Chapter 1
INTRODUCTION

Surface coating is used to protect the substrate from the environment. The coating must adhere to the surface that has been coated so as to decorate or protect any surface, the coating must remain in position. The terms paint and coatings are sometimes used interchangeably; paint is the older term used before the 1940s (e.g. for painting houses) after which new sophisticated synthesized materials were developed for automobiles and aircraft and called coatings.

Paint is the general term for a family of products used to protect and add colour to an object or surface by covering it with a pigmented coating. Paint is used in the production of art, in industrial coating, as driving aid or as preservative. The primary components of paint are binder, diluents, and additives. However, only the binder is absolutely required. The binder is the part which eventually solidifies to form the dried paint film. The diluent serves to adjust the viscosity of the paint. It is volatile and does not become part of the paint film. There are various additives, which are added to improve some properties, such as colour opacity, mattness, pigment dispersion and stability. Pigments or dyes are among the most common additives. They give colour to paint. Pigments may also have the same functions as fillers.

1.1 History

Cave paintings drawn with red and yellow ochre, hematite, manganese oxide and charcoal may have been made by early Homo sapiens as long as 40,000 years ago. Ancient painted walls, to be seen at Dendera, Egypt, although exposed for many ages to the open air, still possess a perfect brilliancy of colour, as vivid as when painted, perhaps 2000 years ago. The Egyptians mixed their colours with some gummy substance, and applied them detached from each other without any blending or mixture. They appeared to have used six colours: white, black, blue, red, yellow, and green. They first covered the field entirely
with white, upon which they traced the design in black, leaving out the lights of
the ground colour. They used minimum for red, and generally of a dark tinge.
Pliny mentioned some painted ceilings in his day in the town of Ardea, which
had been executed at a date prior to the foundation of Rome. He expresses great
surprise and admiration at their freshness, after the lapse of so many centuries.
Paint was made with the yolk of eggs and therefore, the substance would harden
and stick onto the surface applied.²

A pigment is a material that changes the colour of light it reflects as the
result of selective colour absorption. Naturally occurring pigments such as
ochres and iron oxides have been used as colourants since prehistoric times.
Archaeologists have uncovered evidence that early humans used paint for
aesthetic purposes such as body decoration. Pigments and paint grinding
equipment believed to be between 3,50,000 and 4,00,000 years old have been
reported in a cave at Twin Rivers, near Lusaka, Zambia. Before the Industrial
revolution, the range of colour available for art and decorative uses were
technically limited.³

The industrial and scientific revolutions brought a huge expansion in the
range of synthetic pigments, pigments that are manufactured or refined from
naturally occurring materials, available both for manufacturing and artistic
expression. Prussian blue was the first synthetic pigment, discovered accidentially
in 1704.

Discoveries in colour science created new industries and drove changes
in fashion and taste. The discovery in 1856 of mauveine, the first aniline dye,
was a forerunner for the development of hundreds of synthetic dyes and
pigments. Mauveine was discovered by an 18 year-old chemist named William
Henry Perkin, who went on to exploit his discovery in industry and become
wealthy. His success attracted a generation of followers, as young scientists went
into organic chemistry to pursue the riches. Within a few years, chemists had
synthesized a substitute for madder in the production of alizarin crimson. By the
closing decades of the 19th century, textiles, paints, and other commodities in
colours such as red, crimson, blue, and purple had become affordable.
Figure 1.1: Natural ultramarine pigment in powdered form.

Figure 1.2: Synthetic ultramarine pigment is chemically identical to natural ultramarine.

1.2 What are surface coatings?

Surface coatings are used for protection against wear, wear being defined as progressive damage to a solid surface by the action of relative motion with a contacting substance. As most machinery has moving parts or comes into contact with various materials, wear can be a serious industrial problem. Nowadays there are many methods to modify the surface properties of a component and this constitutes the field of ‘surface engineering’. The processes used in surface engineering can be broadly classified into three groups.

- Processes which apply a new material, a coating, to the surface, i.e. lead to the formation of a different phase with a distinct boundary between itself and the substrate.

- Processes that modify the existing surface by inducing a change in composition of the surface engineered layer. This in general leads to a
more diffuse boundary between the substrate and the reaction layer, e.g. as in carburizing.

- Processes that modify the existing surface without a change in composition, e.g. transformation hardening.

1.3 What are paints?

Liquid materials when applied to a substrate in a thin film, dries to form a cohesive, solid film that changes the properties of the substrate are called paint. It is a mechanical mixture or dispersion of pigments or powders, at least some of which are normally opaque, with a liquid or medium known as the vehicle. It must be able to be applied properly, and it must adhere to the surface on which it is applied and form the type of film desired. Paint must also perform the function for which it is being used: protection, decoration or some other function.\(^5,6\)

1.4 Purpose of paints

Coatings are used for protection, decoration, and/or functional purposes on many types of surfaces. The low gloss paint on the ceiling of a room is used for decoration, but it also diffuses light. The coating on the outside of an automobile adds beauty to it and also protects it from rusting. The coating on the inside of a beer can protect the beer from the can; in soft drink cans, the interior coating protects the can from the beverage. Other coatings reduce growth of barnacles on ship bottoms, protect optical fibres against abrasion and so on.

Traditionally, coatings changed slowly in an evolutionary response to new performance requirements and competitive pressures. An important reason for the slow rate of change was the difficulty in predicting product performance. In recent years, there has been increasing research on understanding the basic relationships between composition and performance to permit more rapid responses to the needs for change. Since about 1965, the pace of technical change has increased. A major reason for change has been to reduce VOC (volatile organic compound) emissions. Other factors are the cost of energy for heating curing ovens requiring lower temperature curing, increasingly stringent
regulations of the use of potentially toxic materials, and increased performance requirements. Various approaches to meet the new requirements, particularly to reduce VOC emissions, are being pursued. The use of waterborne coatings has increased substantially and has surpassed solvent borne in volume. Latex paints have been used for many years in architectural coatings. These coatings have had less solvent than traditional solvent borne paints but still contained significant amounts of solvent. Low solvent and solvent-free latex paints are being introduced. Use of waterborne industrial coatings has been dramatically expanded. Solvent borne coatings are still used but solvent levels are being reduced. In many applications, high solids coatings have been successfully adopted. Research is currently directed to making solvent-free coatings. A growth area has been the use of powder coatings for industrial purposes. In many applications, use of powder coatings permits complete elimination of solvent emissions. Radiation curable coatings, particularly UV-cured coatings, have also grown particularly for clear coatings on heat-sensitive substrates. They are solvent free and very low levels of energy are required for curing.

Most coatings are applied as liquids and converted to solid films after application. Powder coatings are applied as solid particles, fused to a liquid, then forming a solid film. Almost all the polymers used in coatings are amorphous and the term solid has no absolute meaning. A useful definition of a solid film is that it does not flow significantly under the pressures to which it is subjected during testing or use. A film can be defined as solid under a set of conditions by stating the minimum viscosity at which flow is observable in the specified time interval.

A way to form films is to dissolve a polymer in solvent(s) at a concentration needed for application, apply the coating, and allow the solvent to evaporate. In the first stage of solvent evaporation, the rate of evaporation is essentially independent of the presence of the polymer. As solvent evaporates, viscosity increases, $T_g$ increases, free volume decreases, and the rate of loss of solvent becomes dependent on how rapidly solvent molecules can diffuse to the surface of a film. If a film is formed at $25{}^\circ\text{C}$ from a solution of a polymer that, when solvent free, has a $T_g$ greater than $25{}^\circ\text{C}$, the film retains considerable solvent even though it is a hard “dry” film.
Chapter 1

Less solvent is needed for a coating based on solutions of lower molecular weight thermosetting resins. After application, the solvent evaporates, and chemical reactions cause cross-linking. A problem with thermosetting systems is the relationship between stability during storage and time and temperature required to cure a film after application. Generally, it is desirable to store a coating for many months without significant increase in viscosity. After application, one would like to have the cross-linking reaction proceed rapidly at the lowest possible temperature. Reaction rates depend on concentration and are reduced by dilution with solvent and increase as solvent evaporates; cross-linking in the applied film after solvent evaporation is initially faster than during storage. As formulations shift to higher solids, there are higher concentrations of functional groups, and there is greater difficulty in formulating storage-stable coatings. To minimize the temperature required for curing while maintaining adequate storage stability, it is desirable to select cross-linking reactions for which the rate depends strongly on temperature.

Design of stable coatings that cure at lower temperatures or shorter times must be based on factors other than kinetics. Several approaches are used, including use of blocked reactants or catalysts (where the blocking group volatilizes with heat, moisture or oxygen curing) use of a volatile inhibitor, use of a cross-linking reaction (that is a reversible condensation reaction involving loss of a volatile reaction product with some of the mono functional volatile reactant used as solvent), use of a reactant that undergoes a phase change over a narrow temperature range; and UV-curing.

