# DEVELOPMENT OF NOVEL SURFACE COATINGS BASED ON ACRYLIC COPOLYMERS

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*by*

**SUMA K.K.**

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
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# Development of novel surface coatings based on acrylic copolymers

Submitted by,

**Suma K.K.**

Dept. of Polymer Science and Rubber Technology

Cochin University of Science and technology

Kochi – 22, Kerala, India

sumarobin@yahoo.co.in

Research Supervisor

**Dr. Rani Joseph**

Professor, Dept. of Polymer Science and Rubber Technology

Cochin University of Science and technology

Kochi – 22, Kerala, India

rani@cusat.ac.in

**Department of Polymer Science and Rubber Technology**
**Cochin University of Science and Technology**
**Kochi - 682022, India.**

**Dr. Rani Joseph**
Professor

Phone: 0484-2575723 (Off)
0484-2577850 (Res)
e mail : rani@cusat.ac.in

# Certificate

This is to certify that the thesis entitled **"Development of novel surface coatings based on acrylic copolymers"** which is being submitted by Mrs.Suma K.K, in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22, is a record of the bonafide research work carried out by her under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Kochi-682022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Rani Joseph

Kochi-22
July, 2009

Dr.Rani Joseph
(Supervising Teacher)

# DECLARATION

I hereby declare that the work presented in this thesis entitled **"Development of novel surface coatings based on acrylic copolymers"** is based on the original research work carried out by me under the guidance and supervision of **Dr. Rani Joseph,** Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-682022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Kochi - 22

July, 2009

Suma K.K.

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# Preface

In recent years considerable developments have taken place in coating industry. Different types of surface coatings are used for various applications, for example architectural paints are mainly used for decoration, but other protective coatings are used for protecting our major assets from natural weathering process. To formulate quality paint, quality raw materials are essential. The property of the paint is mainly determined by the quality of binder. It is one of the most important raw materials that affect almost all properties of coating. The final conversion of film to durable coating involves curing and drying processes depending on the nature of the polymer.

The present study describes the preparation of Vinyl acetate–Butyl acrylate copolymer lattices of varying compositions and solid contents by semicontinuous emulsion polymerization method. This copolymer lattices were used as binder to develop a new surface coating formulation. The properties of this surface coating were improved by using nano $TiO_2$ colloidal sol as a pigment. Antimicrobial activity of surface coatings was improved by the addition of carboxymethyl chitosan as biocide. Uniformly dispersed tyre crumb was used to give a mat finish to the coating. The mechanical properties, adhesive properties, thermal properties etc. of the coatings are presented in thesis.

This thesis is divide into 7 chapters

Chapter 1 is an introduction and a review of the research work done in this field. Scope and objectives of the present work are also discussed.

The specifications of the materials used and the experimental techniques adopted for the preparation and characterization of copolymer, nano $TiO_2$ and paint formulation in the present study are given in Chapter 2.

The preparation, characterization and properties of Butyl acrylate - Vinyl acetate copolymer of different monomer compositions and solid content are described in chapter 3.

The potential use of vinyl acetate – butyl acrylate copolymer as binder for paint formulations and their property evaluation compared with a commercially available paint in Chapter 4. Development of normal paint formulation with vinyl acetate – butyl acrylate copolymers of varying compositions and their property evaluations and comparison with commercial paint is presented in Section 4a. Modification of the paint formulations with tyre crumb and property studies are presented in Section 4b. Development of antimicrobial coating using the copolymer, their property evaluation and comparison of properties with commercial paint are presented in Section 4c.

Synthesis and characterization of nano $TiO_2$ by wet synthesis method is described in chapter 5.

The effect of nano $TiO_2$ in paint formulations using vinyl acetate – butyl acrylate copolymer binder and their properties evaluated and compared with a commercially available paint and paint formulated with conventional $TiO_2$ in Chapter 6. Development of paint formulation of optimized composition of vinyl acetate - butyl acrylate copolymer binder with nano $TiO_2$ is compared with paint formulated with conventional $TiO_2$ and commercially available paint in Section 6a. Preparation of tyre crumb modified coating is present in Section 6b. Antimicrobial coating formulation using nano $TiO_2$ as pigment and comparison of properties with paint formulation with conventional $TiO_2$ and commercial paint are presented in Section 6c.

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# *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.[1] The terms paint and coatings are sometimes used interchangeably; paint is the older term used before the 1940s (eg. 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 accidently 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'.[4] 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 $25^0$C from a solution of a polymer that, when solvent free, has a $T_g$ greater than $25^0$C, the film retains considerable solvent even though it is a hard "dry" film.

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 un reacted 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 $50^0$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.[7]

## 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.[8]

## 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.[9] 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. [10]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.[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 alkoxymethyl 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 $NHCH_2OR$. 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.[13] 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)[14] 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.[15] Nitroalkanes form salts of amines; the salt groups stabilize epoxy-amine emulsions and allow the system to be reduced with water.[16] 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.[17] 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 phthallic 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.[18]

### 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 $T_g$ 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 carbodiimides,[24] or polyfunctional aziridines.[25] $m$-Isopropenyl-$\alpha,\alpha$-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):

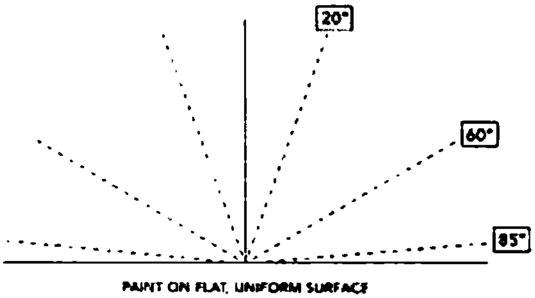

*Figure 1.3: Angles of observation for gloss readings*

The gloss reading at $20^0$ serves to describe the "depth of gloss" is used to describe gloss and semi-gloss paints. The reading at $60^0$ is the measurement of gloss referred to most often and is used with all but dead-flat paints. The $85^0$ 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 $20^0$ gloss reading of 15, and a $60^0$ gloss reading of 55.

*Table 1.1: Gloss ranges*

| Type of Paint | $20^0$ Gloss | $60^0$ Gloss | $85^0$ Gloss (sheen) |
|---|---|---|---|
| Gloss | 20-90 | 70 - 95+ | -- |
| Semi-gloss | 5-45 | 25-75 | -- |
| Satin | -- | 5-25 | 10-40 |
| Eggshell | -- | 2-15 | 5-25 |
| Flat | -- | 0-10 | 0-15 |

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*

| Type of Paint | Typical PVC |
|---|---|
| Gloss | 15% |
| Semi-gloss | 25% |
| Satin | 35% |
| Eggshell | 35-45% |
| Flat | 38 - 80% |

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 straight forward 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 there fore of first (prime) importance. Many metal oxides were found naturally e.g. Red and yellow iron oxides.[33] The colour is also depending on the crystal structure and particle size.[34] 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:**[35]

**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. [36,37]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.

- 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.[40]

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. [11]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 ($Al_2KSi_3\ .12H_2O$), 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, $3MgO \cdot 4SiO_2 \cdot H_2O$) 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 ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). 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:

$$E = E_2 - E_1 = hc/\lambda$$

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.[42]

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*

| Medium | RI | Pigment or extender | RI |
|---|---|---|---|
| Air | 1.0 | Calcium carbonate<br>Chaina clay | 1.58<br>1.56 |
| Water | 1.33 | Talc<br>Barytes | 1.55<br>1.64 |
| Film formers | 1.4-1.6 | Zinc oxide<br>Zinc sulphide<br>Titanium dioxide-<br>Anatase<br>Rutile | 2.01<br>2.37<br><br>2.55<br>2.76 |

### 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.(10) 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-cured 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 deformers 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 Antifloating 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 antifloating agents are used for this purpose. Silicones are sometimes used, but they pose serious bubbling and recoatability problems. Special antifloating 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 discolouration 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 deflocculate 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 between185-255$^0$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 freez-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.[43] 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.[44]

### 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 industrials. 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.[45]

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 ($CH_3COCH_3$): Very strong and very fast evaporating and can cause blushing. It is used in paint and varnish removers.
2. Ethyl acetate ($CH_3COOC_2H_5$): This is a standard fast-evaporating solvent for lacquers. It is relatively low in cost.
3. Butylacetate ($CH_3COOC_4H_9$): This is a very good medium-boiling solvent for lacquers. It has good blush resistance.
4. Ethyl alcohol ($C_2H_5OH$): 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 ($C_4H_9OH$): 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 in to continuous film. This process is called coalescence. The drying mechanism is shown in the following picture.

***Figure 1.4:*** *Drying mechanism of paint film*

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.[46] 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*

| Event | Time |
|---|---|
| Water evaporation | 0-3 hours |
| Coalescing solvent left behind | 0 to 3 hours |
| Resin particles move together | ½-3 hours |
| Coalescing solvent softens resin | ½-3 hours |
| Coalescing solvent softens resin | 1-6 hours |
| Resin particles fuse together | 1-3 hours |
| Coalescing solvent leaves film | 1-5 days |
| Glycols, leave film | 0-5 days |
| Film fully dry | About 1 week |
| Resin properties remain stable | 10 years+ |

## 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 ($TiO_2$) is commonly used as inorganic pigment due to its very high refractive index. $TiO_2$ 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 $TiO_2$ is prepared in the form of colloidal sol. $TiO_2$ in a pre-dispersed form rather than powdered form improves the quality of final dispersion. Nano colloidal $TiO_2$ gives high performance in sunscreen property. More surface area can also be covered compared to the conventional $TiO_2$.

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 lat.ices
- 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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# *Chapter 2*

# MATERIALS USED AND EXPERIMENTAL TECHNIQUES

## 2.1 Materials

1) **Vinyl acetate (VAc):** Manufactured by M/S Loba chemicals were distilled under vacuum to remove the inhibitor.
2) **n-butyl acrylate (BuA):** Manufactured by M/S Loba chemicals were distilled under vacuum to remove the inhibitor.
3) **Sodium carbonate:** AR grade obtained from Merck
4) **Ammonium persulphate:** AR grade obtained from Merck.
5) **Sodium dodecyl benzene sulphonic acid:** HPLC grade from Loba chemi Pvt. Ltd.
6) **Rexol:** Grade N-300 purchased from Laffans petrochemicals limited.
7) **Titanium tetrachloride**: Anhydrous fuming liquid spectrochem Pvt. Ltd.
8) **Distilled, deionized and deoxygenated water**: nice chemicals Pvt. Ltd.
9) **Nitric acid** : Purchased from Rankem with assay of 72%.
10) **Sodium hydroxide** : with 98% assay Purchased from Rankem.
11) **Titanium dioxide** : Travancore titanium products limited.
12) **Tributylphosphate**: with 99% purity purchased from spectrochem pvt.Ltd.
13) **Triton-X-100**: from spectrochem Pvt.Ltd.
14) **Propylene glycol**: with 98% assay from Merck.

15) **Sodium hexa metaphosphate-SHMP:** associated rubber chemicals Pvt. Ltd.

16) **Acticid SPX:** associated rubber chemicals Pvt.Ltd.

17) **Potassiumtripolyphosphate:** LR grade of assay 90% from national chemicals limited.

18) **Kaolin:** assay of 99% Loba chemicals Pvt. Ltd.

19) **Calcium carbonate precipitated:** assay of 99% purchased Merck.

20) **Carboxymethyl cellulose:** assay of 99% purchased from BDH chemicals Ltd. Poole, England.

21) **Carboxymethyl chitosan:** India sea foods limited, Kannamaly India

22) **Rubber crumb:** Rubber Park India Ltd.. Perumbavoor.

## 2.2 Experimental methods

### 2.2.1 Preparation of copolymer latex

The lattices were prepared by semi-continuous emulsion polymerization. The polymerization was carried out in a four necked one liter reactor having a two bladed Teflon (tetrafluoroethelene) coated stirrer and a 25 ml graduated dropping funnel which was immersed in a constant temperature bath kept at 80$^0$C and equipped with water condenser. The recipe used for the synthesis is given in chapter 3. Doubly deionised (DDI) water and emulsifiers were initially charged and maintained under constant agitation of 150 rpm under nitrogen atmosphere for half an hour. The monomers were mixed and then slowly added to stirred solution of surfactant, buffer and DDI water to obtain pre-emulsion. The pre-emulsion was fed to the reactor over a period of 3.5 hours through a dropping funnel at a rate of 0.30 and 0.40 ml/min respectively. No phase separation of pre-emulsion was noticed over the feeding period. The initiator was divided into two portions and the first portion was added to the reactor prior to the addition of the pre-emulsion. Thereafter the second portion of the initiator which was dissolved in deionized water to form a concentrated solution was added to the reactor concurrently with the pre-emulsion. After the addition of all the ingredients the reaction mixture was further heated for 1hr at 80$^0$C. After that the reactor contents was cooled to 28$^0$C, it was filtered to remove any residual coagulum and finally the copolymer latex was obtained. Likewise the lattices containing different monomer composition of VAc-BuA with 85/15, 76/24, 70/30 weight percentage were prepared. Different solid content lattices (35%, 40% and 45%) also prepared for 85/15 weight percent VAc-BuA composition to find out the good performance of lattice binder for paint application.

*Figure 2.1: Experimental setup for the preparation of binder*

*Figure 2.2: Latex obtained after synthesis*

### 2.2.2 Latex paint formulation

The paint formulations were made by mixing appropriate proportions of latex with various ingredients. Lat ices of different compositions were used for the paint formulation. The VAc-BuA copolymers of solid content 45% were used for the preparation. Firstly paints prepared with commercially available $TiO_2$. To find out the effect of nanosized pigment; synthesized nano $TiO_2$ based paints also prepared. Rubber crumb incorporated paints were prepared to get matte finished paints. To improve the resistance of microorganisms (fungus, bacteria etc.) attack, a natural biocide incorporated in all the above formulations. The recipes used for making these formulations are given in the respective chapters.

## 2.3 Results and discussion

### 2.3.1 Characterization of VAc-BuA copolymer

#### 2.3.1.1 IR

The copolymers were precipitated using acetone were washed with methanol and water (1:1ratio). They were then dried in vacuum oven at 60 $^0$C. These samples were dissolved in tetra hydro furan, filtered and dried. These samples were used for the FTIR analysis using Bruker (Tensor 27) instrument.

#### 2.3.1.2 NMR

Copolymer samples were dissolved (5 wt %) in a mixture of deuterated chlorofom and tetrachloroethylene. The $^1$H-NMR spectra were recorded using Bruker advance II NMR spectrometer operating at 100 MHz.

#### 2.3.1.3 Molecular weight

Molecular weight of the synthesized copolymers was determined by size exclusion chromatography with waters HPLC system, 600 series pump, Styragel-HR-5E-4E/2/0.5 columns in series, 2414 refractive index detector (Calibrated using polystyrene standards of molecular weight ($M_p$) 851000/34300/3250). Tetrahydrofuran was used as eluent at a flow rate of

1ml/min. 20µl volume of 0.2% solution of the substance in tetrahydrofuran was injected to get the chromatogram and thus to get the molecular weight.

### 2.3.1.4 Zeta potential

The stability and the particle size of the copolymer lattices were obtained from zeta potential analysis using TSS, NICOMP, particle sizing system (NICOMP 380ZLS)

### 2.3.2 Mechanical tests of dry polymer film

Latex films of 0.2-0.5mm thickness were dried at room temperature in glass petridishes. These films were used for mechanical characterization at room temperature ($28^0$C).

Tensile measurements were made at room temperature using Universal Testing Machine (Shimadzu, AG-I). The specimen size was according to ASTM D 412-98 a. A cross head speed 50 mm/min was found suitable to cover the entire range of compositions of the polymers.

### 2.3.1.5 Thermal properties

The copolymers were precipitated using acetone were washed with methanol and water (1:1ratio). They were then dried in vacuum oven at 60 $^0$C. These samples were used for thermal characterization.

A differential scanning calorimeter (DSC, Q100, TA instruments) was used to measure the glass transition temperatures of the samples. Indium was used for temperature calibration ($T_m$ = 156.6$^0$C, $\Delta H_m$= 28.4 J/g). The analysis was done in nitrogen atmosphere using standard aluminum pans. 5-8 mg specimens were first cooled to -80$^0$C and scan was made from -80$^0$C to 100$^0$C at a heating rate of 10$^0$C/min.

Thermo gravimetric analysis of the samples was carried out in a Q50 Thermo Gravimetric Analyzer (TA Instruments) at a heating rate of 20$^0$C/min. The analysis was done in nitrogen atmosphere and the temperature range was from 50 $^0$C to 800$^0$C.

#### 2.3.1.6 Adhesive properties

**Lap shear and peel strength**

The adhesive property of copolymer lat ices were investigated by lap shear strength. Mild steel substrate used for bonding. Metal strips of size 100×25 mm were machined from 0.60-mm-thick sheets to serve as metal substrates for lap-shear-strength studies on metal-to-metal bonds. Metal strips of size 100×25 mm were machined from 0.11-mm-thick sheets to serve as metal substrates for peel strength studies on metal-to-metal bonds. Mechanical cleaning (surface roughening) was done with a No.100 emery paper. Solvent degreasing with trichloroethylene followed mechanical cleaning. The copolymer latex with different compositions by varying the solid content was used for metal to metal bonding. After applying the copolymer latex, the substrates were kept aside for half an hour to evaporate the solvent. The copolymer latex was applied to a thickness of 0.1 mm on both substrates. The substrates were then subsequently bonded together and the copolymer latex cured at room temperature for two weeks and at $70^0$C for 24hours.

### 2.3.2 Paint evaluation

#### 2.3.2.1 Sample preparation

Mild steel panels were used for the preparation of tests samples according to BS specification 1449 (6x4in). Panels, free from surface imperfection such as rolling marks, scores and corrosion, were thoroughly degreased with trichloroethylene and dried. The panels were then abraded on the test side with 180 grade silicon carbide paper and then wiped with SBPS 40/65 (special boiling point solvent which is the volatile fraction derived from petroleum at the range 40-$65^0$C) to remove any contaminants. Care should be taken that there should not be any time gap between degreasing and painting. The coated panels were air dried as required without any contamination.

#### 2.3.2.2 Water resistance test

This test was used to assess the resistance towards water. It is sometimes referred to as blister resistance. Blistering was assessed by using photographic standards (ASTM D 714-56). It is applied to a wide range of industrial products.

The test is carried out in a thermostatically controlled water bath equipped for mechanical stirring. A rectangular laboratory water bath of 10 liters capacity is used. The water is heated electrically to $38^0C \pm 0.25^0C$. The panels, prepared as described above and are supported in panel racks made of material inert to water. The panels are packed in pairs, back-to-back vertically in the panel racks. The racks are placed across the tank so that the water, which is circulated by a propeller situated at one end, can pass across the face of the panels. After 24 hours immersion the panels are removed from the tank and gently wiped dry with a dry soft cloth. They are examined immediately for blistering and for loss of gloss. Blistering within 12 mm of the edge of the panel is usually disregarded. After examination the panels are replaced in the bath and the immersion continued until the specification limit is reached, usually 7 days at least. The panels are examined every 24 hours up to this point.

#### 2.3.2.3 Salt spray test

This test was used to assess corrosion resistance. It was done according to British standards Institution Method BS 3900 standards.

Salt spray tests are probably the most common tests applicable to corrosion resistance. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates, and it is useful to have information on the behaviour of a particular system in protecting such substrate from corrosion both with intact and damaged paint films. Two tests are in common use: the continuous salt spray test and the intermittent.

The panel(s) is aged for 24 hours before starting the test. Using a scalpel, the coating is cut through to the metal, starting 1 inch (25mm) from the top of the panel and finishing 1 inch (25 mm) from the bottom. The cut should be parallel to the longer side of the panel, and it is important that the surface of the metal should be scored. The test is carried out in a chemically inert container (eg. glass or plastic) with a close-fitting lid. A salt mist is produced by spraying a synthetic sea-water solution through an atomizer. The panels are supported on nonmetallic racks. The spray is so arranged that it does not impinge directly onto the panel surfaces. Panels are examined after 48 hours, 1, 2, and 3 weeks. They are rinsed in running tap water and dried with absorbent paper and examined immediately for blistering. Blistering is assessed as previously described, with reference to photographic standards. The test solution composition is specified as follows (Analytical quality reagents are used for the reproducibility):

*Table 2.1: The ingredients for making synthetic sea water*

| | |
|---|---|
| Sodium chloride (as $NaCl$) | 26.5 g |
| Magnesium chloride (as $MgCl_2$) | 2.4 g |
| Magnesium sulphate (as $MgSO_4$) | 3.3 g |
| Potassium chloride (as $KCl$) | 0.73 g |
| Sodium hydrogen carbonate (as $NaHCO_3$) | 0.20 g |
| Sodium bromide (as $NaBr$) | 0.28 g |
| Calcium chloride (as $CaCl_2$) | 1.1 g |
| Distilled water | 1000ml |

### 2.3.2.4 Alkali and detergent resistance test

Resistance to wards at least three alkali (trisodiumorthophosphate, anhydrous sodiumcarbonate and sodiumhydroxide) was assessed by blistering according to ASTM D 714-56 standards.

At least three alkali resistance tests are in common use. These are based upon the use of trisodiumorthophosphate, sodaash (anhydrous sodium carbonate), and sodium hydroxide respectively. The panels are prepared as described previously. The concentration of solution and temperature of test are as follows.

In these tests the panels are partly immersed in the solutions, at least to a depth of 3-4 inches (75–100mm). As in previously described tests, they are supported in the tank in non-metallic racks. The panels are removed for examination after the first 4 hours' immersion and then subsequently at 24 hour intervals as appropriate. After removal from the tank the panels are rinsed with tap-water, dried with chamois leather, and examined for blistering. They are then allowed to dry at room temperature for 1 hour. They are then re-immersed in the solution and re-examined after 24 hours (and at subsequent intervals), using the same procedure. Blistering is assessed as described previously for water resistance, using the ASTM method.

***Table 2.2:*** *Various reagents and conditions used for alkali resistance test*

| | | |
|---|---|---|
| Trisodiumphosphate | 10% w/w in distilled water | 75°C |
| soda ash | 10% w/w in distilled water | 65°C |
| sodium hydroxide | 5% w/w in distilled water | 25°C |

The detergent test is carried out in a similar manner to the alkali tests. The test is carried out at 74 ± 0.5°C. The panels are examined after 1, 2, 4, 6, 24, and 48 hours from the start of the test. The same criteria for the assessment of deterioration of the paint are adopted as for the alkali tests. The test solution composition is specified as follows

***Table 2.3:*** *The ingredients for making synthetic detergent*

| | |
|---|---|
| Tetrasodiumpyrophosphate anhydrous | 53g |
| Sodiumsulphate anhydrous | 19g |
| Sodiummetasilicate anhydrous | 7g |
| Sodiumcarbonate anhydrous | 1g |
| Potassiumoleate | 20g |

1% solution of the detergent was used for the tests.

### 2.3.2.5 Natural weathering

The panels of dimension 30x6cm are used for making the test specimens as described earlier. The test was conducted for 1 year because natural weathering is a slower degradative process than can be achieved artificially. The test specimens were placed on the top of the roof so that higher sunlight, UV radiation levels impinging on the panels coupled, with, large variations in temperature and humidity.

### 2.3.2.6 Adhesion test[1]

**Cross cut tape test**

This test was carried out according to ASTM D3359-02. The panels are prepared as described earlier. An area free of blemishes and minor surface imperfections are selected. In this test a die with a number of close-set parallel blades is pressed into the test successively in two directions at right angles to each other. The second pressing is superimposed on the first, giving a pattern of squares. A strip of self-adhesive tape (3M Scotch Blue Painters Tape or Sellotape NR Cellulose 1101) stuck over the pattern is removed, and the adhesion of the film is assessed from the amount of the coating removed. The tape is left in contact for 10 seconds and then stripped by pulling the tape back on itself at an angle of approximately $120^{0}$.

### 2.3.2.7 Rheological properties[2]

Determination of apparent viscosity and shear thinning and thixotropic properties of non-Newtonian materials in the shear rate range from 0.1-50 $sec^{-1}$ was carried out using rotational viscometer (Brookfield type RV series). The tests were carried according to ASTM D2196-05 at room temperature ($28^{0}C$).

**Apparent viscosity:** The spindle/speed combination selected to give a minimum scale reading of 10 for various samples.

**Degree of shear thinning and thixotropy:** Set the viscometer at slowest viscometer speed. Start the viscometer and record the scale reading after 30 seconds. Increase the viscometer speed stepwise and record the scale reading after 30 seconds at each speed. After an observation has been made at top speed, decrease the speed in steps to the lowest speed, recording the scale reading after 30 seconds at each speed. After the last reading has been taken at the slowest speed, shut off the viscometer and allow it undisturbed for some time. At the end of the rest period start the viscometer at the slowest speed and record the scale reading after 30 seconds.

$$\text{Shear thinning index} = \frac{\text{Apparent viscosity at low rotational speed}}{\text{Viscosity at 10 times higher speed}}$$

Higher ratio indicating greater shear thinning

### 2.3.2.8 UV-visible spectrum:

The UV-visible spectra were recorded on UV-2550 spectrophotometer.

### 2.3.2.9 Antimicrobial tests[3]

It is important to determine the susceptibility of paint films to microbiological attack on exterior exposure. The growth of fungi and algae on the surface of the paint films cause discoloration and disfigurement of painted surfaces. The tests were done to find out the antimicrobial activity of paint against bacteria, fungi and algae.

#### (a) Algal defacement test

The test is carried out according to ASTM D5589-97. In this method filter paper of diameter 4.2 cm coated with sample paint is used as test substrate. Allen's agar medium is taken in a petridish. The test specimen is placed at the centre of the solidified Allen's agar plates. Algal inoculums are transferred from the flask into a sterilized chromatographic sprayer and apply a thin coat of algae suspension to each specimen making sure the surface is covered. The inoculated plate transferred in to an incubator with a constant fluorescent light having humidity >85% and temperature of $\pm 28^{0}$C. Incubate the samples under the specified condition just stated and examine weekly for growth. Two types of algae are used.

#### (b) Anti-bacterial studies by disc diffusion

Nutrient agar was prepared by 7.5g agar suspended in 250 ml distilled water. It was allowed to soak for 15 minutes and then boiled on a water bath till the agar was completely dissolved. The mixture was autoclaved for 15 minutes at $120^{0}$C and then poured into sterilized petridishes and stored at $40^{0}$C for inoculation. Inoculation was done with the help of platinum wire loop.

The paper disc of diameter 4.2 cm is prepared and is soaked in the samples and dried for 1 hour at 28 $^{0}$C. The discs were applied on bacteria grown in agar plates using a sterilized forceps. The plates were inverted and kept in a bacterial incubater at 37.5$^0$C for 24 hours. Escherichia coli and Bacillus subtills are the bacteria used for inoculation in paint film.

### (c) Fungal defacement test

A spore suspension of each of the test fungi is prepared by pouring one subculture of fungus into sterile 10 mL water. Swirl or gently agitate the slant or plate to loosen the spores. Carefully aspirate the water and spore suspension with a sterile pasteur pipet (trying to avoid obtaining mycelia). Check the collected spore suspension under the microscope for mycelial contamination and make a note of the relative populations of spores versus mycelial forms. Dilute the spores with sterile nutrient salts solution such that the resultant spore suspension contains 0.8 to 1.2 by 10$^6$spores/mL as determined with a counting chamber. Repeat this operation for each organism used in the test. The spore suspension may be prepared fresh each day or may be held in the refrigerator at 3 to 10$^0$C (37 to 50$^0$F) for not more than 4days.

4.2 cm diameter paper disc dipped in sample is used as the test specimen. A thin coat of fungal suspension is applied to each sample using a sterile atomizer or pipet, making sure the surface is covered. but not to over saturate the samples. Alternately, a separate sterile cotton swab may be used to apply and evenly spread the inoculum over the surface of each test sample. Incubate all plates at 28°C under 85 to 90 % relative humidity for 4 weeks.

*Aspergillus fumigates* (MTCC 2483) and *Penicillium citrinium* (MTCC 2553) are the fungal cultures (test organisms) used for the test. Stock cultures of these fungi are maintained separately on an appropriate medium such as potato dextrose agar plates or slants. Subculture individual fungi onto slants or plates 7 to 20 days at 28 to 30$^0$C (82 to 86$^0$F) prior to the experiment, and use these subcultures in preparing the spore suspension.

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# Chapter 3

## PREPARATION AND CHARACTERIZATION OF VINYL ACETATE- BUTYLACRYLATE CO-POLYMER LATICES

### 3.1 Introduction

Polymer latices are colloidal dispersion of rubber/plastic material in aqueous medium. Latices are two types; natural and synthetic. Natural rubber latex is obtained from the botanical source Hevea brasiliensis. The most outstanding property of natural rubber latex is its high wet gel strength. Synthetic latices are produced by emulsion polymerization. Synthetic lattices are aqueous dispersion of polymer particles in water produced by emulsion polymerisation. Synthetic latices are tailored to particular application and therefore have specific properties such as adhesion, solvent resistance, water resistance etc. Preparation of synthetic latex originated in Germany before First World War. During the period of 1930-35 emulsion polymerization was being established as a method of producing synthetic rubber latices. Continuous process for synthetic rubber production was developed for styrene-butadiene and acrylonitrile-butadiene copolymer to alleviate the shortage of natural rubber. Since then many other types have come onto the market of which polyvinylacetate and co–polymers, acrylics, and carboxylic-styrene butadiene type being major products.

Emulsion polymerization is a very important method in the field of chemistry.[1,2] Method of preparation is classified into two groups; operational and chemical. Chemical method depends on type and level of emulsifier, initiator, modifier, electrolyte phase ratio (monomer/water), relative solubility of monomer and relative reactivity of monomers in co-polymerisation. The operational method depends on reactor capacity, stirrer type, speed, temperature, pH and pressure.[3] Commercially, emulsion polymerization technique is divided into three categories based on mode of addition of monomer, initiator, emulsifier etc. They are batch polymerization, semi-continuous polymerization and continuous polymerisation.[4]

In batch polymerisation, complete ingredients are charged into a single stirred reactor. Polymerisation is initiated and continued until the required conversion is attained.[5]

Continuous polymerization is mainly used for the commercial production of synthetic latices such as SBR, nitrile rubber and poly chloroprene.[6]

Semi-continuous is the most widely used emulsion polymerization technique. In this method, single stirred reactor is charged with small portion of required quantity of water and other ingredients. Monomer pre-emulsion and ingredients added to reactor continuously or incrementally over a certain period of reaction time.[7] The controlled addition of monomer emulsion can be used to control particle size distribution and stability of the latex.[8,9]

Large parts of latices are used in coating and adhesives industry. Coating applications depends on the adhesive properties of the polymer. Poly vinyl acetate lattices were developed commercially in West Germany and USA. Vinyl acetate monomers and polymers differ from the majority of commercially used monomers because of its appreciable solubility in water. Poly vinyl acetate, widely used as a binder suffers poor hydrolytic stability especially under alkaline condition, poor weathering stability, poor wet adhesion and high water sensitivity. It has only limited application in coating industry, because of its high $T_g$ ($30^0C$) and minimum film forming temperature (MFT) $20^0C$ making its film hard and inflexible. The hardness of the polymer film has greater significance in the final product. The unmodified polymer latex does not form an integrated continuous film below the MFT and this temperature is influenced the hardness of film. Polymer can be made softer by internal plasticization, which at the same time reduces the MFT, improve freezthaw stability, storage stability, and wet adhesion. There are reports in literature that co-polymerisation of vinyl acetate with other monomers lowers $T_g$ by internal plasticization. This lowering of $T_g$ makes it a suitable binder in surface coating applications. Usually, vinyl acetate is co-polymerised with other polymers like n-butylacrylate, methyl methacrylate etc. for the internal plasticization.[10]

The characteristic feature of free-radical copolymerization of VAc with BuA is poor match in their reactivity ratios. The reactivity ratios of VAc and BuA have values on the order of rVAc _ 0.02-0.07 and rBuA _ 3.07-8.00, respectively. Such a big difference in reactivity ratios leads to phase separation for bulk copolymerization of VAc with BuA. This tendency for rapid polymerization of BuA followed by polymerization of VAc, leading to phase separation, also occurs in batch-emulsion copolymerization of VAc with BuA.[11,12] But in semicontinuos emulsion polymerisation random statistical co-polymer lattices are obtained by controlled pre-emulsion addition.[13,14]

**Mechanism of Film formation**

The formation of latex film arises from the coalescence of the individual latex particles which are normally held apart by stabilising forces (electrostatic and/or steric) resulting from the charged polymer chain end groups or surfactant.[15,16] These forces are overcome by the evaporation of the continuous phase (water).[17] The formation of a continuous film (*i.e.* transparent and crack-free) is then depended on the minimum film formation temperature (MFFT) of the polymer. which in turn is depended on the elastic modulus (resistance to particle deformation), and to a lesser extent, the viscosity of the polymer. If the film is cast above its MFFT, coalescence of the latex particles can occur.[18,19] However, if the film is below its MFFT, a friable discontinuous film or powder compact may form, which is typically opaque due its structured nature and, hence, its ability to diffract light.

