

CHAPTER - III
EXPERIMENTAL DETAILS

In this chapter, the methods of preparation of butyl titanate, epoxy and cashew nut shell liquid (CNSL) resins and paints formulated using these binders and the test methods employed to study the physical and corrosion resistant properties of the paints are described.

3.1. PREPARATION OF THE RESINS

3.1.1. Preparation of butyl titanate resin

The following chemicals are used for the preparation :

- a) Butyl titanate monomer (L.R. grade)
- b) Triethanolamine (A.R. grade)
- c) Tricresyl phosphate (A.R. grade)
- d) Chlorinated paraffin (L.R. grade)
- e) Xylene
- f) Butyl cellosolve
- g) Toluene

Method of preparation

85 gms of butyl titanate monomer, 20 gms of triethanolamine and 50 gms of xylene have been taken together in a round bottom flask and refluxed for two hours. After cooling the solution the butanol formed during the reaction

and the solvent are removed by distillation. 100 gms of titanate complex thus obtained is mixed with 10 gms of tricresyl phosphate and 5 gms of chlorinated paraffin used as plasticizers and dissolved in 100 gms of 1:2 mixture of butyl cellosolve and toluene. The solvent used are commercial grade.

3.2.1. Preparation of Cashew Nut Shell Liquid (CNSL) resin [1]

The following chemicals are used for the preparation :

- a) Cashew Nut Shell Liquid (CNSL) (Indigenous product)
- b) Formaldehyde (40% solution) (A.R. grade)
- c) Hexamine (A.R. grade)
- d) Manganese dioxide (A.R. grade)
- e) Sodium hydroxide (A.R. grade)
- f) Driers of Pb, Co and Mn metals
- g) Xylene
- h) White spirit

Method of preparation

100 gms of CNSL is heated with 3 gms of manganese dioxide in a beaker at 100-110°C, till the foam formation is completely stopped. After the liquid is cooled, the excess manganese dioxide is allowed to settle down. The liquid is transferred to a round bottom flask. It is then

added to a mixture of 5 gms of hexamine, 2 gms of sodium hydroxide in 15 gms of formaldehyde with stirring and heated to 150-160°C for 3 hours. The resin thus obtained is dissolved in 100 gms of 1:1 mixture of xylene and white spirit. 2.2 gms of 0.4% solution of lead naphthanate, 0.5 gms of 0.035% solution of manganese naphthanate, 0.4 gms of 0.025% solution of cobalt naphthanate are added as driers to accelerate the drying property of the resin.

3.1.2(a) Estimation of acid value

Titrimetric method has been employed for the estimation of acid value of the CNSL resin. Accurately 2 gms of the sample is transferred to a 500 ml Erlenmeyer flask and dissolved in 10 ml of xylene and 20 ml of neutral alcohol. It is then titrated against standardised potassium hydroxide solution using phenolphthalein as indicator. The appearance of the pink colour which persists for 30 seconds is the end point.

The calculation of acid value is done using the formula,

$$\text{Acid value} = \frac{A \times N \times 56.1}{B}$$

Where, A = Milliliters of potassium hydroxide solution

N = Normality of potassium hydroxide

B = Grams of sample used.

The acid value of the resin is found to be 9-11.

3.1.3. Preparation of epoxy resin [2]

The following chemicals are used for the preparation :

- a) Epoxy resin (epoxide value : 475 - 500)
- b) Hardener, polyamide (Amine value : 250)
- c) Methyl iso butyl ketone (MIBK)
- d) Butyl cellosolve
- e) Xylene.

The epoxy resin and hardener are supplied by the CIBA Geigy Ltd., Bombay. The solvent used for this preparation is commercial grade.

Method of preparation

66 gms of the epoxy resin is added to a round bottom flask containing 34 gms of 1:1:1 mixture of MIBK, butyl cellosolve and xylene and refluxed to dissolve the resin.

35 gms of polyamide hardener is dissolved in 15 gms of the above solvent mixture.

This coating system is two pack and so the resin and hardener are mixed at the time of application. The mixing ratio of the resin and hardener is 70:30.