Another consideration is the effect of the availability of free volume on reaction rates and reaction completion. If the diffusion rate is greater than the reaction rate, the reaction will be kinetically controlled. If the diffusion rate is slow compared to the kinetic reaction rate, the rate of the reaction will be mobility controlled. If the temperature is well below \( T_g \), the free volume is so limited that the polymer chain motions needed to bring unreacted groups close together are very slow, and reaction virtually ceases. Since cross-linking starts with low molecular weight components, \( T_g \) increases as the reaction proceeds. If the initial reaction temperature is well below the \( T_g \) of the solvent-free coating, little or no reaction can occur after solvent evaporation and a “dry” film forms.
merely as a result of solvent evaporation, without much cross-linking. The result is a weak, brittle film. Mobility control is less likely in baking coatings because the final $T_g$ of the film is below the baking temperature. In powder coatings, mobility control of reaction can be a limitation, since the initial $T_g$ of the reactants has to be over 50°C so that the powder will not sinter during storage.

Dispersions of insoluble polymer particles form films by coalescence of the particles. The largest volume of such coatings uses latex as a binder. The lowest temperature at which coalescence occurs to form a continuous film is called its *minimum film-formation temperature* (MFFT). A major factor controlling MFFT is the $T_g$ of the polymer particles. The MFFT of latex particles can be affected by water, which can act as a plasticizer. Most latex paints contain volatile plasticizers, coalescing solvents, to reduce MFFT. The mechanism of film formation from lattices has been extensively studied. Film formation occurs by three overlapping steps: evaporation of water and water-soluble solvents that leads to a close packed layer of latex particles; deformation of the particles leading to a continuous, but weak, film; and inter diffusion, a slow process in which the polymer molecules cross the particle boundaries and entangle, strengthening the film. A review paper discusses factors affecting development of cohesive strength of films from latex particles. The extent of coalescence has been studied by small-angle neutron scattering, direct energy transfer of particles labelled with fluorescent dyes, and scanning probe microscopy. Coalescing solvents have been necessary to formulate latex coatings to form films at low temperatures while resisting blocking at higher temperatures. Environmental regulations are limiting permissible emissions of VOC.

### 1.5 Classification of paints

Paints can be classified by many methods, and the method chosen is a function of what is to be accomplished. The first purpose of classification is to group those paints that have the property being discussed and have it to the degree considered necessary for inclusion. In this way, they are set apart from paints not having this property or not having it to the required degree.

1. **Water based and Organic solvent based**
2. Synthetic (petroleum derived) and Natural (plant or mineral based)

These divisions cross over each other. As regards the first pair these terms only refer to the solvent. Water based paints can be organic or inorganic, as regards the rest of their ingredients

1.5.1 Comparison between solvent based and water based paints

Advantages of latex paints

- They have a less objectionable odour, which makes them good for repaints and painting in occupied areas, where solvent odour is an issue.
- They clean up with soap and water, there's no need to work with hazardous and/or flammable solvents, and no used solvent to dispose of afterwards.
- Latex paints dry faster, and can be recoated sooner. This makes them a good choice for painting in occupied areas, where someone might touch or brush up against the freshly painted surface.
- Latex paint binders hold up better in sun-exposed areas, because they're more resistant to UV (ultraviolet) radiation. Alkyd and oil binders will absorb more of this radiation and break down more quickly.
- Latex paint films are less prone to yellowing over time, especially with white, light off-white and pastel colours.
- Latex paint films are more breathable, they allow small amounts of water vapour to pass through the film, so the chance of blistering is reduced. This is especially important when the surface being painted is slightly damp.
- Latex paint films have better gloss and colour retention, so they'll keep a 'like-new' appearance longer.
- Latex paint films are more elastic, so they can expand and contract with the substrate better. This means they'll be less likely to crack and peel over time.
Advantages of solvent-based paints

- Solvent-based paints are less sensitive to application conditions, which mean they can be applied over a wider temperature and humidity range (however, the surface must still be dry for good adhesion).
- Solvent-based paints can be applied in a thicker coat with less sagging, for better coverage.
- Solvent-based paints have better flow and levelling characteristics, so they'll dry to a smoother finish, with fewer brush or roller marks (this advantage is reduced somewhat for low V.O.C. alkyd paints).
- Solvent-based paints provide better surface penetration, especially on weathered wood. This implies improved adhesion and better surface protection.
- Solvent-based paints have better adhesion on smooth surfaces.
- Solvent-based paints initially have a sharper, richer-looking gloss (however, they also tend to lose their gloss faster over time).
- Solvent-based paints initially provide a harder, more durable finish (however, they also tend to become more brittle over time).

The major components of a paint formulation are the binder, pigments, solvent and other substances which may be added relatively low levels but have a marked effect on paint. These auxiliary additives can be included thickeners, driers, anti-skin agents, surface-active agents, biocides, fungicides and numerous others. Paint consists of a dispersion of a pigment or a mixture of pigments, extenders, etc., in a binder or polymer. Other materials may be present to achieve specific properties. They may be organic solvents or water to give the required viscosity, suspending agents to keep the paint in good condition during storage, driers and accelerators which provide for rapid cure of the polymer, flow aids, and so on.

1.6 Binders

Binders are materials used to bind together two or more other materials in mixtures. Its two principal properties are adhesion and cohesion. The binder is
the part which eventually solidifies to form the dried paint film. Typical binders include synthetic or natural resins such as acrylics, polyurethanes, polyesters, melamines, epoxy, or oils. Binders can be categorized into three sorts: those that dry, those that cure when they dry, and those that do not depend on drying for curing. Paints that dry contain a solid binder dissolved in a solvent. This forms a solid film when the solvent evaporates, and the film can dissolve in the solvent again. Latex paints, for example, cure irreversibly when they dry, since they undergo polymerization into irreversibly bound networked structures, so that the paint will not redissolve in the solvent. Recent environmental protection requirements discourage the use of evaporating solvents (VOCs), and alternative means of curing have been developed, particularly for industrial purposes. Epoxy coating, for example, is applied by mixing paint and hardener, which cure by forming a hard plastic structure. Such paints do not, strictly speaking, "dry" at all, but harden. In UV curing paints, the solvent is evaporated first, and hardening is then initiated by ultraviolet light. In art, binders have use in painting, where they hold together paints, pastels, and other materials. Binders used include wax, linseed oil, gum arabic, gum tragacanth, methyl cellulose, gums, or protein such as egg white or casein.

The role of the binder is undoubtedly the most important in determining the properties of paint. Paint binders come in a huge range of chemical types and are often tailor made for customers.

Binders have three major jobs to do:

- Provide adhesion to a substrate.
- Form a continuous film.
- Bind the pigments and additives into the paint.

Solvent borne binders are often referred to as resins and waterborne paint binders as latex. Resins are very much like golden syrup in appearance, consistency and stickiness while many waterborne binders resemble milk types. Binders can be labelled as belonging to one of two main categories. They are either convertible or non convertible.
1.6.1 Convertible Binders

Convertible means that as the binder dries it chemically reacts with a hardener, moisture, or oxygen from the air to form a completely new chemical compound that has quite different chemical and physical properties to the starting binder or resin.\textsuperscript{11,12} These types of resins often become very hard and as a consequence are difficult to recoat. This property also gives excellent chemical and abrasion resistance to paint.

Acrylic Epoxy, Acrylic Urethane, Alkyd resins, Epoxies, Ethyl silicate, Linseed Oil, Moisture cured urethane, Polyester Urethane, Special Acrylic Latex, Urethane Alkyd and Amino resins are the examples.

1.6.1.1 Amino Resins

A variety of melamine formaldehyde (MF) resins are made with differences in the ratio of functional groups, the alcohol, and the degree of polymerization. MF resins are classified into two broad classes: I and II. Class I resins are made with relatively high ratios of formaldehyde to melamine, and most of the nitrogen have two alkoxyimethyl substituents. All the resins contain some oligomers: the lowest viscosity ones have high hexamethoxymethyl melamine (HMMM) contents. Class I resins tend to provide tougher films than Class II. Strong acid catalysts are required. Class II resins are made with smaller ratios of formaldehyde to melamine, and many of the nitrogen have only one substituent. The predominant reactive group present in Class II resins is NHCH\textsubscript{2}OR. They yield cross-linked films at temperatures lower than that for Class I resins and are catalyzed by weak acids.

Urea-formaldehyde (UF) resins are made with different ratios of formaldehyde to urea and different alcohols. UF resins are the most economical and most reactive amino resins. With sufficient acid catalyst, coatings formulated with UF resins cure at ambient or mildly elevated temperatures. The coatings have poor exterior durability. UF resins are used in coatings for temperature-sensitive substrates, such as wood furniture, paneling, and cabinetry.
1.6.1.2 Binders Based on Isocyanates

Isocyanates react with any active hydrogen compound. The largest use of polyisocyanates is as cross-linkers for hydroxy-functional acrylic and polyester resins to make urethane coatings. The high reactivity permits ambient or low temperature curing. Because of the intermolecular hydrogen bonding, Polyurethanes generally have good abrasion resistance.

Polyaspartic esters are used in very high solids coatings. Reaction with ketimines and aldimines gives a mixture of a urea from hydrolysis of the ketimine or aldimine and a cyclic unsaturated urea. Aldimines are used in high solids 2K coatings.