**Three stages in the drying process**

**Stage I.** Water evaporates from the latex surface, concentrating the latex: the rate of evaporation has been determined by many researchers[20] as being the same as the rate of evaporation from water alone, or of water from a dilute solution of surfactant + electrolyte, *i.e.*, such as that which constitutes the aqueous phase of latex. This stage is the longest of the three and lasts until the polymer has reached ca 60 - 70% volume fraction, (dependent on the stability of the latex) or until the surface area of the latex's liquid-air interface starts to decrease as a result of solid film formation. Initially, the particles move with

Brownian motion, but this ceases as the electrical double layers undergo significant interaction, once a critical volume of the water has evaporated.

**Stage II.** This starts from the time at which the particles first come into irreversible contact, and iridescence may be observed on the latex surface. The rate of evaporation per unit area of open wet latex remains constant, but the overall rate of evaporation decreases greatly during this stage. Reducing the rate of evaporation can lead to a better quality film by allowing the particles more time to pack into an ordered structure before flocculation occurs. Casting at high temperatures gives the particles sufficient energy to overcome their mutual repulsion and the films are formed before the particles are ordered.[21] Particle deformation occurs in soft lattices, as the particles start to fill inter-particular capillary channels, driven by interfacial forces.

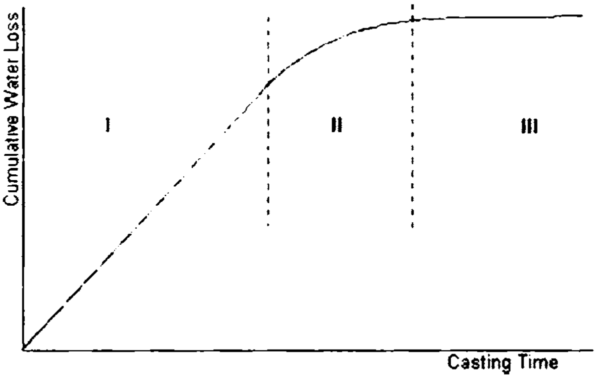

*Figure 3.1: Schematic plot of the water loss occurring on latex drying.*

**Stage III.** This stage starts with the initial formation of a continuous film. The remaining water leaves the film initially via any remaining interparticle channels and by diffusion through the polymer itself, but the rate of evaporation eventually slows to approach that of diffusion alone. It is during this stage that soft latex becomes more homogeneous and gains its mechanical properties. The rate of water removal may be decreased by film additives that are impermeable or hydrophilic.[22]

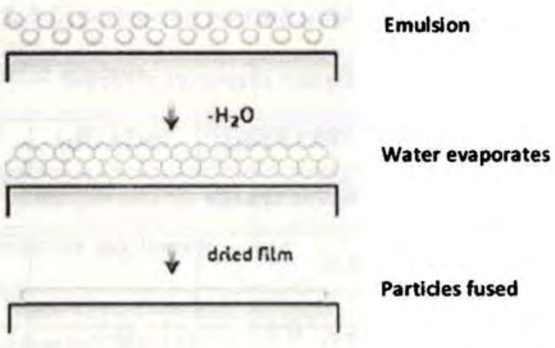

***Figure 3.2:*** *Schematic diagram of film formation of latex*

In the present study, vinyl acetate is co-polymerised with n-butylacrylate. The co-polymer lattices were prepared by using semicontinuous emulsion polymerisation. The solid content, pH, viscosity, particle size, $T_g$, NMR, molecular weight, thermal properties, mechanical properties and adhesive properties were evaluated.

## 3.2 Experimental

Experimental part involves two sections. First section describes the synthesis of VAc –BuA co-polymer latex of different compositions. In second section describes the optimization of solid content and composition.

### 3.2.1 Synthesis of VAc-BuA Co-polymer of varying composition

The lattices containing different monomer composition of VAc-BuA with 85/15, 76/24, 70/30 weight percentage were prepared. The co-polymer lattices were prepared by semi-continuous emulsion polymerization. The details are described in chapter 2. The recipe for the synthesis is given in table 3.1

*Table 3.1: Copolymer preparation recipe*

| **Ingredients** | **85/15 ($B_1$)** | **76/24 ($B_2$)** | **70/30 ($B_3$)** |
|---|---|---|---|
| **Reactor charge** | | | |
| Deionized water (g) | 70 | 70 | 70 |
| Dodecyl benzene sulphonate (DS 10) (g) | 0.5 | 0.5 | 0.5 |
| Ammoniumpersulphate (g) | 0.3 | 0.3 | 0.3 |
| **Monomer feed** | | | |
| Vinylacetate (g) | 153 | 135.9 | 126 |
| Butylacrylate (g) | 27 | 44.1 | 54 |
| DS 10 (g) | 0.25 | 0.25 | 0.25 |
| Deionized water (g) | 105 | 105 | 105 |
| Rexol N-300 (g) | 9 | 9 | 9 |
| $Na_2CO_3$ (g) | 0.12 | 0.12 | 0.12 |
| **Initiator feed** | | | |
| Deionized water (g) | 22.5 | 22.5 | 22.5 |
| Ammoniumpersulphate (g) | 1.2 | 1.2 | 1.2 |

### 3.2.2 Synthesis of VAc-BuA Co-polymer of varying solid content

The properties of latices are also dependent on the solid content. Latices of varying solid content were prepared using the above optimized co-polymer composition to find out the best solid content of latex for the development of surface coating. The recipe for preparing different solid content co-polymer of 85/15 weight percentage VAc-BuA is given in table 3.2

*Table 3.2: Copolymer of varying solid content preparation recipe*

| **Solid content** | **35** | **40** | **45** |
|---|---|---|---|
| **Reactor charge** | | | |
| Deionized water (g) | 90 | 80 | 70 |
| Dodecyl benzene sulphonate (DS 10) (g) | 0.5 | 0.5 | 0.5 |
| Ammoniumpersulphate (g) | 0.3 | 0.3 | 0.3 |
| **Monomer feed** | | | |
| Vinylacetate (g) | 153 | 135.9 | 126 |
| Butylacrylate (g) | 27 | 44.1 | 54 |
| DS 10 (g) | 0.25 | 0.25 | 0.25 |
| Deionized water (g) | 105 | 105 | 105 |
| Rexol N-300 (g) | 9 | 9 | 9 |
| $Na_2CO_3$ (g) | 0.12 | 0.12 | 0.12 |
| **Initiator feed** | | | |
| Deionized water (g) | 22.5 | 22.5 | 22.5 |
| Ammoniumpersulphate (g) | 1.2 | 1.2 | 1.2 |

## 3.3 Results and discussion

0.2 to 0.5 mm thickness films of copolymer lattices synthesized by semi-continuous process were prepared by drying them in glass petridishes. All the films were fond smooth. The filming ability was better for 85/15 wt.% VAc-BuA latex.

### 3.3.1 IR spectroscopy:

Figure 3.1 (a), (b) and (c) shows the IR spectrum of n-Butyl acrylate monomer, Vinyl acetate monomer and VAc-BuA copolymer respectively

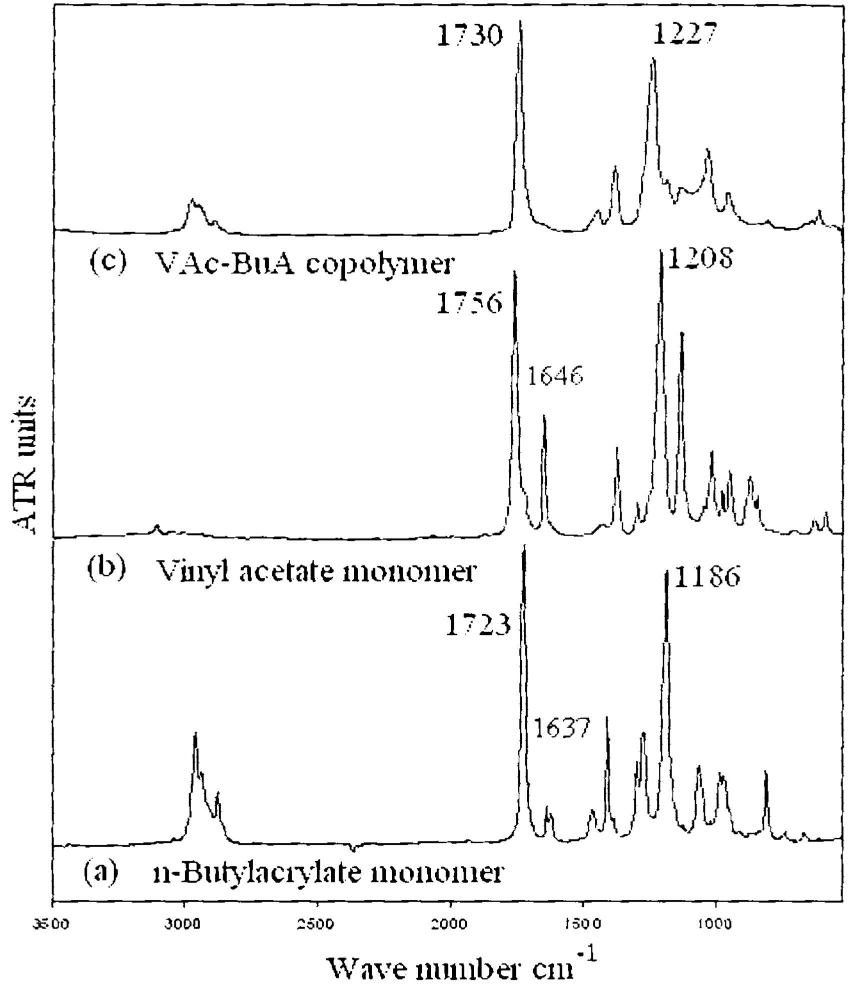

***Figure 3.3:*** *FTIR spectra of (a) n-butylacrylate, (b) vinyl acetate and (c) VAc-BuA copolymer*

The figure show that C=C stretching absorption in the range 1600-1650 cm$^{-1}$ for the monomers disappeared in the IR spectrum of VAc-BuA copolymer.

The C=O stretching absorption in the range 1650-1800 $cm^{-1}$ and C-O stretching absorption in the range 1150-1250 $cm^{-1}$ are present both in the monomers and copolymer. These results show that copolymerization took place between vinyl acetate and butyl acrylate as expected and the functional groups remain unaffected during polymerization. The copolymerization is further confirmed from the single $T_g$ value obtained for the copolymer prepared by semi-continuous emulsion polymerization.

### 3.3.2 NMR

The $^1H$ NMR spectrum of VAc-BuA copolymer is shown in figure 3.2. The peaks at 5.13 ppm and 4.21 ppm correspond to the protons attached to the carbon atom which is directly bonded with oxygen atom. The first broad peak shows the presence of more neighboring hydrogen atoms. This shows that this proton is present in carbon atom of the polymer backbone. But the latter one is a triplet, indicates the presence of two protons on neighboring carbon atom. So it is not present in the polymer back bone but present on the side chain. It shows that this is the proton present on the carbon atom of the butyl group which is directly attached to the oxygen atom. The peaks at 2.53 ppm and 2.04 ppm are of the protons which are present on the carbon atom which is directly attached to >C=O group. The peak at 2.04 is very intense single narrow peak shows the absence of nearby protons. This may be due to the methyl protons of vinyl acetate, since there are no neighboring protons for this methyl group. Other protons in the polymer chain give multiplets which are close together to identify separately and they are present between 2 to 1 ppm values. The peak at 0.94 ppm is a triplet shows the presence of two neighbouring protons. Since this is at very low $\delta$ value the protons should be of the methyl group present at the end of the butyl group. The $^1H$ NMR signals shows that the >C=O group do not take part in the reaction and the side chains are acetyl group and butyl group. This may be the evidence for copolymer formation.

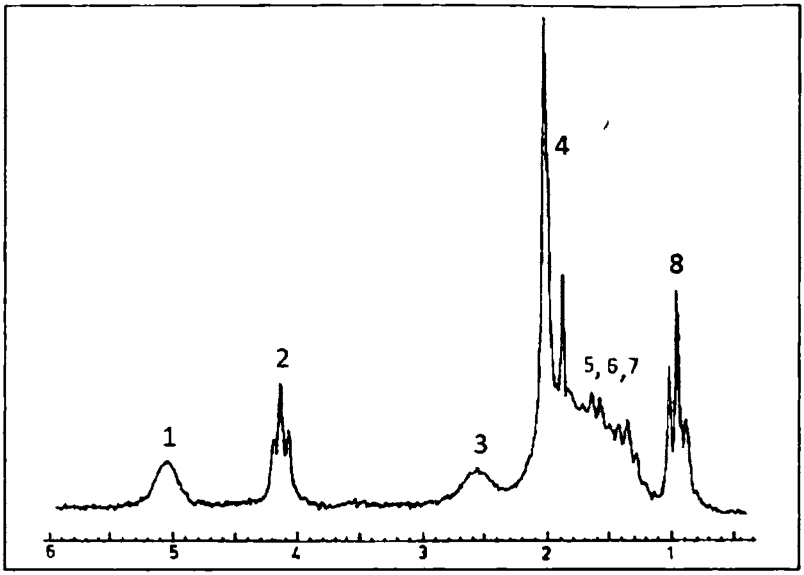

*Figure 3.4: $^1H$ NMR spectrum of vinyl acetate–butyl acrylate co-polymer*

### 3.3.3 Physical properties of copolymer

### 3.3.3.1 Molecular weight

The molecular weight obtained from GPC curve for different compositions are almost same and they are above one lakh. Generally latex polymers have high molecular weight in the region of one lakh to ten lakh. Which provide toughness without the necessity to crosslink.[23]

*Table 3.3: Molecular weight of synthesized VAc-BuA copolymers*

| Property | $B_1$ | $B_2$ | $B_3$ |
|---|---|---|---|
| Molecular weight (Mn) | 1,05,686 | 1,04,220 | 1,02,368 |

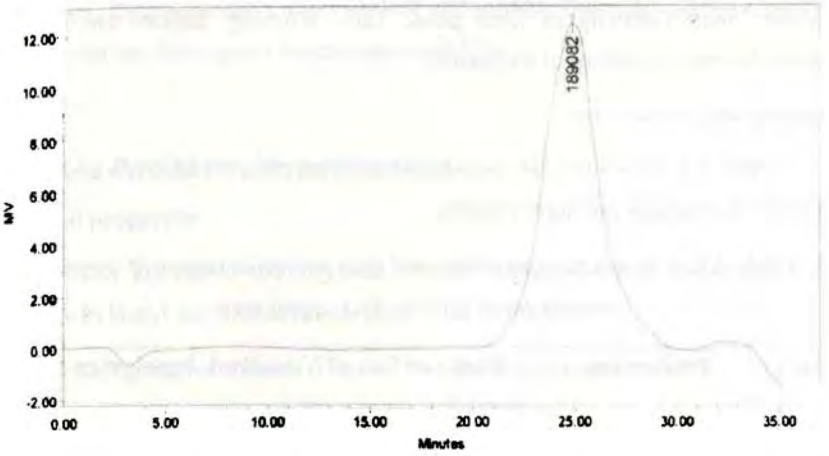

***Figure 3.5:*** *Molecular weight curve of Vinyl acetate   Butyl acrylate co-polymer by GPC*

### 3.3.3.2 VAc-BuA of varying composition

**a) General properties**

***Table 3.4:*** *Physical characteristics of various compositions of VAc-BuA copolymer*

| **Properties** | **Composition of VAc-BuA copolymer** | | |
|---|---|---|---|
| | **$^*B_1$** | **$^{**}B_2$** | **$^{***}B_3$** |
| Appearance | Milky | Milky | Milky |
| Solid content | 45% | 45% | 45% |
| pH | 4.1 | 4.3 | 4.2 |
| Viscosity (centipoises) | 600 | 620 | 615 |

$^*B_1$-85/15 wt.% of VAc-BuA. $^{**}B_2$-76/24 wt.% of VAc-BuA. $^{***}B_3$-70/30 wt.% of VAc-BuA

The table 3.4 shows that all the binders possess solid content 45%. The pH of prepared lat ices shows acidic nature. Viscosity of the latex has no direct correlation with viscosity of final paint. Low viscosity lattices are naturally preferred for easy handling of the paint.

**b) Stability and particle size**

Table 3.5 shows the zeta potential and freeze-thaw stability values. It shows that the lattices are highly stable.

***Table 3.5:*** *Particle size, stability and zeta potential values of various compositions of VAc-BuA copolymer*

| **Properties** | **Composition of VAc-BuA copolymer** | | |
|---|---|---|---|
| | $B_1$ | $B_2$ | $B_3$ |
| Zeta potential (mV) | -53.9 | -47.6 | -44 |
| Freeze-thaw stability | Pass | Pass | Pass |
| Particle size (nm) | 182 | 179 | 140 |

The particle size of the lattices greatly depends on the rate of monomer addition and stirring rate. Usually a decrease of average particle size and glass transition temperature was found by the increase of BuA content in the copolymer.[24] The zeta potential is the overall charge of a particle that acquire in a specific medium. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability. If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. A dividing line between stable and unstable aqueous dispersions is generally taken at either +30 or -30mV. Particles with zeta potentials from ±40 to ±60 have good stability.[25] The zeta potential of prepared lattices found to be in the above cited range. For semi-continuous lat ices, the decrease in BuA content resulted in a proportional increase and, ultimately, dominant role of steric stabilization.[26] Freeze-thaw stability is the zeta potential obtained by freezing the emulsion to -80$^0$C for sixteen hours followed by placing at room temperature for eight hours. Zeta potential values are not affected by freezing and thawing so the prepared lattices have good freeze-thaw stability.

### 3.3.3.3 VAc-BuA of varying solid content

#### a) General properties

Table 3.6 shows the physical characteristics of the co-polymer of Vinyl acetate with Butyl acrylate with varying solid content.

***Table 3.6:*** *Physical characteristics of VAc-BuA copolymer of same composition with varying solid content*

| **Properties** | **Composition of VAc-BuA copolymer** | | |
|---|---|---|---|
| | $*BS_1$ | $**BS_2$ | $**BS_3$ |
| Appearance | Milky | Milky | Milky |
| Solid content | 35% | 40% | 45% |
| pH | 4.3 | 4.2 | 4.1 |
| Viscosity (centipoises) | 480 | 550 | 600 |

$*BS_1$ - 85/15 wt.% of VAc-BuA with 35% solid content. $**BS_2$ - 85/15 wt.% of VAc-BuA with 40% solid content. $***BS_3$ - 85/15 wt.% of VAc-BuA with 45% solid content.

The table 3.6 shows the general properties of lattices of same composition with different solid content. Total solid content below 45% was preferable for better performance of paint than higher solid content emulsion. The pH of prepared lattices found to be in the acidic range. Viscosity of the latex shows small variation with solid content as expected.

**b) Stability and particle size**

*Table 3.7: Particle size, stability and zeta potential values of VAc-BuA copolymer of same composition with varying solid content*

| Properties | Composition of VAc-BuA copolymer | | |
|---|---|---|---|
| | $BS_1$ | $BS_2$ | $BS_3$ |
| Zeta potential (mV) | -54.2 | -50.3 | -53.9 |
| Freeze-thaw stability | Pass | Pass | Pass |
| Particle size (nm) | 172 | 169 | 182 |

The zeta potential and freeze-thaw stability measurements shows that the lattices are stable even at low solid content. The particle size also not shows variation with solid content.

### 3.3.4 Mechanical properties

### 3.3.4.1 VAc-BuA of varying composition

*Table 3.8: Tensile properties of VAc-BuA copolymer latex films with different molar ratio of monomers*

| Property | VAc/BuA copolymer of different compositions | | |
|---|---|---|---|
| | $B_1$ | $B_2$ | $B_3$ |
| Tensile strength (MPa) | 9.68 | 8.77 | 7.37 |
| Young's modulus (MPa) | 34.95 | 12.35 | 8.45 |
| Energy to break(J) | 0.78 | 0.35 | 0.16 |

The tensile properties of the copolymers are given in table 3.8. All the films prepared from the semicontinuous emulsion polymerization process with varying composition show variation in mechanical properties.[27] From table 3.6 we observe that tensile strength, Young's modulus, and elongation at break changed significantly for the semicontinuous latex films. It was observed that the sample $B_1$ has higher tensile strength and Young's modulus than that of the samples $B_2$ and $B_3$.[28,29] Chemical composition distribution and polymerization methods have a tremendous effect on mechanical properties such as elastic modulus, elongation at break and impact strength.[30,31] This may be due to the homogeneously dispersed morphology corresponding to the copolymer composition of 85/15 wt.% VAc/BuA. i.e. Butylacrylate rich regions dispersed in a continuous matrix of vinylacetate rich copolymers.[32,33]

### 3.3.4.2 VAc-BuA of varying solid content

*Table 3.9: Properties of 85/15 VAc-BuA copolymer latex films of different solid contents*

| **Property** | **VAc/BuA copolymer of different solid contents** | | |
|---|---|---|---|
| | **$BS_1$** | **$BS_2$** | **$BS_3$** |
| Solid content | 35% | 40% | 45% |
| Tensile strength (MPa) | 3.54 | 4.77 | 9.68 |
| Young's modulus (MPa) | 7.63 | 9.39 | 34.95 |
| Energy to break (J) | 0.18 | 0.24 | 0.78 |

The tensile properties of co-polymers of varying solid content are given in table 3.9. Form this we observe that even though the vinylacetate-butylacrylate copolymer composition was same the values of tensile strength, Young's modulus, and elongation to break changed considerably for the latex films. We can observe that the sample $BS_3$ has higher tensile strength and Young's modulus than that of the samples $BS_1$ & $BS_2$. The higher solid content samples posse more number of polymer chains, when they dried theses copolymer chains entangled much more and high strength is required to break these chains. This may be the reason for the high tensile properties of higher solid content film.

## 3.3.5 Thermal properties

### 3.3.5.1 DSC

Using DSC we examine the glass transition temperature of the lattices, which is the very important property for coating applications

**a) VAc-BuA of varying composition**

*Table 3.10: $T_g$ values of VAc-BuA copolymerlatex films of different compositions*

| Sample name | $B_1$ | $B_2$ | $B_3$ |
|---|---|---|---|
| Glass transition temperature ($T_g$) | -6.49 | -8.3 | -9.74 |

From table 3.10 we observe that each binder B1, B2 and B3 show single glass transition temperature. This single $T_g$ value for B1, B2 and B3 indicates that the copolymer formed may be either alternate or random copolymer.[34] As per table 5 the decreasing nature of $T_g$ can be seen by increase of BuA content in the copolymer latex. $T_g$ is found to decrease due to loosening of the VAc polymer chain by the addition of BuA having low $T_g$ (-43$^0$C). Glass transition temperature of polymer used in coating industry generally lies between -10$^0$C and 28$^0$C.[35]

**b) VAc-BuA of varying solid content**

*Table 3.11: $T_g$ values of 85/15 VAc-BuA copolymer latex films of different solid content*

| Sample name | $BS_1$ | $BS_2$ | $BS_3$ |
|---|---|---|---|
| Glass transition Temperature (Tg) | -6.1 | -7.6 | -6.9 |

From the table 3.11 we observe that the binders $BS_1$, $BS_2$ and $BS_3$ show a single glass transition temperature. This single $T_g$ value indicates that the copolymer formed may be statistical random copolymer.

### 3. 3.5.2 Thermogravimetry

Thermal stability of the co-polymers was analyzed from thermogravimetric analysis. Thermogravimetric curves (TG) and derivative thermogravimetric curves (DTG) obtained for polyvinyl acetate and polybutyl acrylate are shown in figure 3.6 and 3.7 respectively. Polybutyl acrylate shows single step degradation. Its degradation starts nearly at 300$^0$C and complete at 450$^0$C. Polyvinyl acetate degrades in three stages. The first step degradation occur between 100-200$^0$C, second stage is between 300-370$^0$C and the final stage occurs between 450-500$^0$C.

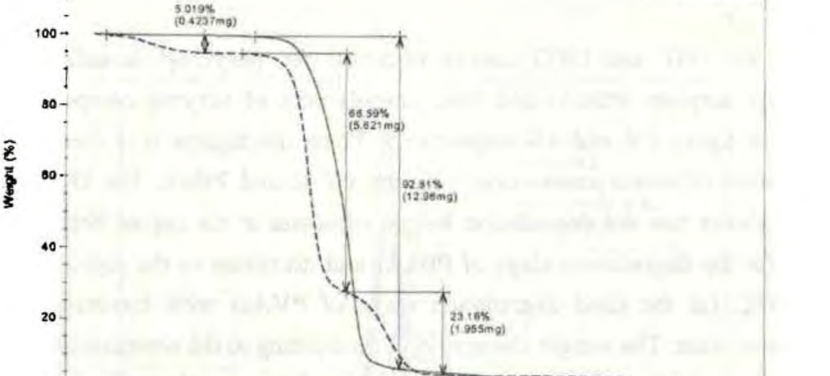

***Figure 3.6:*** *Thermogravimetric traces of polybutyl acrylate and polyvinyl acetate*

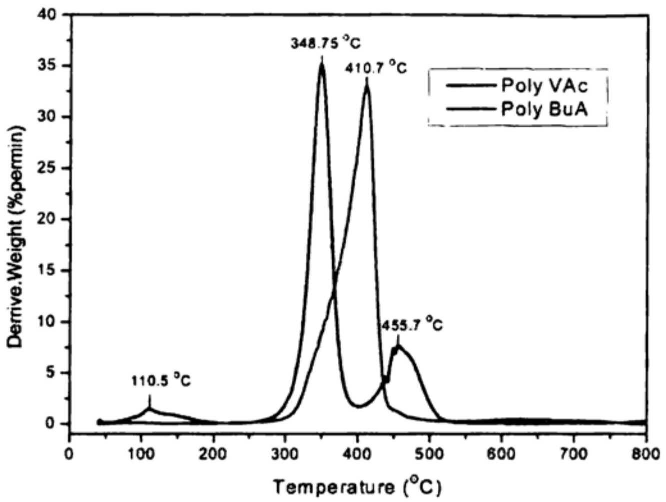

*Figure 3.7: DTG curves of Polybutyl acrylate and polyvinyl acetate*

The TG and DTG curves obtained for polyvinyl acetate (PVAc), polybutyl acrylate (PBuA) and their co-polymers of varying composition are shown in figure 3.8 and 3.9 respectively. From the figures it is clear that the degradation of co-polymers occur between PVAc and PBuA. The DTG curves clearly shows that the degradation weight increases in the region between 300-450$^0$C (at the degradation stage of PBuA) and decreases in the region between 450-500$^0$C (at the third degradation stage of PVAc) with increase of butyl acrylate content. The weight changes occur according to the composition of VAc and BuA content. This indicates that the emulsion copolymerization is very effective to prepare VAc-BuA copolymer of varying composition.

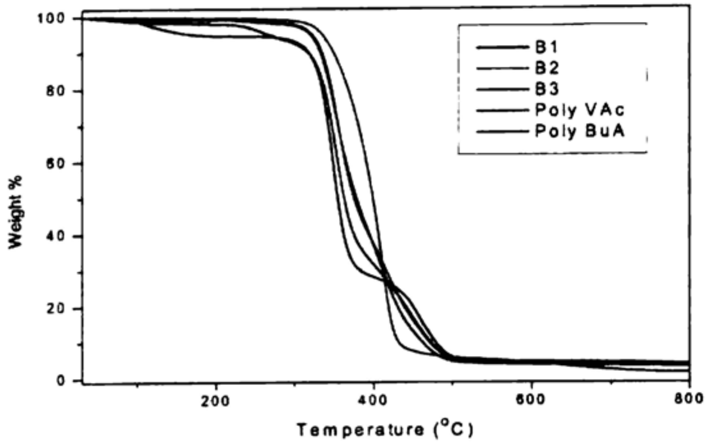

***Figure 3.8:*** *Thermogravimetric traces of Polybutyl acrylate, polyvinyl acetate and varying compositions of copolymer of VAc–BuA*

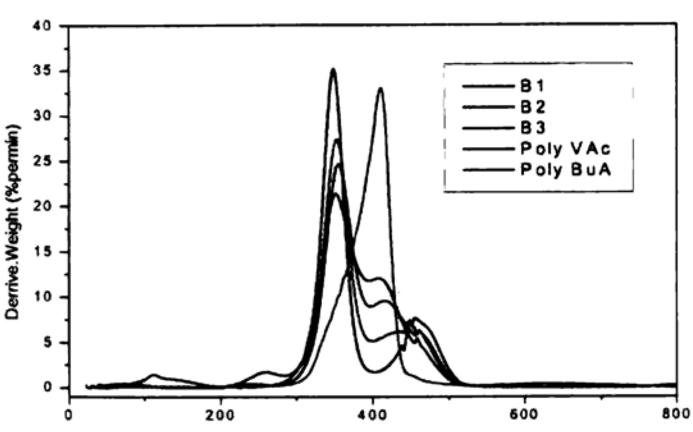

***Figure 3.9:*** *DTG traces of polybutyl acrylate, polyvinyl acetate and copolymers of varying composition*

### 3.3.6 Adhesive properties

#### 3.3.6.1 Lapshear strength

**a) VAc-BuA of varying composition**

Figure 1 & 2 shows the effect of varying the VAc-BuA composition on the metal-to-metal shear strength at room temperature and at 70$^0$C respectively. In both case the shear strength value increases with vinyl acetate content. As the VAc content increases, the modulus of the copolymer latex increases.

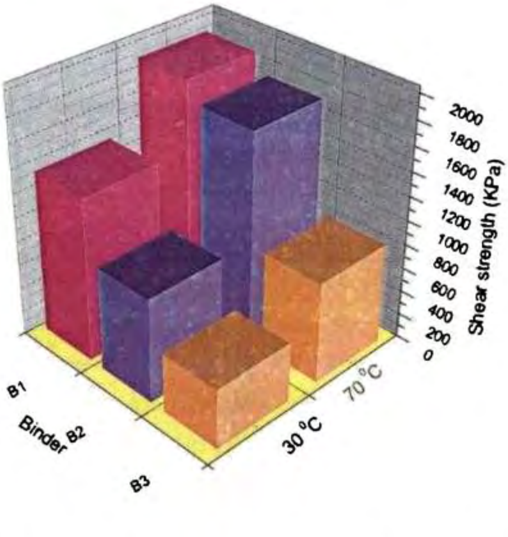

***Figure 3.10:*** *Effect of varying the VAc-BuA composition on shear strength at 30 & 70$^0$C*

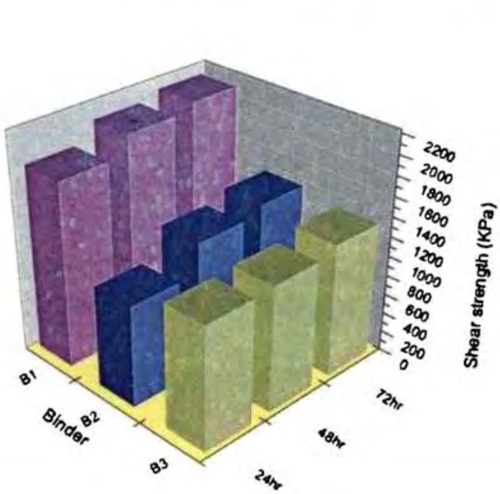

***Figure 3.11:** Effect of varying the VAc-BuA composition on shear strength at 70⁰C (24, 48 and 72 hours)*

All compositions show higher shear strength at 70⁰C on keeping for 72 hours. This shows that as the time increases more drying takes place and this may increase the adhesive strength.

**b) VAc-BuA of varying solid content**

Figure 1 shows the effect of varying the solid content of 85/15 VAc-BuA copolymer on the metal-to-metal shear strength at room temperature (30⁰C) kept for two weeks and at 70⁰C kept for 24hours.

