EXPERIMENTAL DETAILS
CHAPTER - III

EXPERIMENTAL DETAILS

This chapter is exclusively devoted to detailed explanation of experimental works. There are the methods of the preparation of Silicone resin, Cashew nut Shell Liquid-Sulfur (CNSL-S) resin and interpenetrating polymer networks (IPNs) and paint formulations. The test methods employed for the study of the physical characteristics and evaluation of corrosion resistance properties of the paints are also described.

3.1. Preparation of the silicone resins

The following chemicals were used for the preparation of silicone resin

1. Silicone resin          (6407 Rhone Phoulenic Chemie)
2. Xylene             (E-Merck)

3.2. Preparation of cashew nut shell liquid-sulfur resin

The following chemicals were used for the preparation of CNSL-S resin.

1. Cashew nut shell-liquid        : (CNSL) oil- (commercial grade)
2. Formaldehyde              : (E-Merck)
3. Hexamine                  : (E-Merck)
4. Sulfur powder            : (E-Merck)
5. Sodium hydroxide         : (E-Merck)
6. Xylene                   : (E-Merck)
7. Carbon disulfide         : (E-Merck)
Method of preparation

The CNSL resin was synthesized in a round bottom flask. 10 g of sulfur powder was taken in a RB flask and dissolved in carbon disulfide and mixed with 95 g of CNSL oil. The mixture was set aside to stand for one day without any disturbance at room temperature. The RB flask containing CNSL mixture was maintained at constant temperature of 30±5°C for an hour and cooled. Consequently 91.5 g of the above CNSL mixture was refluxed at 140±5°C for an hour with 35 g of hexamine and 29 g of formaldehyde in 78 g of xylene with continuous stirring. Sodium hydroxide was used as a catalyst to carried out the condensation reaction. The resin, thus obtained was cooled and around 50% of xylene, water and other impurities present in it were distilled off and compensate it by freshly purchased xylene.

3.3. Preparation of interpenetrating polymer networks

The suitable IPN polymer was prepared (synthesized) by varying the binders ratio. The following chemicals were used for the preparation of IPN polymer (30/70)

1. Silicone resin : (6407 Rhone Phoulenic Chemie)
2. CNSL-S : (Synthesized)
3. ε-capro lactone : (Cross-linking agent)
4. Xylene : (Solvent)
5. Dibutyltindilaurate (DBTDL) : (Catalyst)

**Method of preparation**

For the preparation of IPN resin, 95 g of 50% CNSL-S solution was added to the round bottom flask containing 5 ml of \(\varepsilon\)-capro lactone taken in the RB flask. The \(\varepsilon\)-capro lactone was used as ring opening agent for CNSL resin. Small amount of DBTDL was added to catalyze the reaction to the CNSL medium, stirred well for half an hour. To the above mixture 105 g of 50% silicone resin was added and refluxed with 75 ml of xylene and distilled off water and impure xylene. The reaction was carried out using N, N’-dimethyl aniline as the catalyst. The loss of xylene and water was compensated by adding fresh xylene with refluxion for three hours. A brown colored resin (IPNs) product was collected in a separate container and preserved it in an airtight clean container for the future studies.

**3.4. Characterization of Binders**

The modern technology mainly focus on the development of reliable high performance coating materials, having superior thermal and mechanical properties ideally suitable for adverse environmental conditions [1]. Hence the FT-IR, GPC and thermal analysis were used to find out the structural and physical properties of the binders.
3.4.1. Fourier-transform Infra-red spectroscopy

Elucidation of silicone, CNSL-S and IPNs structures have been done by Fourier-transform Infra-red spectroscopy. The FT-IR spectra for the synthesized resins were taken on KBr pellets and recorded using a Perkin–Elmer spectrophotometer.

3.4.2. Gel-permeation Chromatography

The number average molecular weight and polydispersity of the silicone, CNSL–S polymeric resins were measured using software controlled GPC of Shimadzu C-R4 A chromatopac, Japan. The GPC was made using polystyrene as standard at ambient conditions, with tetrahydrofuran as the carrier solvent in a carbowax column.

3.4.3. Thermal and XRD analysis

The thermal stability of the different polymers was ascertained through TGA/DTA analysis and the studies were carried out by TGA/DTA model STA 1500, PL thermal analyzer system supplied by the polymer laboratories, UK. The entire system was software controlled (V400), and it can be used for ease of data processing and analysis. The output data for the samples were fed into the computer through analog/digital converter in the form of mV. The thermo gravimetric and differential thermal analysis curves were recorded
simultaneously. Fine powder of samples (coatings) weight ranging from 4-8 mg were placed in the platinum sample pans under a continuous nitrogen atmosphere with a flow of 25 ml/min. The sample and the reference were heated at the rate of 10°C/min. The phase changes and glass transition temperatures of the resins were measured on Perkin-Elmer differential scanning calorimeter, DSC-2. The X-ray diffraction studies were also carried out for the free polymeric powders to characterize their crystallinity.