The aromatic diisocyanates most widely used in coatings are bis(4-isocyanatophenyl)methane (MDI) and toluene diisocyanate (TDI) (2,4-diisocyanato-1-methylbenzene). The higher molecular weight minimizes toxic hazards and the higher functionality increases the rate of cure. Aromatic isocyanate based coatings turn yellow on exposure.

1.6.1.3 Epoxy resins

The largest volume epoxy resins are made by reacting BPA [4,4-(1-methylethylethylidene)bisphenol] with epichlorohydrin (ECH). Waterborne epoxy amine coatings are made using emulsifying agents in either or both the amine and the epoxy package. Proprietary “self-emulsifiable” epoxy resins and polyamides are available; properties approaching those of solvent borne coatings can be achieved. Nitroalkanes form salts of amines; the salt groups stabilize epoxy-amine emulsions and allow the system to be reduced with water. After application, the nitroalkane solvent evaporates, freeing the amine.

1.6.1.4 Acrylic resins

Acrylic resins are used as the primary binder in a wide variety of industrial coatings. Their main advantages are photostability and resistance to hydrolysis. An increase in solids became necessary to meet lower VOC emission requirements. The amount of non- or mono functional resin must be kept to a very low fraction. Molecules with no hydroxyl groups would either volatilize or
remain in the film as plasticizers. Molecules with one hydroxyl group terminate cross-linking reactions, leaving loose ends in the coating.

1.6.1.5 Polyester Resins.

Polyesters for coatings are low molecular weight, amorphous, and branched, with functional groups for cross-linking. Most of the polyesters are hydroxy-terminated polyesters. They are cross-linked with MF resins or polyisocyanates. In general terms, thermosetting polyesters give coatings with better adhesion to metal substrates and better impact resistance than TSAs. On the other hand, TSAs give coatings with superior water resistance and exterior durability.

1.6.1.6 Alkyd resins

These dry by chemically reacting with oxygen in the air to form a different chemical in the dry state. This reaction takes place over the lifetime of the coating and as a result alkyd borne paints tend to become brittle as they age. Alkyd resins are generally made from vegetable oils and other chemicals such as glycerine and phthalic anhydride or their equivalents. The oils such as Soya Bean, Safflower and Linseed oils are usually used. Other common oils such as Safflower and Linseed may also be used depending on price. Resins can be made with high solids but still below in viscosity. These types are ideal for gloss enamel paints. At the other end of the scale resins can be produced at very low solids and in a gel form. These resins can be used as thickening agents. In fact alkyd resins can be tailor made to give a wide range of properties.

1.6.2 Non-convertible binders

This is the category for all binders that do not change chemically when they dry. In this range lacquers and latex paints dominate. The advantage of these types of binders is that because they do not change chemically as they dry we know exactly what they will be like when dried for 1 day or after 10 years. Generally the better performing non convertible binders are of high molecular weight, which gives them good toughness and durability without them having to chemically react further as convertible coatings do. Their advantages are that they are always single pack, their physical properties will not change over time.
and they will always be easy to recoat (at least with themselves). Recoating is easy because the next coat simply dissolves the one underneath and they fuse together as if they had been arc welded together. Coat to coat adhesion (inter coat adhesion) is therefore generally excellent.19

A major disadvantage of non-convertible binders is that they are thermoplastic. This means that they soften when heated and often have poor block resistance. They will also suffer if any grease or oil is deposited on them. They will absorb the contaminant and become soft in that area. Non-Convertible coatings obviously have poor solvent resistance but often have excellent chemical resistance. Acrylic latex, acrylic urethane latex, bitumen, chlorinated rubber solution acrylic, vinyl acrylic, vinyl butyral is the general examples. Non-convertible Binders can be divided into three main groups:

1. Lacquers.
2. Latex types.
3. Specialised latex types.

1.6.2.1 Lacquer binders

These binders dry by solvent evaporation. Once solvent has evaporated from the wet paint there is nothing else that needs to happen. Lacquers can be dissolved after they have dried and in theory you could make them up into the same wet paint again. Note that although lacquers can be redissolved in a solvent they cannot be redissolved in all solvents. A test for chlorinated rubber, for example, is that it dissolves readily in a strong aromatic solvent but is not affected by meths. Lacquers vary widely in type from the old nitro-cellulose types used for car paints to solutions of acrylic resin in aromatic solvent to solutions of very poor durability resin.

1.6.2.3 Latex based binders

Most water-based paints are "latex" paints. The binder in a latex paint is a solid, plastic-like material dispersed as microscopic particles in water. This dispersion is a milky-white liquid, which is called latex in the paint industry, in that it is reminiscent of natural latex from the rubber tree. Latex is also called emulsion, and in some countries, such as England, latex paints are referred to as
emulsion paints. Except for appearance, the latex used in paint is in no way connected with the natural latex used in some kinds of rubber gloves, which reportedly have caused allergic reactions among certain users of the gloves. The paint manufacturer makes a dispersion of the pigments which will go into a batch of paint, and adds the latex binder.20,21

Latex is a dispersion of polymer particles in water. Molecular weights of polymers prepared by emulsion polymerization are generally high; Mw of 1,000,000 or higher is common. The molecular weight does not affect the viscosity of the latex. Latex viscosity is governed by the viscosity of the medium in which the polymer particles are dispersed, by the volume fraction of particles, and by their packing factor. Lattices are used as the vehicle in a majority of architectural coatings. A growing part of the original equipment manufacture (OEM) product and special purpose coatings markets is latex based. Acrylic lattices are used for exterior paints because of their resistance to photo degradation and hydrolytic stability. Acrylic latex paints are useful for alkaline substrates such as masonry and galvanized metal. Acrylic and styrene–acrylic lattices are being used increasingly for industrial maintenance coatings. Acrylic lattices are finding increasing interest for kitchen cabinet finishes and for OEM automotive applications.

Latex paint formulations include coalescing solvents and VOC regulations require use of less coalescing solvents. Various modifications in preparation of lattices have been suggested for reduction of coalescent.22 A promising approach is use of thermosetting lattices. A low Tg thermosetting latex permits coalescence without addition of a coalescing solvent. After film formation, cross-linking increases modulus to give block resistance. If a significant degree of cross-linking occurs before application, coalescence will be adversely affected. Hydroxy-functional lattices can be formulated with MF resins or a water dispersible polyisocyanate for wood and maintenance coatings.23 Carboxylic acid-functional lattices can be cross-linked with carboximidides,24 or polyfunctional aziridines.25 m-Isopropenyl-α, α-dimethylbenzyl isocyanate (TMI) [1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene] reacts slowly with water and can be used to make thermosetting lattices.26
Other thermosetting lattices cross-link at room temperature and are storage stable. Carboxylic acid-functional lattices can be cross-linked with β-(3,4-epoxycyclohexyl)ethyltriethoxysilane.\(^{27}\) A combination of amine-functional and epoxy-functional lattices gives stable one-package coatings.\(^{28}\) A latex with allylic substitution cross-links on exposure to air.\(^{29}\) Hybrid alkyd/acrylic lattices are prepared by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization.\(^{30}\) Stable thermosetting lattices can be prepared using triisobutoxysilylpropyl methacrylate as a comonomer.

Vinyl acetate (VAc) (acetic acid ethenyl ester) is less expensive than (meth)acrylate monomers. VAc lattices are inferior to acrylic lattices in photochemical stability and resistance to hydrolysis and are used in flat wall paints.\(^{31}\) The polymers are more hydrophobic than VAc homopolymers and have superior hydrolytic stability and scrub resistance.

### 1.6.2.4. Specialised latex binders

These are very much like the latex types described previously but are modified to give quite different performance in specialised areas. For example, they may be tailor made to have far superior flexibility or cure to a harder block resistant finish. These binders do not properly fit the non-convertible coating class but are very similar in most features to the latex binders.