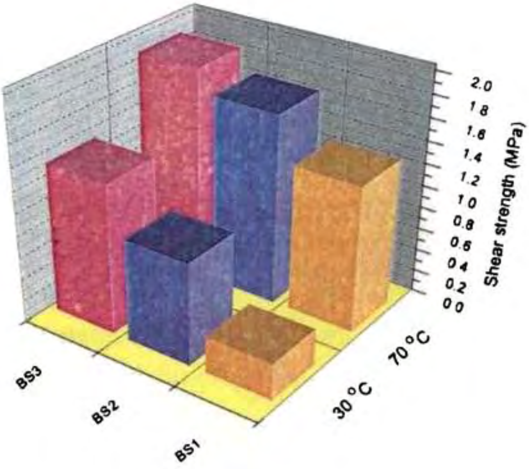

***Figure 3.12:*** *Effect of varying the solid content of 85/15 VAc-BuA copolymer on shear strength*

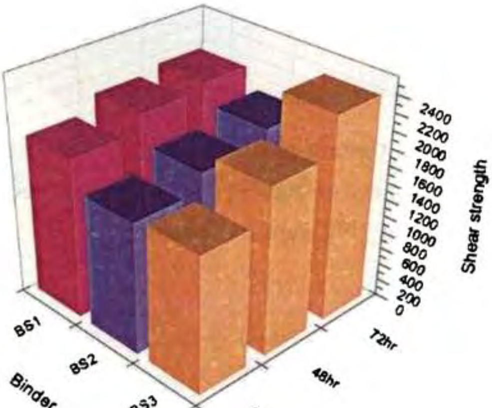

***Figure 3.13:*** *Effect of varying the solid content of 85/15 VAc-BuA copolymer on shear strength (24, 48 and 72 hrs)*

All above studies shows that the shear strength value increases with increasing the solid content at different temperatures. As the solid content increases, the modulus of the copolymer increases. Furthermore, the copolymer has a high affinity towards metal surfaces, and this result in better metal–metal bonds.

### 3.3.6.2 Peel strength

#### a) VAc-BuA of varying composition

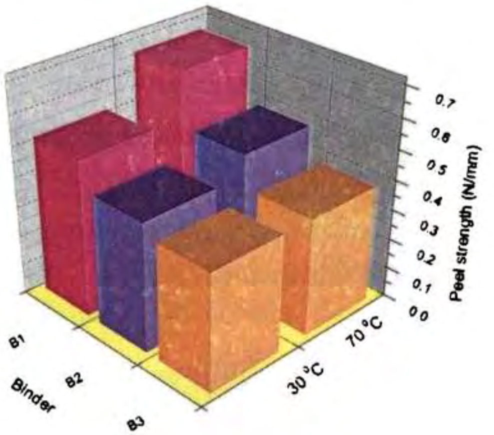

**Figure 3.14:** Effect of varying the VAc-BuA composition on peel strength at 30 & 70$^0$C

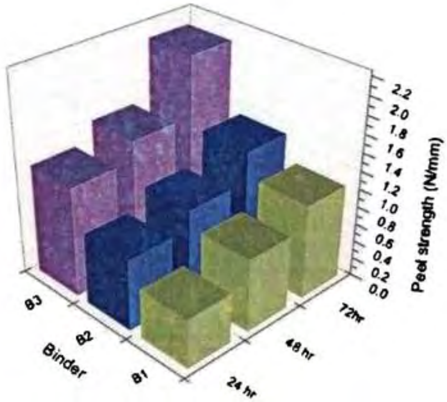

**Figure 3.15:** Effect of varying the VAc-BuA composition on peel strength at 70⁰C (24, 48 and 72 hrs)

**) VAc-BuA of varying solid content**

Figure 4 shows the effect of varying the solid content of 85/15 VAc-BuA copolymer on the metal-to-metal peel strength at room temperature (30⁰C) kept for two weeks and at 70⁰C kept for 24hours.

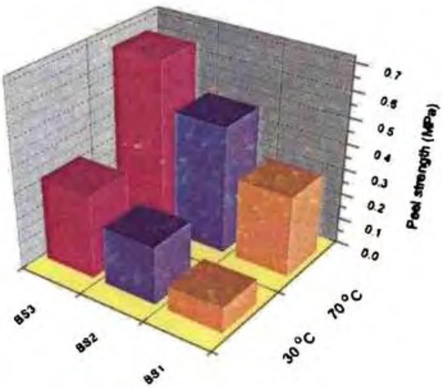

***Figure 3.16:*** *Effect of varying the solid content of 85/15 VAc-BuA copolymer on peel strength at 30 & 70⁰C*

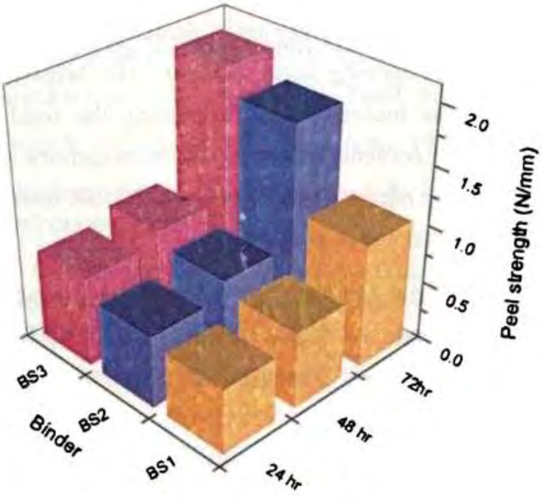

***Figure 3.17:** Effect of varying the solid content of 85/15 VAc-BuA copolymer on peel strength at $70^0C$ (24, 48 and 72 hrs)*

The peel strength also found to increases with increasing solid content. The higher peel strength was obtained at higher solid content. As the BuA content increases the flexibility of the latex film increases, which leads to inferior peel strength values.

## 3.4 Conclusion

The rate of monomer addition and co-monomer composition is found to have considerable effect on the thermal, mechanical and adhesive properties of vinylacetate-butylacrylate copolymer latex. All compositions showed good film forming property. The tensile strength, young's modulus and shear strength are found to get decreased with the increasing percentage of BuA. Better shear and peel strength at $70^0C$ showed stability of copolymer lattices. 85/15 weight percentage of VAc/BuA latex is more suitable binder in coating. The single Tg value of copolymer lattice increases with increasing butyl acrylate content. The rate of monomer addition, water content and the amount of surfactant are found to have considerable effect on the solid content and mechanical properties of vinylacetate-butylacrylate copolymer latex films. Good filming ability is found for all the films with varying solid content. The tensile strength, Young's modulus is found to be increases with increasing the solid content. Single $T_g$ found at higher solid content indicates the homogenous morphology of the copolymer latex. Hence higher solid content VAc/BuA latex is more suitable to be used as binder in water based coating.

For metal-to-metal bonding, vinylacetate-butylacrylate copolymer latex shows high shear strength. At higher temperature, VAc/BuA copolymer latex showed better shear and peel strength compared to room temperature. This shows the thermal stability of VAc/BuA copolymer latex for bonding applications. Both the peel and shear strength values increased with increasing solid content. Hence, higher solid content VAc/BuA latex is more suitable to use as binder for water based surface applications.

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# *Chapter 4*

# PREPARATION AND PROPERTY EVALUATION OF SURFACE COATINGS

## 4a: Paint formulations with VAc-BuA copolymer of varying compositions

### 4a.1. Introduction

Surface coatings are used for both surface decoration and protection. In the context of decoration, it is essential that the surface is uniformly and completely covered. This is most readily achieved by using a pigment of high refractive index such as $TiO_2$. Polymer lattices are used as binder. Binder is used for the adhesion of pigment firmly to the surface.[1] $TiO_2$ (rutile) has been used as white pigment due to its very high refractive index 2.76, relatively low density and maximum scattering of visible light and they absorb little energy in the visible part of the spectrum.[2]

Latex coatings are developed by dispersing $TiO_2$ in latex. Latex based coating is also known as water based coating. The main constituents of water based paints are pigment, binder, dispersing agent, extender, protective colloid, defoamer, biocide, coalescing solvent. Dispersing agents are used to the preparation of higher solids, lower viscosity dispersions.[3] Extenders are low cost materials used to replace more expensive prime pigment. Commonly used extenders are white mica, talc, kaolin etc. Water based coating would still be found to be deficient in open time (wet edge) and difficulty would be experienced in making uniform application to large area. This problem can be solved by the addition of colloid. Defoamers are used for the prevention of foam formation. The ingredients in water based coatings degrade in presence of micro organism which is prevented the addition of the biocide. Coalescing solvents are also called temporary plasticizer which ensures good film formation at low temperatures. Besides, the ingredients in coating formulation other criteria for water based coating are pigment volume concentration (PVC) and critical pigment concentration. Lower PVC is better for exterior coatings. Generally, in interior and exterior coating 40-65 % PVC is being used.

$$\text{PVC\%} = \frac{\text{Volume of pigment and extenders}}{\text{Volume of (Pigment+extenders+polymer+other non-volatile ingredients}} \text{ X } 100$$

CPVC is the point at which there is just sufficient binder present to satisfy the pigment surface and fill the void space between pigment particles.[4] Many factors which affect the water based coating. They are film forming property of binder, particle size of binder, pigmentation etc. Particle size of polymer lattices has greater significance in surface coatings. The particle size affects the pigment binding, opacity, flow property and gloss. Latex polymers have molecular weight in the region of 1,00,000-10,00,000, which provides toughness without crosslinking.[5] Most of the latex coatings based on vinylacetate co-polymers have a pH about 7-8, at this pH polymeric emulsion prevent hydrolysis.[6]

A new paint is being formulated with Vinyl acetate - butyl acrylate copolymer lattices of varying compositions as binder and conventional $TiO_2$ as pigment. Different properties of formulated paints are evaluated and compared with commercially available paint.

## 4a.2 Experimental

Paints were made by mixing proportions of latex with various ingredients in the formulation given in table 4a.1. The VAc-BuA used in this paint (solid content 45%) was prepared by the semi-continuous emulsion polymerization. According to table 4a.1 various latex paints were prepared by different monomer composition i.e, 85/15, 76/24, 70/30 wt.

*Table 4a.1: Paint formulation*

| Ingredients | Weight (g) | | |
|---|---|---|---|
| | $^{*}PB_1$ | $^{**}PB_2$ | $^{***}PB_3$ |
| Water | 35 | 35 | 35 |
| Triton-X100 | 0.42 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0.42 | 0.42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 | 0.42 |
| Volcastab | 0.42 | 0.42 | 0.42 |
| Silicone emulsion | 1.34 | 1.34 | 1.34 |
| Propylene glycol | 4 | 4 | 4 |
| Acticid SPX | 0.32 | 0.32 | 0.32 |
| Above ingredients are to be combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added | | | |
| Kaolin | 17 | 17 | 17 |
| Calcium carbonate | 18.64 | 18.64 | 18.64 |
| $TiO_2$ (Rutile) | 44.6 | 44.6 | 44.6 |
| Mix the above ingredients at high speed for 20 minutes. While stirring the mixture the following ingredients were added | | | |
| Carboxymethyl cellulose | 0.74 | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 | 0.92 |
| Ammonia | 0.42 | 0.42 | 0.42 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added. | | | |
| Polymer emulsion | 75 | 75 | 75 |

$^{*}PB_1$ - Paint formulated with VAc-BuA copolymer (85/15 wt.%). $^{**}PB_2$ - Paint formulated with VAc-BuA copolymer (76/24 wt.%). $^{***}PB_3$ - Paint formulated with VAc-BuA copolymer (70/30 wt.%)

Triton-X100 – Isooctylphenoxypolyethoxyethanol. Volcastab- Phenolethoxylate condensate. Acticid SPX – Methylchloroisothiazolinone

## 4a.3 Results and Discussion

The most important tests for evaluating the durability and quality of paints are water resistance, salt spray resistance, alkali resistance, detergent resistance, weather resistance and adhesion tests. These tests were conducted according to standard procedures described in chapter 2. The specimens for the tests were prepared by coating the paint samples in mild steel panels of size 6inx4in (BS specification).

The observations for various tests are summarised in the respective tables. For each test and the appearance of the coated samples (photographs) before and after the tests are also shown under the respective tests. The properties of the formulated paints are compared with a commercially available paint.

### 4a.3.1 Water resistance test

Water resistance test was conducted at 38$^0$C using distilled water.

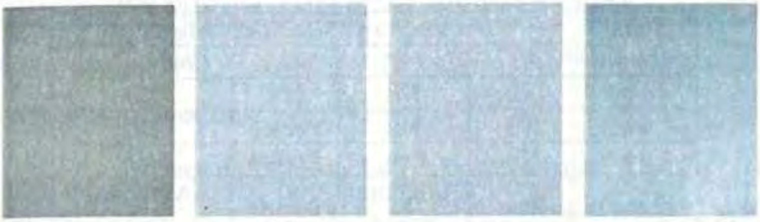
*Table 4a.2: Blister formation in water resistance test*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | *$PB_1$* | *$PB_2$* | *$PB_3$* | **Commercial* |
| 24 hrs | Nil | Nil | Nil | Nil |
| 4 days | Nil | Nil | Few | Nil |
| 1week | Nil | Few | Medium | Nil |
| 3 week | Nil | Medium | Medium dense | Few |
| 12week | Few | Medium dense | Dense | Medium |

**Commercially available emulsion paint*

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are shown in figure 4a.1.

Initial appearance



Final appearance

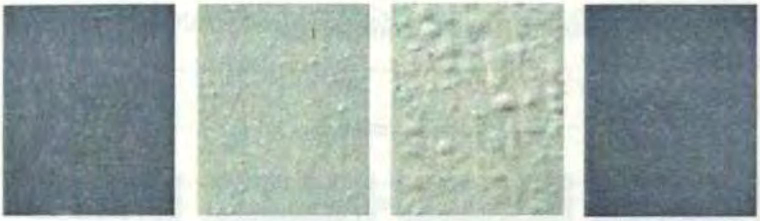


***Figure 4a.1:** Appearance of specimens before and after the water resistance test*

The figure 4a.1 and table 4a.2 clearly shows that sample $PB_1$ is highly resistant to water because it shows only few blisters of very small size even after 12 weeks. Commercially available paint also shows similar result. The sample $PB_2$ shows dense small sized blisters and the sample $PB_3$ shows dense larger sized blisters.

### 4a.3.2 Salt spray test

Salt spray test was conducted at $28^0$C using the salt water prepared as per procedure in chapter 2 for getting uniform test atmosphere always.

***Table 4a.3:*** *Blister formation in salt spray test*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***$PB_1$*** | ***$PB_2$*** | ***$PB_3$*** | ***Commercial*** |
| 48 hrs | Nil | Nil | Nil | Nil |
| 1 week | Nil | Nil | Peeled | Nil |
| 4 week | Nil | Few | Peeled | Few |
| 12week | Few | Medium dense | Peeled | Medium dense |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are given in figure 4a.2.

Initial appearance

$PB_1$ $PB_2$ $PB_3$ Commercial

Final appearance

$PB_1$ $PB_2$ $PB_3$ Commercial

***Figure 4a.2:*** *Appearance of specimens before and after the salt spray test*

By analyzing the observations shown in table 4a.3 and the photographs depicted in figure 4a.2 we can see that the sample $PB_3$ is easily affected by salt spray and is peeled off from the mild steel panel within 1 week. The specimen $PB_2$ shows small sized blisters of medium dense. Commercially available paint shows medium sized blisters of dense. The sample $PB_1$ shows only very few blisters and is more resistant to attack of salt water (sea water).

### 4a.3.4 Alkali resistance test

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at 75°C, $Na_2CO_3$ at 65 °C and NaOH at 28 °C) according to standard procedure as described in chapter 2.

*Table 4a.4: Blister formation in $Na_3PO_4$ resistance test (75°C)*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB₁*** | ***PB₂*** | ***PB₃*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Medium | Nil |
| 8 hrs | few | medium | Peeled | few |
| 16 hrs | medium | dense | Peeled | dense |
| 24 hrs | dense | peeled | Peeled | peeled |

*Table 4a.5: Blister formation in $Na_2CO_3$ resistance test (65°C)*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB₁*** | ***PB₂*** | ***PB₃*** | ***Commercial*** |
| 4 hrs | Nil | few | few | Nil |
| 8 hrs | few | medium | Peeled | few |
| 16 hrs | medium | dense | Peeled | dense |
| 24 hrs | dense | peeled | Peeled | peeled |

*Table 4a.6: Blister formation in NaOH resistance test (28$^0$C)*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***$PB_1$*** | ***$PB_2$*** | ***$PB_3$*** | ***Commercial*** |
| 4 hrs | Nil | Few | Medium | Nil |
| 8 hrs | medium | Dense | Peeled | dense |
| 16 hrs | dense | Peeled | Peeled | peeled |

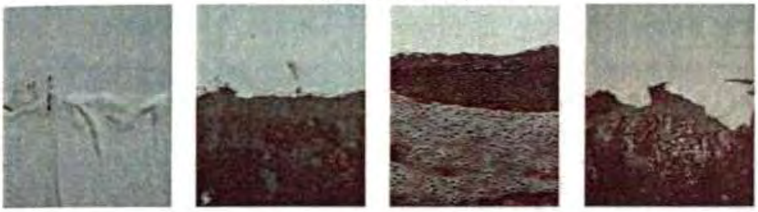
Tables 4a.4, 4a.5 and 4a.6 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, 24h for $Na_2CO_3$, 16h for NaOH) are shown in figure 4a.3.

From the figures and the tables we can see that the resistance of the specimens varied with the nature of the alkali. The sample $PB_1$ showed higher resistance to the attack of all alkalies when compared to all other samples.

Initial appearance

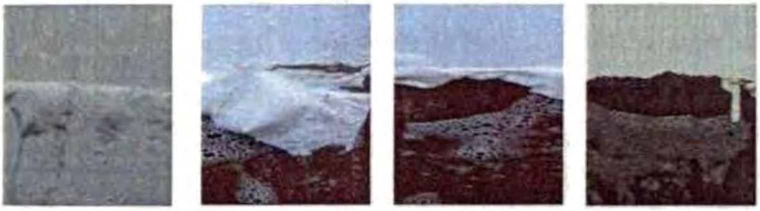
PB$_1$ PB$_2$ PB$_3$ Commercial

Final appearance $Na_3PO_4$



PB$_1$ PB$_2$ PB$_3$ Commercial

Final appearance $Na_2CO_3$



PB$_1$ PB$_2$ PB$_3$ Commercial

Final appearance NaOH

PB$_1$ PB$_2$ PB$_3$ Commercial

***Figure 4a.3:*** *Appearance of specimens before and after alkali resistance test*

### 4a.3.5 Detergent resistance test

Detergent resistance test was conducted at 28$^0$C using a standard detergent.

***Table 4a.7:*** *Blister formation during detergent resistance test*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB1*** | ***PB2*** | ***PB3*** | ***Commercial*** |
| 1day | Nil | Few | Medium | Nil |
| 3 days | Few | Medium | Medium | Medium |
| 1 week | Medium | Medium dense | Medium dense | Medium dense |

The photographs of initial appearance (before the test) and final appearance (after 1 week) of the coated samples for detergent resistance test are shown in figure 4a.4.

Initial appearance

PB$_1$ PB$_2$ PB$_3$ Commercial

Final appearance

PB$_1$ PB$_2$ PB$_3$ Commercial

***Figure 4a.4:*** *Appearance of specimens before and after detergent resistance test*

Table 4a.7 and figure 4a.4 shows that sample $PB_1$ and commercially available paint are more resistant to detergent. Sample $PB_3$ shows rusting.

### 4a.3.6 Natural weather resistance

Weather resistance test was conducted to know the effect of natural weather on the paint surface. The specimens were prepared by coating the paints on mild steel panels of size 12x6in. The test was conducted for a period of 10 months from March to December. This time period was selected because the samples were exposed to all seasons during the test.

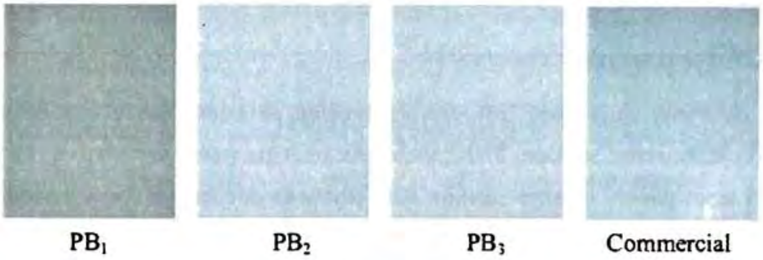
***Table 4a.8:*** *Chalking formation in weather resistance test*

| **Time interval** | **Chalking observed** | | | |
|---|---|---|---|---|
| | ***$PB_1$*** | ***$PB_2$*** | ***$PB_3$*** | ***Commercial*** |
| 1month | Nil | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil | Nil |
| 10 months | Nil | Staining | Staining | Nil |

The photographs of initial appearance (before the test) and final appearance (after 10 months) of the coated samples for weather resistance test are shown in figure 4a.5.

The figure 4a.5 and table 4a.8 shows that all the samples are very stable towards natural weather. The samples $PB_2$ and $PB_3$ show slight stains on the surface.

Initial appearance



Final appearance

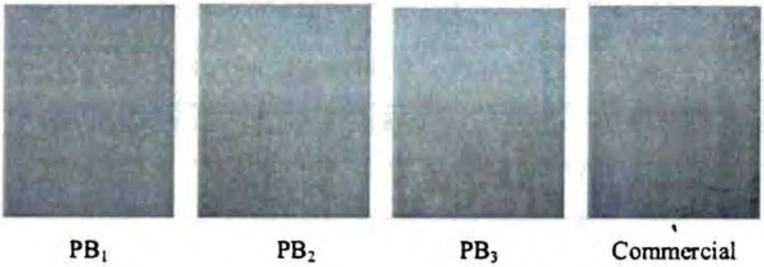


***Figure 4a.5:*** *Appearance of specimens before and after weather resistance test*

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample PB$_1$ is having superior resistance towards all test conditions. PB$_1$ is the paint formulated with binder 85/15 wt.% of VAc-BuA. From the results we can also conclude that the binder have a key role in determining the properties of paints.

Architectural paints based on auto oxidisable binders have seeds of degradation within them. The oxidation process does not stop when the film has dried. Oxidation proceeds, giving an increasingly cross linked film. The durability of exterior paint is due to the careful choice of binder which aims to keep the oxidisability of the film to the minimum. Failure of paints may due to either of chemical resistance and optimum mechanical properties or to combinations of them. The binder B1 has minimum oxidisability, high chemical resistance and optimum mechanical properties. Hence PB$_1$ shows better performance in paint formulation.

### 4a.3.7 Scotch test

The adhesive strength of the paints was determined using scotch resistance test. The tests were carried out as described in chapter 2.

*Table 4a.9: Adhesion rating during scotch test*

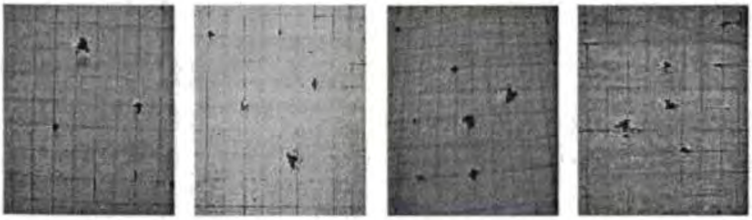
| Sample name | Classification | % removal |
|---|---|---|
| $PB_1$ | 4B | Less than 5% |
| $PB_2$ | 3B | 5 – 15% |
| $PB_3$ | 2B | 15 – 35% |
| Commercial | 3B | 5 – 15% |

The photographs of test specimens before and after the test are shown in figure 4a.6.

Initial appearance

$PB_1$ $PB_2$ $PB_3$ Commercial

Final appearance



$PB_1$ $PB_2$ $PB_3$ Commercial

***Figure 4a.6:*** *Appearance of specimens before and after scotch test*

The figure 4a.6 and table 4a.9 show that the adhesive strength of all samples is high. But sample $PB_1$ shows slightly higher adhesive strength.

## 4a.4 Viscosity of paint

The viscosity of a complex system such as paint is governed by the interaction of all the ingredients in the formulation. The viscosity of a paint formulation controls its storage stability, ease of application and the subsequent flow after the application. The viscosity adopted for paint at the formulation state is determined largely by the storage requirements as well as its application characteristics.

Viscosity and shear thinning behaviour are important properties of paint. It depends on size of colloidal particles. The paint displaying flow behaviour is typical for thixotropic paints, *i.e.*, time-dependent reduction in viscosity with shear rate. Paints exhibiting such rheology do not drip from the applicator (eg., brush or lamb's wool roller). Under the shearing forces which normally arise in the course of processing (painting) of low viscosity paints make un-evenness, eg., brush lines or brush furrows, are able largely to flow out. Left at rest, the paint then regains a relatively high viscosity with sufficient rapidity that it is impossible for "curtaining" to develop when the paint is applied to vertical surfaces. Moreover, a paint having such rheology allows paint application in a single operation in a substantially greater film thickness than is possible in the case of paints having more simple flow behaviour.

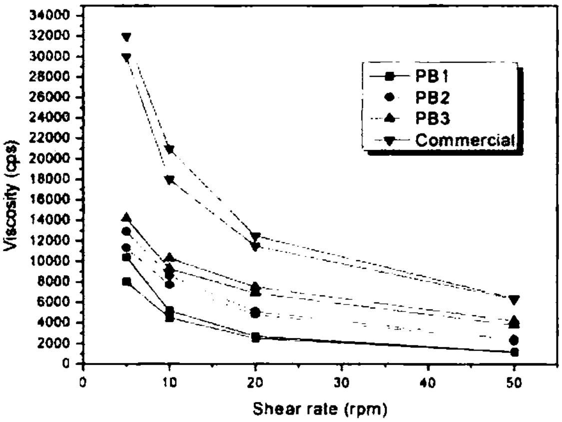


*Figure 4a.7: Effect of shear rate on the viscosity of Paint*

Shear thinning index is the ratio viscosity of paint at a low rotational speed to the viscosity at a speed ten times high. It gives an idea of the degree of shear thinning over that range of rotational speed. Higher ratio indicates greater shear thinning.

To avoid sagging on vertical surfaces the paints must exhibit non-Newtonian rheology, that is, they must have the property of shear thinning to facilitate flow through the gun and atomization, but must rapidly develop structure in the liquid film. Thus they may have a viscosity of about 500-1000 cps at1000 rpm, and will probably reach a viscosity of ~1,00,000 cps at the low shear rate applicable to flow under gravity on a vertical surface.

Shear thinning index of $PB_1$, $PB_2$ and $PB_3$ at two different speeds 5 and 50 are given in table 4a.10.

***Table 4a.10:*** *Shear thinning index of the samples*

| **Sample** | **Shear thinning index** |
|---|---|
| $PB_1$ | 8.67 |
| $PB_2$ | 5.37 |
| $PB_3$ | 3.76 |
| Commercial | 5 |

## 4a.5 Thermogravimetry

Thermal stability of the paint was found out using thermogravimetry. Samples $PB_1$, $PB_2$ and $PB_3$ contains the same binder but with different compositions of vinyl acetate and butyl acrylate. We have already found in chapter 2 that the thermal stability of these binders is almost same. Hence the thermal stability of the samples PB1 and commercially available paints were analysed and the thermograms obtained are shown in figure 4a.8 and its derivative is shown in figure 4a.9.

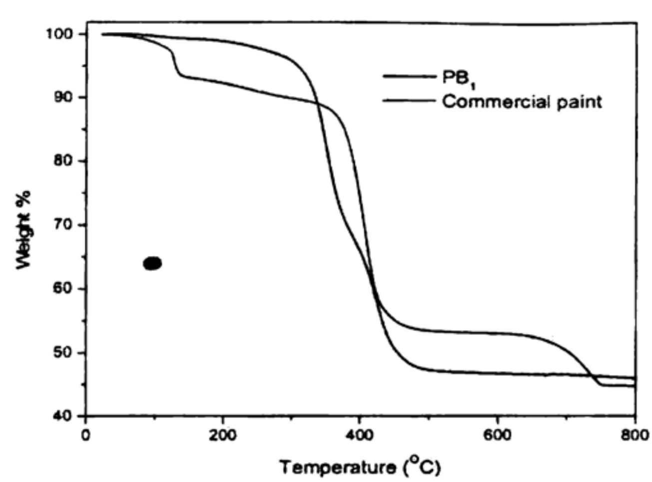


***Figure 4a.8:** TG traces of $PB_1$ and commercial paint*

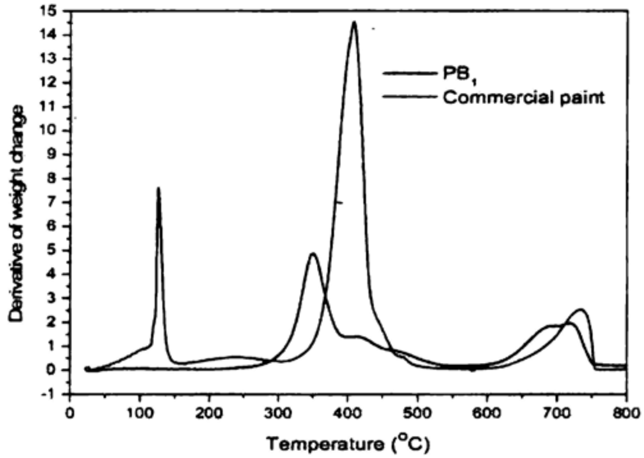


**Figure 4a.9:** DTG traces of $PB_1$ and commercial paint

From the figures we can see that the commercially available paint start to degrade at 120°C but the degradation of the formulated paint starts only at 300°C. This shows that the formulated paint has superior thermal stability compared to commercially available paint.

## 4a.6 Conclusion

A new paint formulation was developed with different compositions of vinyl acetate - butyacrylate copolymer. Properties of these paints were evaluated for 3 compositions namely 70/30, 76/24 and 85/15. Out of these different paints prepared, the formulation prepared with 85/15 wt.% VAc-BuA showed best performance in durability tests such as water resistance, alkali resistance, detergent resistance test, salt spray tests, weather resistance and scotch test compared to commercial paint and the other two compositions.

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# 4b: Paint formulation with rubber crumb

## 4b.1. Introduction

Matt paints are used on large areas such as walls and ceilings, including plaster boards, hard board, brick, cement rendering, foamed polystyrene and most wall papers, where the easy application, quick dry, and lower odour of water-borne dispersion paints are major advantages. The consequences of poorer flow and lapping are not readily visible and were never seen as an insurmountable disadvantage.[1] The consequences of flow deficiencies were more visible, and durability requirements more demanding, e.g. for cleaning in corridors of schools, hospitals, factories, and in areas of high condensation such as kitchens and bathrooms.[2-4] As a consequence, this sector was split between water- and solvent-based technologies.

Matt formulations contain a resin system and a matting agent. The matting agent has a surface moiety. Paints with low amounts of binder have a high ratio of pigment volume to binder volume, a condition referred to in the coatings literature as a high pigment volume concentration (high PVC). These paints may have poor cohesive and adhesive properties. They normally have a matte appearance and are often in a powdery, friable, and flaking condition. Their treatment requirements differ from paints containing higher proportions of binder (such as commonly encountered linseed oil or acrylic paints) in that consolidants are easily absorbed into the paint and fill voids between the pigment particles. However, although cohesion of the paint and adhesion to the substrate are promoted by added amounts of resin, filling void spaces between pigment particles may cause changes in the appearance of the paint by a treatment that is practically irreversible. The matte paint is to use a consolidation system that distributes the consolidant in a manner that minimizes changes in appearance, introduces the minimum quantity necessary to achieve effective cohesion of the paint and adhesion of the paint to the substrate, and is compatible with the paint and support materials in the long term.[5-11]

The matting agent used for the present study is rubber powder (made from used rubber products). Rubber crumb contain 50% rubber hydrocarbon and the rest is carbon black, oil etc. The typical composition of crumb rubber obtained is shown in table 4b.1.

***Table 4b.1:*** *Composition of rubber crumb*

| Ingredients | Percentage |
|---|---|
| Natural rubber | 35 % |
| Synthetic rubber | 15% |
| Carbon black | 30% |
| Oil | 10% |
| Accelerators, Antiozonants, etc. | 10% |

Crumb rubber has essentially two effects interaction effect (IE) and particle effect PE). The IE is the effect of the crumb absorbing the aromatic oils from the binder. The PE is the effect of the crumb as a filler .As with any filler, the addition of crumb affects the rheology of the binder by increasing the viscosity and reinforcing the binder to some extent (Wypych, 2000). Crumb rubber used as filler for reducing cost and also modifying properties of the end products. Crumb rubber modified by surface active agents. Surface activation improves the dispersion of crumb rubber particles. The increased adhesiveness makes it possible to use as fillers. In some applications, surface activated crumb rubber can be moulded by itself, without binders or other additives.[12-22]

The surface active powder has large surface area compared to ordinary rubber. Surface activation was done by water. The water activation was not expected to have a great affect on the surface morphology, as the goal of this procedure is the removal of light oils from the crumb rubber particles, not morphology changes. According to ASTM D-297, test results support the theory that oil extraction occurred as results the activation process.