3.5. Preparation of primers

The ingredients used for the preparation of the primers based on silicone, CNSL-S, IPNs resins are for the preparation of primers given in the Table.3.1. The following chemicals were purchased from different companies such as Zinc dust was purchased from metal powder company ltd., Thirumangalam, Madurai, India; particle size of the paint grade zinc dust is 3-5 micron, Manganese flake was supplied by Burgoyne Burbidges and Co., (India), Bombay. The stainless steel flake pigment was supplied by United States. The different ratios of PVC were used to formulate the suitable primer with different combinations of paint ingredients.
Table 3.1

The ingredients used for the preparation of primers

<table>
<thead>
<tr>
<th>Binder</th>
<th>Pigments</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNSL-S</td>
<td>Zinc dust, Stainless steel, Aluminium paste, Manganese powder</td>
<td>Xylene, Carbon disulfide</td>
</tr>
<tr>
<td>Silicone -6407</td>
<td>Zinc dust, Stainless steel, Aluminium paste, Manganese powder</td>
<td>Xylene</td>
</tr>
<tr>
<td>IPNs</td>
<td>Zinc dust, Stainless steel, Aluminium paste, Manganese powder</td>
<td>Xylene</td>
</tr>
</tbody>
</table>
Preparation of primers using various types of binders

Zinc dust and ZnO were taken in an attritor Jar (Szegvari Attritor system, supplied by union process, Ohio, U.S A) and mixed with silicone resin. The ingredients were ground with ceramic balls for an hour to get the Hegman Gauge value of six. Primer with various pigments weight percentage ranging from 50% to 80% have prepared by taking required weight of pigments and binder for suitable pigment volume concentration.

Manganese mixed with MnO₂ and ground well in the attritor jar as stated above for the zinc primer preparation procedure with various pigment weight percentage ranges from 50% to 80%. Similarly the stearic acid was (dispersing agent) mixed with other metallic powder pigments such as leafing aluminium paste and stainless steel flakes paste were used for the preparation of primers with various pigment volume concentration ranging from 20% to 50%.

As per the above procedure, stainless steel, aluminium, manganese and zinc were incorporated in the CNSL-S and IPN resins. A typical primer formulation for 70% pigment volume concentration of zinc, manganese in the binders are given in Tables 3.2 and 3.3. The physical properties of these
Table 3.2

Typical primer formulation of PVC 70% of zinc in different binders

<table>
<thead>
<tr>
<th>Binders</th>
<th>Pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNSL-S (g)</td>
<td>Silicone (g)</td>
</tr>
<tr>
<td>13.8</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>17.6</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.3

Typical primer formulation of PVC 70%, of manganese in CNSL-S & Silicone resins and 60% in IPN binder

<table>
<thead>
<tr>
<th>Binders</th>
<th>Pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNSL-S (g)</td>
<td>Silicone (g)</td>
</tr>
<tr>
<td>6.9</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
primers such as specific gravity, viscosity, dry film properties per coat and non volatile matter were measured and presented in Tables 3.4 & 3.5.

3.6. Silicone resin (commercial)—finish coat

Two types of finish coat paints were prepared, one based on ceramic blue pigment containing cobalt and alumina and the other ceramic green pigment containing cobalt and silica. For the preparation of finish coat, the following ingredients were used.

1. Silicone resin : (commercial)
2. Cobalt carbonate : (E-Merck)
3. Alumina pigment : (E-Merck)
4. TiO₂ white pigment : (Commercial)
5. Xylene : (E-Merck)
6. Water : (E-Merck)

Preparation of ceramic pigments

Ceramic pigments were prepared by direct calcination of cobalt and alumina compounds. In this process, oxides of their elements were used as the raw material for the ceramic pigment preparation. These raw materials were mixed thoroughly and calcined at very high temperatures and the product was crushed into 300 mesh sieve size [2]. The required size of the particle can be obtained by changing the following parameters during the
Table 3.4
Liquid paint properties of zinc based primers in different binders