### 1.7. Pigments

Pigments were in use before the birth of civilisation. Coloured minerals, and materials such as charcoal, were used to colour the bodies and living spaces of primitive man. As his skill grew, the use of minerals expanded to include the colouring of pottery, ceramics, and eventually glass, and the preparation of mixtures with media such as natural oils, and other resinous materials, to make paints. A pigment can be defined as a solid, insoluble, material that is added to a binder to produce colour, reduce gloss, provide physical properties (such as sandability), reduce permeability to moisture, produce texture or even act to prevent corrosion. Pigments usually have a particle size of about 0.5 to 5 μms in standard paints but can be as small as 0.01 μms in the case of some bright organic pigments.\(^{32}\)
From the early beginnings of the use of paint for decorative and artistic purposes has come the highly technical and commercially important paint industry of today. A pigment is a coloured or non-coloured, black or white, particulate compound which can be dispersed in a medium, resin or polymer, without being dissolved or appreciably affected chemically or physically. When paint is applied as a thin film over a substrate, the dispersed pigment will absorb and scatter light. Dyes or dyestuffs, on the other hand, are usually soluble in paint media and give transparent or translucent films. This property obviously limits the utility of dyes in the coatings industry to products such as inks and stains. Pigment reduces the shininess or gloss of the binder. By gradually increasing pigment levels, and by using larger particle pigments, the following gloss levels are achieved:

1. gloss (least amount of pigment)
2. semi-gloss
3. satin or "silk"
4. eggshell
5. flat (greatest amount of pigment)

Paint gloss is determined by using instrument readings of reflectivity taken at different angles from the vertical (polished glass = 100):

\[ \begin{align*}
\text{20°} & \hspace{1cm} \text{60°} \\
\text{85°} & \\
\end{align*} \]

\text{PAINT ON FLAT, UNIFORM SURFACE}

\textit{Figure 1.3: Angles of observation for gloss readings}
The gloss reading at 20\(^{\circ}\) serves to describe the "depth of gloss" is used to describe gloss and semi-gloss paints. The reading at 60\(^{\circ}\) is the measurement of gloss referred to most often and is used with all but dead-flat paints. The 85\(^{\circ}\) reading describes the "sheen" of flat, eggshell and satin paints. Paints described as flat, satin, semi gloss and gloss will have sheen and gloss values falling into the ranges tabulated below. This is not to say that a given product will vary within their angle; rather, each value for the product will be designed to be in the range described below. For example, particular semi gloss paint might have a 20\(^{\circ}\) gloss reading of 15, and a 60\(^{\circ}\) gloss reading of 55.

Table 1.1: Gloss ranges

<table>
<thead>
<tr>
<th>Type of Paint</th>
<th>20(^{\circ}) Gloss</th>
<th>60(^{\circ}) Gloss</th>
<th>85(^{\circ}) Gloss (sheen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gloss</td>
<td>20-90</td>
<td>70 - 95+</td>
<td>--</td>
</tr>
<tr>
<td>Semi-gloss</td>
<td>5-45</td>
<td>25-75</td>
<td>--</td>
</tr>
<tr>
<td>Satin</td>
<td>--</td>
<td>5-25</td>
<td>10-40</td>
</tr>
<tr>
<td>Eggshell</td>
<td>--</td>
<td>2-15</td>
<td>5-25</td>
</tr>
<tr>
<td>Flat</td>
<td>--</td>
<td>0-10</td>
<td>0-15</td>
</tr>
</tbody>
</table>

The paint chemist uses a figure called the PVC (pigment volume concentration) to indicate the relative proportion of pigment to binder for the paint formulation. The PVC is a comparison of the relative volumes (not weights) of total pigment and binder, and is calculated as follows:

\[
\text{PVC\%} = \frac{\text{Volume of Pigments}}{\text{Volume of Pigments} + \text{Volume of Binder}} \times 100
\]

Typical PVC values associated with different levels of paint gloss are given in table 1.2.
Table 1.2: PVC values for different types of paint

<table>
<thead>
<tr>
<th>Type of Paint</th>
<th>Typical PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gloss</td>
<td>15%</td>
</tr>
<tr>
<td>Semi-gloss</td>
<td>25%</td>
</tr>
<tr>
<td>Satin</td>
<td>35%</td>
</tr>
<tr>
<td>Eggshell</td>
<td>35-45%</td>
</tr>
<tr>
<td>Flat</td>
<td>38 - 80%</td>
</tr>
</tbody>
</table>

Thus, a broad range of pigmentation levels is utilized in designing flat paint formulations. Higher quality flat paints, both interior and exterior, will generally have PVCs in the 38 - 50 percent. Because these flat paints have more binder available per unit of pigment, they will have better durability than higher PVC flats, all else being equal, as measured by properties such as scrub resistance and dirt resistance for interior use and colour retention, chalk resistance, mildew resistance, and general durability for exterior applications.

1.7.1 Types of Pigments

Today, many compounds are still obtained from natural sources and treated to give pigments for paint and other uses. The vast majority of such pigments, however, are nowadays the so called extender pigments. These extenders, or fillers, as they are sometimes known, play a very important role in the formulation of paint, and although they are less costly than coloured pigments or other special pigments, their total contribution to the properties of paint must not be ignored. The ‘prime’ pigments, including coloured pigments, anti-corrosive pigments, and other manufactured pigments, are produced by the chemical industry as inorganic metallic salts, metallic and non-metallic organic compounds. Coloured organic compounds, in general, have come from the dye industry that has developed and is continuing to develop dyes for the textile and wool industries. It is a straightforward matter to design insoluble pigment
molecules and the manufacture of pigments is now a worldwide business of huge economic importance.

The pigments can be classified into three main groups:

1. Prime pigments provide colour (Either inorganic or organic).
2. Extender pigments control gloss level, texture, etc.
3. Anti-corrosive and special function pigments.

1.7.2. Prime pigments - inorganic

The term prime means colour giving when used with the word pigment. The term inorganic means the pigment is of mineral origin. Inorganic prime pigments are usually metal oxides. They are called prime because the first use of paints was for decoration and colour was therefore of first (prime) importance. Many metal oxides were found naturally e.g. Red and yellow iron oxides. The colour is also depending on the crystal structure and particle size. Today most are made synthetically to get the cleanest colours possible. Titanium dioxide is the white pigment that colours just about everything we see that is white.

Main inorganic pigments:

White: Titanium Dioxide, exist in three forms anatase, rutile and brookite. The most important pigment in use today is titanium dioxide. Titanium dioxide, as we use it in paint, first came into commercial production in 1941. Since then its sales have climbed and its superb properties have seen it established as being far superior to any other white pigment. It has had no rivals since the banning of white lead in the early 1970's. Any white paint, plastic or paper you see will contain titanium dioxide. Today it has been refined to such an extent that you can get it in a wide range of "flavours" depending on whether you wish to have a paint with minimum chalking or maximum gloss or whatever. What grade is chosen depends on the skill of the humble designer paint chemist. Although titanium dioxide is far ahead of any other white pigment for hiding power it is still relatively poor compared to most other inorganic pigments.
Red: Red iron oxide is used as red pigment. This is the colour seen on old farm barns throughout the country. It comes in differing shades, which are determined by the pigment particle size.

Yellow Ochre: A yellow form of iron oxide.

Green: Chrome Oxide.

Characteristics of inorganic pigments:

- Excellent opacity or hiding power.
- Excellent light fastness or resistance to fading.
- They are relatively inexpensive and easy to mix into paint mill bases.
- The colours are generally dirty in tone.
- There are bright clean inorganic red, orange and yellow pigments but these have mostly slipped into obsolescence because of their toxicity. These include lead chromate type pigments; cadmium and selenium based pigments and of course white lead and red lead.

- They are quite dense pigments and will tend to settle out unless precautions are taken.
- They are relatively heat stable and chemical resistant.
- Largish particle size of 0.3 to 1 μms.
- Durability depends on the type of chemical treatment these pigments are given during manufacture.

1.7.3. Prime pigments - organic

The term organic mean that the pigment is based on the chemical element carbon. It was once thought that all organic chemicals could only be obtained from living things and hence the name. Today there are millions of different organic chemicals most of which can be produced synthetically without the need to source raw materials from living things. Most organic pigments are not naturally occurring and are made from petroleum by-products in very complicated chemical processes by clever chemists. Organic pigments are the brightly coloured ones used for the clean colours red, yellow, bright green
and blue, purple and magenta. Organic pigments have really sprung into prominence in the last 10-20 years for two main reasons: 38, 39

1. The awareness of the dangers of lead in the older bright red and yellow lead chromate type pigments meant that these pigments had to be replaced.

2. The advancing technology in manufacturing and chemical engineering in the organic pigment industry.

Main organic pigments:

Black: A form of carbon that resembles the soot in your grannies old chimney. Surprisingly comes in quite a range of shades that can be clearly seen when it is reduced with white. Extremely good hiding power and light fastness.

Blue: Most durable blue organic pigments have a little bit of copper to help them. This is chemically bound into the pigment. Good light fastness and excellent tinting strength.

Green: There are yellow and blue shades available. Good light fastness and tint strength. Malachite green is an example.

Orange: Orange organic pigments are generally very poor in hiding power and very poor in light fastness. Dinitro anilines are generally used as orange pigment.

Magenta: 2,9-dimethylquinacridone is an example. They are very expensive but poor tint strength and hiding power. It has good light fastness.

Characteristics of organic pigments:

• Available in bright vivid colours to match all shades of the rainbow.

• Generally at least 10 times as expensive as the closest inorganic pigment.

• Very difficult to get clean reds and yellows with good opacity and good exterior light fastness.
Introduction

• Often these pigments are very difficult to grind into paint mill bases.
• Pigments are generally low in density and not prone to settling out.
• Organic pigments often have a very high oil absorption or demand for binder. This means that in many paints only so much pigment can be added until the paint becomes low in gloss and very thick. This results in paints with poor opacity.
• Low density and may tend to float to top of paint.
• Excellent to very poor hiding power.
• Excellent to very poor light fastness.
• Colours are usually very bright and clean toned (apart from black).
• Poor hiding power means that many organic pigments have transparency properties. This makes them ideal for automotive type metallic finishes when they are used to tint aluminium flake containing bases.
• Generally the pigment particle size is very small 0.01 to 0.1 μms. This makes handling in the factory difficult as spilling just a few grams can contaminate a large area. Some of these pigments are more like gases to handle than powders.