3.1.4. Preparation of chlorinated rubber resin [3]

The following chemicals are used for the preparation :

- a) Chlorinated rubber - 10
- b) Chlorinated paraffin (L.R. grade)
- c) Castor oil (Commercial grade)
- d) Xylene
- e) Toluene

Chlorinated rubber-10 is supplied by Rishiroop Polymers Pvt. Ltd., Nasik, India.

Methods of preparation

60 gms of chlorinated rubber-10 is dissolved in 60 gms of xylene solvent. 24 gms of chlorinated paraffin is added to it with stirring and 8 gms of castor oil is added as plasticizers. 15 gms of toluene as solvent is added to the resin solution.

3.1.5. Elucidation of structure

Elucidation of structure of butyl titanate, CNSL and epoxy resin have been done by Infra-red spectral analysis. This spectra is taken on KBr pellets and recorded using a Perkin-Elmer spectrophotometer.

3.2. PREPARATION OF PRIMERS

The ingredients used for the preparation of the primers based on butyl titanate, CNSL and epoxy-polyamide resins are given in the table 3.1.

Zinc dust is supplied by the Metal Powder Company Ltd., Thirumangalam, Madurai, India; particle size of the paint grade zinc dust is 3 - 5 micron, manganese flake powder is supplied by Burgoyne Burbidges and Co (India), Bombay. Nickel flake powder is supplied by INCO EUROPE Ltd., U.K. the specification number of the powder is INCO NICKEL POWDER - 255. The stainless steel flake pigment is supplied by United State Bronze Powder Incorporated, Flemington, the grade of the powder is 316 stainless steel grade x. Extender pigment Alumina - Titania is supplied by the Metallizing Equipments (P) Ltd., Jodhpur, India. The solvents used are commercial grade.

3.2.1. Method of preparation

Zinc dust and Alumina - Titania are taken in an attritor jar (Szegvari Attritor system, supplied by Union Process, Ohio, U.S.A) and mixed with butyl titanate resin. Steel balls are added into it and the ingredients are ground and mixed well in the attritor for 30 minutes to get the Hegman Gauge value of five. Primer with various pigment weight percentage ranging from 10% to 95% have

Table 3.1

The ingredients used for the preparation of primers

Binder	Pigments	Solvents
(1) Butyl titanate resin	Zinc dust Manganese flake Nickel flake	Toluene Butyl cellosolve
(2) Cashew Nut Shell Liquid (CNSL) resin	316 Stainless steel flake Alumina - Titania (extender pigment)	Xylene White spirit
(3) Epoxy-polyamide resin		Xylene Butyl cellosolve Methyl Isobutyl ketone

been prepared by taking required weight of pigments and binder required for that pigment weight percentage.

Similarly the other metallic powder pigments such as manganese, nickel and stainless steel flakes are used for the preparation of primers with various pigment weight percentage ranging from 10% to 95%.

In this way the primer based on CNSL and epoxy-polyamide resins are prepared. A typical primer formulation for 60% pigment weight percentage of zinc in the binders are given in table 3.2 and these primers' physical properties are given in table 3.3.

3.2.2. Chlorinated rubber - finish coat

Two types of finish coat are prepared. One based on TiO_2 pigment and the other based on micaceous iron oxide pigment. For this, the following ingredients are used.

- a) Chlorinated rubber - 10
- b) Chlorinated paraffin
- c) Castor oil
- d) Micaceous iron oxide (MIO)
- e) Titanium dioxide (TiO_2)
- f) Barytes
- g) Zinc oxide

Table 3.2
 Typical primer formulation for 60% pigment weight
 percentage of zinc in different binders

Binders			Pigments		Sol- vents gms
Butyl Titanate (50% solu- tion) gms	CNSL resin (50% solu- tion) gms	Epoxy polyamide (66% solu- tion) gms	Zinc dust gms	Alumina Titania gms	
80	-	-	160	4	60
-	80	-	160	4	60
-	-	resin=33.3 hardener=15	120	3	45

