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 I.aiian 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) Potassium tripolyphosphate: 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 latexes were prepared by semi-continuous emulsion polymerization. The polymerization was carried out in a four necked one liter reactor having a two bladed Teflon (tetrafluoroethylene) coated stirrer and a 25 ml graduated dropping funnel which was immersed in a constant temperature bath kept at 80°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°C. After that the reactor contents was cooled to 28°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.
2.2.2 Latex paint formulation

The paint formulations were made by mixing appropriate proportions of latex with various ingredients. Latexes 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 TiO₂. To find out the effect of nanosized pigment; synthesized nano TiO₂ 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 (1:1 ratio). They were then dried in vacuum oven at 60 °C. These samples were dissolved in tetrahydrofuran, 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 chloroform and tetrachloroethylene. The ¹H-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 (Mₚ) 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°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 (1:1 ratio). They were then dried in vacuum oven at 60°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 ($T_m = 156.6^\circ C$, $\Delta H_m = 28.4$ J/g). The analysis was done in nitrogen atmosphere using standard aluminum pans. 5-8 mg specimens were first cooled to -80°C and scan was made from -80°C to 100°C at a heating rate of 10°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°C/min. The analysis was done in nitrogen atmosphere and the temperature range was from 50°C to 800°C.
2.3.1.6 Adhesive properties

Lap shear and peel strength

The adhesive property of copolymer latices 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°C for 24 hours.

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°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°C ± 0.25°C. 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**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride (as NaCl)</td>
<td>26.5 g</td>
</tr>
<tr>
<td>Magnesium chloride (as MgCl₂)</td>
<td>2.4 g</td>
</tr>
<tr>
<td>Magnesium sulphate (as MgSO₄)</td>
<td>3.3 g</td>
</tr>
<tr>
<td>Potassium chloride (as KCl)</td>
<td>0.73 g</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate (as NaHCO₃)</td>
<td>0.20 g</td>
</tr>
<tr>
<td>Sodium bromide (as NaBr)</td>
<td>0.28 g</td>
</tr>
<tr>
<td>Calcium chloride (as CaCl₂)</td>
<td>1.1 g</td>
</tr>
<tr>
<td>Distilled water</td>
<td>1000 ml</td>
</tr>
</tbody>
</table>

### 2.3.2.4 Alkali and detergent resistance test

Resistance towards at least three alkali (trisodium orthophosphate, anhydrous sodium carbonate and sodium hydroxide) 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 trisodium orthophosphate, 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
Materials used and experimental techniques

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

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trisodiumphosphate</td>
<td>10% w/w</td>
<td>75°C</td>
</tr>
<tr>
<td>Soda ash</td>
<td>10% w/w</td>
<td>65°C</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>5% w/w</td>
<td>25°C</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrasodium pyrophosphate anhydrous</td>
<td>53g</td>
</tr>
<tr>
<td>Sodium sulphate anhydrous</td>
<td>19g</td>
</tr>
<tr>
<td>Sodium metasilicate anhydrous</td>
<td>7g</td>
</tr>
<tr>
<td>Sodium carbonate anhydrous</td>
<td>1g</td>
</tr>
<tr>
<td>Potassium oleate</td>
<td>20g</td>
</tr>
</tbody>
</table>

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

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°.

2.3.2.7 Rheological properties

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°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 lowest
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.
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

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 algal 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 ±28°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°C and then poured into sterilized petridishes and stored at 40°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 °C. The discs were applied on bacteria grown in agar plates using a sterilized forceps. The plates were inverted and kept in a
Chapter 2

bacterial incubater at 37.5°C for 24 hours. Escherichia coli and Bacillus subtilis 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°C (37 to 50°F) for not more than 4 days.

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 citrinum (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°C (82 to 86°F) prior to the experiment, and use these subcultures in preparing the spore suspension.

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Reference

1 (a) Annual Book of ASTM Standards Vol. 06.01
(b) Annual Book of ASTM Standards, Vol.15.09

2 (a) Annual Book of ASTM Standards Vol.06.01
(b) ASTM sub committee D01. 24 on Physical properties of Liquid Paints and Paint materials.

3 (a) Annual Book of ASTM Standards, Vol.06.01
(b) Annual Book of ASTM Standards Vol.06.02