CHAPTER – 3

EXPERIMENTAL DETAILS

3.1 Introduction

This episode is absolutely committed to detailed clarification of experimental works. There is a method of preparation of epoxy polyol from a modified epoxy resin. Two pack polyurethane coatings are prepared from a prepared epoxy polyol and a polyisocyanates. Polyisocyanates which includes Aliphatic (HexamethyleneDiisocyanate-HDI), Aromatic (TolueneDiisocyanate-TDI) and Cycloaliphatic (Isophorne Diisocyanate – IPDI) isocyanates. The coatings industry needs analytical methods that allow the assessment of coating characteristics before and after their exposure to a wide variety of service conditions. This assessment may help to predict the service lifetime of a coating material or to verify when it meets requirements for a particular application and/or commercialization \(^{(1)}\).

An analytical method FT IR (Fourier-Transform Infra-Red Spectroscopy) is employed for the conformation of the presence of functional groups. For changing the stockiometry of the hydroxyl groups (-OH Group) in the epoxy polyol resin and isocyanate groups (N=C=O groups) in the hardener by keeping the ratio of Epoxy Polyol consistent and changing the ratio of isocyanate from 0.80 to 1.20, a total of seven types of experiments were conducted.
All these experiments were based on the solid contents of the hydroxyl equivalent weights of epoxy polyol and NCO equivalent weight of polyisocyanates. After the film coated with the prepared polyurethane coatings, the various physical properties and mechanical properties are measured and compared. The Electrochemical Impedance Spectroscopy (EIS) is used for the characterization of the coated film.

3.2 Preparation of Hydroxyl terminated epoxy resin

The following chemicals are used for the preparation of epoxy polyol resin,

1. Epoxy resin (Bisphenol-A type – Epoxide equivalent weight-450-550),
2. Diethanolamine,
3. Xylene,

A homogeneous solution of epoxy resin GT 6071-X-75 from Ciba gaey, Mumbai, Diethanol amine from Spectrum Baroda, Xylene, cellosolve acetate from E-Merck has been selected for the present investigation. Cold rolled mild steel panels were used for this study. A three necked flask (500 ml), equipped with a mechanical stirrer, condenser and a thermometer was placed in a water bath.
Epoxy resin GT 6071-X75-(266.67G), Cellosolve acetate(40 G), Xylene (93.33 G), Diethanolamine(42 G) were placed in a three necked flask and stir well at room temperature for 5 min. Gradually the temperature increases from 60°C to 70°C, active hydrogen of diethanolamine to open up the oxirane ring of epoxy resin to generate secondary alcohol. The reaction mixture heated upto 120°C and reflexes for 6 Hrs with stirring and secondary hydroxyl terminated epoxy polyol are prepared.

3.3 Test methods

3.3.1 Test method for hydroxyl value for the resin sample

Definition

This test method determines the number of hydroxyl groups present which can be acetylated under the condition of test. Hydroxyl value is defined as the number of milligrams of potassium hydroxide necessary to neutralize the acetic acid which combines on the acetylation of one gram of sample.

Procedure:

Weigh 5 g of sample of the resin in Erlen meyer flask. Pipette out accurately 5 ml of Pyridine-Acetic anhydride reagent (3:1 volume ratio) into a flask contains the sample for acetylation. The contents are thoroughly mixed by gentle swirling. Pipette out 5 ml Pyridine-Acetic anhydride reagent into an empty flask for the reagent blank. Keep the flask on a stream bath under reflex condensers and heat it for one Hour. (Add a porcelain pieces to prevent bumbing).
Add 10 of water through condenser into the flask and heated on the steam bath for 10 min. with reflex condenser attached. Allow the flask to cool up to a room temperature with a condenser attached. Add about half of 25 ml of neutralized butanol, through the condenser into the flask. Remove the condenser and use the remaining butanol to wash down the sides of the flask. Add 1 ml of phenolphthalein indicator solution and titrate the contents in the flask to a faint pink end point with 0.5N alcoholic KOH solution.

The hydroxyl value is calculated as follows,

\[
\text{Hydroxyl value} = \frac{(B-S) \times N \times 56.10}{W} + \text{Acid value}
\]

Where,

B = ml of KOH solution required for the reagent blank,

S = ml of KOH solution required for the titration of the acetylated sample,

N = Normality of alcoholic KOH solution,

W = Weight of sample used for the acetylation.
3.3.2 Test method for acid value of organic coating materials

Scope:

This test method covers the measurement of the free acidity present in the nonvolatile portion of varnishes, oils, certain resins and paint vehicles by the reaction with standard alkali solution.

Procedure:

Weigh about 20 g of the resin sample accurately into two conical flasks. Add 50 ml of the mixture of isopropyl alcohol and toluene to dissolve the resin by swirling the flask. Add 3-4 drops of phenolphthalein indicator solution and titrate the mixture against the standard KOH until the permanent pink color is appeared. Acid value is calculated from the following equation,

\[
\text{Acid value} = \frac{\text{ML of KOH Solution} \times \text{Normality of KOH} \times 56.1}{\text{Weight of the sample (Solids) in Grams}}
\]
3.3.3 Test method for isocyanate groups in urethane materials or prepolymer

Scope:
This test method covers the determination of the isocyanate group (NCO) content of a urethane intermediate of prepolymer.