Table 3.3
Liquid paint properties of 60% zinc rich primers
in different binders

No.	Properties	Primers based on		
		Butyl titanate	CNSL	epoxy polyamide
1.	Specific gravity	1.89	1.75	2.04
2.	Viscosity (B4 Ford Cup) (sec)	80	120	132
3.	Dry film thickness per coat (μm)	40 \pm 5	40 \pm 5	45 \pm 5

- h) Xylene
- i) Toluene

Methods of preparation

Titanium dioxide, barytes and zinc oxide are taken in the jar of attritor and mixed with chlorinated rubber resin solution. Steel balls are added into it and the attritor is run for 30 minutes till the Hegmann Gauge value of 7 is reached.

Similarly MIO pigmented finish coat is prepared in the same manner. Typical paint formulations of these two finish coat with 25% PVC and 36% PVC are given below [4].

MIO based (25% PVC) finish coat

Chlorinated rubber - 10 (50% solution)	: 145 gms
Chlorinated paraffin	: 28.5 gms
Castor oil	: 9 gms
MIO	: 140 gms
Barytes	: 31.5 gms
Zinc oxide	: 3.5 gms
Xylene:Toluene (1:4 mixture)	: 125 gms
Specific gravity	: 1.57
Viscosity (B4 Ford cup)	: 220 sec
Thickness per coat (DFT)	: 40 ± 5 µm

TiO₂ based (36% PVC) finish coat

Chlorinated rubber - 10 (50% solution)	: 145 gms
Chlorinated paraffin	: 28.5 gms
Castor oil	: 9 gms
Titanium dioxide	: 151 gms
Barytes	: 115 gms
Zinc oxide	: 3.5 gms
Xylene:Toluene (1:4 mixture)	: 125 gms
Specific gravity	: 1.80
Viscosity (B4 Ford cup)	: 280 sec
Thickness per coat (DFT)	: 45 ± 5 µm

3.3. PREPARATION OF PAINTED SPECIMENS

Mild steel panels of various sizes (2.5 x 2.5 cms, 5 x 7.5 cms, 10 x 15 cms, 10 x 10 cms) have been degreased with trichloroethylene and then sand blasted to remove rust and mill scale from the surface of the iron. The primers (pigment weight percentage 10% to 95%) have been applied over mild steel specimens by brush, in such a manner to build up the dry film thickness of the primer coat to 80 ± 5 µm. B. Del Amo et.al's [5] studies indicate that the zinc rich primer with 80 - 90 µm thickness offered best protection to M.S. substrates. The painted panels are allowed to dry for about 15 days before carrying out the actual tests.

Best primer is selected by the potentiodynamic polarisation method, this is top coated with the two types of chlorinated rubber paint and allowed to dry for further 15 days before carrying out the tests. The thickness of the top coat should be $80 \pm 5 \mu\text{m}$. For the electrochemical measurements the coated panels of $1 \times 1 \text{ cm}^2$ at the centre were exposed after masking the remaining portion with bee waxes.

3.4. TESTING OF LIQUID PAINTS

The liquid paint is standardised by the following tests; specific gravity, fineness of grind and dry film thickness and viscosity.

3.4.1. Specific gravity

The specific gravity of the liquid paint is determined by means of weight per gallon cup [6]. The cup has a known volume. The difference in weight of the cup filled with paint and the empty cup gives the weight of the known volume of paint. The ratio of the weight of the known volume of the paint to that of the known volume of water is the specific gravity of the paint.

3.4.2. Viscosity

Viscosity measures the fluidity of the paint. Tests for viscosity are quantitative but the method of measure-

ment 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 is filled at a standard temperature and the time required for the paint to flow completely through the orifice is measured. The Ford cup is widely used for viscosity determination [7]. The Ford cup No.B4 is used in the present study.

3.4.3. Fineness of grind

The test is based on the use of Hegman Gage [8]. It is employed as a manufacturing control test to ascertain whether the pigment is dispersed properly and uniformly into the resin or not. The paint paste is placed into the grooves in a carefully machined steel block and a scraper is 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 is taken at the point at which the specks (large particle) in the film appeared to predominate.