1.7.4 Extender Pigments.

The binders used in protective coatings dry or cure at ambient temperatures either by solvent evaporation, air oxidation or by chemical reaction to form continuous films and are porous to a greater or lesser degree to oxygen, water, chlorides, sulphates, carbon dioxide etc. In other words, as clear films, they are not entirely suitable for long-term protection of substrates against corrosion. They have to be reinforced by pigments.

There are several other minerals that have been used in paints for many years. These were called extenders, and were considered as cheap materials that reduced the cost of the finished paint. However, experience has shown that the so called extender pigments are of great value in giving improved water
resistance, improved durability, easier application and good storage stability to paints, as well as improving commercial viability by lowering costs.  

Extender pigments are generally white, naturally occurring minerals with very low solubility in water and preferably inert to the action of acids and alkalis. This does not exclude coloured minerals such as iron oxides that have use in primer formulations as extending pigments. The minerals are won by mining operations and are crushed, cleaned and segregated as products with particles from sub-micron to a few microns in size. The minerals cover a wide range of chemical compounds such as sulphates, oxides and silicates. Carbonates of calcium and magnesium are used extensively in paints for decorative purposes but because of their solubility, especially in acid solutions, are not formulated into coatings requiring high durability and high water resistance.

Aluminium flake (manufactured from high purity metal by milling aluminium powder in a solvent such as white spirit, with stearic acid as a lubricant with a size of about 1 to 100 nm in the longer dimensions and 0.05 to 2 mm in thickness) when distributed in a polymer, remain dispersed in the body of the film, reduce the permeability of polymers by causing ions or molecules to follow a long, tortuous path to the substrate, as compared with a direct path through an unfilled polymer. It also has the advantage of excellent resistance to ultraviolet radiation. These metallic finishes are widely used in the automotive industry where their characteristic ability to show a different colour when viewed from different angles has a strong bearing on body design. Thin flakes of chemical-resistant glass can also be used in a similar manner to aluminium flakes. The media used for these coatings are essentially solvent-free materials, with two-pack epoxy and peroxide cured polyester being preferred. Many structures, some going back to Victorian times and including the Eiffel Tower, have been maintained with MIO-based coatings since they were built, with excellent results. German and British railways used the pigment for many years.

Mica, an aluminium potassium hydrated silicate (Al₂KSi₃.12H₂O), is found in several forms, the most important for the paint industry being muscovite. Mica particles have a high aspect ratio, i.e. diameter to thickness ratio, of greater than 25, but the pigment has high oil absorption and this limits
its loadings in paint films to relatively low levels. Additions of mica to zinc-based primers have been shown to improve the performance of these products.

Talc (Magnesium silicate, 3MgO·4SiO₂·H₂O) is the most widely used extender pigment. It can have a fibrous or needle-like structure, be plate-like, or amorphous, depending upon the source. Talc is non reinforcing type filler but improves the impermeability of films. The fibrous structures confer good storage properties on paint by preventing settlement of pigments. They are generally hydrophobic, have good colour and are easily dispersed in paint media.

The mineral form of barium sulphate (Barytes) is an inert compound with a low oil absorption and used in build coats and primers at high loadings. It has a relatively low cost and finds use in chemical resistance coatings. The precipitated form of barytes is used as an extender for coloured pigments. Barium sulphate has the disadvantage of a high relative density and this can lead to settlement problems.

Synthetic silica is suitable as a matting agent for coatings due to its high surface area. Kaolin or China clay is a hydrous aluminium silicate (Al₂O₃·2SiO₂·2H₂O). The calcined form has found considerable use as an extender in water-based systems. It is a lamellar pigment with a relatively high oil absorption and low relative density. Nepheline syenite is a nodular form of potassium sodium aluminium silicate. It has a low oil absorption, similar to Wollastonite, and finds use in high solids anti-corrosive primers.

1.7.5 Anti-corrosive pigments

As the name implies, these materials are used to prevent the corrosion of the substrate. Corrosion occurs because metals are not homogeneous materials. Heterogeneities are introduced at grain boundaries, by stress and surface contamination and by differences in composition. When in contact with an electrolyte, areas of higher potential behave as anodes and those of lower potential as cathodes, thereby creating a corrosion cell. Metal ions are formed at the anodic areas and dissolve into the electrolyte. The electrons produced pass through the metal to the cathodic areas for subsequent reaction and so the process continues. Interrupting or slowing down any aspect of this process reduces the rate of corrosion.
Traditional anti-corrosive pigments such as zinc chromate work by chemically or electrically interfering with the process of rusting. Metallic zinc pigments work by sacrificing themselves for the steel in the corrosion process. As the zinc sacrifices itself zinc corrosion products are formed which are commonly referred to as white rust. These types of priming paints are sometimes referred to as cold galv. This is a reference to galvanised iron, which is steel coated with zinc.

Barrier pigments are used in high build paints and the idea is that they provide a physical barrier to any water and oxygen that tries to wriggle through the paint film. If a steel surface can be starved of water and/or oxygen no corrosion can take place. Barrier pigments are plate like in structure. Typical examples are leafing aluminium flakes, glass flake and micaceous iron oxide. The extender pigments talc and mica also act as barrier pigments because of their plate like structure.

1.7.6 Properties of pigments

1.7.6.1 Appearance

Most pigments are used to provide a visual effect, mainly colour and opacity. Having achieved the required colour and opacity, it is important to ensure the pigment will remain essentially insoluble in the system in which it is used and will give the required physical properties, such as light fastness, weather ability and resistance to chemicals.

1.7.6.2 Colour of pigments

The colour of a pigment is mainly dependent on its chemical structure. The selective absorption and reflection of various wavelengths of light that impinge on the pigmented surface determines its hue. A blue pigment appears so because it reflects the blue wavelengths of the incident white light that falls upon it and absorbs all of the other wavelengths. Black pigments absorb almost all the light falling upon them, whereas white pigments scatter and reflect virtually all the visible light falling on their surfaces. Fluorescent pigments have an interesting characteristic as well as having high reflection in specific areas of the visible spectrum; they also absorb light in areas outside the visible spectrum.
The differing absorption and reflection characteristics of compounds are attributed to the arrangements of the electrons within their molecules and to their energy and frequency vibration. A molecule will absorb electromagnetic radiation from part of the spectrum. This absorption excites the electrons, resulting in the promotion of an electron from its ground state, $E_1$, to an orbital of higher energy $E_2$. The wavelength of the light absorbed is determined by the difference in energy $E$ between the two orbital concerned:

$$E = E_2 - E_1 = h\nu/\lambda$$

where $h$ is Planck's constant, $c$ is the velocity of light, and $\lambda$ is the wavelength of light.

A given molecule has a limited number of orbitals, each with its own characteristic energy. This means that the energy difference $E$ described above has certain definitive values. The pigment molecule is therefore only able to absorb light at particular wavelengths, determined by the energy difference $E$ that is characteristic of the given molecule. As the electronic excitation is accompanied by a multitude of rotational and vibrational transitions, the absorption is not at a single wavelength, but over a wide band. The wavelengths not involved in the absorption are reflected and determines the colour of the molecule, and therefore produce the complementary colour to the wavelengths absorbed.

Fluorescent pigments are the fluorescent dyes that have been dissolved into a resin, often achieving good migration fastness on account of their reacting with the resin. The dyes themselves are often basic dyes, with poor light fastness, and while as 'pigments' they have improved durability, nevertheless they are still considered poor and are limited to interior applications. They also have poor opacity and are quite expensive. There is an exception, (azomethine), which is a true pigment and has been known since the end of the nineteenth century.

The main cause of colour of inorganic pigments is the charge transfer spectra and/or d-d transition spectra, especially of the 3d transition metals. However, this does not explain all inorganic pigments. It is well known that molecules containing a metal in two valency states can be intensely coloured.
e.g. Prussian blue. It is thought that the deep colour of such compounds is due to transfer of an electron from ions in the lower valency state to a higher one. Another cause of colour is the trapping of a cation in the three-dimensional lattice carrying a negative charge. Therefore, within these cavities there is room for positive and negative ions and neutral molecules. Ultramarine is an example of such a molecule.

It is not only the pigment's chemical nature that determines its colour. The crystal structure is now recognized as playing an important role. Several pigments can exist in more than one crystal form, a property known as polymorphism, and these forms can be of very different colours. The clearest examples are linear trans-quinacridone, which exists in three different crystal forms. Polymorphism is not limited to organic pigments. Titanium dioxide exists in three crystal forms and other polymorphic pigments such as lead chromates and lead molybdates also have more than one crystal form. Particle size also influences colour. Smaller particles are usually brighter in shade and change the hue of a pigment.

