$$\textbf{\textit{Hydroxyethyl cellulose}}$$

Nitrocellulose is used to prepare nitrocellulose lacquer. Cellulose acetate is used in flare coatings. Ethyl cellulose is combined with silicone to prepare air-dry heat-resistant coatings. Hydroxyethyl cellulose is used as a protective colloid in latex paints.

1.1.1. Nitrocellulose

Nitrocellulose can be esterified to varying degrees. The mononitrate, dinitrate and trinitrate of a $C_6H_7O_2(OH)_3$ unit correspond to nitrogen contents of 6.76%, 11.11% and 14.14%, respectively. Nitrocellulose with a nitrogen content below 10.5% has poor solubility in organic solvents. The nitrogen content used in coating formulations is in the range of 11.2–12.2%, especially 11.7–12.2%. Nitrocellulose is highly flammable, but the fire hazards it presents can be reduced by storing it dampened with various liquids, such as ethanol or isopropanol, but it is insoluble in these alcohols.

The molecular weight of nitrocellulose is controlled by the hydrolysis degree of the cellulose. High molecular-weight nitrocellulose imparts good mechanical strength, cold resistance and durability, but low solid content and poor levelling. Low molecular-weight nitrocellulose has good hardness and sanding properties, but suffers severe degradation under exposure to sunlight.

Nitrocellulose cannot be used alone because of its low solid content, as well as the low gloss and poor adhesion of its dry film. The coating need be modified by resins compatible with nitrocellulose (such as short or medium oil length alkyd resins) to overcome these defects.

Inexpensive nitrocellulose coatings usually have a drying time of ten minutes. As wood coatings, nitrocellulose coating films have a high gloss and improve the appearance of wood grains.

However, besides high VOC content, other disadvantages of nitrocellulose coatings, such as wood discoloration (yellowing), flammability and toxicity, are opening the door to new technologies that include waterborne and radiation curable acrylics.
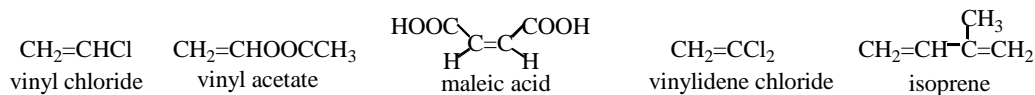
1.1.2 Cellulose acetate butyrate

Cellulose acetate butyrate (CAB) has good colour retention, and the fire hazards of CAB are much less than those of nitrocellulose. CAB with 2.2 acetate groups, 0.6 butyrate groups and 0.2 unreacted hydroxyl groups in each glucose unit is used to control wet film flow and promote the orientation of aluminium pigment sheets in flare coatings.

1.2. Chlorinated polymer

Chlorinated polymers, such as polyvinyl chloride (PVC), have good resistance to chemicals and weather. Since the atomic weight of the chlorine atom (35.5) is far higher than that of C (12) and H (1), the introduction of chlorine atoms and the polarity of C-Cl bonds in chlorinated polymer cause a substantial increase in intermolecular interactions. Thus, chlorinated polymers can form dense films with low water permeability and are mainly used as anti-corrosive topcoats.

PVC is a linear polymer with a high structural regularity, resulting in a high degree of crystallization. PVC with $T_g = 78\ °C$ is an odourless and tasteless resin.

$CH_2=CHCl$	$CH_2=CHOOCCH_3$	$\underset{H}{\overset{HOOC}{>}}C=C\underset{H}{\overset{COOH}{<}}$	$CH_2=CCl_2$	$CH_2=CH-\underset{}{\overset{CH_3}{C}}=CH_2$
vinyl chloride	vinyl acetate	maleic acid	vinylidene chloride	isoprene

Monomers for chloranated polymers

Crystalline PVC is rarely used alone to formulate coatings. PVC can be modified by chlorination or the incorporation of co-monomers to obtain thermoplastic chlorinated polymers, and the modification destroys PVC's structural regularity and improves solvent dissolution and adhesion to metals. The higher the chlorine content of the chlorinated polymers, the lower is the permeability and the better is the flame retardancy, but the lower are the flexibility and impact resistance.