<table>
<thead>
<tr>
<th>No</th>
<th>Properties</th>
<th>CNSL-S</th>
<th>Silicone</th>
<th>IPN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Specific gravity (g/cc)</td>
<td>1.2084</td>
<td>1.5068</td>
<td>1.5244</td>
</tr>
<tr>
<td>2</td>
<td>Viscosity (B4 Ford cup) sec</td>
<td>62</td>
<td>135</td>
<td>104</td>
</tr>
<tr>
<td>3</td>
<td>Dry film thickness per coat (μm)</td>
<td>75±5</td>
<td>80±5</td>
<td>80±5</td>
</tr>
<tr>
<td>4</td>
<td>Non volatile matter</td>
<td>54.3%</td>
<td>87.3%</td>
<td>75.5%</td>
</tr>
</tbody>
</table>

Table 3.5
Liquid paint properties of manganese based primers in different binders

<table>
<thead>
<tr>
<th>No</th>
<th>Properties</th>
<th>CNSL-S</th>
<th>Silicone</th>
<th>IPN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Specific gravity (g/cc)</td>
<td>1.2352</td>
<td>1.8514</td>
<td>1.5524</td>
</tr>
<tr>
<td>2</td>
<td>Viscosity (B4 Ford cup) sec</td>
<td>73</td>
<td>156</td>
<td>112</td>
</tr>
<tr>
<td>3</td>
<td>Dry film thickness per coat (μm)</td>
<td>65±5</td>
<td>80±5</td>
<td>80±5</td>
</tr>
<tr>
<td>4</td>
<td>Non volatile matter</td>
<td>54.3%</td>
<td>87.3%</td>
<td>75.5%</td>
</tr>
</tbody>
</table>
process, including raw materials, their proportions, the processing stages, and their conditions.

Cobalt blue pigment was produced by mixing 81% of $\alpha$-Al$_2$O$_3$, cobalt carbonate 15% thoroughly and the remaining 4% H$_2$O was added ground well for consistency. All the carbonate present in the mixture was converted into cobalt oxide and CO$_2$ by roasting the mixture in open air for 30 minutes. The roasted materials were calcined at 1100°C for an hour in a muffle furnace.

The ceramic blue and TiO$_2$ pigments were taken into the attritor jar and mixed with silicone resin solution. Ceramic balls were added into it and the attritor was run for 20 minutes to get the Hegmann gauge value reached to six. Similarly ceramic green pigments were prepared by the above procedure and finish coats formulated. Typical paint formulations prepared of these two finish coat with 15% PVC are given below.

**Ceramic blue pigment based (15% PVC)–finish coat**

1. Silicone resin : 76.5 g  
2. TiO$_2$ : 2.83 g  
3. Ceramic Blue : 24.40 g  
4. Xylene : 15.9 g  
5. Specific gravity : 1.4096 g/cc  
6. Viscosity (B4 cup) : 180 sec  
7. Thickness per coat : 45±5 μm
Ceramic green pigment based (15% PVC)–finish coat

1. Silicone resin 26.60 g
2. TiO₂ 2.83 g
3. Ceramic green 26.30 g
4. Xylene 18.2 g
5. Specific gravity 1.6750 g/cc
6. Viscosity (B4 cup) 205 sec
7. Thickness per coat 45±5 μm

3.7. Preparation of painted specimens

The mild steel panels of various sizes (2.5x2.5 cm, 5x7.5 cm, 10x10 cm) have sand blasted to remove rust and mill scale from the surface of the MS and degreased with Trichloroethylene. The primers (pigment volume concentration 50% to 80%) have applied over the mild steel specimens by hand brush method to build up the dry film thickness of the primer coat up to 80±5 μm. B del Amo et al. [3] studies have indicated that the zinc rich primer with 80-90 μm thickness offered best protection to mild steel substrates. The painted panels were allowed to dry in hot air oven for backing at 190°C for 20 minutes before carrying out the regular tests.

The best performance of the primer was chose from the potentiodynamic polarization study results. The primer panels were top coated.
with the ceramic pigmented silicone resins paint and allowed to dry in hot air oven at 190°C for 20 minutes before the tests.

3.8. Evaluation of coating properties

The evaluation of performances of the primer and paint films were done by subjecting the coatings to physiochemical and electrochemical tests. The important physical properties, which are normally assessed for finding out the suitability of the coating for practical applications are the hardness, flexibility, impact to loads, adhesion of the film to the substrate material and abrasion resistance. In addition to physical properties the performance of the coated system in corrosive and chemical environments were also studied through the electrochemical accelerating test methods.