## 4b.2 Experimental

### 4b.2.1 Modification of crumb rubber (activation in hot water)

The low surface area present in crumb rubber, particularly cryogenically produced, tends to decrease the reactivity of the crumb rubber. This results in as lower gelation period, and ultimately less compatibility between crumb rubber and binder (Liang 1998). Therefore, research has been undertaken for of improving the compatibility of crumb rubbers binder. One possible alternative to this procedure is the treatment of the crumb rubber using hot water to generate an activated rubber surface (Memon 1999a).The activation was achieved by soaking the crumb rubber particles in hot water thus allowing the excess oils and chemicals present in the crumb rubber particles to be removed in the hot water slurry. This was accomplished by mixing 400 g of crumb rubber with 800 g of distilled water, the mixture was then heated up to 85 °C and blended for a period of 60 min. Following this, the slurry was filtered and dried at room temperature

### 4b.2.2 Development of surface coating with rubber crumb

The same formulations used for surface coatings in sections 4a is used by additionally adding the rubber crumb. The rubber crumb was dispersed in different mediums such as water, aqueous solutions of carboxy methyl cellulose, sodium hexametaphosphate and dodecyl benzene sulphonicacid. Figure 4b.1 shows the dispersion stability of rubber crumb in water in presence of different dispersing agents after 1 week.

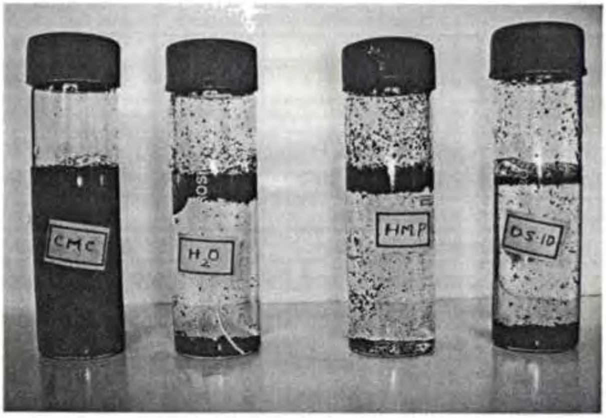


***Figure 4b.1:*** *Dispersions of rubber crumb in water with different dispersing agents (CMC - carboxymethyl cellulose, $H_2O$ - water, HMP - sodium hexametaphosphate, DS-10-* dodecylbenzenesulphonic acid)

Rubber crumb is found to be uniformly dispersed only in aqueous solution of carboxy methyl cellulose. The dispersion containing the rubber crumb and latex was prepared first and mixed with other ingredients. Different proportions of rubber crumb were used for making the surface coating and the optimum level was found out for the easy brushing and good dispersion. For all formulations the VAc-BuA copolymer of 45% solid content was used. Table 4b.2 shows the quantities of different ingredients used for the formulations.

*Table 4b.2: Paint formulation with rubber crumb*

| **Ingredients** | **Weight (g)** | |
|---|---|---|
| | ***PB** | ***PBR** |
| Water | 35 | 35 |
| Triton-X100 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0.42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 |
| Volcastab | 0.42 | 0.42 |
| Silicone emulsion | 1.34 | 1.34 |
| Propylene glycol | 4 | 4 |
| Acticid SPX | 0.32 | 0.32 |
| Above ingredients are to be combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added | | |
| Kaolin | 17 | 17 |
| Calcium carbonate | 18.64 | 18.64 |
| $TiO_2$ (Rutile) | 44.6 | 44.6 |
| Mix the above ingredients at high speed for 20 minutes. While stirring the mixture the following ingredients were added | | |
| Carboxymethyl cellulose | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added. | | |
| Polymer emulsion | 75 | 75 |
| Rubber crumb | 0 | 3 |

*PB-Paint with VAc-BuA copolymer (85/15 wt.%) without crumb. **PBR- VAc-BuA copolymer (85/15 wt.%) and crumb rubber.

## 4b.3 Results and discussion

The durability tests, adhesion test and viscosity of the matt finish paint (paint formulated with rubber crumb, PBR) were carried out and compared with paint formulated without rubber crumb and commercially available emulsion paint. The procedures of the tests are described in chapter 2. The specimens for the tests were prepared by coating the paint samples in mild steel panels of size 6inx4in (BS specification).

The observations for various tests are summarised in the respective tables for each test and the appearance (photographs) of the coated paint samples before and after the tests are also shown under the respective tests. The properties of the formulated paints are compared with a commercially available paint.

### 4b.3.1 Water resistance test

***Table 4b.3:*** *Blister formation in water resistance test at $38^0C$*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | ***PB*** | ***PBR*** | ***Commercial*** |
| 24 hrs | Nil | Nil | Nil |
| 4 days | Nil | Nil | Nil |
| 1week | Nil | Nil | Nil |
| 3 week | Nil | Nil | Few |
| 12week | Few | Nil | Medium |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are shown in figure 4b.1.

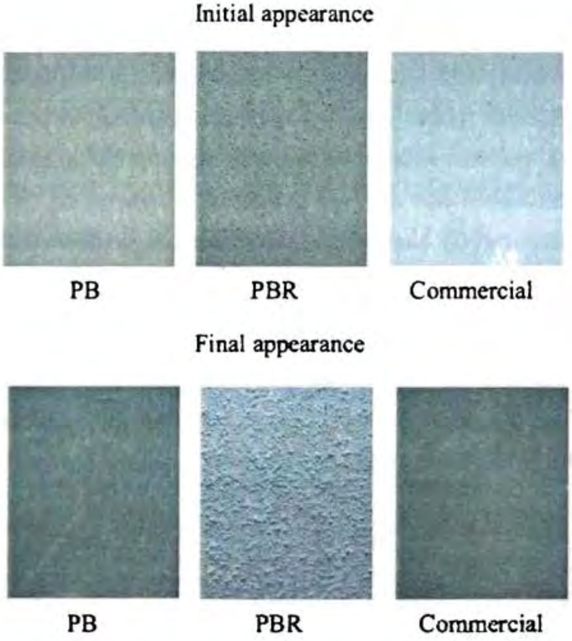


***Figure 4b.2:*** *Appearance of specimens before and after water resistance test*

The figure 4b.2 and table 4b.3 clearly shows that sample PBR is highly resistant to water and is not shows any blister even after 12 weeks. The sample PB and commercially available paint show a little blistering.

### 4b.3.2 Salt spray test

***Table 4b.4:*** *Blister formation in salt spray test at $28^0C$*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***PBR*** | ***Commercial*** |
| 48 hrs | Nil | Nil | . Nil |
| 1 week | Nil | Nil | Nil |
| 4 week | Nil | Nil | Few |
| 12week | Few | Nil | Medium dense |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are shown in figure 4b.3

Initial appearance

PB PBR Commercial

Final appearance

PB PBR Commercial

***Figure 4b.3:*** *Appearance of specimens before and after salt spray test*

By analyzing the observations shown in table 4b.4 and the photographs shown in figure 4b3 it can be seen that the sample PBR is very stable and is not affected by salt spray. Samples coated with PB and commercially available paint than are more affected by the salt water.

### 4b.3.4 Alkali resistance test

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at 75°C, $Na_2CO_3$ at 65°C and NaOH at 28°C) according to standard procedure as described in chapter 2.

*Table 4b.5: Blister formation in $Na_3PO_4$ resistance test (75°C)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | *PB* | *PBR* | *Commercial* |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Few | Few |
| 16 hrs | Medium | Medium | Dense |
| 24 hrs | Dense | Medium | Peeled |

**Table 4b.6:** Blister *formation in* $Na_2CO_3$ resistance test (65°C)

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | *PB* | *PBR* | *Commercial* |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Few |
| 16 hrs | Medium | Few | Dense |
| 24 hrs | Dense | Few | Peeled |

Initial appearance

PB PBR Commercial

Final appearance $Na_3PO_4$

PB PBR Commercial

Final appearance $Na_2CO_3$

PB PBR Commercial

Final appearance NaOH

PB PBR Commercial

***Figure 4b.4***: *Appearance of specimens before and after alkali resistance test*

*Table 4b.7: Blister formation in NaOH resistance test (28$^0$C)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***PBR*** | ***Commercial*** |
| 4 hrs | Nil | Few | Nil |
| 8 hrs | Medium | Medium | Dense |
| 16 hrs | Dense | Dense | peeled |

Tables 4b.5, 4b.6 and 4b.7 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, for 24h $Na_2CO_3$, 16h for NaOH) are shown in figure 4b.3.

From the photographs (figure 4b.3) it can be seen that the resistance of the sample PBR is better than all the other samples in the three alkalies tested.

### 4b.3.5 Detergent resistance test

*Table 4b.8: Blister formation in detergent resistance at 28$^0$C*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***PBR*** | ***Commercial*** |
| 1day | Nil | Nil | Nil |
| 3 days | Few | Nil | Medium |
| 1 week | Medium | Few | Medium |

The photographs of initial appearance (before the test) and final appearance (after 1 week) of the coated samples for detergent resistance test are shown in figure 4b.5.

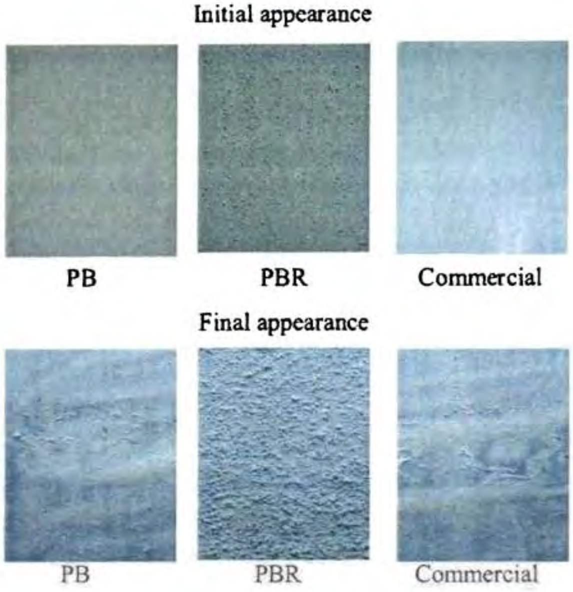


***Figure 4b.5:*** *Appearance of specimens before and after detergent resistance test*

Table 4b.8 and figure 4b.5 shows that sample PBR is more resistant to detergent attack than PB and commercially available paint.

### 4b.3.7 Natural weather resistance

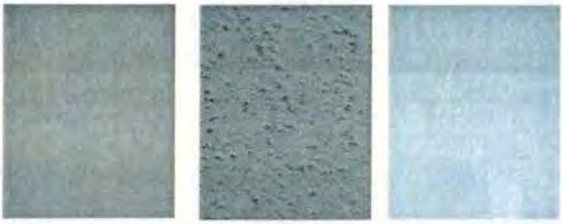
Weather resistance test was conducted for a period of 10 months from March to December. This time period was selected because the samples were exposed to all seasons during the test.

***Table 4b.9:*** *Blister formation in weather resistance test*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | ***PB*** | ***PBR*** | ***Commercial*** |
| 1month | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil |
| 10 months | Nil | Nil | Nil |

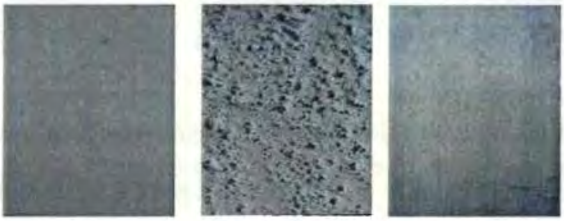
The photographs of initial appearance (before the test) and final appearance (after 10 months) of the samples exposure to weather test are shown in figure 4b.6

Initial appearance



PB PBR Commercial

Final appearance



PB PBR Commercial

***Figure 4b.6*** *Appearance of specimens before and after weather resistance test*

The figure 4b.6 and table 4b.9 shows that all the samples are very stable towards natural weather and did not any colour change or degradation during the test.

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample PBR is having good resistance towards various chemicals. The presence of rubber crumb may actively resist the attack of chemicals and climate conditions due to its inherent resistance. Rubber crumb is already a vulcanized form and also contains fillers such as carbon black, ZnO, silica etc. this is the reason for the inherent resistance.

### 4b.3.8 Scotch test

The cross cut adhesion test is carried out to know the adhesion of paint films on the substrate. The adhesion rating according to ASTM standards is shown in the table 4b.10.

***Table 4b.10:*** *Adhesion rating assessed by scotch test*

| Sample name | Classification | % removal |
|---|---|---|
| PB | 4B | Less than 5% |
| PBR | 5B | 0% |
| Commercial | 3B | 5 – 15% |

The photographs of test specimens before and after the test are shown in figure 4b.7

Initial appearance

Final appearance

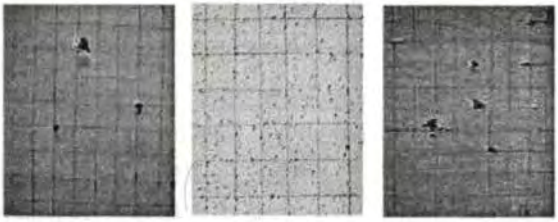


***Figure 4b.7:*** *Appearance of specimens before and after scotch test*

The figure 4b.7 and table 4b.10 show that the adhesive strength of all samples is high. The sample PBR has no peeling by the scotch test, but trace peeling in PB and commercial sample are observed. The presence of matting agent (activated rubber crumb) may not allow the scotch tape to adhere on the surface of paint. This may be the reason for the good result obtained for the scotch test. This shows that the adhesive materials will not adhere on the matt finished paint film.

### 4b.5 Viscosity of paint

Viscosity and shear thinning behaviour is an important property of paint for ease of application. It is depend on the size of the colloidal particles in paint. The viscosity of newly formulated paint is found to be independent of the presence of activated rubber crumb as it is uniformly distributed in the paint.

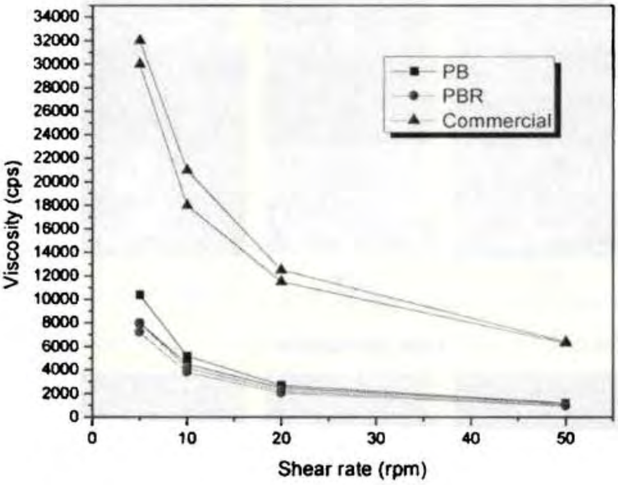


*Figure 4b.8: Variation of viscosity with shear rate*

Shear thinning index of $PB_1$, $PB_2$ and $PB_3$ at two different speeds 5 and 50 are given in table 4b.11.

*Table 4b.11: Shear thinning index of specimens*

| Sample | Shear thinning index |
|---|---|
| PB | 8.67 |
| CPBR | 7.84 |
| Commercial | 5 |

## 4b.5 Conclusion

A new matt finish paint formulation was developed with Vinyl acetate - butyacrylate copolymer (85/15) using activated tyre crumb. The paint showed better durability, water resistance, alkali resistance and detergent test, salt spray tests and weather resistance compared to commercial grade paint. The adhesion property is better than the other paints.

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# 4c: Paint formulation with natural biocide

## 4c.1 Introduction

Biocides are required in paint formulation to prevent microbial degradation during shipment, storage and use. Biocides are also required to protect the coated substrate from harmful microorganisms such as bacteria, fungi and the like. Microorganisms are ubiquitous in the environment. Many of them have simple requirements for the growth that can be met by most waterborne coatings. Adding an in-can preservative will protect these coatings in the wet state during storage and transport. After the coating has been applied and dried, most waterborne and solvent-borne coatings are susceptible to colonization by fungi or algae. The addition of a dry-film preservative (fungicide or algaecide) will ensure long-term performance of the coating.

Biocides used in paint products may be grouped into three major classes: preservatives, mildewcides and antifoulants. Preservatives are widely used in water-based paint systems to prevent in-can bacterial and fungal degradation during storage and shipment. They are particularly useful in latex systems such as synthetic rubber, polyacrylate, and natural rubber lattices. Mildewcides are used to prevent degradation of the dried paint films and underlying substrate by microorganisms. Antifoulant paints are used to prevent the growth of organisms on the hull of both commercial and pleasure boats. The attachment of such organisms decreases the operating efficiency of the boats and increases their maintenance costs.

Mercurial-type biocides have been widely used as both preservatives and mildewcides in paints. They have excellent performance in both functions in many situations. They offer the fast kill time and can control high levels of bacterial contamination. Unfortunately, they are hazardous to handle and may cause environmental problems. Thus, they cannot be used for common applications. A wide variety of biocides have been tried as marine antifoulants, but the marketplace has been dominated by cuprous oxide and organotin compounds for this use. Cuprous oxide has been popular because it is efficient, relatively economical, and is specified in many military antifouling paint formulations as the exclusive biocide. However, this chemical causes micro porosity in the paint film, which adversely affects efficiency, and it limits the paint colors to dark reddish brown. The organotin are more expensive than cuprous oxide and also more difficult to incorporate in paint formulations. Furthermore, they do not leach out completely during use so that when ships are sandblasted the disposal of the contaminated sand poses difficulties. However, organotins yield uniform, tight films without the micro porosity problems associated with cuprous oxide and may be formulated in a wide variety of bright or light colors. For the latter reasons, they are widely used on pleasure boats. Since both cuprous oxide and organotin compounds present technical or environmental problems, there is a need for new and better antifoulant paint biocides.

However, merely blending these biocides into paint formulations may result in problems. Some of the major problems are their miscibility with other constituents of the system and their water solubility. Their insolubility may cause agglomeration of the biocide in the dried film. Their water solubility may cause leaching from the paint film or migration of the biocide in the film. These lead to uneven biocidal protection, environmental problems and reduced service life. Accordingly, it is an objective of this study to make a class of bioactive polymers which are effective as preservatives, mildewcides and marine antifoulants in paints.

Industrial water-based formulations usually require protection against microbial spoilage. Examples of such formulations include lattices, emulsions, paints, adhesives, caulks, and sealing mastics. Microbial contaminants can be introduced by water (process water, wash water), raw materials (latex, fillers, pigments, etc.), and poor plant hygiene. Bacteria are the most common spoilage organisms, but fungi and yeasts are sometimes responsible for product deterioration. Among the most common contaminants are *Aeromonas* sp., *Bacillus* sp., *Desulfovibrio* sp., *Escherchia* sp., *Enterobacter* sp., and *Pseudomonas* sp. Microbial growth is usually manifested as a loss in functionality and may include gas formation, pH changes, offensive odour, and changes in viscosity and color.[1] Spoilage of the water-based products, which can go unnoticed until the product reaches the consumer, can result in significant economic loss to the manufacturer. Good plant hygiene and manufacturing practices, when combined with the use of a compatible broad spectrum biocide, will minimize the risk of microbial spoilage of the coating.[2] In selecting an in-can preservative, cost effectiveness, compatibility, stability, handling, and eco-toxicity are important factors to take into account. Intrinsic properties of the coating, such as pH, viscosity, redox potential, and the presence of certain ingredients may also affect the effectiveness of biocides. Typical use levels for in-can preservatives are in the range of 0.05 to 0.5 weight percent. The examples of in-can preservatives are Aldehyde (Biocheck 80), Amide (Biochek 20), Amino acid adducts (Nuosept 44), Blends of actives (Acticides) etc.

Both water-based and solvent-based coatings are susceptible to the colonization of fungi and algae upon drying. The type of microorganisms that can colonize the coating will depend on several factors, including the moisture content of the surface, the presence of nutrients, the substrate, and the type of coating.[3,4] For example, the moisture content of the surface is affected by factors such as climatic (amount of rainfall, dew, humidity, temperature, and period of the year) as well as local conditions (surfaces sheltered from winds and shaded areas will contain higher moisture content).[5] The presence of nutrients may include constituents of the coating (such as polymers, thickener residues, etc.), biodegraded substances produced by other microorganisms (e.g., complex substrates may be attacked by a succession of microorganisms), or simply material deposited on the coating from the atmosphere, such as dirt. The substrate is also of importance. It provides, for example, a suitable pH environment. In this regard, fungi favour more acidic conditions, such as those provided by wood. Algae, on the other hand, favour more alkaline conditions, such as those provided by masonry. Last, the type and properties of the coating (water repellency, hardness, chalking, and roughness) will also play an important role in determining which type of microorganism could colonize the coating.

On exterior surfaces, *Aureobasidium pullulans* and *Alternaria* sp. are common fungal isolates. In general, fungi found on exterior surfaces are able to withstand high temperatures and dry conditions, are tolerant to UV exposure, and can adhere well to surfaces.[6] On interior surfaces, the fungi *Aspergillus* sp.

and *Penicillium* sp. are frequently isolated. Algae are mainly isolated from exterior surfaces. Green algae species (*Chlorella* sp. Or *Stichococcus* sp.) are usually isolated in temperate regions. *Trentepohlia* sp.(which can be orange or green in color) is very common in tropical regions. Blue-green algae (*Gloeocapsa* sp., *Nostoc* sp.) have been isolated from various regions. Several blue-green algae (*Calothrix* sp., *Sytonema* sp.) are black in color and are, thus, easily mistaken for fungal discoloration.

The growth of microorganisms on coatings, also known as defacement, not only affects the appearance of the coating (discoloration), but it may also compromise its performance (biodeterioration). Fungi can penetrate coatings, resulting in cracking, blistering, and hampering the coatings' adhesion properties, thus leading to decay or corrosion of the underlying substrate. Algae colonies, which seem to grow more rapidly on porous substrates such as stucco, cement, and bricks, may be able to hold water. The freezing and thawing of this entrapped water may induce cracking or may increase the permeation properties of the coating, leading to failure. Also, the presence of water may encourage colonization by other microorganisms, which, in turn, may cause biodeterioration.[7]

There are several dry-film fungicides and algaecides in the market. Dry-film fungicides should be UV stable and resistant to leaching. Typical use levels for dry-film biocides are in the range of 0.5 to 2.0 percent by weight. As with the in-can preservatives, performance and compatibility with a specific coating formulation should be tested. Accelerated laboratory tests are usually recommended to test outdoor coatings.[8,9] These tests involve coating an inert surface that is then inoculated with various fungal or algae species. The most common fungicide active ingredients in the market include benzimidazoles, carbamic acid derivatives (e.g., IPBC), chlorothalonil, isothiazolones (eg., OIT), pyridines-*N*-oxide derivatives, thiazoles, and thiophthalamides (eg., fopet). The most common algaecides include S-triazines and ureaderivatives (eg., Diuron).

Chitosan is a polycationic polymer with specific structure and properties.[10] It contains more than 5,000 glucosamine units and is obtained commercially from shrimp and crab shell chitin (a *N*-acetylglucosamine polymer) by alkaline deacetylation[11,12] (NaOH, 40–50%). [13]Chitosan is inexpensive and nontoxic containing reactive amino groups. It has been shown to be useful in many different areas as an antimicrobial compound in agriculture, as a potential elicitor of plant defence responses, as a flocculating agent in wastewater treatment,[14,15] as an additive in the food industry,[16,17] as a hydrating agent in cosmetics,[18,19] and more recently as a pharmaceutical agent[20,21] in biomedicine.[22,23] The antimicrobial activity of chitosan was observed against a wide variety of microorganisms including fungi, algae, and some bacteria.[24] Chitosan films are tough, long lasting, flexible, and very difficult to tear. Most of their mechanical properties are comparable to many medium-strength commercial polymers.[25] It was reported that chitosan films have moderate water permeability and could be used to increase the storage life of fresh produce and foodstuffs with higher water activity values.[26]

To improve the antimicrobial properties of the surface coating without affecting the film formation property of surface coating, a natural biocide is introduced instead of synthetic biocide. Carboxy methyl chitosan having good film forming ability and excellent antimicrobial activity is selected for this. The antimicrobial properties of thus formulated paint was then compared with the paint formulated without natural biocide (Chapter 4a) and commercially available paint.

## 4c.2 Experimental

### 4c.2.1 Development of surface coating with natural biocide

Paints were made with various quantities of carboxymethyl chitosan as biocide to test the antimicrobial activity and optimized the quantity of chitosan required for the antimicrobial activity. The VAc-BuA copolymer latex of 45% solid content was selected for this paint formulation. Table 4c.1 shows the paint formulation recipe with carboxymethyl chitosan as natural biocide and without chitosan dervative.

Table 4c.1: Paint formulation

| Ingredients | Weight (g) | | |
|---|---|---|---|
| | *PB | **CPB | **CPBR |
| Water | 35.0 | 35.0 | 35.0 |
| Triton-X100 | 0.42 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0.42 | 0.42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 | 0.42 |
| Volcastab | 0.42 | - | - |
| Silicone emulsion | 1.34 | 1.34 | 1.34 |
| Propylene glycol | 4.00 | 4.00 | 4.00 |
| Acticide SPX | 0.32 | - | - |
| Above ingredients were mixed by mechanical stirring for 10 minutes. After that the following ingredients were added to the mixture with stirring | | | |
| Kaolin | 17.0 | 17.0 | 17.0 |
| Calcium carbonate | 18.64 | 18.64 | 18.64 |
| $TiO_2$ (Rutile) | 44.60 | 44.60 | 44.60 |
| Mix the above ingredients at high speed for 20 minutes. While stirring the mixture the following ingredients were added | | | |
| Carboxymethyl cellulose | 0.74 | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 | 0.92 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added. | | | |
| Polymer emulsion | 75.0 | 75.0 | 75.0 |
| Carboxymethyl chitosan | 0 | 0.60 | 0.60 |
| Activated rubber crumb | 0 | 0 | 3.00 |

*PB - Paint formulated with VAc-BuA copolymer (85/15 wt.%) without chitosan derivative. **CPB - Paint formulated with VAc-BuA copolymer (85/15 wt.%) and carboxymethyl chitosan as natural biocide. ***CPBR - Paint formulated with VAc-BuA copolymer (85/15 wt.%) with carboxymethyl chitosan and rubber crumb.

## 4c.3 Results and Discussion

Antimicrobial properties, durability properties, adhesive strength and viscosity of the paint CPB and CPBR formulated using natural biocide carboxymethyl chitosan is compared with the sample PB and commercially available paint.

### 4c.3.1 Antimicrobial studies

Surface coatings are usually attacked by various micro organisms such as fungus, algae and or bacteria. To know the antimicrobial activity of the formulated paints antialgal, antifungal and antibacterial tests were carried out according to the standard procedures described in chapter 2.

This test method attempts to provide a means to comparatively evaluate different coating formulations for their relative performance under a given set of conditions. It does not imply that a coating that resists growth under these conditions will necessarily resist growth in the actual application. This test method covers an accelerated method for determining the relative resistance of two or more paints or coating films to algae, fungus and bacterial growth

The results obtained from antimicrobial tests, durability tests, adhesion test and viscosity of the paint formulated using natural biocide (carboxymethyl chitosan) are compared with the paint without natural biocide and commercially available paint.

### 4c.3.1a. Antialgal studies

The algal species such as *Chlorella pyrenoiclosa* (Unicellular green algae), *Oscillaforia subrivis* (Filamentous blue green algae) are used for the study antialgal study. The nuisance growth of terrestrial algae on painted surface is a ruining problem.

Antialgal tests were conducted for four weeks. The growth of algae after 1 week and 4 weeks are shown in the photographs. The observations for the growth of microorganisms are described by standard ratings in the respective tables.

**A. Green algae**

*Table 4c.2: Rate of growth of green algae on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Traces of growth (1—10 %) | 1 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | Traces of growth (1—10 %) | 1 |
| **WeekK 4** | | |
| PB | Light growth (10-30%) | 2 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | moderate growth (30-60%) | 3 |

The photographs to show the growth of the green algae on the specimens after 1 week and after 4 weeks are shown in figure 4c.1.

**B. Blue green algae**

*Table 4c.3: Rate of growth of blue green algae on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Traces of growth (1—10 %) | 1 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | Traces of growth (1—10 %) | 1 |
| **Week 4** | | |
| PB | Light growth (10-30%) | 2 |
| CPB | Traces of growth (1-10%) | 1 |
| CPBR | None | 0 |
| Commercial | Moderate growth (30-60%) | 3 |

The photographs to know the growth of the blue green algae on the specimens after 1 week and after 4 weeks are shown in figure 4c.2.

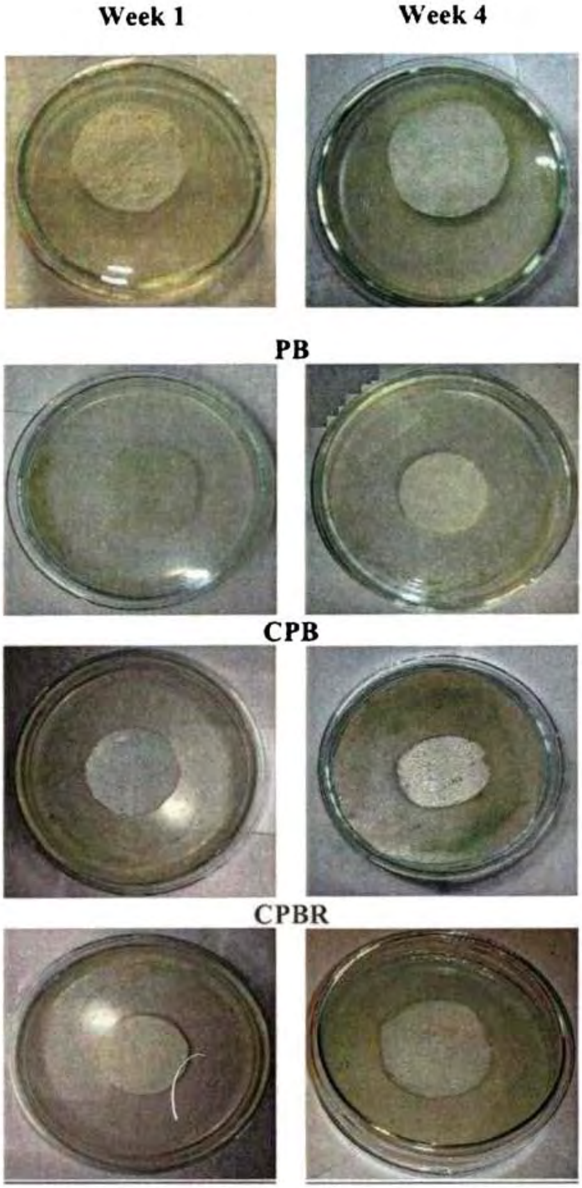


***Figure 4c.1:*** *Photographs for showing the growth of green algae on the specimens after 1 week and four weeks at the test*

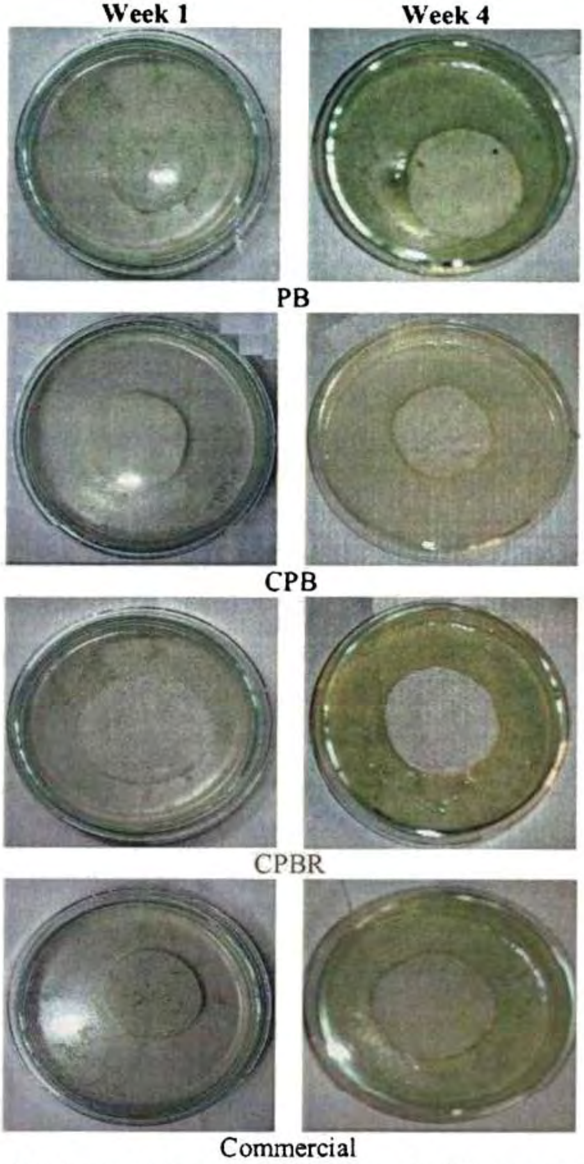


***Figure 4c.2:*** *Photographs for showing the growth of blue green algae on the specimens after 1 week and four weeks at the test*

The growth rate of both types of algae observed as in tables 4c.2 and 4c.3 shows that carboxymethyl chitosan based paint exhibit greater antialgal activity compared to other samples.