1.7.6.3 Tinctorial strength

Tinctorial strength must be considered when choosing a pigment. The higher the tinctorial strength, the less pigment is required to achieve a standard depth of shade, therefore it has economic implications. The chemical structure is fundamental to the tinctorial strength of the pigment molecule. Highly conjugated molecules show increased tinctorial strength. Inorganic pigments that are coloured because of their metals in two valency states, show high tinctorial strength, whereas those that have a cation trapped in a crystal lattice are weakly coloured. Particle size can make a dramatic difference to the tinctorial strength of a pigment. smaller particles yielding higher tinctorial strength. The paint manufacturer can increase tinctorial strength by efficient dispersion, which is particularly important for pigments with a very small particle size.

1.7.6.4 Insolubility

In the definition of a pigment, it was stated that it must be 'insoluble in, and essentially physically and chemically unaffected by the vehicle or substrate'. Therefore, when a pigment is incorporated into paint formulation, it must not
significantly dissolve in either the vehicle or solvents. Nor must it react with any of the components, such as crosslinking agents. In the dried film the pigment must also remain unaffected by the substrate and to agents, with which it comes into contact, including water, which may simply be in the form of condensation, or acidic industrial atmospheres. Although we have defined pigments as being insoluble, in practice they may dissolve under certain conditions leading to application problems. The application problems associated with a pigment being soluble in a system include the following.

**Blooming:** If the pigment dissolves in the solvent, as the paint dries, the solvent comes to the surface and evaporates, leaving crystals of the pigment on the surface in the form of a fine powder. This deposit looks very much like the bloom seen on the surface of soft fruit hence its name. As solubility increases with temperature, this phenomenon is made worse at elevated temperatures, such as in stoving paints. As the pigment has also dissolved in the binder, usually in the form of a supersaturated solution, it continues to migrate even when the solvent has evaporated and continues to appear on the surface even after being wiped clear.

**Bleeding:** Pigments in a dried paint film may dissolve in the solvent contained in a new coat of paint applied on top of the original film. If this topcoat is the same colour this will be of little on sequence. However, if the topcoat is a different colour, particularly a white or pale colour, the result can be disastrous. It is most noticeable when a white paint is applied over a red paint. The red pigment bleeds into the new white paint film, staining it pink. Subsequent coats will not cover the original, as the pigment continues to dissolve. Again elevated temperatures exacerbate the problem. Although usually associated with red pigments, it is possible with any pigment possessing only poor to moderate solvent fastness.

**Recrystallization:** This phenomenon was almost unknown until the introduction of bead mills. During the milling stage heat is generated, which dissolves a portion of the pigment. The paint often goes through quality control without a problem, appearing strong and bright, because
the pigment is acting as a dye in a supersaturated solution. However, over a period of time the dissolved ‘pigment’ starts to precipitate out, losing brilliance and colour strength. This becomes especially noticeable in the case of paints containing two differently coloured pigments, e.g. a blue and a yellow, that have different solubility characteristics. The more soluble yellow pigment dissolves and then as it comes out of solution and precipitates, the paint will go bluer in shade. Recrystallization can even take place in aqueous systems. It can be avoided by using less soluble pigments and or by controlling the temperature during the dispersion.

1.7.6.5 Opacity

The terms ‘hiding power’ and ‘opacity’ are often interchanged, but there is a subtle and important difference. Hiding power is the ability of a pigmented coating to obliterate the surface. It is dependent on the ability of the film to absorb and scatter light. Naturally, the thickness of the film and the concentration of the pigment play a essential role. At the other extreme, titanium dioxide absorbs almost no light, yet its ability to scatter light ensures that at a high enough concentration it will cover the substrate being coated. Even certain types of paint may require transparency, especially wood finishes, certain can coatings and in metallic and pearlescent finishes, now so popular in automotive finishes. A key factor in the opacity of a pigment is its refractive index (RI), which measures the ability of a substance to bend light. The opacifying effect is proportional to the difference between the refractive index of the pigment and that of the medium in which it is dispersed. This is one of the main reasons why titanium dioxide is now almost universally used as the white pigment in paint. In Table 1.3 the refractive index is given for white pigments, important extender pigments and for media in which they may be incorporated. The refractive index is fundamental to a given compound providing it retains the same crystal structure. As most inorganic pigments have a high refractive index and organic pigments have much lower values, it follows that most inorganic pigments are opaque, whereas organic pigments are transparent.

Particle size of the pigment also affects the opacity. As the particle size increases, the ability of the particle to scatter light increases, up to a maximum.
It then starts to decrease. This ability to scatter light increases the hiding power of the pigment, and therefore the hiding power also reach a maximum and then decreases as the particle size increases. Whereas the refractive index of a compound cannot be altered, the pigment manufacturer can influence the particle size of pigments; consequently particle size selection has become one of the principal developments in pigment technology in recent years. The particle size that gives optimum opacity can be calculated for any given wavelength. For maximum opacity, the desired particle size is approximately half the dominant wavelength. There has even been the development of organic pigments that have even larger particles, moving them beyond this point of maximum opacity, in order to combine transparency with the higher light fastness one sees from larger particles. This phenomenon has been called ‘ultra transparency’, but has the disadvantage that such pigments have low tinctorial strength. The organic pigments have a particle size of between 0.1 and 0.5mm, inorganic pigment can be much larger. Titanium dioxide manufacturers often try to reduce the size of their pigment particles, down to around 0.25mm, thereby enhancing opacity.

**Table 1.3: Refractive index of pigments**

<table>
<thead>
<tr>
<th>Medium</th>
<th>RI</th>
<th>Pigment or extender</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.0</td>
<td>Calcium carbonate</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chaina clay</td>
<td>1.56</td>
</tr>
<tr>
<td>Water</td>
<td>1.33</td>
<td>Tale</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barytes</td>
<td>1.64</td>
</tr>
<tr>
<td>Film formers</td>
<td>1.4-1.6</td>
<td>Zinc oxide</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc sulphide</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Titanium dioxide-Anatase</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rutile</td>
<td>2.76</td>
</tr>
</tbody>
</table>
1.7.6.6 Transparency

Transparency is obtained by producing as small pigment particle as possible. This is achieved by surrounding the particles as soon as they are formed with a coating, which prevents the growth of crystals. For higher-quality pigments that are required to have better mechanical stability, alternative coatings such as more complex resin derivatives with higher melting points and greater resistance to oxidation or other surface treatments are used. Although iron oxide pigments are normally opaque, they can be made in a transparent form. The transparent form is widely used for metallic finishes, where its high transparency not only gives an attractive finish, but its excellent weather ability can actually improve the weather ability of pigments with which they can be combined. Transparent iron oxides depend on the particles being unusually small, and also having a specific crystal shape. The dispersion process can influence the transparency obtained, as it consists of breaking up clusters of particles to individual primary particles. Good dispersion will make maximum use of a small particle's transparency.

1.7.6.7 Durability

For most paint applications, pigments are required to be durable. They should neither fade nor darken to any extent. The pigment concentration and other pigments used in the paint play a role. Durability must also be considered in terms of the end use. Pigments must not weaken the film formed by the binder. Indeed, in a well formulated paint it is likely to assist in producing a cohesive, hard, elastic film, protecting the substrate and increasing the life expectancy of the paint film. This will also be dependent on whether the paint film is sufficiently thick. For corrosion-resistant paints, the pigment is a fundamental component; often providing chemical protection to the substrate.

1.7.6.9 Chemical stability

The requirements of a pigment to withstand any chemicals with which it may come into contact may well be a critical factor in the selection process. One has to consider two aspects of chemical attack. First it can come from within the paint itself. The resin, crosslinking agents, UV-initiators, and any other additive may react with the pigment and change its performance. In the early days of UV-
coatings, additives on the pigment drastically reduced storage stability, resulting in the coating gelling in the can. For powder coatings the initiator can change their shade and reduce fastness properties. The second possible attack can come from chemicals with which the coating comes into contact. Water, in the form of condensation, can seriously affect a paint film, including domestic situations such as bathrooms and kitchens. Many of the detergents used for cleaning paintwork are harsh and aggressive towards the pigment. Most test methods associated with chemical stability consist of applying the chemical to the surface of the coating, keeping them in contact for a given time, then measuring the discolouration of the coating and/or the staining of the chemical concerned.

1.7.6.10 Heat stability

Few pigments degrade at temperatures normally associated with coatings. However, several pigments will change shade because they become more soluble as the temperature is increased. Therefore for organic pigments, heat stability is closely related to solvent fastness. Elevated temperatures can also result in a modification in the crystal structure of pigments. Pigments with a highly crystalline structure are usually more heat stable than polymorphic pigments, where the different crystal modifications may respond differently to heat. Generally, inorganic pigments have superior heat stability an exception is yellow iron oxide, which loses water from the crystal at elevated temperatures.