Specific gravity

The specific gravity of the liquid paints and the primer was determined by means of weight per gallon cup [4]. The volume of cup is known and constant. The difference in weight of the cup filled with paint and the empty cup gives the weight of the known volume of the paint to that of the known volume of water is the specific gravity of the paint.
Viscosity

Viscosity measures the fluidity of the paint. Tests for viscosity are quantitative, but the method of measurements must be chosen according to the properties of the paint. The test instrument consists of a cup with an orifice at the bottom. Both cup and orifice are of controlled volume, diameter and length. The cup was filled with paint at a standard temperature and the time required for the paint to flow completely through the orifice was measured. The Ford cup is widely used for viscosity determination [5] and in the present study Ford cup no. B4 was used.

Fineness of grind

The test was performed based on the use of Hegman gauge [6]. It was employed as a quality control test, to ascertain whether the pigment was dispersed properly and uniformly into the resin or not. The paint paste was placed on the grooves in a carefully machined steel block and scraper was drawn over the block in the direction of grooves. The grooves are graduated uniformly in-depth from zero at one end to 10 μm at the other end. The reading was taken at the point at which the specks (large particle) in the film appeared to predominant.
Dry film thickness

Many methods are used to find out the dry film thickness. In the present work, instrument based on magnetic function was used [7]. Magnetic thickness gauge was used for finding the thickness of the coatings on the metallic surfaces. If the attractive force between a permanent magnet in the gauge and a coated specimen is high, the distance between them is low. Elcometer is working based on the above principle and it is used to measure the thickness of the paint coatings.

3.9. Determination of Mechanical properties of painted specimens

Abrasion (Taber Abrasion)

Abrasion resistance is the ability of a coating material to withstand mechanical action such as rubbing, scarping or erosion that tends to remove materials from its surface progressively. It is not an isolated property in the coating but also is related to other physical properties like wear resistance, cohesive strength, hardness, tensile strength and toughness. Several methods have been evolved to determine the abrasion resistance such as abrasive blasts, rotating disks and rotating wheels etc. In this test [8], the painted specimens of 10x10 cm square were mounted on a turntable that rotates at 100 rpm. The pre-weighed painted specimens were placed below the abrading wheels closely. Abrasion resistance of coatings were measured by applying 1000
revolution under 1000g load. The abrasion resistance of the primer coated panels were also determined using this method.

**Flexibility (Conical Mandrel Bend Test)**

Conical mandrel bend test method gives an idea of adhesion and extensibility of coatings when applied to flat sheet metal of uniform surface texture [9]. In this test, the primer was coated on thin (930-32 gauge) cold rolled carbon steel strip of the dimensions of 10 cm width and 19 cm of length. The test specimens were kept up right on its lengthwise position between the mandrel and draw bar (with the finish side towards the draw bar). It was then tightly clamped in the right position in such a way that, end of the coated specimens adjacent to the narrow end part of the conical mandrel almost touching the side of the draw bar level frame. The lever was moved through about 180 degree at uniform velocity to bend the specimen approximately in about 15 seconds. The bend surface of the specimen was examined for any damage to the film. The flexibility of the paints and primer were tested using the above procedure. The percentage of elongation is calculated using the formula,

\[
\text{Percentage elongation} = \frac{t}{2r + t} \times 100
\]
where, ‘t’ is the thickness of the panel and ‘r’ is the radius of the mandrel at which the coating passes the test

**Impact resistance (Falling Weight Method)**

A number of tests have been exist based on falling weight, for finding the impact resistance of the coatings. They provide a means of adjusting the height of standard weight, usually hemispherical at the base. For any given weight and height of fall to the resultant distortion or damage of the paint film will depend on the characteristics of the surface. The paint is required to be undamaged under a blow delivered by a defined weight falling from a fixed height. The maximum height from which the load is impinge without damage to the coating is noted and the impact resistance is expressed as kg/cm\(^1\) which can be used for comparative assessment of the coatings. The painted panels were placed on the hemispherical base, 1 pound of weight was released to fall on the specimen from 10cm height. The height was increased to 60cm by a step value of 5 cm. Impact resistance of the coatings were measured by falling weight method [10].

**Hardness (Cross-Hatch test)**

In this method, the assessment of adhesion was made by the area of film detached from the substrate [11]. A 5 Sq cm\(^2\) coated paint was cut through its
thickness to the substrate by means of close parallel cuts and then another set of parallel cuts made right angles to the former. An adhesive tape was pressed over the surface of the cut film and sharply pulled off. The number of squares of film detached was counted and used as a comparative measure of the adhesion.