The tests conducted for antifungal activity of various paint samples shows that the algal defacement is more predominant for the samples CPB and CPBR which contains natural biocide when compared to other samples. From the rating tables 4c.2 & 4c.3 and figures 4c.1 & 4c.2 for the growth of green and blue green algae we can observe that the samples CPB and CPBR are not attacked by algae. The growth of the algae can be observed on PB and commercially available paint samples. This shows that carboxymethyl chitosan can effectively control the growth of algae in paints.

### 4c.3.2 Antifungal studies

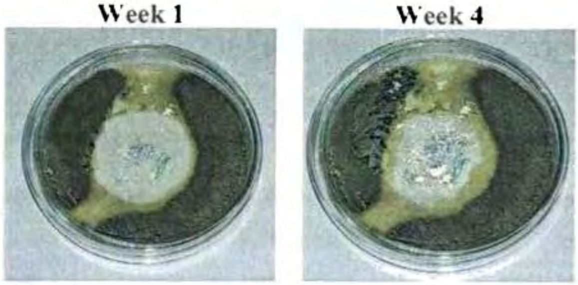
The fungal species such as *Aspergillus* and *Penicillium citrinium* are used for the study of antifungal activity of paint samples.

Antifungal tests were conducted for four weeks. The growth of fungi after 1 week and 4 weeks are shown in the photographs. The observations for the growth of fungi are described by standard ratings in the respective tables.

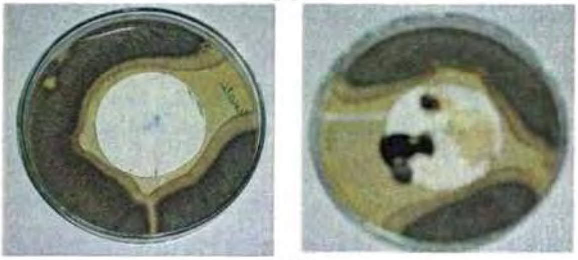
### A. Aspergillus

*Table 4c.4: Rate of growth of Aspergillus on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Light growth (10—30 %) | 2 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | Light growth (10—30 %) | 2 |
| **Week 4** | | |
| PB | Moderate growth (30-60 %) | 3 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | Heavy growth (60 % to 100%) | 4 |



**PB**



**CPB**

**CPBR**

**Commercial**

***Figure 4c.3:*** *Photographs showing the growth of Aspergillus on the specimens after 1 week and four weeks at the test*

### b. *Pencillium citrinium*

*Table 4c.5: Rate of growth of Penicillium citrinium on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Traces of growth (1—10 %) | 1 |
| CPB | None | 0 |
| CPBR | None | 0 |
| Commercial | Traces of growth (1—10 %) | 1 |
| **Week 4** | | |
| PB | Moderate growth (30-60 %) | 3 |
| CPB | Light growth (10—30 %) | 2 |
| CPBR | None | 0 |
| Commercial | Heavy growth (60 % to 100%) | 4 |

Table 4c.5 shows the growth rate of two types of algae, which shows grater fungal defacement observed for chitosan based paint than commercial paint. The photographs shows the growth of *Penicillium citrinium* on the specimens after 1 week and after 4 weeks are shown in figure 4c.4

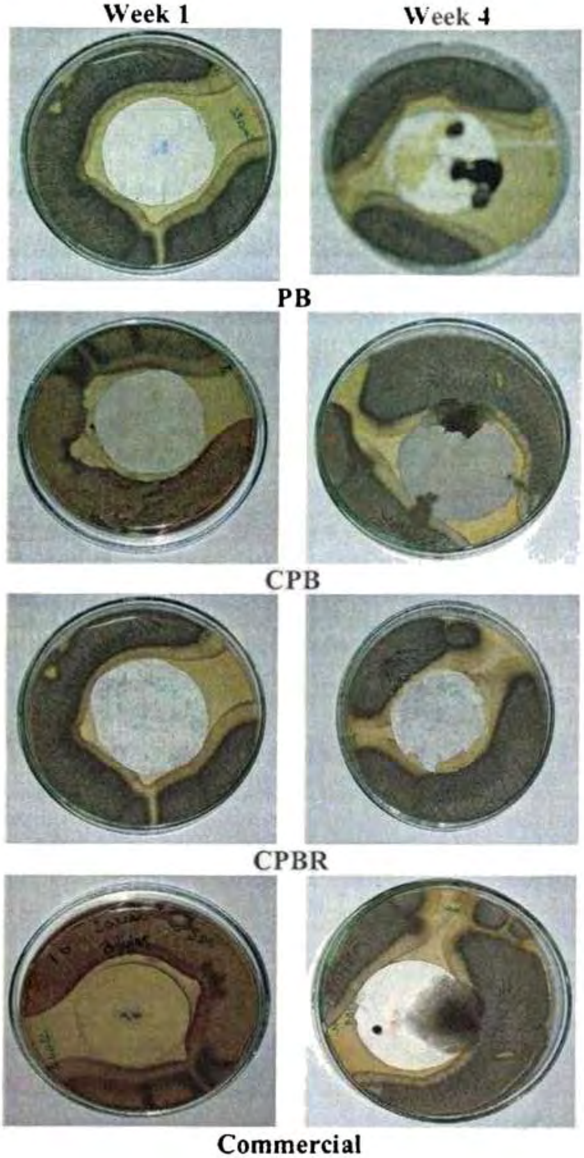


***Figure 4c.4:*** *Photographs for showing the growth of Penicillium citrinium on the specimens after 1 week and four weeks at the test*

Fungi are present on the surface of coated paint in two forms. They may be present as thread-like structures, mycelia or as clusters of spherically, black coloured spores. The mycelia structures are observed when conditions under fungi are relatively growing and reproducing. Spore clusters are found when conditions for growth and reproduction are less favourable. Spores are more resistant to environmental changes and anti-microbial agents than the mycelia forms. Growth of two type of fungi spore on paint film is observed after 4 weeks, as shown in photograps. The carboxymethyl chitosan based coating shows better resistance to fungi attack than commercial paint film.

### 4c.3.3 Antibacterial studies

The antibacterial tests were conducted in accelerated lab conditions. The bacterial species such as *Escherichia colli* and *Bacillus cereus* are used for the study of antibacterial activity of paint samples.

Antibacterial tests were conducted for two days. The photographs of paint films immediately after inoculation of bacteria (initial) and the growth of bacterial colonies after 48 hours are shown in respective figures. The observations for the growth are described by standard ratings in the respective tables.

#### A) *Escherichia colli*

***Table 4c.6:*** *Rate of growth of Escherichia colli on the samples*

| Sample | Growth of bacterial colonies on Samples | Rating |
|---|---|---|
| **Initial** | | |
| PB | No growth | 0 |
| CPB | No growth | 0 |
| CPBR | No growth | 0 |
| Commercial | No growth | 0 |
| **After 48 hours** | | |
| PB | No growth | 0 |
| CPB | No growth | 0 |
| CPBR | No growth | 0 |
| Commercial | No growth | 0 |

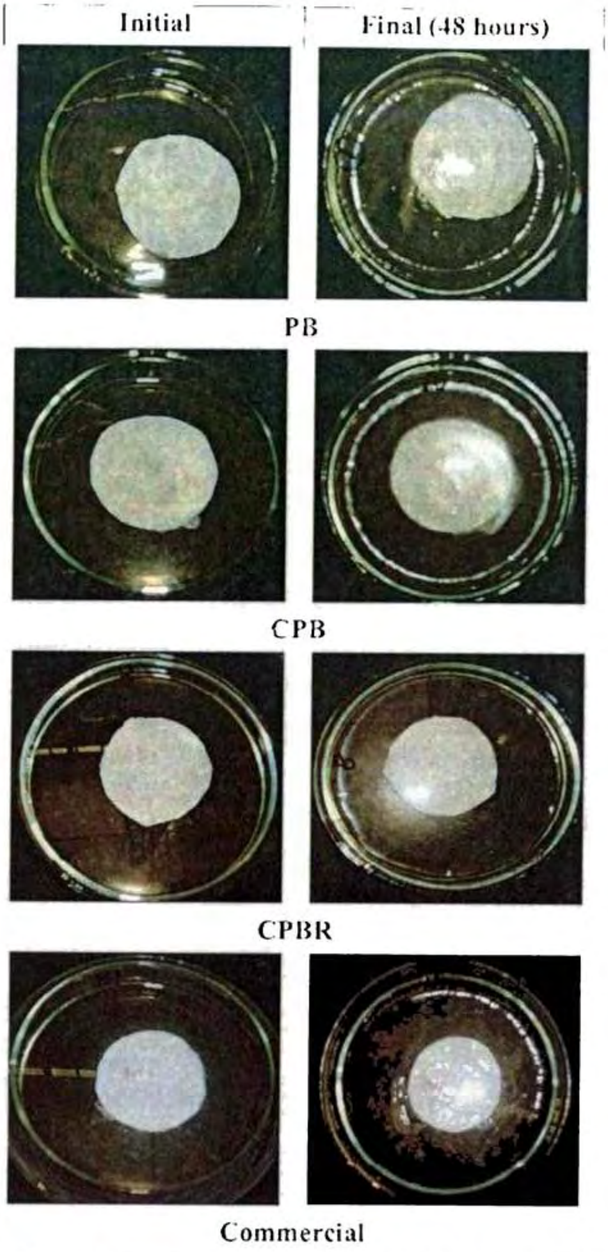


***Figure 4c.5:*** *Photographs for showing the growth of Escherichia colli on the specimens before and after 48 hours at the test*

### b. *Bacillus cereus*

*Table 4c.7: Rate of growth of Bacillus cereus on the samples*

| Sample | Growth of bacterial colonies on Samples | Rating |
|---|---|---|
| **Initial** | | |
| PB | No growth | 0 |
| CPB | No growth | 0 |
| CPBR | No growth | 0 |
| Commercial | No growth | 0 |
| **After 48 hours** | | |
| PB | No growth | 0 |
| CPB | No growth | 0 |
| CPBR | No growth | 0 |
| Commercial | No growth | 0 |

The photographs show the growth of *Escherichia colli* on the paint films at the time of inoculation and after 48 hours is shown in figure 4c.5. The photographs show the growth of *Bacillus cereus* on the paint films at the time of inoculation and after 48 hours is shown in figure 4c.6.

The bacterial growth increases under conditions of stress such as heat, cold, dehydration, some are able to form spores which are resistant to high temperature and dry environment and more resistant to bactericides. The photograps show the growth of two types of bacteria on the surrounding agar medium but colonial growth of bacteria is not observed on the paint film after 48hours. This shows that all paint films have good resistance to bacterial attack.

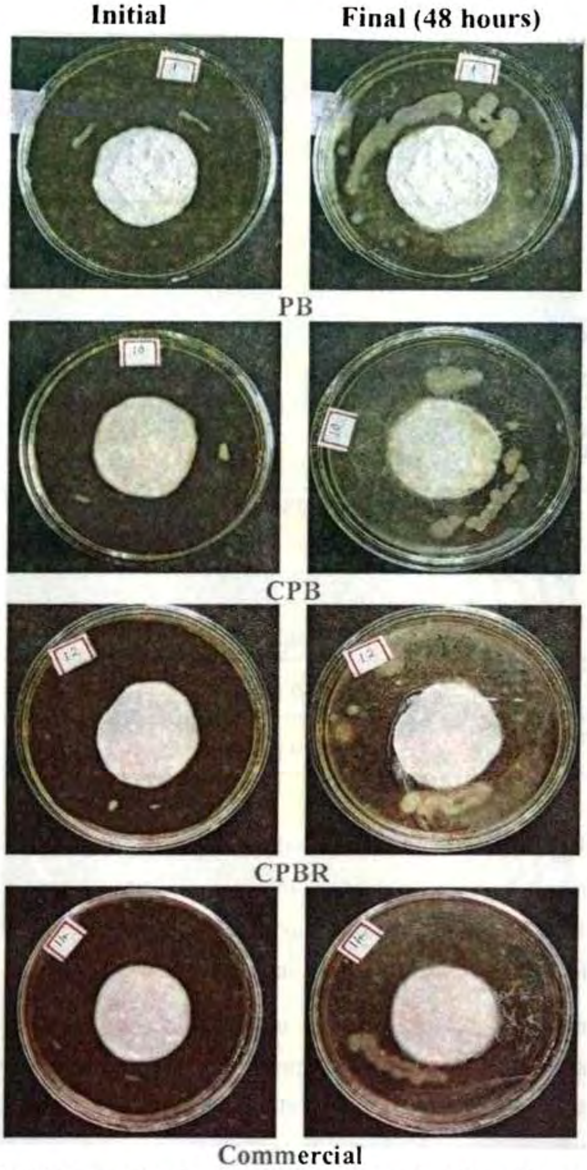


***Figure 4c.6:*** *Photographs for showing the growth of Bacillus cereus on the specimens before and after 48 hours at the test*

Most of the chemical agents used in paint films effectively control fungi, algae and bacteria by interfering with their metabolic functions.

The exact mechanism of the antimicrobial action of carboxymethyl chitosan is still unknown, but different mechanisms have been proposed. Interaction between positively charged chitosan molecules and negatively charged microbial cell membranes leads to the leakage of proteinaceous and other intracellular constituents.[27] Chitosan acted mainly on the outer surface of the bacteria. At a lower concentration (<0.2 mg/mL), the polycationic chitosan does probably bind to the negatively charged bacterial surface to cause agglutination, while at higher concentrations, the larger number of positive charges may have imparted a net positive charge to the bacterial surfaces to keep them in suspension.[28]

### 4c.3.2 Durability tests

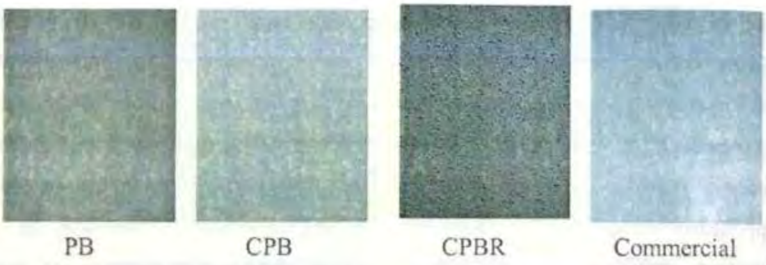
#### 4c.3.2a Water resistance test:

***Table 4c.8:*** *Blister formation in water resistance test at 38°C*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 24 hrs | Nil | Nil | Nil | Nil |
| 4 days | Nil | Nil | Nil | Nil |
| 1week | Nil | Nil | Nil | Nil |
| 3 week | Nil | Few | Nil | Few |
| 12week | Few | Few | Nil | Medium |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are shown in figure 4c.7.

Initial appearance



Final appearance

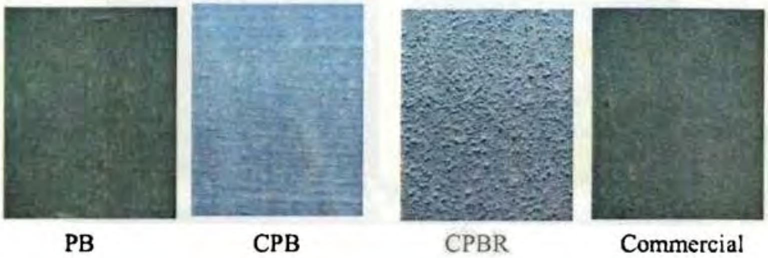


*Figure 4c.7: Appearance of specimens before and after the water resistance test*

The figure 4c.7 and table 4c.8 clearly shows that sample CPBR is highly resistant to water and is not shows any blister even after 12 weeks. The sample CPB and commercially available paint show only slight blistering.

### 4c.3.2b Salt spray test:

*Table 4c.9: Blister formation in salt spray test at $28^0C$*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | *PB* | *CPB* | *CPBR* | *Commercial* |
| 48 hrs | Nil | Nil | Nil | Nil |
| 1 week | Nil | Nil | Nil | Nil |
| 4 week | Nil | Few | Nil | Few |
| 12week | Few | Medium | Few | Medium |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are shown in figure 4c.8.

Initial appearance

PB CPB CPBR Commercial

Final appearance

PB CPB CPBR Commercial

***Figure 4c.8:*** *Appearance of specimens before and after the salt spray test*

By analyzing the observations shown in table 4c.9 and the photographs shown in figure 4c.8 we can see that the sample CPBR is very stable and not much affected by salt spray. Salt water resistance is found to be better for CPBR compared to commercially available paint.

4c.3.2c **Alkali resistance test:**

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at $75^0$C, $Na_2CO_3$ at $65^0$C and NaOH at $28^0$C) according to standard procedure as described in chapter 2.

*Table 4c.10: Blister formation in $Na_3PO_4$ resistance (75$^0$C)*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Nil | Few |
| 16 hrs | Medium | Few | Few | Dense |
| 24 hrs | Dense | Medium | Medium | Peeled |

*Table 4c.11: Blister formation in $Na_2CO_3$ resistance (65$^0$C)*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Nil | Few |
| 16 hrs | Medium | Few | Nil | Dense |
| 24 hrs | Dense | Medium | Few | Peeled |

*Table 4c.12: Blister formation in NaOH resistance (28$^0$C)*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil | Nil |
| 8 hrs | Medium | Few | Medium | Dense |
| 16 hrs | Dense | Medium | Dense | Peeled |

Tables 4c.10, 4c.11 and 4c.12 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, for 24h $Na_2CO_3$, 16h NaOH) are shown in figure 4c.9.

From the photographs in figure 4c.9 we can see that the alkali resistance of the sample CPBR is more in all three alkalies compared to other samples.

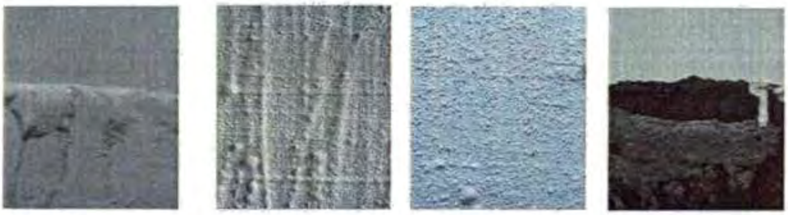
Initial appearance

PB CPB CPBR Commercial

Final appearance $Na_3PO_4$

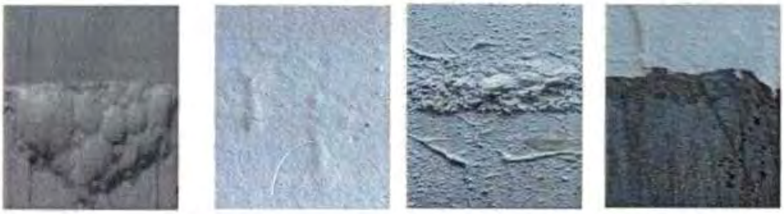
PB CPB CPBR Commercial

Final appearance $Na_2CO_3$



PB CPB CPBR Commercial

Final appearance NaOH



PB CPB CPBR Commercial

***Figure 4c.9:*** *Appearance of specimens before and after alkali resistance test*

### 4c.3.2d Detergent resistance test

***Table 4c.13:*** *Blister formation in detergent resistance at $28^0C$*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 1 day | Nil | Nil | Nil | Nil |
| 3 days | Few | Nil | Nil | Medium |
| 1 week | Medium | Few | Nil | Dense |

The photographs of initial appearance (before the test) and final appearance (after 1 week) of the coated samples during detergent resistance test are shown in figure 4c.10.

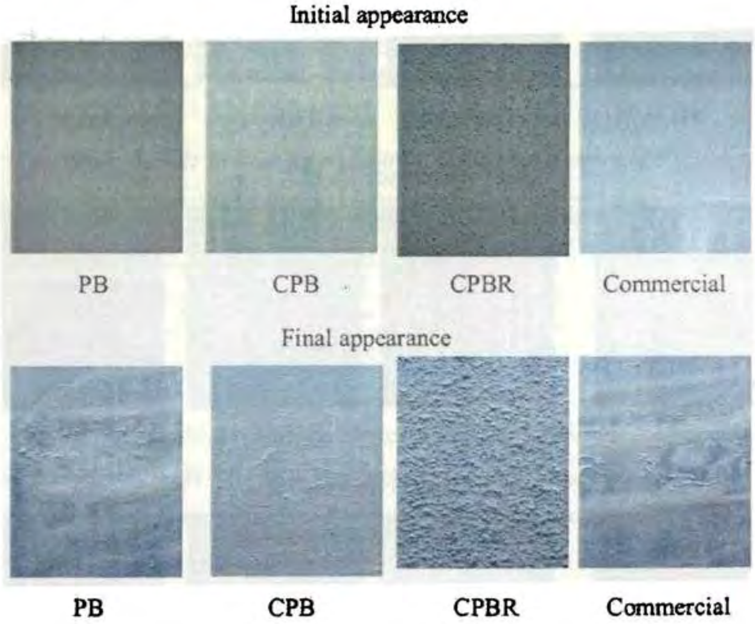


***Figure 4c.10:*** *Appearance of specimens before and after detergent resistance test*

Table 4c.13 and figure 4c.10 shows that sample CPB and CPBR is more resistant to detergent attack than PB and commercially available paint.

### 4c.3.2e Natural weather resistance

Weather resistance test was conducted for a period of 10 months from March to December. This time period was selected because the samples were exposed to all seasons during the test.

***Table 4c.14:*** *Chalking formation in weather resistance test*

| Time interval | Chalking observed | | | |
|---|---|---|---|---|
| | ***PB*** | ***CPB*** | ***CPBR*** | ***Commercial*** |
| 1 month | Nil | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil | Nil |
| 10 months | Nil | Nil | Nil | Nil |

The photographs of initial appearance (before the test) and final appearance (after 10 months) of the coated samples during weather resistance test are shown in figure 4c.11.

Initial appearance

PB CPB CPB Commercial

Final appearance

PB CPB CPB Commercial

***Figure 4c.11:*** *Appearance of specimens before and after weather resistance test*

The figure 4c.11 and table 4c.14 shows that all the samples are very stable towards natural weather and not shows any colour change or degradation during the test.

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample CPBR is having good resistance towards various chemicals. The presence of rubber crumb and chitosan may actively resist the attack of chemicals and climate conditions due to the inherent resistance of rubber crumb and film forming ability of chitosan.

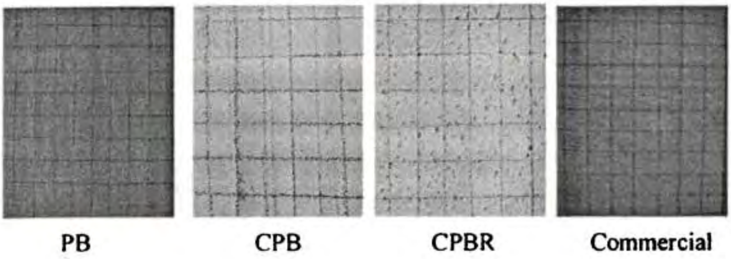
### 4c.3.3 Scotch test

The cross cut adhesion test is carried out to know the adhesion of paint films on the substrate. The adhesion rating according to ASTM standards is shown in the table 4c.15.

*Table 4c.15: Adhesion rating assessed for scotch test*

| Sample name | Classification | % removal |
|---|---|---|
| PB | 4B | Less than 5% |
| CPB | 5B | 0% |
| CPBR | 5B | 0% |
| Commercial | 3B | 5 - 15% |

The photographs of test specimens before and after the test are shown in figure 4c.12.


Initial appearance

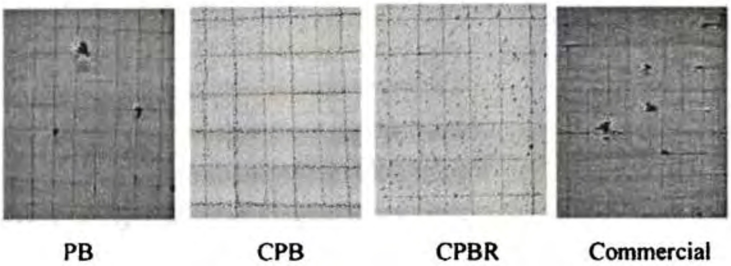

Final appearance

***Figure 4c.12:*** *Appearance of specimens before and after the scotch test*

The figure 4c.12 and table 4c.15 shows that the adhesive strength of all samples is high. The sample PBR has no peeling by the scotch test, but trace peeling in PB and commercial sample are observed. The presence of matting agent (activated rubber crumb) may not allow the scotch tape to adhere on the surface of paint. This may be the reason for the good result obtained for the scotch test. This shows that the unwanted materials will not adhere on the matt finished paint film.

### 4c.3.4 Viscosity

Viscosity and shear thinning behaviour is an important property of paint for ease of application. It is depend on the size of the colloidal particles in paint. The viscosity of newly formulated paint is independent of the presence of activated rubber crumb.

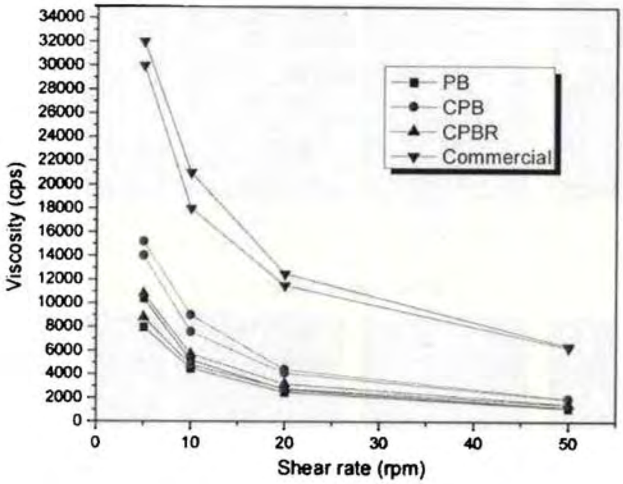


**Figure 4c.13:** Variation of viscosity with shear rate

Shear thinning index of PB, CPB, CPBR and commercial paint at two different speeds 5 and 50 are given in table 4c.16.

**Table 4c.16:** Shear thinning index of the specimens

| Sample | Shear thinning index |
|---|---|
| PB | 8.67 |
| CPB | 7.83 |
| CPBR | 6.4 |
| Commercial | 5.0 |

## 4c.4 Conclusion

A new paint formulation was developed with Vinyl acetate - butyacrylate copolymer as binder and carboxyl methyl chitosan as biocide. The paint gave good durability in water resistance, alkali resistance and detergent test, salt spray tests, weather resistance and scotch test compared to commercial paint. The paint shows better resistance to algae, fungi and bacterial growth due to the presence of carboxyl methyl chitosan.

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# *Chapter 5*

# PREPARATION AND CHARACTERIZATION OF NANO TITANIUM DIOXIDE

## 5.1 Introduction

The word pigment derived from the Latin word pigmentum. The definition concentrates on the products used to give an aesthetic effect such as colour and opacity. Extenders do not usually affect the colour or opacity of a paint film, but play an important role in the film properties such as reinforcement, gloss, hardness etc. They affect the properties of the paint itself such as rheology, settling characteristics or cost.[1] Most pigments are used to provide a visual effect, mainly colour and opacity. Important to ensure that pigment will remain essentially insoluble in the system in which it is used and will give required physical properties such as light fastness, weather ability and resistance to chemical.[2] Colour of pigments depends on its chemical nature. The selective absorption and reflection of various wave length of light that impinge on the pigmented surface determines its hue. Black pigments absorb almost all the light falling upon them where as white pigments scatter and reflect all the visible light falling on their surfaces. The differing absorption and reflection characteristics of compounds are attributed to arrangement of the electrons within their molecule and to their energy and frequency vibration. A molecule will absorb electromagnetic radiation from part of spectrum. This absorption excites the electron from ground state $E_1$ to an orbital of higher energy orbital $E_2$. The wave length of light absorbed is determined by the difference in energy E between two orbital concerned.

$$E=E_2-E_1=hc/\lambda.$$

Opacity is the hiding ability of a pigmented coating, depends on the ability of the film to absorb and scatter light. A key factor of the opacity of a pigment is its refractive index, 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 medium in which it is dispersed.[3,4,5]

Pigments are classified into two inorganic and organic pigments. In organic pigments have high refractive index, high chemical and high heat stability than inorganic pigments. Commonly used white inorganic pigment is titanium dioxide ($TiO_2$), due to its very high refractive index 2.76, relatively low density and maximum scattering of visible light and they absorb little energy in the visible part of the spectrum. The conventional $TiO_2$ has some disadvantages. The untreated $TiO_2$ pigment is not sufficiently basic. Acidic product will be formed when reacted and as a result of photo-oxidation and thus do not help to maintain integrity of film. It has no fungicidal or bacteriostic properties. $TiO_2$ has much attention in the application field such as sunscreen properties, catalytic supporter, coating industry, photo catalyst and solar energy converters.[6,7]

$TiO_2$ exists mainly in 3 naturally occurring crystallographic forms are Anatase (tetragonal), Brookite (orthorhombic), and Rutile(tetragonal). Anatase and rutile form are manufactured on a large scale. Rutile has much closer atomic packing in its crystalline pattern and is more stable.[8] Conversion of anatase to rutile occurs only at elevated temperature (~1000°C). Anatase has very high photo activity and is therefore not suitable for exterior finishes because it may cause rapid degradation of the paint film. $TiO_2$ based coating has UV shielding ability due to UV ray absorption and UV ray scattering.[9] Light scattering depends on the particle size and the wavelength of corresponding light. Due to the reduction of particle size UV ray absorption increases. "Larger-sized $TiO_2$ particle exhibit less effectiveness as a sunscreen agent".[10] Particle size increases the ability of the particle to scatter light increases up to a maximum and then decreased.[11,12] The ability of a scatter light increases the hiding power of the pigment and therefore the hiding power also reaches the maximum and then decreased as the particle size increased. The sunscreen performance depends on how well the ultrafine particles are dispersed in the formulation. $TiO_2$ in a predispersed form rather than powdered form improves the quality of final dispersion. $TiO_2$ colloidal sol would be expected to high performance in sunscreen property. Different methods are used for preparation of nano-sized colloidal sol such as sol-gel process and hydrothermal process. However, we adopt wet synthesis process[13,14] as it is cost effective.

[15]For $TiO_2$ preparation usually titanium hydroxide is precipitated by hydrolysis and then calcinated at 900°C. But the straight hydrolysis yields only anatase on calcination. Rutile form of $TiO_2$ is obtained by alkaline hydrolysis of titanylsulfate or titanium tetrachloride.[16]

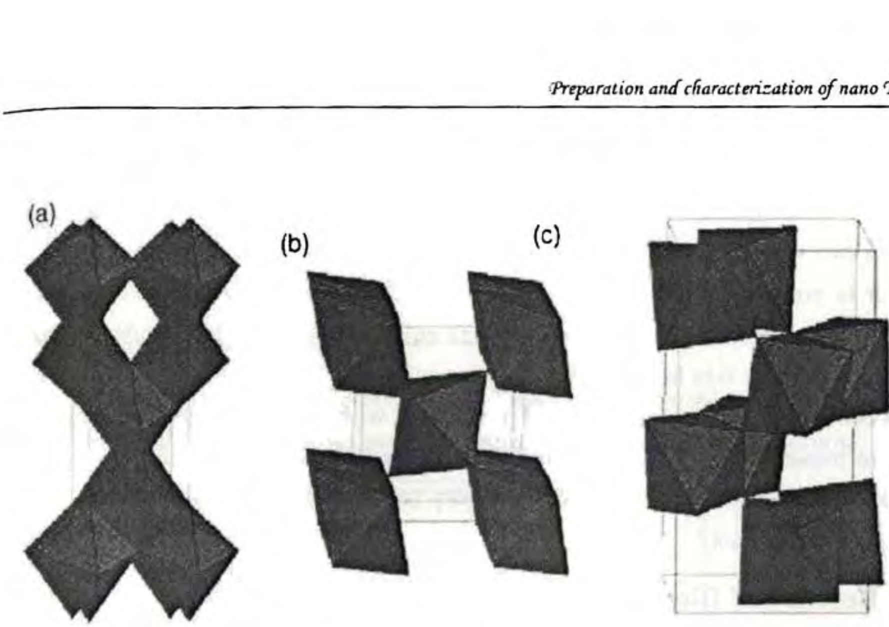

*Figure 5.1: Crystallographic forms of $TiO_2$ (a) Anatase (b) Brookite & (b) Rutile*

In order to achieve UV-ray shielding property we developed nano $TiO_2$ colloidal sol by wet synthesis process. The present study deals with an optimum design of $TiO_2$ colloidal sol regarding appropriate particle size, stabilize in a neutral pH region[17] and suppression of photo catalytic activity.