Procedure:
Weigh about 3 to 3.5 g of the sample accurately into a 250 ml Erlenmeyer flask. Add 20 ml of dry toluene followed by 25 ml of Dibutyl amine solution (diluted 260G of dry Dibutyl amine to one liter with dry toluene). Swirl the flask during the addition of the Dibutyl amine solution. Wash the sides of the flask with 5 ml of dry toluene. Stopper the flask and allow it to stand at room temperature for 15 min. add 110 ml of isopropanol from a graduated cylinder and 0.4 ml of bromocresol green indicator from a graduated 1 ml pipette. Titrate it then against 1 N hydrochloric acid solution while swirling the flask contents to effect a rapid mixing. Note the end point by disappearance of the blue color and the reappearance of a yellow color which persists for at least 15 sec. run a blank under identical condition omitting the sample.

The NCO content calculated using the following formula,

\[
\text{NCO} \% = \frac{(B-V) \times N \times 0.042}{W} \times 100
\]

Where,
- \(B\) = Volume of HCl for titration of the blank in ml,
- \(V\) = Volume of HCl for titration of the specimen in ml,
- \(N\) = Normality of HCl,
- 0.042 = Milliequivalent weight of NCO,
- \(W\) = Grams of specimen weight.
3.4. Characterization of binders

The modern technology mainly focuses on the development of reliable high performance coating materials, having superior mechanical properties ideally suitable for adverse environment conditions\(^{(5)}\). Hence, the FT IR analysis is used to find out the presence of functional groups in the binders and its products.

3.4.1 Fourier-Transform Infra –Red Spectroscopy

The proposed structures for the epoxy polyol, HexamethyleneDiisocyanate (HDI), TolueneDiisocyanate (TDI) and Isophorne Diisocyanate (IPDI) have been done by Fourier-Transform Infra –Red Spectroscopy. The composition of epoxy polyol and its respective hardener like HDI, TDI, IPDI to form the polyurethane product, for air drying and stoving applications have been done by Fourier-Transform Infra –Red Spectroscopy.

3.5 Evaluation of the coating properties

3.5.1.0 Wet film properties

The evaluation of performances of coated films is done by subjecting the coated panels 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 drying time, hardness, flexibility, impact on loads, adhesion of the film to the substrate and gellation time.
In addition to physical properties, the performances of the coated system in corrosive and chemical environments are also studied through the electrochemical accelerating test methods.

3.5.1.1 Specific gravity

The specific gravity of the liquid paints is determined by means of weight per gallon cup\(^6\). The volume of the 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 the water is the specific gravity of the paint.

3.5.1.2 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 properties of the paint. The test instrument consists of a cup with an orifice at the bottom called ford cup which is widely used for viscosity determination\(^7\). Both the cup and orifice are of controlled volume, diameter and length. The cup is filled with the paint at a standard temperature and the time required for the paint to flow completely through the orifice is measured. Here We are using the ford cup number B4 for our studies.
3.5.1.3 Gellation time

Gellation time is the most important test for the applicators. Adjust the base and hardener at a temperature of 20°C ± 1°C. Mix the base and hardener in the ratio stated on the formula sheet to a total volume of 200 ml in a 250 ml can. Note the time. Place the can in the insulating case immediately after mixing of the two components. Note the time when the mixed components changes from liquid to solid phase. The gel time is recorded as the time elapsed from the mixing of the two components to the change from liquid to solid phase (8).

3.5.2.0 Dry film properties

3.5.2.1 Dry film thickness

Many methods are used to find out the dry film thickness. In the present work, instrument based on magnetic function is used (9). Magnetic thickness gauge is used for finding the thickness of the coatings on the metallic surfaces for more accuracy. If the attractive force between a permanent magnet in the gauge and the coated specimen is high, the distance between them is low.
3.5.2.2 Gloss measurement

The degree to which a painted surface possesses the property of reflecting light in a mirror-like manner (specular reflection). The extent to which this property is developed depends mainly on the composition of the paint, surfaces ranging from dead flat to full gloss being obtainable. Calibrate the gloss meter (Figure 3.1) at the start and completion of every period of operation. To calibrate, adjust the instrument to read correctly the gloss of a standard, primary or secondary, whose assigned value is approximately that of the glossiest specimens to be measured. Measure at least three portions of the surface of the specimen to obtain an indication of uniformity. Report the average of gloss readings. Gloss level measured in two angles namely 20° and 60° respectively.