However, chlorinated polymers have poor photochemical degradation resistance and heat stability. Above 140 °C, PVC starts to decompose by the removal of hydrogen chloride in an autocatalytic chain reaction. Stabilizers, such as dibutyltin dilaurate, a soap of metal ions (barium, cadmium and strontium),

maleic ester or epoxy compounds, are added to improve photochemical stability and heat stability.

1.2.1. Polyvinyl chloride acetate

Polyvinyl chloride acetate (PVCA) is the copolymer of vinyl chloride and vinyl acetate monomers. Vinyl acetate imparts a lower T_g and improved solvency in organic solvents. Maleic acid is also used to increase adhesion to metals. The terpolymer with a weight ratio of vinyl chloride: vinyl acetate: maleic acid = 86:13:1 (mole ratio of 81:17:1) has $\bar{M}_w$= 75000, and terpolymer-based coatings have good storage stability and are used in the interior walls of drinks cans.

Hydroxyl PVCA can be prepared by the hydrolysis of PVCA. A hydroxyl PVCA resin with $\bar{M}_n$= 23000 and T_g= 79 ℃ is dissolved in butanone, and its coating film has good mechanical properties. In order to achieve the viscosity of 0.1Pa s used for spray painting, the PVCA content should be below 19 wt% and 12% NVV (Non-volatile Volume-Volume percent solids).

It is observed that even if the coating film has been dried at room temperature for several years, there are still 2–3％ residual solvents in the film. When the film is dried at a temperature higher than the T_g of the resin, the solvents can be completely removed.

1.2.2. Vinylidene chloride copolymer

Vinylidene chloride copolymer is prepared by the copolymerization of vinyl chloride (70–45％) and vinylidene chloride (30–55％). Copolymer coatings have good adhesion and flexibility. Consequently, plasticizers are not needed in the copolymer coating formulation. When non-toxic pigments are used, the coatings are harmless to humans, and thus they can be used in drinks and food containers.

1.2.3. Perchloroethylene

PVC (53–56％ chlorine) can be modified by chlorination, which increases its chlorine content to 67%. The resulting resin is called perchloroethylene or chlorinated polyvinyl chloride (CPVC).

CPVC is produced by the chlorination of aqueous suspension of PVC particles followed by exposure to UV light, which initiates the free-radical chlorination. Compared with chlorinated rubber films, CPVC films are denser and more structurally regular, and have better chemical resistance, but the solid content is lower.

1.2.4. Chlorinated polyolefin

Polypropylene (PP) or polyethylene (PE) is partially chlorinated to obtain chlorinated polypropylene (CPP) or chlorinated polyethylene (CPE).

CPP has two types: 20–40% or 63–67% chlorine content, and the two types can be dissolved in halogenated hydrocarbon, toluene or butyl acetate. The solution has good adhesion to PP, PE, paper sheets and aluminium films.

CPE is used to prepare printing inks for PP films, adhesives between PP and papers, and coatings used for PP products.

1.2.5. Chlorinated rubber

Chlorinated rubber is produced by the direct chlorination of natural rubber (isoprene polymer) in CCl_4 solution and has a molecular weight in the range of 3500–20000. The molecular weight of natural rubber is degraded, and the chlorination process involves complex organic reactions, such as addition, substitution and cyclization.

Non-flammable chlorinated rubber has specific adhesion to many surfaces and very low water-vapour permeability (e.g. about one-tenth of that of alkyd resin films) and exhibits excellent solvent-release properties.

Chlorinated rubber coatings can be applied at temperatures as low as –20 ℃. A coat of a thixotropic chlorinated rubber coating yields a film with a thickness of up to 125μm. The coatings are mainly used