## 5.2 Experimental

### 52.1 Preparation of colloidal nano $TiO_2$

The preparation procedure for $TiO_2$ colloidal sol in nano form consists of two steps: (1) hydrolysis process of $TiCl_4$ and (2) acid treatment process.

**Hydrolysis Process**

NaOH solution at a concentration of 64.5g/l and $TiCl_4$ solution at a concentration of 200 g/l was added drop wise to water with stirring. The solution was maintained at a pH range 6 to 8. After the completion of addition the pH was adjusted to 7, the resulting slurry was filtered, and the residue of $TiO_2$ was washed until the electro conductivity of the filtrate was below 100mS/cm.

**Acid Treatment Process**

The synthesized $TiO_2$ contain sodium ions, soluble $TiO_2$ and other impurities were removed by acid treatment .The washed cake was redispersed in water to prepare 2 mol/l of $TiO_2$ slurry. Resulting $TiO_2$ slurry and an aqueous 2 mol/l $HNO_3$ solution were placed in a flask equipped with a reflux condenser, and then the mixture was heated at 95$^0$C. After aging for 2 hours at 95$^0$C, the mixture was cooled to room temperature and neutralized with 28% of aqueous ammonia to obtain treated slurry. Then, the slurry was filtered, and the filter cake of treated $TiO_2$ was washed until electro conductivity of the filtrate was 100mS/cm. Thus we get colloidal sol.

## 5.3 Results and Discussion

### 5.3.1 Bulk density

The primary identification of the size of the material was done by determining the bulk density. The bulk density value of synthesized nano $TiO_2$ powder sample is compared with conventionally available $TiO_2$ in table 5.1.

*Table 5.1: Bulk densities of $TiO_2$*

| Sample name | Bulk density (g/cm$^3$) |
|---|---|
| Conventional $TiO_2$ | 1.45 |
| Nano $TiO_2$ | 0.98 |

### 5.3.2 Surface area

The surface area of the samples determined using BET method is given in the table 5.2.

*Table 5.2: Surface area of $TiO_2$ samples*

| Sample name | Surface area (m$^2$/g) |
|---|---|
| Conventional $TiO_2$ | 8.[illegible] |
| Nano $TiO_2$ | 234 |

From the surface area analysis it is clear that the synthesised $TiO_2$ has very high surface area compared to conventional $TiO_2$. This may be due to the reduction in size to nano scale.

### 5.3.3 X-Ray Diffraction (XRD)

The XRD patterns of conventional $TiO_2$ samples are given in figures. The figure shows the characteristics peaks of rutile, thus confirmed the structure.

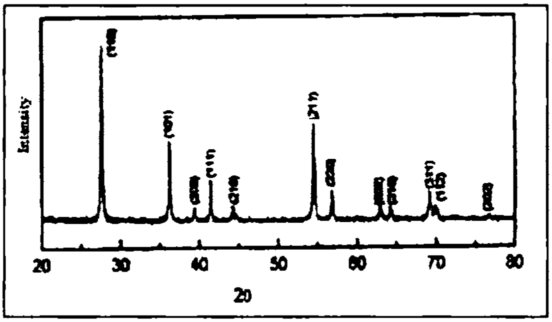

*Figure 5.2: XRD pattern of conventional rutile $TiO_2$*

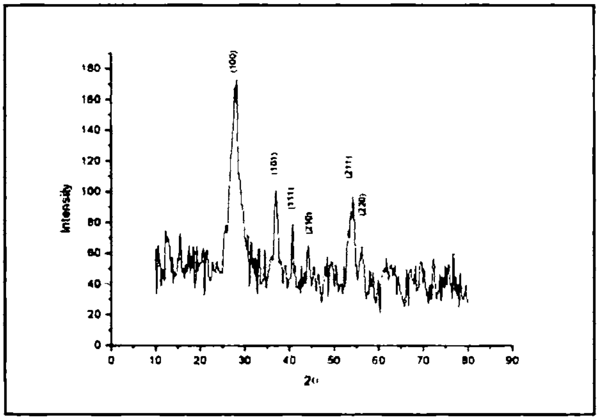

*Figure 5.3: XRD pattern of synthesized nano $TiO_2$*

The XRD pattern of nano $TiO_2$ is shown here. It shows characteristic peaks of rutile $TiO_2$. The peaks are wide compared to conventional $TiO_2$ and some peaks are not clear for nano colloidal $TiO_2$. This happens when reduction in particle size. The average particle size of nano and conventional TiO2 calculated by Debye Scherrer equation is shown in table 5.3.

***Table 5.3:*** *Average particle size of $TiO_2$ samples*

| Sample | Particle size (nm) |
|---|---|
| Nano $TiO_2$ | 29 |
| Conventional $TiO_2$ | 262 |

$$D=\frac{0.9\lambda}{\beta Cos\theta}$$

λ - wavelength of the X-ray source, β - full width at half maximum of the diffraction peaks in radians, θ - the diffraction angle.

### 5.3.4 UV-Visible spectroscopy

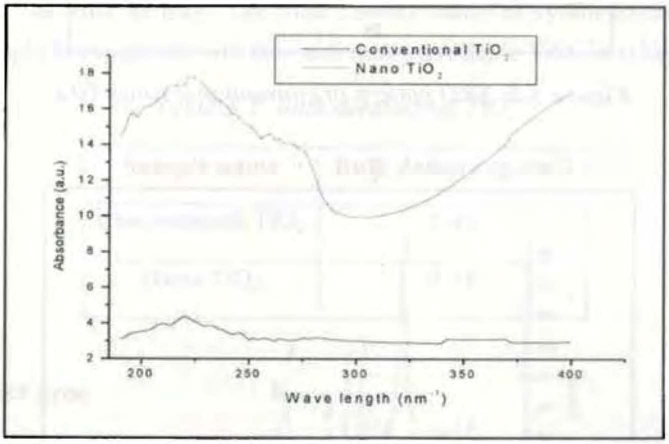

***Figure 5.4:*** *UV-Visible absorption spectrum of nano & conventional $TiO_2$*

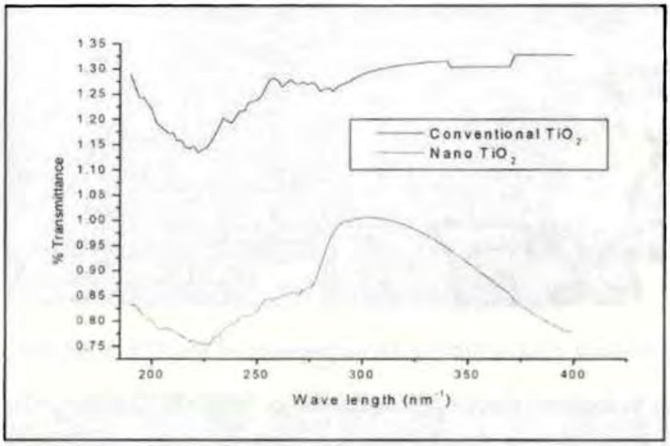

***Figure 5.5:*** *UV-Visible transmittance spectrum of nano & conventional $TiO_2$*

The UV shielding ability of nano $TiO_2$ is compared with conventional $TiO_2$. The figure 5.4 shows the UV absorption of nano and conventional $TiO_2$. The absorption of UV radiation is three times higher for nano $TiO_2$ compared to conventional $TiO_2$. The figure 5.5 shows the UV ray transmittance of nano $TiO_2$ and conventional $TiO_2$. The transmittance of UV radiation by nano $TiO_2$ is very low compared to conventional $TiO_2$. These observations show that nano sized $TiO_2$ has better UV ray shielding ability compared to conventional $TiO_2$. Hence it can be use as UV ray protector in surface coatings.

### 5.3.5 Scanning electron microscopy

Scanning electron microscopy (SEM) allows the visualization of materials at very high magnifications. Depending on the instrument and materials properties, it is capable of providing resolutions down to the nanometre scale.

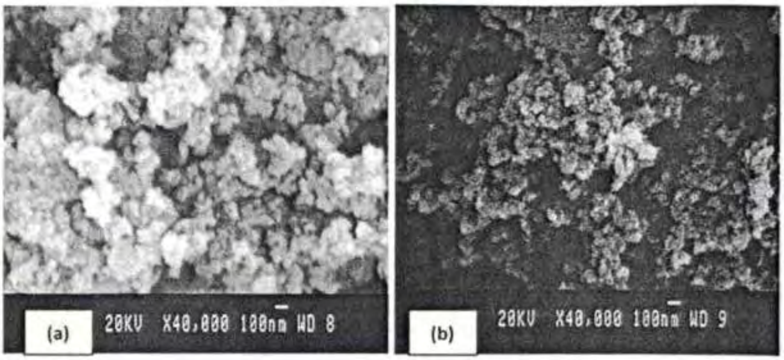

***Figure.5.6:** SEM micrograph of (a) conventional and (b) nano $TiO_2$ powder*

The scanning electron microscopy is helpful to understand the morphology of the surface. The micrograph pictures revels that when the colloidal solution dried the particles become agglomerated. So it is better to keep as colloidal dispersion and thus to add in paint to retain particles integrity.

### 5.3.6 Transmission electron microscopy

The TEM image of the$TiO_2$ sample is given in figure. The size of the particle was determined from the scale bar given in the picture. The average particle size was calculated and found to be equal to 20nm. The corresponding diffraction pattern is also shown in fig. Diffraction pattern of colloidal form show concentric rings which indicate the crystalline nature of synthesised nano $TiO_2$.

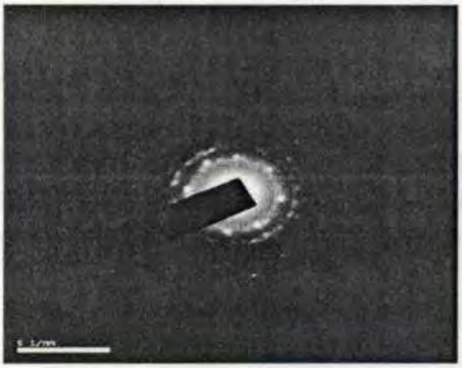

***Figure 5.7:** Diffraction pattern of synthesized nano $TiO_2$*

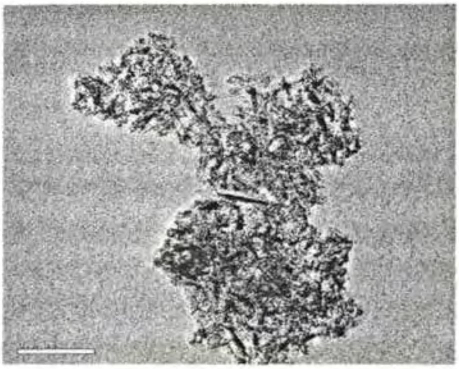

*Figure 5.8:* *TEM image of synthesized nano $TiO_2$ powder*

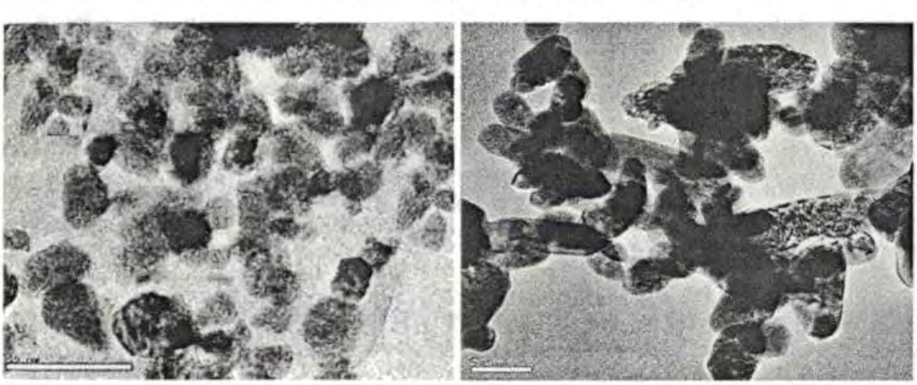

*Figure 5.9:* *TEM images of synthesized colloidal nano $TiO_2$*

### 5.3.7 Thermo gravimetric analysis

Thermal analysis of the prepared $TiO_2$ nano particles was carried out to know the possible changes occurring when the materials were subjected to heat treatment. TGA shows weight reduction at initial temperature due to the absorption of moisture. Above $200^0$C the weight remains same. This shows that synthesized rutile nano $TiO_2$ is pure.

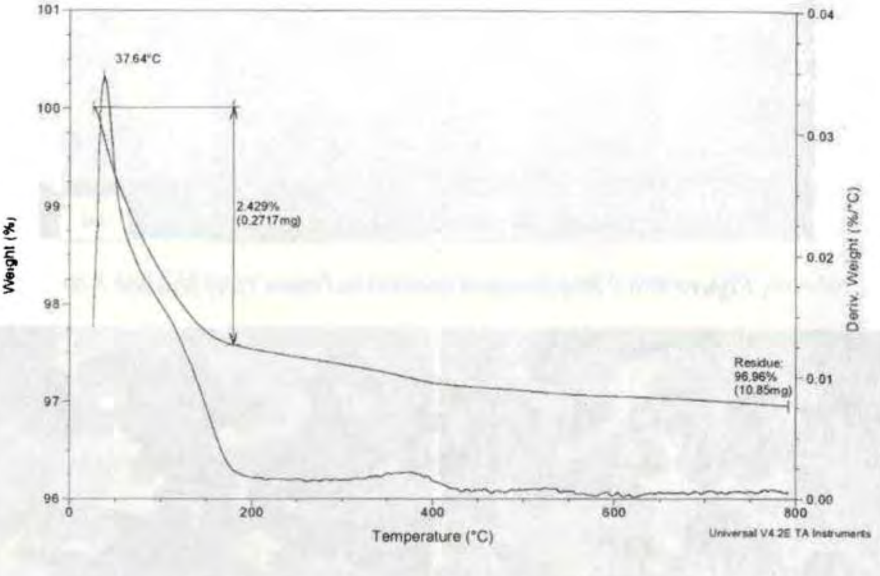

*Figure 5.10: Thermogravimetric trace of synthesized nano $TiO_2$*

## 5.4 Conclusion

Titanium dioxide with high degree crystallinity was prepared from titanium tetrachloride. SEM picture shows the morphology of the powder. TEM and SEM studies revealed that the synthesized particle sizes are in the nanometre region. The particle size of the nano $TiO_2$ is much lower than that of conventional $TiO_2$. Surface area of the nanoparticles was very high compared to that of conventional $TiO_2$. The UV-Visible spectra show that UV ray protection efficiency of the synthesized nano $TiO_2$, which is the very important property for paint. Thermo gravimetric analysis shows that the synthesized samples are pure. This method is very simple and can save energy because this does not require the calcinations at very high temperature.

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# *Chapter 6*

# PREPARATION AND PROPERTY EVALUATION OF SURFACE COATING BASED ON NANO $TiO_2$

## 6a: Development of paint formulation of VAc-BuA copolymer with nano $TiO_2$ as pigment

### 6a.1 Introduction

Paints are required to be both decorative and protective. In the decorative context, it is essential that the surface is uniformly and completely covered. This is most readily achieved by using a pigment of high refractive index such as $TiO_2$. Binder is used for the adhesion of pigment firmly to the surface. $TiO_2$ (rutile) has been used as white colour pigment due to its very high refractive index (2.72), relatively low density and maximum scattering of visible light and they absorb little energy in the visible part of the spectrum. The commercial $TiO_2$ has some disadvantages. The untreated $TiO_2$ pigment is not sufficiently basic. When react, acidic product will be formed as a result of photo-oxidation and thus does not help to maintain integrity of film. It has no fungicidal or bacteriostic properties. $TiO_2$ has much attention in the application field such as sunscreen properties, catalytic supporter, coating industry, photo catalyst and solar energy converters. $TiO_2$ based coating has UV shielding ability due to UV ray absorption and UV ray scattering.[1] The ultraviolet spectrum is divided into three regions: UVC (200 - 290 nm), UVB (290-320 nm) and UVA (320--400 nm). UVC has the highest energy but is completely absorbed by ozone in the stratosphere. UVB is the most damaging UV light. UVA has the longest wavelength and lowest energy. Light scattering depends on the particle size and the wavelength of corresponding light.[2] Due to the reduction of particle size UV ray absorption increases. "Larger-sized $TiO_2$ particle exhibiting less effectiveness as a sunscreen agent". The sunscreen performance depends on how well the ultrafine particles are dispersed in the formulation.[3]

$TiO_2$ absorbs light with wavelength of 405 nm or shorter. Since it has very high refractive index, it is very effective in scattering. Both scattering and absorption are important in attenuating UV light, each mechanism predominating at different ends of spectrum. Theoretical study proved that for submicron $TiO_2$, the UVB attenuation is predominately due to its absorption while the UVA attenuation is predominately due to its scattering. In another words, $TiO_2$ is a UVB absorber and a UVA scatterer.[4] The smaller size is better for UVB attenuation. For larger particle, UV radiation is primarily absorbed in the outer layer of the particle and the material in the interior is not fully utilized. A smaller particle size means larger specific surface area, more $TiO_2$ exposure to UV light for higher absorption.[5] The larger specific surface area also gives the sunscreen more in coating area. Thus, it can be concluded that at same active concentration smaller particle sizes. The smaller PPS (primary particle size) gives more transparency and larger PPS results in more opacity. Good formulation with appropriate PPS (15-35nm) can easily boost the sunscreen performance and decrease the transparency.[6]

$TiO_2$ in a predispersed form rather than powdered form improves the quality of final dispersion. $TiO_2$ colloidal sol would be expected to high performance in sunscreen property. In this chapter, development of new paint formulation with nano colloidal $TiO_2$ as pigment is developed.

## 6a.2 Experimental

### 6a.2 Development of surface coating

Paints were made by mixing latex with various ingredients as per the formulation given in Table 6a.1. Various latex paints were prepared by using conventional $TiO_2$ and synthesized nano $TiO_2$ colloidal sol.

Nano $TiO_2$ has higher surface area when compared with conventional $TiO_2$. Hence lower amount is enough for getting required property for the paint the formulation.

*Table 6a.1: Paint formulation with nano $TiO_2$*

| **Ingredients** | **Weight (g)** | |
|---|---|---|
| | *PB | **nPB |
| Water | 35 | 35 |
| Triton-X100 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0 .42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 |
| Volcastab | 0.42 | 0.42 |
| Silicone emulsion | 1.34 | 1.34 |
| Propylene glycol | 4 | 4 |
| Acticid SPX | 0.32 | 0.32 |
| Above ingredients were combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added | | |
| Kaolin | 17.32 | 20.97 |
| Calcium carbonate | 18.64 | 29.59 |
| $TiO_2$ (Rutile) | 44.6 | 30 |
| The above ingredients mixed at high speed for 20 minutes. The following ingredients were added while stirring the mixture | | |
| Carboxymethyl cellulose | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added | | |
| Polymer emulsion | 75 | 75 |

*PB- Paint formulation using conventional $TiO_2$, **nPB- Paint formulation using nano $TiO_2$

## 6a.3 Results and discussion

The properties of the paint formulated with nano $TiO_2$ pigment is compared with the paint formulated with conventional $TiO_2$.

The UV shielding ability of the paints and the durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance, weather resistance and adhesion tests are also carried out to know the effect of nano sized effect of pigment. These tests were conducted according to standard procedures described in chapter 2. The specimens for the tests were prepared by coating the paint samples in mild steel panels of size 6in x 4in (BS specification).

The observations for various tests are summarised in the respective tables. For each test the appearance (photographs) of the coated samples before and after the tests are shown under the respective tests. The properties of the formulated paints are compared with a commercially available paint.

### 6a.3.1 UV visible spectrum

The UV-Visible absorbance and transmittance spectrum obtained for the paint formulated with conventional & nano $TiO_2$ are given in figures 6a.1 and 6a.2 respectively.

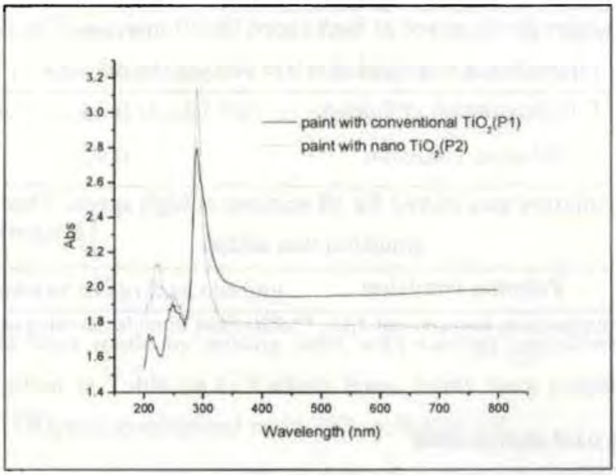


*Figure 6a.1: Absorption spectrum of formulated paints.*

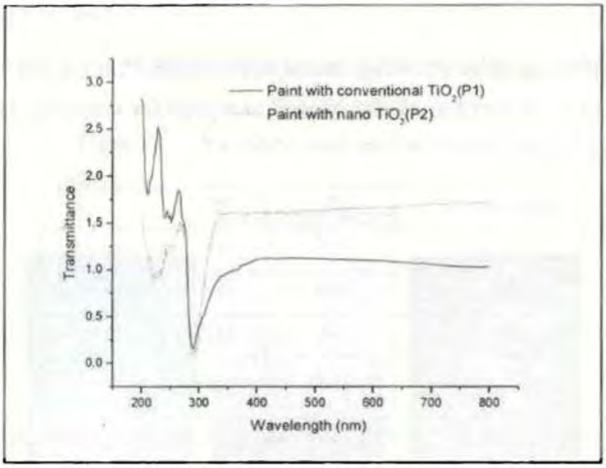


***Figure 6a.2:*** *Transmittance spectrum of formulated paints*

Figure 6a.1 shows that absorbance of UV ray is higher for the paint formulated with colloidal nano $TiO_2$. Figure 6a.2 shows that the transmittance for the paint formulated with colloidal nano $TiO_2$ is low compared to the paint formulated using conventional $TiO_2$. The higher absorption and low transmittance of UV region for nPB is more significant from 270-200nm. This shows that the paint formulated with nano$TiO_2$ have more UV shielding capability.

### 6a.3.2 Water resistance test

***Table 6a.2:*** *Blister formation in water resistance test at 38 °C*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ****Commercial*** |
| 24 hrs | Nil | Nil | Nil |
| 4 days | Nil | Nil | Nil |
| 1week | Nil | Nil | Nil |
| 3 week | Nil | Nil | Few |
| 12week | Few | Few | Medium |

*Commercially available emulsion paint

The photographs showing initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are given in figure 6a.3.

Initial appearance

Final appearance

***Figure 6a.3:*** *Appearance of specimens before and after water resistance test*

The figure 6a.3 and table 6a.2 clearly shows that even after 12 weeks sample nPB is highly resistant to water as like PB and commercially available paint. This shows that nano sized pigment not affect the water resistance property of the paint film.

### 6a.3.3 Salt spray test

***Table 6a.3:*** *Blister formation in salt spray test at 28$^0$C*

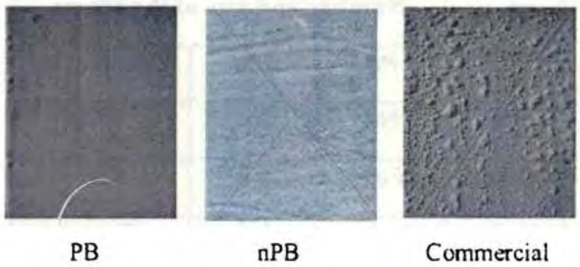
| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 48 hrs | Nil | Nil | Nil |
| 1 week | Nil | Nil | Nil |
| 4 week | Nil | Nil | Few |
| 12week | Few | Nil | Medium dense |

The photographs showing initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are given in figure 6a.4.

Initial appearance

PB nPB Commercial

Final appearance



PB nPB Commercial

***Figure 6a.4:*** *Appearance of specimens before and aftersalt spray test*

By analyzing the observations shown in table 6a.3 and the photographs depicted in figure 6a.4 we can see that the sample nPB is not affected by salt spray even after 12 weeks. The specimens PB and commercially available paint shows more blistering than nPB. This shows that the nano sized pigment intimately and uniformly mixed with the paint and this gives more integrity to the paint films. This may be the reason for the good stability off paint film containing nano $TiO_2$.

### 6a.3.4 Alkali resistance test

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at 75°C, $Na_2CO_3$ at 65°C and NaOH at 28°C) according to standard procedure as described in chapter 2.

*Table 6a.4: Blister formation in $Na_3PO_4$ resistance test (75°C)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Few |
| 16 hrs | Medium | Nil | Dense |
| 24 hrs | Dense | Nil | Peeled |

*Table 6a.5: Blister formation in $Na_2CO_3$ resistance test (65°C)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Few |
| 16 hrs | Medium | Nil | Dense |
| 24 hrs | Dense | Few | Peeled |

*Table 6a.6: Blister formation in NaOH resistance test ($28^0C$)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Medium | Few | Dense |
| 16 hrs | Dense | Medium | Peeled |

Tables 6a.4, 6a.5 and 6a.6 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, for 24h $Na_2CO_3$, 16h for NaOH) are shown in figure 6a.5.

From the figures and the tables we can see that the resistance of the specimens varied with the nature of the alkali. The sample nPB showed lower number and size of blisters when compared to PB and commercially available paint. This again shows that when ingredients of paint are taken in nano sized form the integrity of the paint film improved, which in turn increase the resistance towards chemicals.

Initial appearance

PB nPB Commercial

Final appearance $Na_3PO_4$

PB nPB Commercial

Final appearance $Na_2CO_3$

PB nPB Commercial

Final appearance NaOH

PB nPB Commercial

***Figure 6a.5:*** *Appearance of specimens before and after alkali resistance test*

### 6a.3.5 Detergent resistance test

***Table 6a.7:*** *Blister formation in detergent resistance test*

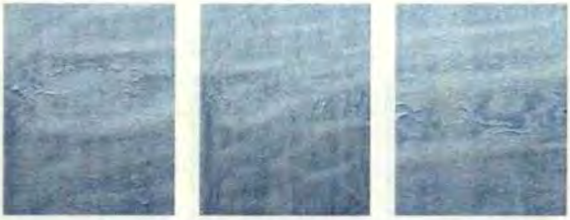
| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 1day | Nil | Nil | Nil |
| 3 days | Few | Few | Medium |
| 1 week | Medium | Medium | Medium |

The photographs of initial appearance (before the test) and final appearance (after 1 week) of the coated samples for detergent resistance test are shown in figure 6a.6.

Initial appearance

PB nPB Commercial

Final appearance



**PB nPB Commercial**

***Figure 6a.6:*** *Appearance of specimens before and after detergent resistance test*

Table 6a.7 and figure 6a.6 shows that sample nPB have detergent resistance similar to sample PB and commercially available paint.

### 6a.3.6 Natural weather resistance

Weather resistance test was conducted to know the effect of natural weather on paint surface. The specimens were prepared by coating the paint on mild steel panels of size 12x6in. The test was conducted for a period of 10 months from March to December. This time period was selected because the samples were exposed to all seasons during the test.

***Table 6a.8:*** *Chalking formation in natural weather resistance test*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPB*** | ***Commercial*** |
| 1 month | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil |
| 10 months | Nil | Nil | Nil |

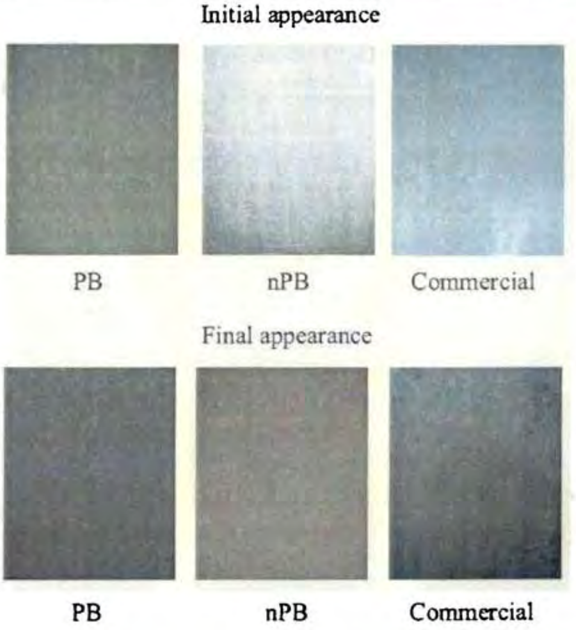


***Figure 6a.7:*** *Appearance of specimens before and after weather resistance test*

The figure 6a.7 and table 6a.8 shows that all the samples are very stable towards natural weather.

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample nPB is have good resistance towards all test conditions as like PB and commercially available paint. In the case of alkali resistance and salt spray resistance nPB is superior to the other samples. From the results we can conclude that the pigment in nano sized form enhance the surface integrity of paint films.

Rutile $TiO_2$ is the most thermodynamically stable allotropic form and is generally obtained by a high temperature process. Calcination at high temperature is usually accompanied by sintering among particles. This can adversely affect the optical properties and dispersion stability. In this study nano $TiO_2$ colloidal sol never heated at above $100^0C$. So that particle size retained even after the preparation. Therefore nano colloidal $TiO_2$ sol in paint formulation gave better dispersions stability and better surface integrity.

### 6a.3.7 Scotch test

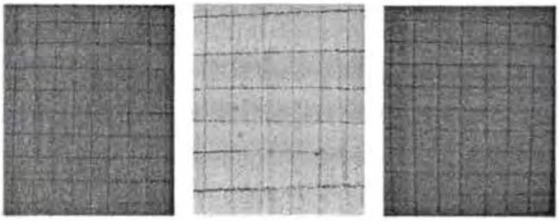
The adhesive strength of the paints was determined using scotch resistance test. The tests were carried out as described in chapter 2.

*Table 6a.9: Adhesion rating during scotch test*

| Sample name | Classification | % removal |
|---|---|---|
| PB | 4B | Less than 5% |
| nPB | 4B | Less than 5% |
| Commercial | 3B | 5 - 15% |

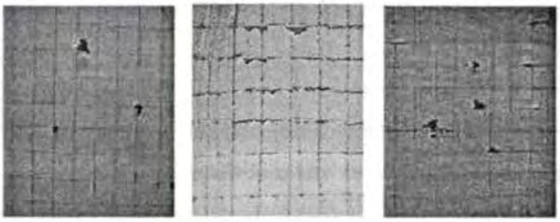
The photographs of test specimens before and after the test are given in figure 6a.8

Initial appearance



PB nPB Commercial

Final appearance



PB nPB Commercial

***Figure 6a.8:*** *Appearance of specimens before and after the scotch test*

The figure 6a.8 and table 6a.9 shows that the adhesive strength of nPB is same as that of PB.

### 6a.4 Viscosity of paint

Viscosity and shear thinning behaviour are important properties of paint. It depends on the size of colloidal particles. Figure 6a.9 shows reduction in paint viscosity. This may be due to the reduced particle size of pigment. The paint viscosity found to be increased by the addition of more amount of thickener.

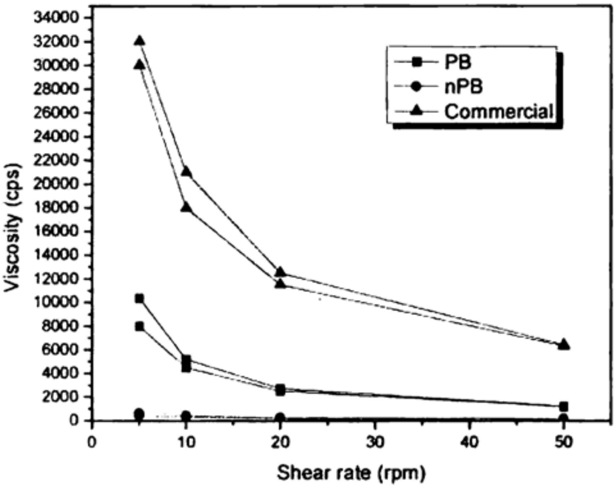


*Figure 6a.9: Effect of shear rate on the viscosity of Paint*

Shear thinning index of PB, and nPB at two different spindle speeds of 5 and 50 are given in table 6a.10.