1.8 Additives

This group of raw materials is used in relatively small amounts to give coatings certain necessary properties. The role of the paint formulator is to bring together the required constituents in a stable, cost-effective composition that can be conveniently applied to the substrate. Most additives are a nuisance and we would rather not have them. Often they are there because we have too much of another ingredient. For example we need to add deformer to waterborne paints because of the large amounts of wetting agents (soap or detergent type chemicals) needed to make a tinting system work. Paint additives used in paint industry are:
1.8.1 Antisettling agents

This group of agents is used to prevent the separation or settling of the pigment from the vehicle. Most commonly this is done by using additives that set up a gel structure with the vehicle, trapping the pigment within the gel and preventing it from settling to the bottom.

1.8.2 Antiskinning agents

An important additive for enamel paints is the anti-skinning agent. Without this ingredient all enamel paints would skin in the can. Note that excessive stirring of alkyd paints or leaving lids improperly sealed can result in permanent loss of the volatile antiskinning agent. Never shake up old cans of enamel paint that have been in storage. In most cases skins can be removed by carefully cutting away from the top of the paint layer. These are essentially volatile antioxidants that prevent oxidation, drying, or skinning of the paint while it is in the can but volatilize and leave the paint film, allowing it to dry properly once it has been applied. The most common antiskinning agents are methyl ethyl ketoximine, very effective in alkyds, and butyaldoxine, effective in oleo resinous liquids. Phenolics are sometimes used, but they can slow the drying time of the coating.

1.8.3 Thickeners and rheology modifiers

It provides adequate viscosity (thickness), so that the paint may be applied properly. The impact of thickener depends on how thick the paint goes on and how well it flows out when applied. The modern rheology modifiers help latex paints to resist spattering when applied by roller and flow out smoothly.

Misconception about paint and quality is the perception by many painters that the thicker a paint is, the better the quality. But especially if a large volume of thinner is needed to get the paint to a useable consistency. Be aware that there is nothing natural about the thickness of paint. All paint is artificially thickened and we can make most paints as thick or as thin as we like. You should be aware that the thickeners used to thicken paint also control other paint properties and that if paint is thinned more than a few percent these properties can be compromised. Thick does not necessarily mean high quality. Cheaper paints are
often disguised by making them thicker than necessary. Paint thickeners have two main roles.

1. Prevent the paint solids from settling out in storage and to prevent the paint from sagging during application. The use of too much will result in poor flow and the paint being full of brush marks.

2. Make the paint harder to spread and to impart what we call brush drag. In enamel paints this property is often built into the particular binder rather than being given by a special thickener. This allows the painter to apply the correct amount of paint by applying the paint at a natural spreading rate. These thickeners also act to minimise roller fly off (paint spattering everywhere when roller applied)

Waterborne paints use special thickeners called rheology modifiers, which give excellent flow and levelling and also impart brush drag. In water-based paints, the most common bodying agents are methyl cellulose, hydroxyethyl cellulose, the acrylates, and the bentonites. These agents also tend to improve the stability of the emulsion.

1.8.4 Antifoaming agents

Most colours used in the paint industry are a blend of colours. Thus, to form a gray some black is added to a white paint. It is important that one colour not separate from the other and antifoaming agents are used for this purpose. Silicones are sometimes used, but they pose serious bubbling and recoatability problems. Special antifoaming agents are sold under various trade names.

1.8.5. Levelling Agents

Sometimes paint does not flow properly and shows brush or roller marks. These can often be corrected by special wetting agents that cause the vehicle to set the pigment better.

1.8.6. Antifoaming

This is much more of a problem in water-based than in solvent-based paints. The presence of bubbles not only makes for an unsightly paint when applied, but results in a partially filled paint can when the bubbles leave the paint
while it is in the can. Latex paints are stabilized with surfactants and colloids which, unfortunately, also help to stabilize air introduced during manufacture or during application, and thus form stable foam. Non-aqueous paints (indeed any liquid other than a pure one) may also show bubbling. Sometimes two antifoam additions are made, one at an early stage of manufacture and the other just prior to filling-out. Usually antifoams are of high surface activity and good mobility while not being actually soluble in the foaming liquid. Commonly they work by lowering the surface tension in the neighbourhood of the bubble, causing them to coalesce to larger, less stable bubbles which then break. At their simplest, these additives may be solutions of single substances such as pine oil, dibutyl phosphate, or short chain (C6–C10) alcohols.

1.8.7 Biocides

They are two types used in latex paints

1. A preservative to keep bacteria from growing in the paint. This is especially important for paint stored in containers that are repeatedly opened and closed, because contamination can occur.

2. A mildewcide, to discourage mildew from growing on the surface of the paint after it has been applied. This is used mainly in exterior products, although some interior paints, such as those formulated for use in damp areas, e.g., kitchens and baths, may also contain mildewcide.

Most exterior paints will suffer a blackish-greenish discoloration caused by the growth of fungi or mildew on the surface. Until now this condition has been prevented by the inclusion of a mercurial in the paint, often in combination with zinc oxide. Today non mercurial also are available.

1.8.9 Wetting and dispersing agents

Wetting agents and dispersing agents are essential for getting pigments into paints. They are related to the detergents used for washing dishes and act to wet the pigments and allow them to be more easily dispersed into paint. They are more often needed in latex type paints than in solvent borne paints where the binder can often do a very good pigment-wetting job by itself. Latex binders tend to become extremely aerated and can gel if subjected to too much
mechanical stress such as is needed to disperse pigments. Organic pigments in particular can be very difficult to grind up into paint and need quite specialised, individually tailored, wetting and dispersing agents to achieve this. Our architectural tinters are loaded with wetting agents. Not only are they needed to wet the pigments in the tinter, but a lot of extra wetting agent is also needed to allow the tinters to be added to both solvent and water based paints. The level of these machine tinters in our paint should be kept as low as practicable. The presence of glycols, wetting agents and surfactants in our latex roof paints is the reason were commend that roofs used for collecting drinking water are disconnected for the first few rains. These materials make water foamy and give a slightly unpleasant taste.

Many different types of wetting agents are necessary in water-based paints. Some are used for improved pigment dispersions, whereas others are employed to improve adhesion to a poor surface such as a slick surface. A dispersing agent in latex paint is used to defloculate pigment and extender particles, while at the same time reducing the viscosity of pigment/extender dispersion. Anionic and non-ionic surfactant is commonly used dispersing agent. Sodium and potassium polyphosphates are widely used as anionic dispersing agent.

1.8.10 Freeze-Thaw Stabilizers

These are necessary in water-based paints to prevent coagulating or flocculating when the paints are subjected to freezing temperatures. The stabilizers, such as ethylene or propylene glycol, lower the temperature at which the paint will freeze. Another way of accomplishing this goal is to use an additive that improves the stability of the emulsion.

1.8.11 Coalescing Agents

Coalescing agents are temporary plasticisers which are used to reduce MFT of the polymer. They are high boiling liquids which have boiling points between 185-255°C. The purpose of these agents in water-based paints is to soften and solvate partially the latex particles in order to help them flow together and form a more nearly continuous film, particularly at low temperatures. This can be done with poly alcohols such as ethylene glycol, propylene glycol etc.
Water-soluble coalescents are used to modify other properties such as wet edge and freeze-thaw stability. In gloss paint high level of propylene glycols are incorporated primarily to improve wet edge. Solubility of coalescent in the water phase or polymer phase is good to coalescent efficiency. Coalescing solvent has a vital part in drying process of the latex paints. The coalescing solvent is needed to soften the solid suspended acrylic binder particles in order for them to fuse or stick together in one unified mass. The coalescing solvent is a lot slower to evaporate than water in normal conditions. Normally the water evaporates quickly and the drying paint becomes quite thick making it difficult for the coalescing solvent to escape. In cold conditions this is not the case. The paint remains quite liquid (because the water is not evaporating) and the coalescing solvent are given much more freedom with which to escape the paint film. There is never any coalescing solvent vapour in air (unless you live in a paint factory) so in times all the coalescing solvent will evaporate from the coating leaving the water behind. It may take about 3-5 hours for this to happen. As a result the latex particles are left surrounded by only water. When the weather eventually warms up the water will evaporate leaving behind a poorly coalesced acrylic paint. The severity of this poor coalescence on the paints physical properties varies depending on time and temperatures. The worst that can happen is that the paint dries as a powder. In real life this may not be the case and the actual result will be something in between a powder and a normal paint film. The visible results may be a patchy appearance with possible loss of gloss and adhesion. The next rain may result in blistering, or the entire coating could be washed off.

1.9 Solvents

Solvents are liquids that can dissolve other substances in the same way you dissolve. The dissolved material can be reclaimed from a solution in the solvent by evaporating the solvent off. Solvent is the medium, in which the pigment and binder are carried, which is then evaporates when paint is on the substrate. There are essentially three types of volatile solvents a true solvent (which tends to dissolve the basic film former), a diluent, and a nonsolvent (tolerated by the coating). Thus, in a lacquer, ethyl acetate is the true solvent.
ethyl alcohol is the latent solvent, and petroleum hydrocarbon is the diluent. In a latex paint water might be considered a true solvent, but in alkyd enamel it would be a diluent. Paint simply could not be applied without a solvent, for in most instances the result would be a semisolid mass. It can therefore be said that the most important property of a solvent is to reduce viscosity sufficiently so that the coating can be applied, whether by brush, roller, dipping, or spraying. Besides this most important property, the solvent has other significant features. It controls the setting time of the paint film, which, in turn, controls the ability of one panel of paint to blend with another panel applied later. In addition, it controls important properties such as levelling or flow, gloss, drying time, durability, sagging tendencies, and other good or bad features in the wet paint or paint film.