**Water absorption**

The weighed primer coated glass plates were immersed in water. After 24 hours shocking, they were taken out and the excess water was removed by gentle wiping with filter paper and weighed. This procedure was repeated till the identical values obtained. From the amount of water absorbed the percentage of water uptake was calculated.

**3.10. Accelerated test**

**Salt spray (fog) test**

The salt spray (fog) test [12] was carried out as per the ASTM specification B 117. Salt spray chamber has been used to simulate atmospheric marine exposure with in a defined area. The paint/primer specimens were suspended in the salt spray (fog) test chamber on horizontal rods parallel to the flow of the fog and interface between specimens and the direct impingement was avoided. The liquid used for the corrosion environment was 5% NaCl solution and clean compressed air was used for the atomization. The atomized
solution was continuously sprayed to the test chamber and the temperature of
the chamber was maintained at 35°C. Periodic examination of the specimens
was made. After 720 hours of this test, the specimens were taken out and the
corrosion spots counted with the help of a magnifying lense.

3.11. Electrochemical methods of evaluation

1. Potential –time measurements

The simplest of the entire electrochemical test, is the measurement of
the electrode potential of the painted metal as a function of immersion time
[13]. For the electrochemical measurements, 1x1 Sq. cm area of coated panels
were exposed and the remaining portion masked with bee waxes. The painted
panel was immersed in 3% NaCl solution at 35±2°C and the change in
potential of the painted metal was followed by means of electrometer with time
using saturated calomel electrode (SCE) as the reference for 6 months duration.

2. Galvanic current measurement

The painted metal can be made either anode or cathode in a galvanic
current cell by coupling it with a more cathodic or anodic metal to the painted
metal article [14]. The coated panels with one square centimeter area exposed
at the center were used for this study. Similarly an uncoated mild steel panel
with one square centimeter area exposed at the center after masking the
remaining part with bee wax was used as coupling metal. The galvanic current
between the primer coated electrode and the uncoated mild steel panel immersed in 3% NaCl was measured periodically with the help of zero resistance ammeter.

3. Potentiodynamic polarization measurement

Polarization measurements were carried out using BAS 100B electrochemical analyzer software interfaced for data acquisition and analysis. The polarization measurements were made to evaluate the corrosion resistance property of the primer/paints [15]. A 5 ml of 3% NaCl solution was taken in the electrochemical cell and 1 square centimeter exposed area of painted electrode was immersed for one day to attain a constant potential, which was used as the working electrode. A platinum electrode with an area of 1 sq. cm and saturated calomel electrode (SCE) were used as the counter and reference electrode respectively, to carry out the polarization experiments. The electrode was polarized 200 mV cathodically and 300 mV anodically from the OCP in the test medium with a scan rate of 1 mV/sec towards the anodic direction. The results were plotted as log current density against potential. These measurements were made periodically for 150 days and the loss of NaCl solution volume made up by adding distilled water during the study period.
4. Electrochemical impedance measurements

Impedance measurements were carried out with the help of PAR model 6310 EG & G instruments A.C impedance analyzer [16]. Three electrode electrochemical cell setup used for this study was the similar one that used for the polarization measurements. The impedance measurements were carried out over the frequency range of 10 mHz to 100 KHz at the open circuit potential. An A.C signal of 5 mV amplitude was superimposed over the OCP of the working electrode. These measurements were made with a regular interval for 150 days. The charge transfer resistance ($R_t$) was obtained from the Nyquist plots. The values of $R_t + R_s$ correspond to the point where the plot cuts $Z'$ axis at low frequency and $R_s$ (solution resistance) corresponds to the point where the plot cuts $Z'$ axis at high frequency. The double layer capacitance ($C_{dl}$), values were calculated from the relation $C_{dl} = \frac{1}{2 \pi f_{max} R_t}$. where, $f_{max}$ is the maximum frequency at which the imaginary part is maximum. $R_t$ is the charge transfer resistance.

3.12. Surface examination techniques

Morphological studies by SEM

The surface examination studies were carried out using scanning electron microscopy (SEM) model Hitachi S-3000, Version-1, Japan. The SEM photographs [17] of the primers before and after heat treatment were taken at 500 and 1000 time magnifications and the change in surface
morphology of these coatings were examined. The morphology of synthesized silicone, CNSL-S and IPNs was studied through SEM technique. The formation of IPNs was also confirmed through the SEM photographs. It shows the combined nature of the silicone and CNSL-S resins morphology.
References


8. ASTM Specification: D-6192


10. ASTM Specification: G-477

11. ASTM Specification: D-3359-23