**Table 6a.10:** Shear thinning index of the samples

| Sample | Shear thinning index |
|---|---|
| PB | 8.67 |
| nPB | 4.2 |
| Commercial | 5 |

### 6a.5 Thermogravimetry

Thermal stability of the paints was found out using thermogravimetry. Samples PB and nPB contains the same binder. The thermal stability of the samples PB, nPB and commercially available paints were analysed and the thermograms obtained are shown in figure 6a.10 and its derivative is shown in figure 6a.11.

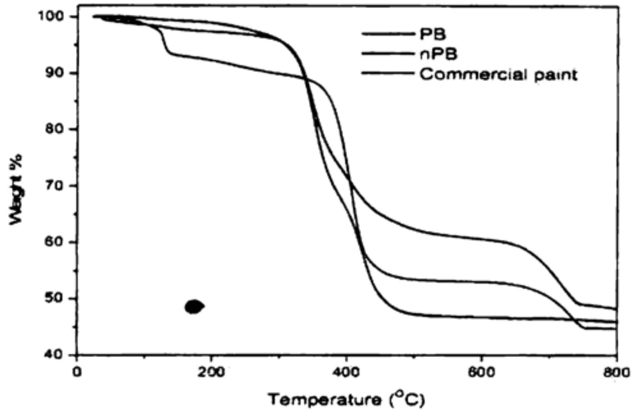


**Figure 6a.10:** TG traces of PB, nPB and commercial paint

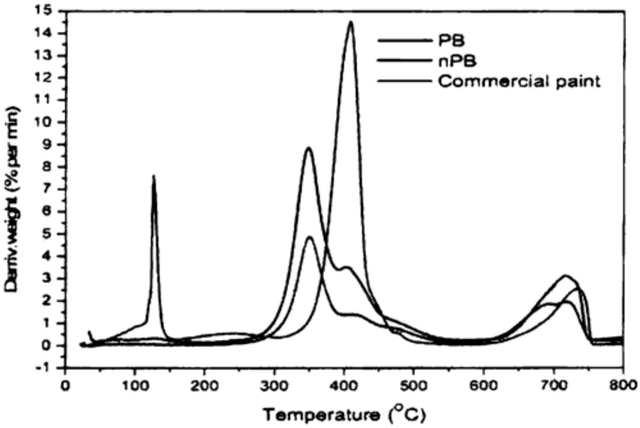


**Figure 6a.11:** DTG traces of PB, nPB and commercial paint

From the figures we can see that the commercially available paint start to degrade at 120$^0$C but the degradation of PB and nPB starts only at 300$^0$C. This shows that the formulated paint has superior thermal stability compared to commercially available paint.

## 6a.5. Conclusion

The paint formulation using binder based on VAc-BuA copolymer and pigment nano $TiO_2$ sol was found to give better properties compared to commercially available paint and paint formulated with conventional $TiO_2$. The paint prepared with nano $TiO_2$ sol shows higher transparency of visible light and better UV shielding ability compared to the paints prepared with conventional $TiO_2$. Thus, the size of $TiO_2$ should be reduced to the minimum (15-35nm) to boost sunscreen property and thus to achieve appropriate transparency. $TiO_2$ has excellent protection against UVB. However, in order to balance UVA protection, the size should be adjusted to slightly larger dimension, because the scattering becomes an important contributor. At right size, $TiO_2$ can be very effective in UVA protection. Viscosity and shear thinning behavior depend on the size of the colloidal particles in paint.

## Reference

1 Lowe NJ, Fredlander J; "*Sunscreens: Rationale for Use to Reduce Photodamage and Phototoxicity*", *Sunscreens*, 2nd Ed., Lowe NJ, Shaath NA, Pathak MA (Eds.), Marcel Dekker Inc, New York, **1997**, 35.

2. Kelly KA, Ewing GD, Dromgoole SH, Lichtin JL, Sakr AA; *J Soc Cosmet Chem* **1993**, 44, 139.

3 Kligman LH, Kligman AM; "*Ultra Radiation-Induced Skin Aging*", *Sunscreens*, 2nd Ed., Lowe NJ, Shaath NA, Pathak MA (Eds.), Marcel Dekker Inc, New York, **1997**, 117.

4 Flairhurst D, Mitchnick MA; "*Particulate Sun Blocks: General Principle*", *Sunscreens*, 2nd Ed., Lowe NJ, Shaath NA, Pathak MA (Eds.), Marcel Dekker Inc, New York, **1997**, 313.

5 Stamatakis P, Palmer BR; *J Coating Tech* **1990**, 62, 789, 95.

6 Sakamoto M, Okuda H, Futamata H, Sakai A, Iida M; *J Jpn Soc Mater* **1995**, 68, 4, 203.

# 6b: Paint formulation with nano $TiO_2$ and rubber crumb

## 6b.1 Introduction

The paint formulation developed with colloidal nano $TiO_2$ give gloss surface. $TiO_2$ in nano form will effectively screen the radiations from sun.[1] The surface nature is modified with a matting agent activated rubber crumb[2] as in chapter 4 part b. The properties of the formulated paint were studied.

## 6b.2 Experimental

Rubber crumb is found to be uniformly dispersed in aqueous solution of carboxy methyl cellulose. The dispersion containing the rubber crumb and latex was prepared and is mixed with other ingredients. The optimum level of matting agent was used for the easy brushing and good dispersion stability. For all formulations the VAc-BuA copolymer of 45% solid content was used. Table 6b.1 shows the quantities of different ingredients used for the formulation.

*Table 6b.1: Paint formulation with nano $TiO_2$ and rubber crumb*

| Ingredients | Weight (g) | |
|---|---|---|
| | ***PB** | ****nPBR** |
| Water | 35 | 35 |
| Triton-X100 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0.42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 |
| Volcastab | 0.42 | 0.42 |
| Silicone emulsion | 1.34 | 1.34 |
| Propylene glycol | 4 | 4 |
| Acticid SPX | 0.32 | 0.32 |
| Above ingredients are to be combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added | | |

| | | |
|---|---|---|
| Kaolin | 17 | 17 |
| Calcium carbonate | 18.64 | 18.64 |
| $TiO_2$ (Rutile) | 44.6 | 30 |
| Mix the above ingredients at high speed for 20 minutes. While stirring the mixture the following ingredients were added | | |
| Carboxymethyl cellulose | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added. | | |
| Polymer emulsion | 75 | 75 |
| Rubber crumb | 0 | 3 |

*PB-Paint formulation using VAc-BuA copolymer (85/15 wt.%), conventional $TiO_2$, **nPBR-Paint formulation using VAc-BuA copolymer (85/15 wt.%), nano $TiO_2$ and crumb rubber.

## 6b.3 Results and discussion

The durability tests, adhesion test and viscosity of the matt finish paint (paint formulated with rubber crumb and nano $TiO_2$, nPBR) were carried out and compared with paint formulated without rubber crumb and commercially available emulsion paint. The procedures of the tests are described in chapter 2. The specimens for the tests were prepared by coating the paint samples in mild steel panels of size 6inx4in (BS specification).

The observations for various tests are summarised in the respective tables for each test. For each test the appearance (photographs) of the coated paint before and after the tests are also shown under the respective tests. The properties of the formulated paints are compared with a commercially available paint.

### 6b.3.1 Water resistance test

***Table 6b.2:*** *Blister formation in water resistance test at $38^0C$*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | **PB** | **nPBR** | ***Commercial** |
| 24 hrs | Nil | Nil | Nil |
| 4 days | Nil | Nil | Nil |
| 1week | Nil | Nil | Nil |
| 3 week | Nil | Nil | Few |
| 12week | Few | Nil | Medium |

The photographs showing initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are given in figure 6b.1.

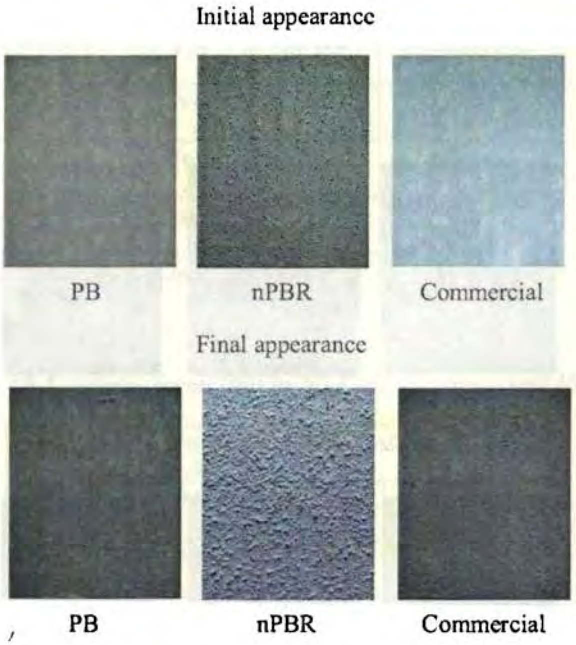


***Figure 6b.1:*** *Appearance of specimens before and after water resistance test*

The figure 6b.1 and table 6b.2 clearly shows that sample nPBR is highly resistant to water and is not shows any blister even after 12 weeks. The sample PB and commercially available paint show a little blistering.

### 6b.3.2 Salt spray test

***Table 6b.3:*** *Blister formation in salt spray test at $28^0C$*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 48 hrs | Nil | Nil | Nil |
| 1 week | Nil | Nil | Nil |
| 4 week | Nil | Nil | Few |
| 12week | Few | Few | Medium dense |

The photographs showing initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are given in figure 6b.2.

Initial appearance

PB nPBR Commercial

Final appearance

PB nPBR Commercial

***Figure 6b.2:*** *Appearance of specimens before and after salt spray test*

By analyzing the observations shown in table 6b.3 and the photographs shown in figure 6b.2 we can see that the sample nPBR is stable as PB. The sample coated with commercially available paint is more affected by salt water.

### 6b.3.3 Alkali resistance test

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at 75°C, $Na_2CO_3$ at 65°C and NaOH at 28°C) according to standard procedure as described in chapter 2.

***Table 6b.4:*** *Blister formation in $Na_3PO_4$ resistance test (75°C)*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Few |
| 16 hrs | Medium | Few | Dense |
| 24 hrs | Dense | Medium | Peeled |

***Table 6b.5:*** *Blister formation in $Na_2CO_3$ resistance test (65°C)*

| **Time interval** | **Number and size of the blister** | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Few |
| 16 hrs | Medium | Nil | Dense |
| 24 hrs | Dense | Few | Peeled |

*Table 6b.6: Blister formation in NaOH resistance test (28$^0$C)*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil |
| 8 hrs | Medium | Medium | Dense |
| 16 hrs | Dense | Dense | Peeled |

Tables 6b.4, 6b.5 and 6b.6 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, for 24h $Na_2CO_3$, 16h NaOH) are shown in figure 6b.3.

From the photographs (figure 6b.3) it can be seen that the resistance of the sample nPBR is better than all other samples.

Initial appearance

PB nPBR Commercial

Final appearance $Na_3PO_4$

PB nPBR Commercial

Final appearance $Na_2CO_3$

PB nPBR Commercial

Final appearance NaOH

PB nPBR Commercial

***Figure 6b.3:*** *Appearance of specimens before and after alkali resistance test*

### 6b.3.4. Detergent resistance test

***Table 6b.7:*** *Blister formation in detergent resistance test at $28^0C$*

| Time interval | Number and size of the blister | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 1day | Nil | Nil | Nil |
| 3 days | Few | Nil | Medium |
| 1 week | Medium | Nil | Medium |

The photographs showing initial appearance (before the test) and final appearance (after 1 week) of the coated samples for detergent resistance test are given in figure 6b.4.

Initial appearance

PB nPBR Commercial

Final appearance

PB nPBR Commercial

***Figure 6b.4:*** *Appearance of specimens before and after detergent resistance test*

Table 6b.7 and figure 6b.4 shows that sample nPBR is more resistant to detergent attack than PB and commercially available paint.

### 6b.3.5 Natural weather resistance

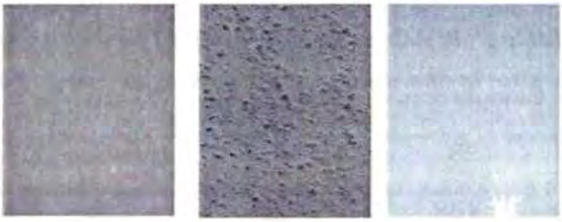
Weather resistance test was conducted for a period of 10 months from March to December in a year. This time period was selected because the samples were exposed to all seasons during the test.

**Table 6b.8:** Chalking formation during weather resistance test

| Time interval | Chalking observed | | |
|---|---|---|---|
| | ***PB*** | ***nPBR*** | ***Commercial*** |
| 1month | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil |
| 10 months | Nil | Nil | Nil |

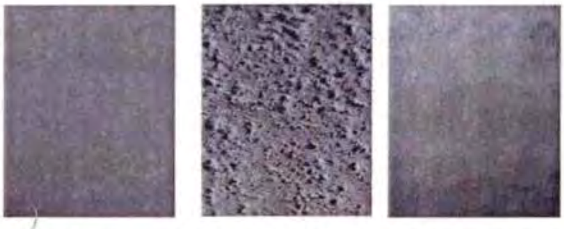
The photographs showing initial appearance (before the test) and final appearance (after 10 months) of the coated samples for weather resistance test are shown in figure 6b.5.

Initial appearance



PB nPBR Commercial

Final appearance



PB nPBR Commercial

***Figure 6b.5:*** *Appearance of specimens before and after weather resistance test*

The figure 6b.5 and table 6b.8 shows that all the samples are very stable towards natural weather and did not show any colour change or degradation during the test.

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample nPBR is having good resistance towards various chemicals. The presence of rubber crumb may actively resist the attack of chemicals and climate conditions due to the inherent resistance of rubber crumb.

### 6b.3.6 Scotch test

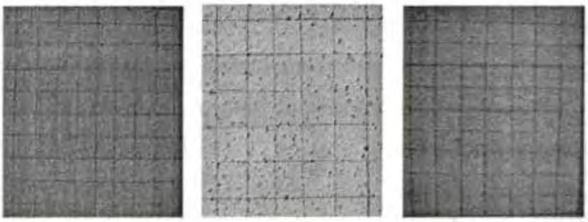
The cross cut adhesion test is carried out to know the adhesion of paint films on the substrate. The adhesion rating according to ASTM standards is shown in the table 6b.9.

***Table 6b.9:*** *Adhesion rating assessed by scotch test*

| Sample name | Classification | % removal |
|---|---|---|
| PB | 4B | Less than 5% |
| nPBR | 5B | 0% |
| Commercial | 3B | 5 - 15% |

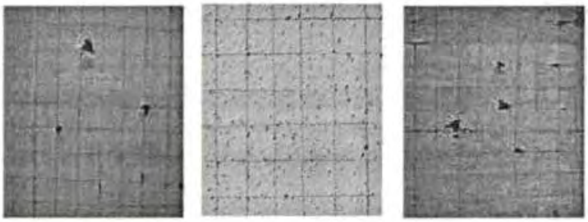
The photographs of test specimens before and after the test are shown in figure 6b.6

Initial appearance



PB nPBR Commercial

Final appearance



PB nPBR Commercial

***Figure 6b.6:*** *Appearance of specimens before and after the scotch test*

The figure 6b.6 and table 6b.9 shows that the adhesive strength of all samples is high. The sample nPBR has no peeling by the scotch test, but trace peeling in PB and commercial sample are observed. The presence of matting agent (activated rubber crumb) may not allow the scotch tape to adhere on the surface of paint. This may be the reason for the good result obtained for the scotch test. This shows that the unwanted materials will not adhere on the matt finished paint film.

### 6b.4. Viscosity

Viscosity and shear thinning behaviour is an important property of paint for ease of application. The viscosity of newly formulated paint found to be independent of the presence of activated rubber crumb as it is uniformly distributed in the paint.

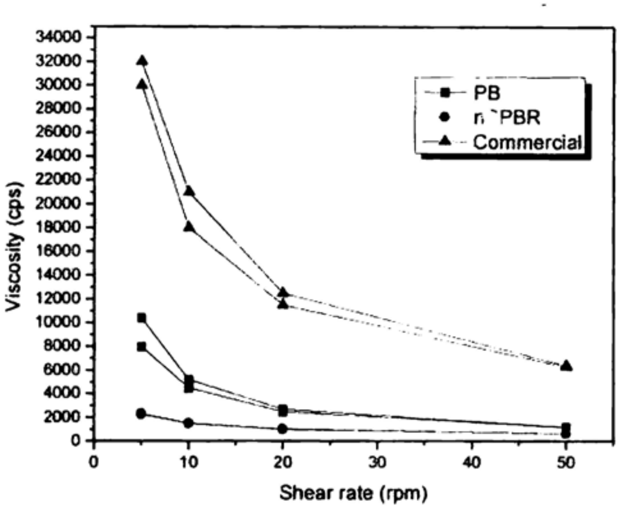


***Figure 6b.7:** Variation of viscosity with shear rate*

Shear thinning index of PB, nPBR and commercially available emulsion paint at two different rotational speeds 5 and 50 are given in table 6b.10.

***Table 6b.10:** Shear thinning index of specimens*

| Sample | Shear thinning index |
|---|---|
| PB | 8.67 |
| nPBR | 3.63 |
| Commercial | 5 |

## 6b.5. Conclusions

The paint formulation using the binder based on VAc-BuA copolymer, pigment nano $TiO_2$ sol and activated rubber crumb as a matting agent was found to give better performance compared to commercially available paint and paint formulated with conventional $TiO_2$. The newly developed coating has good UV shielding ability and durability compared to the paints prepared with conventional $TiO_2$.

## Reference

1 (a) Flairhurst D, Mitchnick MA; "*Particulate Sun Blocks: General Principle*", *Sunscreens*, 2nd Ed., Lowe NJ, Shaath NA, Pathak MA (Eds.), Marcel Dekker Inc, New York, **1997**, 313.

(b) Kligman LH, Kligman AM; "*Ultra Radiation-Induced Skin Aging*", *Sunscreens*, 2nd Ed., Lowe NJ, Shaath NA, Pathak MA (Eds.), Marcel Dekker Inc, New York, **1997**, 117

2 (a) Putman BJ; *Quantification of the Effects of Crumb Rubber in CRM Binders*, Dissertation, Clemson University, Clemson, SC, **2005**.

(b) Rubber Manufacturers Association (RMA), US Scrap Tire Markets **2003** Edition, Rubber Manufacturers Association, Washington, D.C., **2004**.

# 6c: Paint formulation with nano $TiO_2$ and natural biocide

## 6c.1 Introduction

The synthesised colloidal nano $TiO_2$ sol has high sunscreen capability, appropriate particle size, stabilization in a neutral pH region, and suppression of photo catalytic activity. $TiO_2$-based surface coating has ultraviolet ray (UV-ray) shielding ability due to UV-ray absorption and UV-ray scattering. Since the extent of light scattering depends on the relationship between the particle size and the wavelength of corresponding light, reduction of $TiO_2$ particle diameter achieves high transparency in visible light, while UV-ray absorptivity increases with the extension of the geometric area occupied by $TiO_2$.

The particle size of conventional ultrafine $TiO_2$ is about 20 to 50 nm, which is designed in consideration of ideal sunscreen capability based on powdery $TiO_2$.[1] For further UV-ray absorption and visible light transparency, particle size is required to be much smaller.[2] However, the reduction of particle size causes an aggregation, which behaves as though it is one larger-sized $TiO_2$ particle, there by exhibiting less effectiveness as a sunscreen agent.[3,4] The sunscreen performance is dependent on how well the ultrafine particles are dispersed in the paint formulation. It is well known that employing the $TiO_2$ in a predispersed form rather than powder form improves the quality of final dispersion.TiO2 colloidal sol, which is an ultimate dispersion, would be expected to facilitate the preparation of high UV shielding coating.

Carboxymethyl chitosan used as biocide for improving the antimicrobial activity of paint formulated with nano colloidal sol as pigment.

## 6c.2 Experimental

Paints were made by mixing latex with various ingredients as per the formulation given in Table 6c.1. Various latex paints were prepared by using conventional $TiO_2$ and synthesized nano $TiO_2$ colloidal sol.

*Table 6c.1: Paint formulation*

| Ingredients | Weight (g) | | |
|---|---|---|---|
| | *PB | **nCPB | ***nCPBR |
| Water | 35.0 | 35.0 | 35.0 |
| Triton-X100 | 0.42 | 0.42 | 0.42 |
| Potassium tripolyphosphate | 0 .42 | 0.42 | 0.42 |
| Sodium hexametaphosphate | 0.42 | 0.42 | 0.42 |
| Volcastab | 0.42 | 0.42 | 0.42 |
| Silicone emulsion | 1.34 | 1.34 | 1.34 |
| Propylene glycol | 4.00 | 4.00 | 4.00 |
| Acticid SPX | 0.32 | - | - |
| Above ingredients were combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added | | | |
| Kaolin | 17.32 | 20.97 | 20.97 |
| Calcium carbonate | 18.64 | 29.59 | 29.59 |
| $TiO_2$ (Rutile) | 44.6 | 30.0 | 30.0 |
| The above ingredients mixed at high speed for 20 minutes. The following ingredients were added while stirring the mixture | | | |
| Carboxymethyl cellulose | 0.74 | 0.74 | 0.74 |
| Silicone emulsion | 0.92 | 0.92 | 0.92 |
| The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added | | | |
| Polymer emulsion | 75.0 | 75.0 | 75.0 |
| Carboxymethyl chitosan | - | 0.60 | 0.60 |
| Activated rubber crumb | - | - | 3.0 |

*PB - Paint formulation using conventional $TiO_2$. **nCPB- Paint formulation using nano $TiO_2$ and carboxymethyl chitosan. ***nCPBR- Paint formulation using nano $TiO_2$, carboxymethyl chitosan and rubber crumb.

## 6c.3 Results and Discussion

Antimicrobial properties, durability properties, adhesive strength and viscosity of the paint nCPB and nCPBR formulated using natural biocide carboxymethyl chitosan is compared with the sample PB and commercially available paint.

### 6c.3.1 Antimicrobial studies

Surface coatings are usually attacked by various micro organisms such as fungus, algae and or bacteria. To know the antimicrobial activity of the formulated paints antialgal, antifungal and antibacterial tests were carried out according to the standard procedures described in chapter 2.

This test method attempts to provide a means to comparatively evaluate different coating formulations for their relative performance under a given set of conditions. It does not imply that a coating that resists growth under these conditions will necessarily resist growth in the actual application. This test method covers an accelerated method for determining the relative resistance of two or more paints or coating films to algae, fungus and bacterial growth

The results obtained from antimicrobial tests, durability tests, adhesion test and viscosity of the paint formulated using natural biocide (carboxymethyl chitosan) are compared with the paint without natural biocide and commercially available paint.

### 6c.3.1a. Antialgal studies

The algal species such as *Chlorella pyrenoiclosa* (Unicellular green algae), *Oscillaforia subrivis* (Filamentious blue green algae) are used for the study antialgal study. The nuisance growth of terrestrial algae on painted surface is a ruining problem.

Antialgal tests were conducted for four weeks. The growth of algae after 1 week and 4 weeks are shown in the photographs. The observations for the growth of microorganisms are described by standard ratings in the respective tables.

### a. Green algae

*Table 6c.2: Rate of growth of green algae on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **WEEK 1** | | |
| PB | Traces of growth (1—10 %) | 1 |
| nCPB | None | 0 |
| nCPBR | None | 0 |
| Commercial | Traces of growth (1—10 %) | 1 |
| **WEEK 4** | | |
| PB | Light growth (10-30%) | 2 |
| nCPB | None | 0 |
| nCPBR | None | 0 |
| Commercial | moderate growth (30-60%) | 3 |

The photographs to show the growth of the green algae on the specimens after 1 week and after 4 weeks are shown in figure 6c.1.

### B. Blue green algae

*Table 6c.3: Rate of growth of blue green algae on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Moderate growth (30—60 %) | 0 |
| nCPB | None | 0 |
| nCPBR | | |
| Commercial | Moderate growth (30—60 %) | 0 |
| **Week 4** | | |
| PB | Moderate growth | 0 |
| nCPB | None | 0 |
| nCPBR | None | 0 |
| Commercial | Moderate growth | 0 |

The photographs to show the growth of the blue green algae on the specimens after 1 week and after 4 weeks are shown in figure 6c.2.

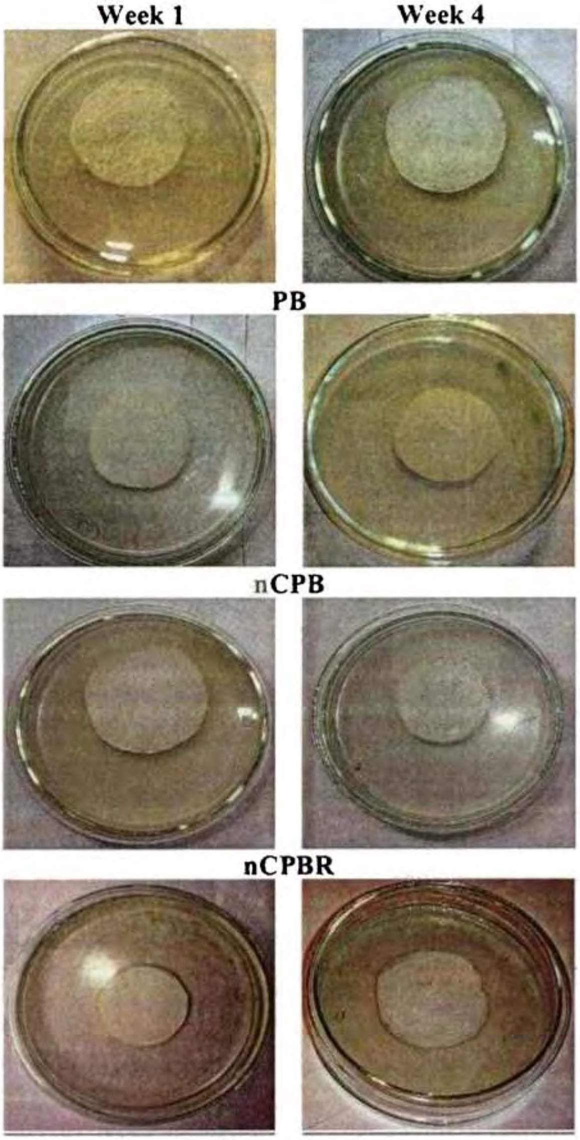


***Figure 6c.1:*** *Photographs showing the growth of green algae on the specimens after 1 week and four weeks at the test*

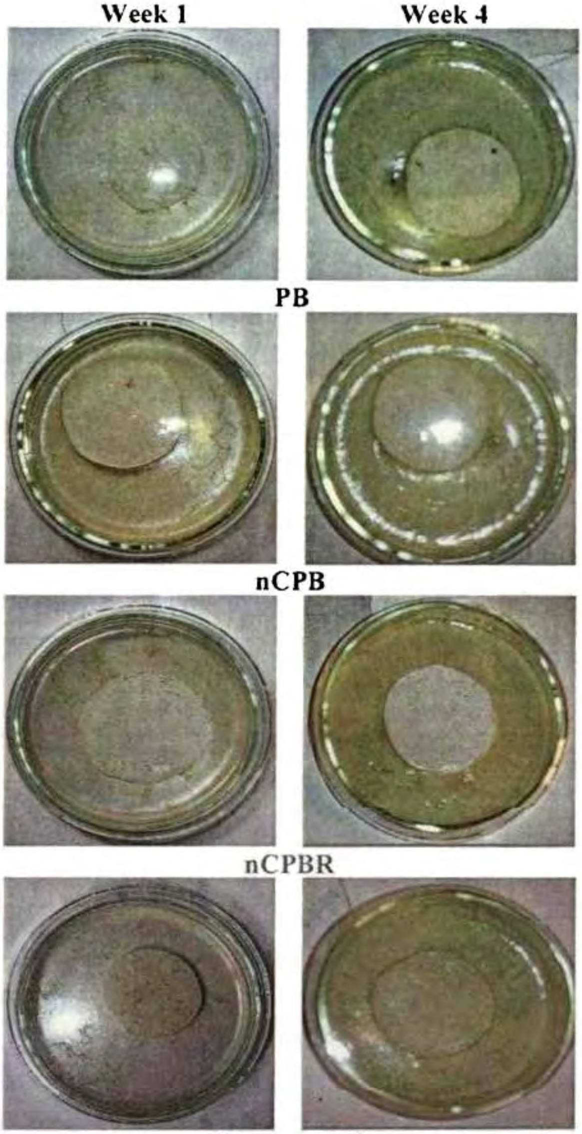


***Figure 6c.2:*** *Photographs showing the growth of blue green algae on the specimens after 1 week and four weeks at the test*

The tests conducted for antifungal activity of various paint samples shows that the algal defacement is more predominant for the samples nCPB and nCPBR which contains natural biocide when compared to other samples. From the rating tables and figures for the growth of green and blue green algae we can observe that the samples ηCPB and ηCPBR are not attacked by algae. The growth of the algae can be observed on PB and commercially available paint samples. This shows that carboxymethyl chitosan can effectively control the growth of algae in paints.

### 6c.3.2 Antifungal studies

The fungal species such as *Aspergillus* and *Penicillium citrinium* are used for the study of antifungal activity of paint samples.

Antifungal tests were conducted for four weeks. The growth of fungi after 1 week and 4 weeks are shown in the photographs. The observations for the growth of fungi are described by standard ratings in the respective tables.

#### A. Aspergillus

***Table 6c.4:*** *Rate of growth of Aspergillus on the samples*

| Sample | Observed Growth on Samples | Rating |
|---|---|---|
| **Week 1** | | |
| PB | Light growth (10—30 %) | 2 |
| η CPB | None | 0 |
| η CPBR | None | 0 |
| Commercial | Light growth (10—30 %) | 2 |
| **Week 4** | | |
| PB | Moderate growth (30-60 %) | 3 |
| η CPB | None | 0 |
| η CPBR | None | 0 |
| Commercial | Heavy growth (60 % to 100%) | 4 |

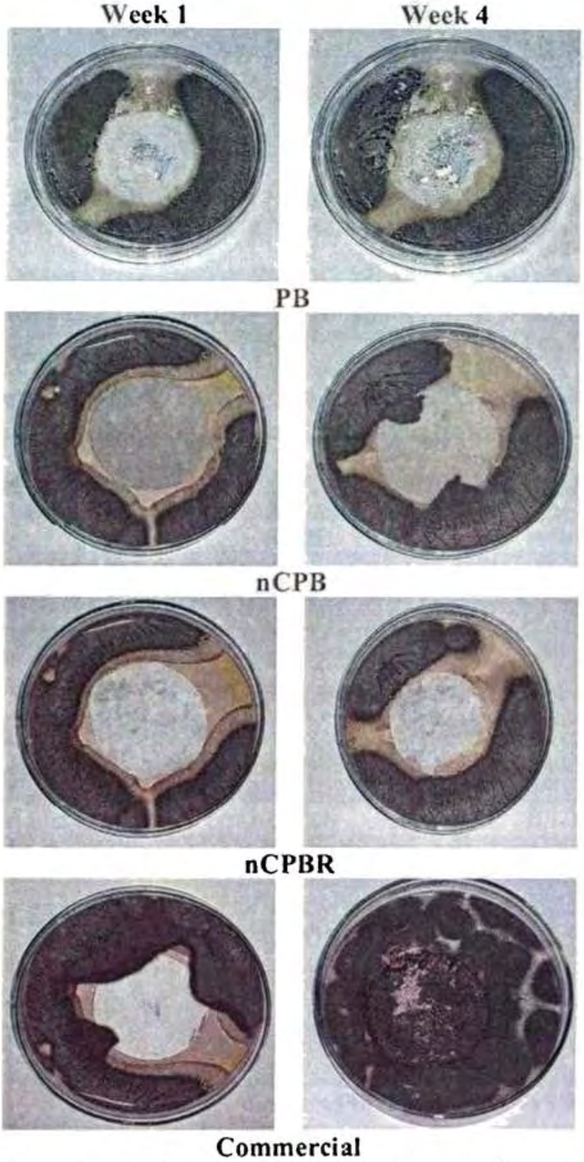


***Figure 6c.3:*** *Photographs showing the growth of Aspergillus on the specimens after 1 week and four weeks at the test*

### b. *Pencillium citrinium*

*Table 6c.5: Rate of growth of Penicillium citrinium on the samples*

| **Sample** | **Observed Growth on Samples** | **Rating** |
|---|---|---|
| **Week 1** | | |
| PB | Moderate growth (30—60 %) | 3 |
| nCPB | None | 0 |
| nCPBR | None | 0 |
| Commercial | Moderate growth (30—60 %) | 3 |
| **Week 4** | | |
| PB | Heavy growth (60 % to 100%) | 4 |
| nCPB | None | 0 |
| nCPBR | None | 0 |
| Commercial | Heavy growth (60 % to 100%) | 4 |

Table 6c.5 shows growth rate of algae, which shows grater fungal defacement observed for chitosan based paint than commercial paint. The photographs showing the growth of *Aspergillus* and *Penicillium citrinium* and on the specimens after 1 week and after 4 weeks are shown in figure 6c.3 and 6c.4 respectively.