1.9.1 Petroleum Solvents

These constitute the most popular group of solvents used in the coatings industry. They consist of a blend of hydrocarbons obtained by the distillation and refining of crude petroleum oil. The faster-evaporating types, which come off first, are used as diluents in lacquers or as solvents in special industrial paints. Solvents of the intermediate group are used in trade sales paints. Members of the slowest group, beginning with kerosene and going into fuel oils, are used for heating, lubrication, and other applications.

The most important group used in trade sales paints and varnishes consists of mineral spirits and heavy mineral spirits. They are sometimes considered a turpentine substitute because the distillation ranges are approximately the same. Because of their low price, proper solvency, and correct evaporation rate, mineral spirits are probably the most popular solvents used by the coatings industry. Normally they are the sole solvents in all interior and exterior paints with the exception of flat finishes. Special grades that pass antipollution regulations are now being sold. Heavy mineral spirits are a slower-evaporating petroleum hydrocarbon and an ideal solvent for flat-type finishes. During cold winter weather, the formulator might use a combination of regular and heavy mineral spirits. Architects switching to new high-solids coatings should work closely with the manufacturer to assure proper performance and be certain that application personnel are properly trained to handle the more
complex systems. In many coatings it gives satisfactory spraying and dipping properties. Because of regulations regarding air pollution, the straight types of hydrocarbon solvents that hitherto have been the backbone of the coatings industry are being phased out and replaced by mixtures that will pass the stringent regulations of various states.

1.9.2 Alcohols, Esters, and Ketones

A great many of these types of solvents are used in industrials and especially in lacquers. Among the more popular solvents of this type are the following:

1. Acetone (CH₃COCH₃): Very strong and very fast evaporating and can cause blushing. It is used in paint and varnish removers.

2. Ethyl acetate (CH₃COOC₂H₅): This is a standard fast-evaporating solvent for lacquers. It is relatively low in cost.

3. Butyl acetate (CH₃COOC₄H₉): This is a very good medium-boiling solvent for lacquers. It has good blush resistance.

4. Ethyl alcohol (C₂H₅OH): Used only in a denatured form, it is a good latent solvent for lacquers and also is used to dissolve shellac. It is relatively low in cost.

5. Butyl alcohol (C₄H₉OH): This is a medium-boiling popular latent solvent for lacquers.

The presence of toxic solvents in the atmosphere of the work-place is not the only problem giving concern in recent years. It is now well established that the emission of volatile organic compounds (VOCs) into the atmosphere can have serious environmental implications. Thus, effects on the concentration of ozone in the stratosphere resulting in the depletion of ozone (particularly in the Polar Regions) have been much publicized as 'holes in the ozone layer', which give rise to increased ultraviolet radiation penetration of the earth's atmosphere. The mechanism of this process, in which chlorinated hydrocarbons play an important part, is well understood. A consequence of the increased intensity of UV light in
the troposphere is an increase in the incidence of skin cancers. The formation of summer smogs (associated with large conurbations such as Los Angeles and Athens) is a result of ozone creation in the troposphere which is also encouraged by VOC emissions. It has also been observed that smog can be formed at substantial distances from the original emission source.

Water is the most powerful solvent known to exist that can dissolve more material than any other liquids.

1.10 Drying Mechanism of Latex Paint

Film formation of latex paint occurs when the paint is applied and the water evaporates. During this process, the particles of pigment and binder come closer together with great force, causing them to fuse and bind the pigment into continuous film. This process is called coalescence. The drying mechanism is shown in the following picture.

![Drying mechanism of paint film](image)

This mechanism of film formation is that allows water-thinning and cleanup with latex paints, while providing prompt development of a water and
weather resistant film shortly after application. The latex paint film retains microscopic openings that allow it to “breath”, through which moisture is entering. The latex paint film is thus more tolerant of moisture coming inside the building than oil paint. Latex paints may blister from rain, dew or other sources of water on the outside of the coating, if the paint with limited adhesion capability was applied over a chalky or unclean surface has not enough time to dry thoroughly.

**Table 1.4: Drying times of various ingredients in paints**

<table>
<thead>
<tr>
<th>Event</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water evaporation</td>
<td>0-3 hours</td>
</tr>
<tr>
<td>Coalescing solvent left behind</td>
<td>0 to 3 hours</td>
</tr>
<tr>
<td>Resin particles move together</td>
<td>½-3 hours</td>
</tr>
<tr>
<td>Coalescing solvent softens resin</td>
<td>½-3 hours</td>
</tr>
<tr>
<td>Coalescing solvent softens resin</td>
<td>1-6 hours</td>
</tr>
<tr>
<td>Resin particles fuse together</td>
<td>1-3 hours</td>
</tr>
<tr>
<td>Coalescing solvent leaves film</td>
<td>1-5 days</td>
</tr>
<tr>
<td>Glycols leave film</td>
<td>0-5 days</td>
</tr>
<tr>
<td>Film fully dry</td>
<td>About 1 week</td>
</tr>
<tr>
<td>Resin properties remain stable</td>
<td>10 years+</td>
</tr>
</tbody>
</table>

1.11 The Scope and Objectives

During the last two decades, lot of research works have been undertaken on the development of water based coating due to environmental concern about solvents and other volatile organic compounds (VOC) being emitted in to the atmosphere and causing ozone depletion, acid rain and possibly a chemical imbalance of the earth’s ecosphere.
Paint properties will be influenced by the effect of monomer ratio, particle size, and stabilizer system. In general, softer polymers favour extensibility, exterior durability, film integration whereas harder polymers favour lower dirt retention, glow retention and scrub resistance. Most lattices using in the decorative market are copolymers or terpolymers with the ratios chosen to suit specific sector.

The objective of the study was to prepare the latex based on Vinylacetate and Butylacrylate as good binder using semicontinuous emulsion polymerisation method. Vinylacetate-Butylacrylate copolymer of different compositions was prepared. Polyvinylacetate is a hard polymer which is widely used for the preparation of paints and adhesives due to their low cost and adhesive properties. This polymer softened by internal plasticization by butylacrylate. Polybutylacrylate is a soft polymer. The polymerization conditions were optimized to get a good stable co-polymer lattice with 85/15 wt.% VAc-BuA content.

Water-based paints usually require protection against microbial spoilage. Microbial growth is usually manifested as a loss in functionality and may include gas formation, pH changes, offensive odour, and changes in viscosity and colour. To improve the antimicrobial properties of the surface coating without affecting the film formation property of surface, a new natural biocide (Chitosan derivative) is introduced instead of using synthetic biocide. Chitosan has good film forming ability and excellent antimicrobial activity. Paints made by carboxymethyl chitosan as biocide are eco-friendly, cost effective and durable.

Conventional titanium dioxide (TiO₂) is commonly used as inorganic pigment due to its very high refractive index. TiO₂ based coating has UV shielding ability due to UV ray absorption and scattering. Light scattering depends on the particle size. The reduction of particle size increases the UV ray absorption. Nano sized TiO₂ is prepared in the form of colloidal sol. TiO₂ in a pre-dispersed form rather than powdered form improves the quality of final dispersion. Nano colloidal TiO₂ gives high performance in sunscreen property. More surface area can also be covered compared to the conventional TiO₂.
Matt finishing paints are used on large areas such as walls and ceilings. Matt formulation contains a resin system and a matting agent. The matting agent has a surface moiety. The matting agent used for the present study is activated rubber crumbs. Rubber crumb is usually contains 50% rubber content. Different proportions of rubber crumb are used for making the surface coating and the optimum level of addition was found out for the easy brushing and good dispersion formation.

New coating formulations are developed with vinyl acetate - butyl acrylate as binder, conventional TiO$_2$ or nano TiO$_2$ as pigment, activated rubber crumb as matting agent and carboxymethyl chitosan as biocides. The performance of the above formulated paints is compared by comparing their properties with commercially available paints.

The salient objectives of the current investigation are:

- Synthesis of vinyl acetate butyl acrylate copolymer lattices
- Synthesis of nano TiO$_2$ by cost effective method
- Study the effect of carboxy methyl chitosan as natural biocide for surface coatings
- Using activated rubber crumbs as matting agent
- Development of different paint formulations
  - with conventional TiO$_2$ as pigment.
  - with conventional TiO$_2$ as pigment and carboxymethyl chitosan as biocide.
  - with conventional TiO$_2$ as pigment, carboxy methyl chitosan as biocide and activated rubber crumb a matting agent.
  - with nano TiO$_2$ as pigment.
  - with nano TiO$_2$ as pigment, carboxy methyl chitosan as biocide.
  - with nano TiO$_2$ as pigment, carboxy methyl chitosan as biocide and activated rubber crumb a matting agent.
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