3.4.4. Dry film thickness

Many methods are used for dry film thickness measurements. In the present work [9], instrument based on magnetic function is used. Magnetic thickness gauges are

based on the principle that attractive force between a permanent magnet and a magnetic material is inversely proportional to the distance between them. Elcometer is based on the above principle and it is used for measuring the thickness of the coating.

3.5. DETERMINATION OF PHYSICAL PROPERTIES OF PAINTED METAL

3.5.1. Abrasion test (Taber Abraser)

In this test [10], the painted specimens of 10x10 cm square is mounted on a turn table that rotates at 100 rpm. Under a pair of weighed abrading wheels of closely controlled composition in such a manner as to cause side slip between the abrading wheels and surface of the test specimen. Abrasion resistance of coatings is generally expressed in terms of weight loss per 1000 revolution under a 1000 gms load. Abrasion resistance of the primer coated panels were determined.

3.5.2. Conical mandrel test

This method gives an idea of adhesion and extensibility of coatings when applied to flat sheet metal of uniform surface texture [11]. In this test, the primer is coated on thin (30 - 32 gauge) cold rolled carbon steel strip of the dimensions of 10 cms width, with a maximum length of 19 cm. The test specimen is kept up right on its length wise position between the mandrel and draw

bar (with the finish side towards the draw bar). It is then tightly clamped in position in such a way that end of the coated specimens adjacent to the narrow end part of the conical mandrel is almost touching the side of the draw bar level frame. The lever is moved through about 180 degree at uniform velocity to bend the specimen approximately in about 15 seconds. The bend surface of the specimen is examined for any damage to the film. The percentage of elongation is calculated by using the formula, $(t / 2r + t) \times 100$, where 't' is the thickness of the panel and 'r' is the radius of the mandrel at which the coating passes the test.

3.5.3. Impact resistance test

This was measured by falling weight method [12]. In this test, a tub of weight 2 pound is allowed to fall

film and sharply pulled off. The number of squares of film detached is counted and used as a comparative measure of the adhesion.

3.5.5. Water absorption

Primer coated weighed glass plates are immersed in a water bath. After 24 hours, it is taken out and the excess water is removed by filter paper and then weighed. This procedure is repeated till the identical values are obtained. From the amount of water absorbed the percentage of water uptake is calculated.

3.6. ACCELERATED TEST

(i) Salt spray (fog) test [14]

Salt spray chamber has been used to simulate atmospheric marine exposure. The specimens are suspended in the salt spray (fog) test chamber from horizontal rods parallel to the flow of the fog and the interface between specimens and the direct impingement is avoided. The solution used is 5% sodium chloride. Clean compressed air is used for atomisation. The atomised solution is continuously supplied to the test chamber and the temperature of the chamber is maintained at 30 - 35°C. Periodic examination of the specimens were made. After 720 hours of this test, the specimens are taken out and the corrosion spots are counted with the help of a magnifying lense.

3.7. ELECTROCHEMICAL METHODS OF EVALUATION

3.7.1. Potential - time measurements [15]

The simplest of all the electrochemical test is the measurements of the electrode potential of the painted metal as a function of immersion time. The painted panel was immersed in 3% sodium chloride solution at $35 \pm 2^\circ\text{C}$ and the potential of the painted metal was followed by means of electrometer with time using Saturated Calomel Electrode (SCE) for 6 months duration.

3.7.2. Galvanic current measurement [16]

The painted metal can be made either anode or cathode in a galvanic current cell by coupling it with a more anodic or cathodic metal. The coated panels with one square centimeter area exposed at the centre were used for this study. Similarly an uncoated mild steel panel with one square centimeter area exposed at the centre 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% sodium chloride was measured periodically with the help of zero resistance ammeter.