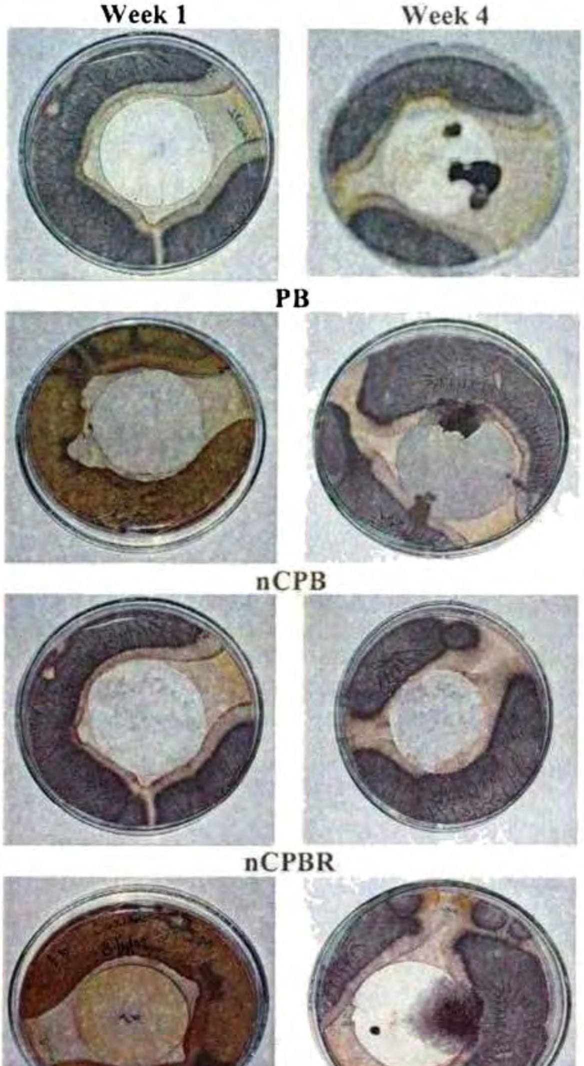


***Figure 6c.4:*** *Photographs showing the growth of Penicillium citrinium on the specimens after 1 week and four weeks at the test*

Fungi are present on the surface of coated paint in two forms. They may be present as thread-like structures, mycelia or as clusters of spherically, black coloured spores. The mycelia structures are observed when conditions under fungi are relatively growing and reproducing. Spore clusters are found when conditions for growth and reproduction are less favourable. Spores are more resistant to environmental changes and anti-microbial agents than the mycelia forms. Growth of two type of fungi spore on paint film is observed after 4 weeks, as shown in photograps. The carboxymethyl chitosan based coating shows better resistance to fungi attack than commercial paint film.

### 6c.3.3 Antibacterial studies

The antibacterial tests were conducted in accelerated lab conditions. The bacterial species such as *Escherichia colli* and *Bacillus cereus* are used for the study of antibacterial activity of paint samples.

Antibacterial tests were conducted for two days. The photographs of paint films immediately after inoculation of bacteria (initial) and the growth of bacterial colonies after 48 hours are shown in respective figures. The observations for the growth are described by standard ratings in the respective tables.

### A) *Escherichia colli*

*Table 6c.6: Rate of growth of Escherichia colli on the samples*

| Sample | Growth of bacterial colonies on Samples | Rating |
|---|---|---|
| **Initial** | | |
| PB | No growth | 0 |
| nCPB | No growth | 0 |
| nCPBR | No growth | 0 |
| Commercial | No growth | 0 |
| **After 48 hours** | | |
| PB | No growth | 0 |
| nCPB | No growth | 0 |
| nCPBR | No growth | 0 |
| Commercial | No growth | 0 |

The photographs show the growth of *Escherichia colli* on the paint films at the time of inoculation and after 48 hours are given in figure 6c.5

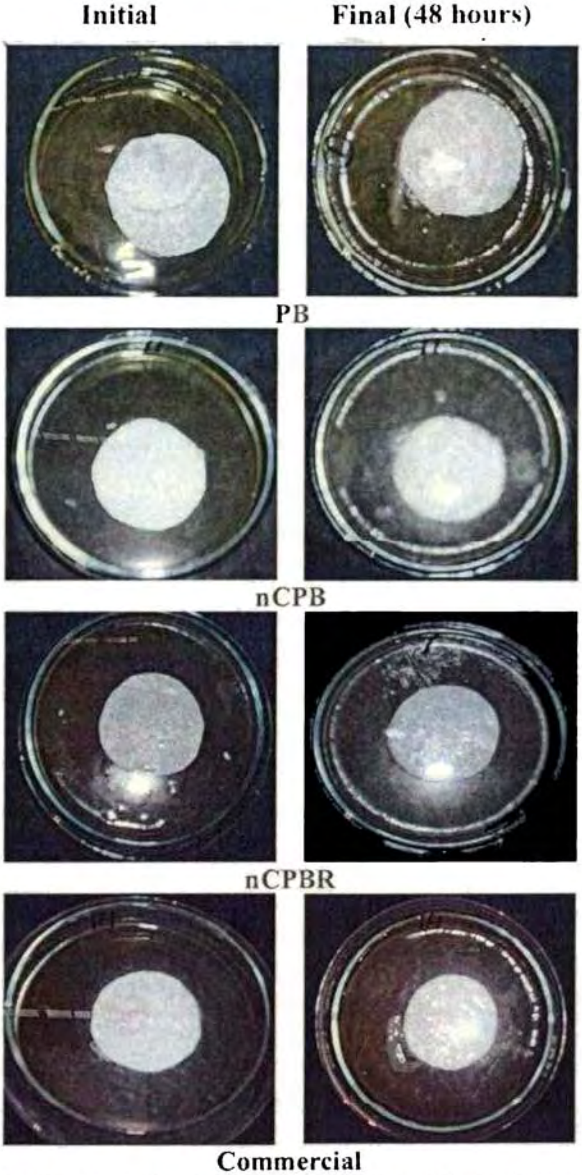


***Figure 6c.5:*** *Photographs showing the growth of Escherichia colli on the specimens before and after 48 hours at the test*

**b. *Bacillus cereus***

**Table 6c.7: Rate of growth of Bacillus cereus on the samples**

| Sample | Growth of bacterial colonies on Samples | Rating |
|---|---|---|
| | **Initial** | |
| PB | No growth | 0 |
| nCPB | No growth | 0 |
| nCPBR | No growth | 0 |
| Commercial | No growth | 0 |
| | **After 48 hours** | |
| PB | No growth | 0 |
| nCPB | No growth | 0 |
| nCPBR | No growth | 0 |
| Commercial | No growth | 0 |

The photographs show the growth of *Bacillus cereus* on the paint films at the time of inoculation and after 48 hours are shown in figure 6c.6

The bacterial growth increases under conditions of stress such as heat, cold, dehydration, some are able to form spores which are resistant to high temperature and dry environment and more resistant to bactericides. The photograps show the growth of two types of bacteria on the surrounding agar medium but colonial growth of bacteria is not observed on the paint film after 48hours. This shows that all paint films have good resistance to bacterial attack.

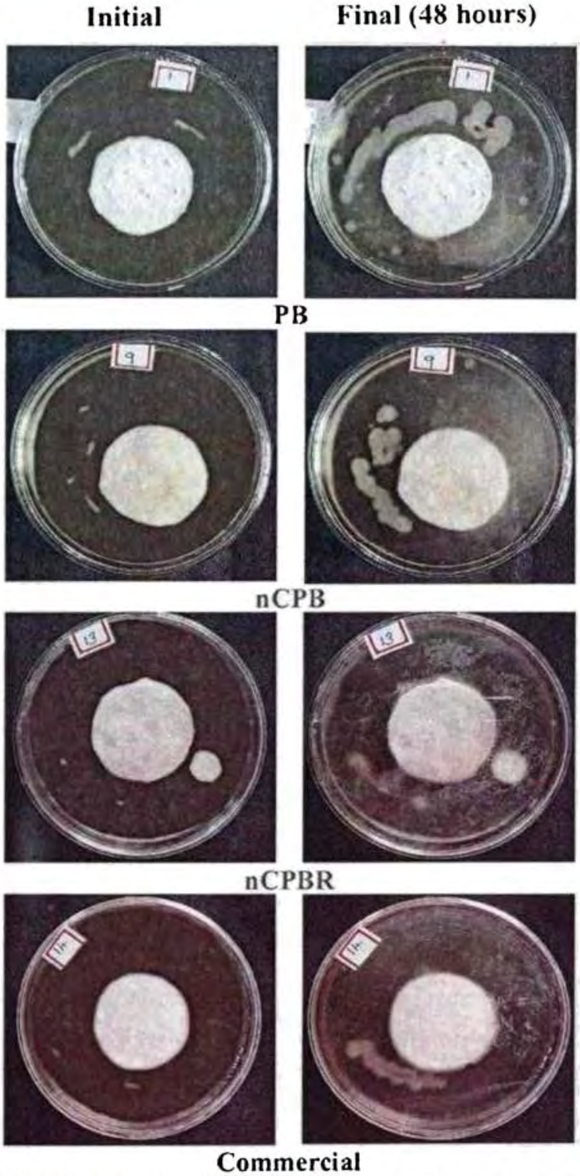


***Figure 6c.6:*** *Photographs showing the growth of Bacillus cereus on the specimens before and after 48 hours at the test*

Most of the chemical agents used in paint films effectively control fungi, algae and bacteria by interfering with their metabolic functions.

The exact mechanism of the antimicrobial action of carboxymethyl chitosan is still unknown, but different mechanisms have been proposed. Interaction between positively charged chitosan molecules and negatively charged microbial cell membranes leads to the leakage of proteinaceous and other intracellular constituents.[5] Chitosan acted mainly on the outer surface of the bacteria. At a lower concentration (<0.2 mg/mL), the polycationic chitosan does probably bind to the negatively charged bacterial surface to cause agglutination, while at higher concentrations, the larger number of positive charges may have imparted a net positive charge to the bacterial surfaces to keep them in suspension.[6]

### 6c.3.2 Durability tests

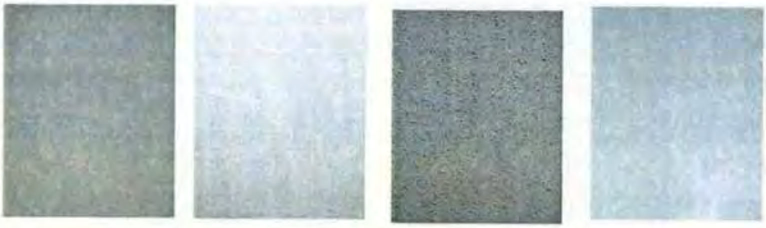
#### 6c.3.2.1 Water resistance test

***Table 6c.2:*** *Blister formation in water resistance test at 38$^0$C*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ****Commercial*** |
| 24 hrs | Nil | Nil | Nil | Nil |
| 4 days | Nil | Nil | Nil | Nil |
| 1week | Nil | Nil | Nil | Nil |
| 3 week | Nil | Nil | Nil | Few |
| 12week | Few | Nil | Nil | Medium |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for water resistance test are shown in figure 6c.1.

Initial appearance



Final appearance

***Figure 6c.7:*** *Appearance of specimens before and after water resistance test*

The figure 6c.7 and table 6c.2 clearly shows that sample nCPB and nPBR is highly resistant to water and is not shows any blister even after 12 weeks. The sample PB and commercially available paint show only slight blistering.

### 6c.3.2.2 Salt spray test

***Table 6c.3:*** *Blister formation in salt spray test at $28^0C$*

| **Time interval** | **Number and size of the blister** | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ***Commercial*** |
| 48 hrs | Nil | Nil | Nil | Nil |
| 1 week | Nil | Nil | Nil | Nil |
| 4 week | Nil | Nil | Nil | Few |
| 12week | Few | Nil | Nil | Medium |

The photographs of initial appearance (before the test) and final appearance (after 12 weeks) of the coated samples for salt spray test are shown in figure 6c.8

Initial appearance

Final appearance

***Figure 6c.8:** Appearance of specimens before and after salt spray test*

By analyzing the observations shown in table 6c.3 and the photographs shown in figure 6c.8 it can be seen that the sample nCPB & nCPBR are very stable and is little affected by salt spray. Salt water resistance is found to be better for nCPB & nCPBR compared to PB and commercially available paint.

### 6c.3.2.3 Alkali resistance test

Alkali resistance test was conducted for three types of alkalies ($Na_3PO_4$ at $75^0C$, $Na_2CO_3$ at $65^0C$ and NaOH at $28^0C$) according to standard procedure as described in chapter 2.

*Table 6c.4: Blister formation in $Na_3PO_4$ resistance test ($75^0C$)*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Nil | Few |
| 16 hrs | Medium | Nil | Nil | Dense |
| 24 hrs | Dense | Few | Few | Peeled |

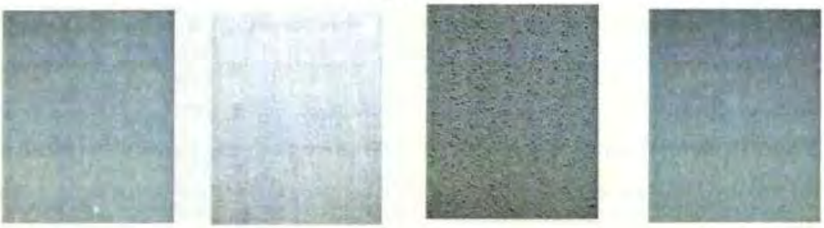
*Table 6c.5: Blister formation in $Na_2CO_3$ resistance ($65^0C$)*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ***Commercial*** |
| 4 hrs | Nil | Nil | Nil | Nil |
| 8 hrs | Few | Nil | Nil | Few |
| 16 hrs | Medium | Nil | Nil | Dense |
| 24 hrs | Dense | Few | Few | Peeled |

*Table 6c.6: Blistering formation in NaOH resistance test ($28^0C$)*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ***Commercial*** |
| 4 hrs | Nil | Few | Medium | Nil |
| 8 hrs | Medium | Dense | Peeled | Dense |
| 16 hrs | Dense | Medium | Dense | Peeled |

Initial appearance

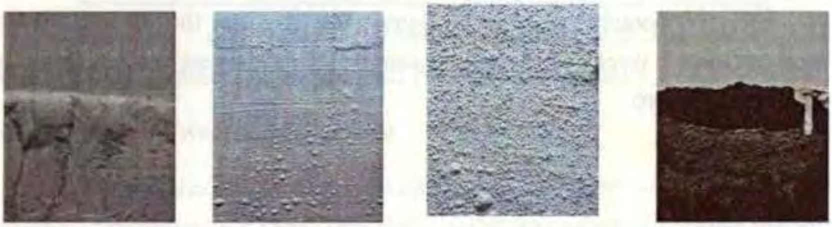


PB nCPB nCPBR Commercial

Final appearance $Na_3PO_4$

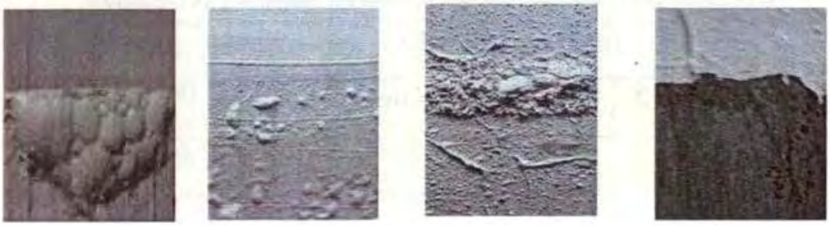
PB nCPB nCPBR Commercial

Final appearance $Na_2CO_3$



PB nCPB nCPBR Commercial

Final appearance NaOH



PB nCPB nCPBR Commercial

***Figure 6c.9:*** *Appearance of specimens before and after alkali resistance test*

Tables 6c.4, 6c.5 and 6c.6 describe the appearance of specimens at different time intervals of test conducted for $Na_3PO_4$, $Na_2CO_3$ and NaOH respectively. The photographs of coated samples before the test (initial appearance) and after the test (final appearance, 24h for $Na_3PO_4$, for 24h $Na_2CO_3$, 16h NaOH) are shown in figure 6c.9. From the photographs we can see that the alkali resistance of the sample nCPB and nCPBR are better than other samples.

### 6c.3.2.4 Detergent resistance test

*Table 6c.7: Blister formation in detergent resistance test at 28$^0$C*

| Time interval | Number and size of the blister | | | |
|---|---|---|---|---|
| | *PB* | *nCPB* | *nCPBR* | *Commercial* |
| 1 day | Nil | Nil | Nil | Nil |
| 3 day | Few | Nil | Nil | Medium |
| 1 week | Medium | Few | Nil | Medium |

The photographs of initial appearance (before the test) and final appearance (after 1 week) of the coated samples for detergent resistance test are shown in figure 6c.40

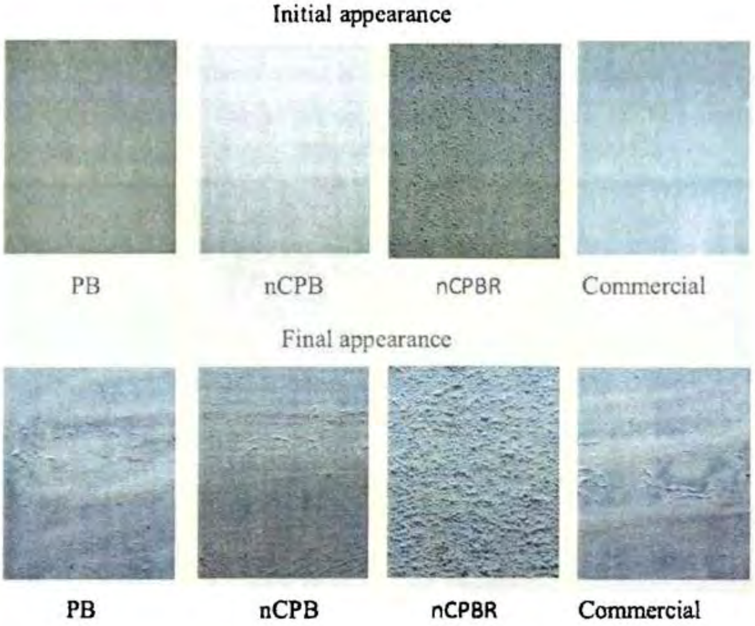


***Figure 6c.10:*** *Appearance of specimens before and after detergent resistance test*

Table 6c.7 and figure 6c.10 shows that sample nCPB and nCPBR are more resistant to detergent attack than PB and commercially available paint.

### 6c.3.2.5 Natural weather resistance

Weather resistance test was conducted for a period of 10 months from March to December in a year. This time period was selected because the samples were exposed to all seasons during the test.

***Table 6c.8:*** *Chalking formation during weather resistance test*

| **Time interval** | **Chalking observed** | | | |
|---|---|---|---|---|
| | ***PB*** | ***nCPB*** | ***nCPBR*** | ***Commercial*** |
| 1 month | Nil | Nil | Nil | Nil |
| 5 months | Nil | Nil | Nil | Nil |
| 10 months | Nil | Nil | Nil | Nil |

The photographs of initial appearance (before the test) and final appearance (after 10 months) of the coated samples for weather resistance test are shown in figure 6c 11

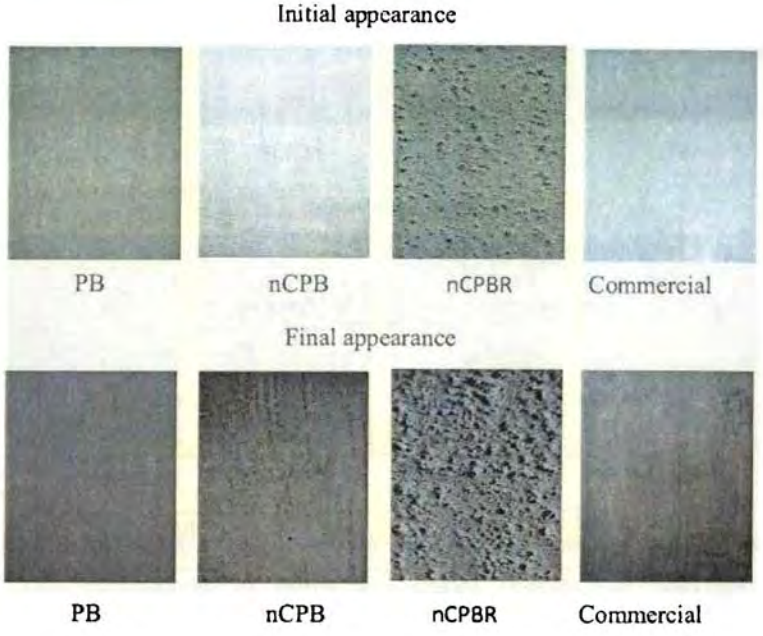


***Figure 6c.11**: Appearance of specimens before and after weather resistance test*

The figure 6c.11 and table 6c.8 shows that all the samples are very stable towards natural weather and did not show any colour change or degradation during the test.

The durability tests such as water resistance, salt spray resistance, alkali resistance, detergent resistance and weather resistance tests carried out for different specimens shows that the sample nCPB and nCPBR have good resistance towards various chemicals. The presence of rubber crumb may actively resist the attack of chemicals and climate conditions due to the inherent resistance of rubber crumb

### 6c.3.4 Scotch test

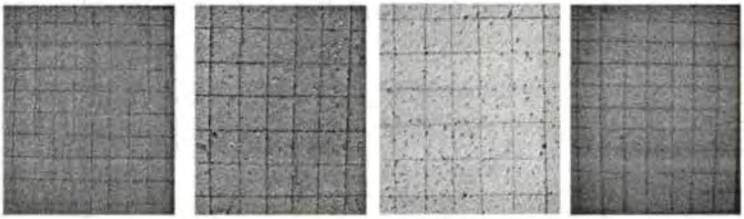
The cross cut adhesion test is carried out to know the adhesion of paint films on the substrate. The adhesion rating according to ASTM standards is shown in the table 6c.9.

***Table 6c.9:*** *Adhesion rating assessed by scotch test*

| Sample name | Classification | % removal |
|---|---|---|
| PB | 4B | Less than 5% |
| nCPB | 5B | 0% |
| nCPBR | 5B | 0% |
| Commercial | 3B | 5 – 15% |

The photographs of test specimens before and after the test are shown in figure 6c.12

Initial appearance



PB nCPB nCPBR Commercial

Final appearance

PB nCPB nCPBR Commercial

***Figure 6c12:*** *Appearance of specimens before and after scotch test*

The figure 6c.12and table 6c.9 show that the adhesive strength of all samples is high. The sample nCPB and nCPBR has no peeling by the scotch test, but slight peeling for PB and commercial sample are observed. The presence of matting agent (activated rubber crumb) may not allow the scotch tape to adhere on the surface of paint. This may be the reason for the good result obtained for the scotch test. This shows that the unwanted materials will not adhere on the matt finished paint film.

### 6c.3.5 Viscosity

Viscosity and shear thinning behaviour is an important property of paint for the ease of application. It depends on the size of the colloidal particles in paint. Viscosity of newly formulated paint is independent of carboxymethyl chitosan.

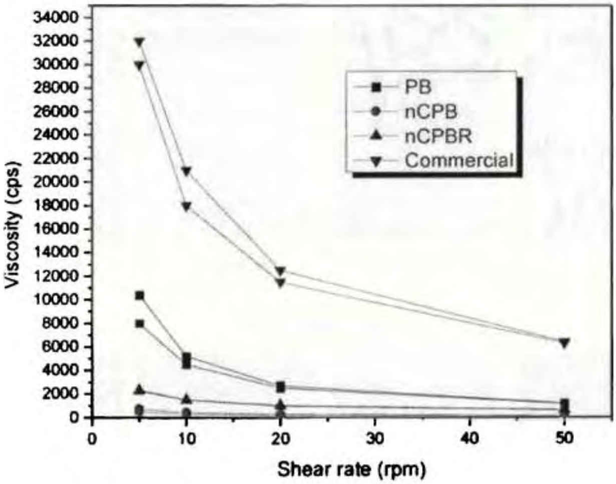


***Figure 6c.13:*** *Variation of viscosity with shear rate*

Shear thinning index of PB, nCPB, nCPBR and commercially available emulsion paint at two different rotational speeds 5 and 50 are given in table 6c.10.

*Table 6c.10: Shear thinning index of specimens*

| Sample | Shear thinning index |
|---|---|
| PB | 8.67 |
| nCPB | 4.5 |
| nCPBR | 4.7 |
| Commercial | 5 |

## 6c.4. Conclusion

The paint formulated using the binder based on VAc-BuA copolymer with 85/15 weight percentage with pigment nano $TiO_2$ sol and carboxymethyl chitosan as a biocide. The paint showed better antimicrobial properties and durability due to the presence of carboxymethyl chitosan.

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# Chapter 7

## Summary and conclusions

The most recent developments on coatings are related to environmental considerations and need to confirm the safety legislations. Cost and benefit relationship have also become significantly important in an increasingly competitive world market. Ecological pressure and legislation in many countries force the paint industry to reduce the level of volatile organic solvent in modern paint systems. Water borne binders are used to complete these demands. The era of water based coatings began with the Clean Air Act of 1990. The architectural coating market will respond to the latest challenge. The water based binder is used to decrease the volatile organic content. Vinyl acetate-Butyl acrylate (Vac-BuA) copolymer lattices were used as a binder in coating formulation. The most important application of VAc-BuA copolymer lattices is based on their adhesive property, softness, low MFT, freeze-thaw stability, storage stability, wet adhesion and low volatile organic content.

In the present investigation, an attempt has been made to prepare water based coatings based on novel formulations. Attempts were made to modify of the performance and characteristics of paint through the incorporation of water based binder and carboxy methyl chitosan, as antimicrobial agent. The excellent antimicrobial properties and adhesive strength is capable of giving a new face to coating industry.

In the first part of the study, varying compositions of Vinyl acetate-Butyl acrylate copolymer lattices were synthesized by semi-continuous emulsion polymerization. The rate of monomer addition and co-monomer composition were found to have considerable effect on the thermal, mechanical and adhesive properties of vinyl acetate-butyl acrylate copolymer latex. All compositions have shown good film forming property. The single $T_g$ value indicates that the copolymer formed may be statistical random copolymer. The synthesized lattices have been characterized by FTIR, NMR, GPC, DSC, TGA and measurement of zeta potential, mechanical strength and adhesive properties.

As the second part of the study, a new coating formulation is tested with varying compositions of synthesized vinyl acetate-butyl acrylate copolymer lattices, as a binder was investigated. The synthesized copolymer lattices containing compositions such as 85/15, 76/24 and 70/30 weight percentage are used. The durability tests of three formulated paints were compared with commercially available paints. The property of the paint varies with vinyl acetate content in the copolymer lattice. Paint formulated with 85/15 weight percentage of VAc-BuA composition shows better performance in the durability tests.

The quality of the paint is strongly linked to the pigment chosen for that paint. Rutile titanium dioxide is the most important pigment in use today. Titanium dioxide is superior to any other white pigment. $TiO_2$ based coating has UV shielding ability due to UV ray absorption and UV ray scattering. Light scattering depends on the particle size and the wavelength of corresponding light. Due to the reduction of particle size, UV ray absorption increases. The sunscreen performance depends on how well the ultrafine particles are dispersed in the formulation. The nano $TiO_2$ colloidal sol was prepared by a wet synthesis process. The present study deals with an optimum design of $TiO_2$ colloidal sol regarding appropriate pH, particle size, stabilize in neutral pH. $TiO_2$ is in a predispersed form rather than powdered form improves the quality of final dispersion. $TiO_2$ colloidal sol is used as a pigment in the formulated paint. The UV ray shielding ability of this formulated coating is enhanced by the presence of nano $TiO_2$ colloidal sol. The nanosized colloidal pigment gives better gloss property to the surface coating. This paint formulation has better durability. The matt paint was used as a consolidation system. The minimum quantity of matting agent required to achieve effective cohesion of the paint and adhesion of the paint to the substrate, and which is compatible with the paint and support materials in the long term was determined. In the new coating formulation, activated rubber crumb is used as a matting agent. Activated rubber crumb enhances all the properties of paint film.

Architectural coatings are required to fulfill demand for improved environmental compatibility. Water-borne emulsion paints can experience viscosity loss, gas formation, colour change, and pH drift as a result of the degradation of organic constituents. This deterioration can be caused by microorganisms. This can destroy both the decorative and protective properties of paint films. The antimicrobial properties of newly formulated paints are enhanced by using carboxymethyl chitosan as the antimicrobial agent. Carboxymethyl Chitosan has good film forming ability and excellent antimicrobial activity. These properties of arboxymethyl chitosan enhance water resistance, alkali resistance, detergent resistance and adhesive strength.

Thus, antimicrobial agent carboxymethyl chitosan has been proved to be a promising candidate to modify the performance characteristics of developed coating formulations.

# Abbreviations and symbols

| | |
|---|---|
| ASTM | American standards and testing methods manual |
| BET | Brunauer, Emmett and Teller |
| BuA | Butyl acrylate |
| cm | centimetre |
| CPBR | Paint formulated using VAc-BuA copolymer (85/15 wt.%) with carboxymethyl chitosan and rubber crumb |
| CPVC | Critical Pigment Volume Concentration |
| DSC | Differential scanning calorimetry |
| DTA | Differential thermal analysis |
| DTG | Derivative thermogravimetry |
| FTIR | Fourier Transform infrared |
| GPa | Giga Pascal |
| GPC | Gel permeation chromatography |
| HPLC | High performance liquid chromatography |
| hrs | Hours |
| IR | Infra Red Spectroscopy |
| L.R. | Laboratory reagent |
| m | metre |
| MFFT | Minimum film forming temperature |
| MHz | Mega hertz |
| min | Minutes |
| mm | millimetre |
| mol | Mole |
| μm | Micrometer |
| MPa | Mega Pascal |
| $Na_2CO_3$ | Sodium carbonate |
| NaOH | Sodium hydroxide |
| $Na_3PO_4$ | trisodiumphosphate |
| nCPB | Paint formulated using VAc-BuA copolymer (85/15 wt.%) with nano $TiO_2$ |

| | |
|---|---|
| nCPBR | Paint formulated using VAc-BuA copolymer (85/15 wt.%) with nano $TiO_2$, carboxymethyl chitosan and rubber crumb |
| nm | Nanometre |
| Nm | Newton meter |
| NMR | Nuclear magnetic resonce |
| PB | Paint formulated with VAc-BuA copolymer (85/15 wt.%) |
| $PB_1$ | Paint formulated with VAc-BuA copolymer (85/15 wt.%) |
| $PB_2$ | Paint formulated with VAc-BuA copolymer (76/24 wt.%) |
| $PB_3$ | Paint formulated with VAc-BuA copolymer (70/30 wt.%) |
| PBR | PBR- VAc-BuA copolymer (85/15 wt.%) and crumb rubber |
| phr | Parts by hundred parts by weight of resin |
| ppm | parts per million |
| PVC | Pigment Volume Concentration |
| r | Reactivity ratio |
| rpm | Revolutions per minute |
| SBR | Styrene butadiene rubber |
| $SiO_2$ | Silica |
| T | Temperature |
| $T_g$ | Glass transition temperature |
| TGA | Thermo gravimetric analysis |
| $TiO_2$ | Titanium dioxide |
| Tm | Melting temperature |
| UTM | Universal Testing Machine |
| UV | Ultra Violet |
| VAc | Vinyl acetate |
| VAc-BuA | Vinyl acetate-Butyl acrylate copolymer |
| VOC | Volatile organic content |
| Wt | Weight |
| XRD | X- ray diffraction |
| ZnO | Zinc oxide |

## Publications in International Journals

1. Paint Formulation Using Water Based Binder and Property Studies, Suma K.K., Sinto Jacob, Rani Joseph; *Macromolecular Symposia* **2009**, 277(1), 144.
2. Modification of Polypropylene/Glass Fiber Composites with Nanosilica, Sinto Jacob, Suma K.K., Jude Martin Mendaz, Abhilash George, K.E.George; *Macromolecular Symposia*, **2009**, 277(1), 138.
3. Studies on the effect of nano $TiO_2$ on Vinylacetate-Butylacrylate latex based surface coating, Suma K.K, Sinto Jacob, Rani Joseph; *Material Science and Engineering: Part.B* , communicated (2009).

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