3.7.3. Polarisation studies : Tafel extrapolation method

Figure 3.1 shows the set up used for potentiodynamic polarisation. The measurements are made with the

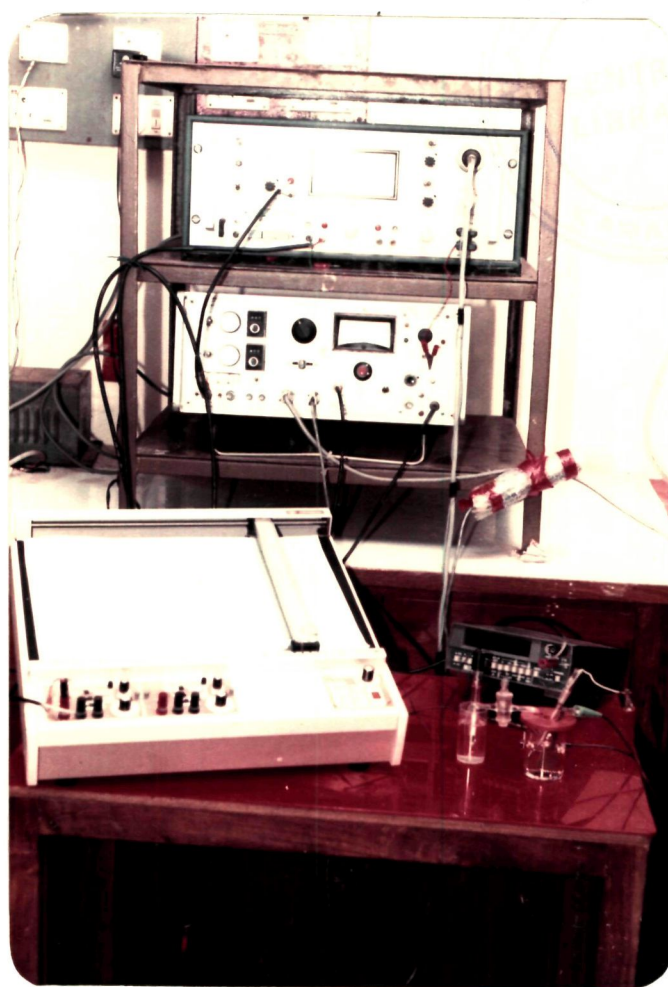


Fig.3.1: Set-up for polarisation studies.

PARC, Corrosion measurement system. The potential of the electrode is varied by the universal programmer (Model 175 PARC, USA) through the potentiostat (Model 173 PARC, USA). The potential Vs log current plots are made using the X-Y recorder (Model RE 0074 PARC, USA).

50 ccs of 3% sodium chloride solution was taken in the electrochemical cell. One square centimeter exposed painted electrode was then introduced and held for one day to attain a constant potential, which is used as working electrode, a platinum electrode of 10 cm^2 area as counter and a SCE as reference electrode to carry out the polarisation experiment. At the beginning of the polarisation study, the electrode was kept at 200 mV cathodic to its open circuit potential for 10 minutes. Then the potential is scanned at a rate of 1 mV/sec towards the anodic direction. The results are plotted on the X-Y recorder as log current density Vs over potential. These measurements are made periodically. The loss occurred in the electrolyte is made up with triple distilled water.

The values of corrosion current are obtained by extrapolation of the plots of over potential Vs log current density of the linear portion to the corrosion potential.

3.7.4. Impedance studies

Impedance measurements are carried out with the help of PAR model 368-1 A.C. Impedance system. The set up is shown in the Fig.3.2. The electrochemical cell used for this study is the similar one used for the polarisation measurements. Impedance measurements are carried out at the open circuit potential. An a.c. signal of 10 mV amplitude is applied to the working electrode. The frequency is varied from 100 KHz to 0.1 Hz. These measurements are made periodically.

The charge transfer resistance (R_t) is obtained from the Nyquists 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 the Z' axis at high frequency. The difference gives the R_t value. The capacitance (C_{dl}), values are obtained from the Nyquist plots from the following 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.



Fig.3.2: Set-up for impedance studies

3.8. PHYSICAL METHODS

(i) Surface morphology by SEM method

The SEM studies are carried out by using SEM of JEOL, JSM 35 CF, Japan. The SEM photograph of the primers before and after 60 days immersion in 3% sodium chloride solution are taken and the surface morphology of these coatings are studied at 1000 time magnification.

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