3.5.2.3.0 Hardness testing

3.5.2.3.1 Scratch hardness

The resistance to scratching under a specified load of a dried film of the paint is tested. The test conducted by using the scratch hardness apparatus (Figure 3.2) (11). Place the panel in the test device and clamp test panel, with the coating uppermost, to the sliding panel of the apparatus with the longer side of the sliding panel parallel to the direction in which the scratch will be made. Fix the needle in the chuck so that the position of operation is normal to the coating. Place weights on the holder above the needle to obtain the specified load. Start the motor of the apparatus and allow the scratch to be made on the coating. Remove the panel and inspect the scratch to see if the coating has been penetrated to the substrate (which is indicated by the deflection on voltmeter). Care must be taken on needle and fresh portion on the test panel for repeated tests.
Figure 3.1 - Gloss meter

Figure 3.2 - Scratch hardness apparatus
3.5.2.3.2 Cross hatch testing

In this method, the assessment of adhesion is made by the area of film detached from the substrate\(^{12}\). The test conducted by using the cross hatch tester (Figure 3.3). 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 stuck over the pattern is removed sharply and the adhesion of the film is assessed from the amount of the coating removed.

3.5.2.3.3 Pencil hardness testing\(^{13}\)

Pencils are prepared such that approximately \(\frac{1}{4}\) inch of lead is exposed from the wood. The lead is cylindrical in shape with the end squared off with a fine grade abrasive paper. In the test, the pencil lead is pushed firmly along the surface of the paint film at 90° to the surface, using the maximum force i.e. just less than sufficient to break off the lead for a distance of 6 mm. The hardness of the film is equated with that of the pencil that just fails to damage the coating. A good quality set of pencil ranging from 6B – 9H should be used.
Figure 3.3 - Cross hatch tester

Figure 3.4 - Impact tester
3.5.2.3.4 Flexibility Test-impact tester (Falling weight method)\textsuperscript{(14)}

This test is devised to determine the degree to which paint on a metal surface can accommodate rapid deformation. The test conducted by using the Impact tester (Figure 3.4). A number of tests have been exists 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 impringe without damage to the coating is noted. The painted panels are placed on a hemispherical base; 1 pound of weight was released to fall on the specimen from 10 cm height. The height is increased to 60 cm by a step value of 5 cm. impact resistance of the coatings are measured by falling weight method.

3.5.2.3.5 Flexibility Test-Conical mandrel test

Conical mandrel bend test method gives an idea of adhesion and extensibility of coatings when applied to flat sheet metal to uniform surface texture \textsuperscript{(15)}. The test specimen is kept up the right on its lengthwise position between the mandrel and draw bar (with the finish side towards the draw bar). It is 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 is moved through about 180 degrees at uniform velocity to bend specimen approximately in about 15 seconds. The bend surface of the specimen is examined for any damage to the film.

3.5.2.4.0 Resistance test

3.5.2.4.1 Chemical resistance test\(^{(16)}\)

The coated panels are immersed to a depth of 4” in a tank of the appropriate liquid, whilst being maintained in a near vertical position. All of these tests are carried out at an ambient temperature. The panels are removed for examination till the coating fails to pass the test. Blistering, hardness, adhesion and discoloration of the coated film are examined. After taking out from the immersion tank, the panels are kept for five minutes for recovery in the normal conditions. In Chemical resistance test, acetic acid, sodium chloride and hydrochloric acid are being used at 10% solution in demonized water.

3.5.2.4.2 Solvent resistance test

In solvent resistance test, Xylene, Methyl Ethyl Ketone(MEK) drops are placed on the tested panel with covered watch glass. These panels are examined for every five minutes.
3.5.3.0 Accelerated test

3.5.3.1 Salt spray (fog) test

The salt spray (fog) test (Figure 3.5)\(^{(17)}\) is 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 coated specimen are 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 is avoided. The liquid used for the corrosion environment is 5% NaCl solution and clean compressed air is used for the atomization. The atomized solution is continuously sprayed to the test chamber and the temperature of the chamber is maintained at normal atmospheric conditions. Periodic examination of the specimen is made by using the help of magnifying lens.

3.5.3.2 Electrochemical methods of evaluation

Electro chemical impedance spectroscopy (EIS) measurements: An insulating material like paints are applied on a metallic substrate and it is immersed in an aggressive electrolyte such as water, NaCl etc. The noticeable changes are observed as the electrolytes penetrated through the bulk of the coating. The durability of the materials depends on the coating adhesion, humidity, scratch and chemicals etc. all the polymers are permeable to corrosive species like oxygen and water\(^{(18)}\) and the adhesion is lost or decreased by the absorption of electrolytes by coatings\(^{(19)}\) resulting in the corrosive attack of the underlying metal and the consequent changes in the resistance and capacitance values which can be followed through EIS(Figure 3.6)\(^{(20)}\).
Figure 3.5 - Salt spray chamber

Figure 3.6 - Electrochemical Impedance Spectroscopy (EIS)
EIS provides more detailed information for comparison on the long term behavior of organic coatings. EIS having a small signal perturbation is proved to be a powerful tool for detecting the performance of coatings \(^{(21)}\). Recently, a number of authors have published on the characterization of coatings through EIS \(^{(22,23)}\). An AC voltage of small amplitude is applied across the coating film, and the resulting impedance to the a.c. current is measured. Measurements are made over wide frequency ranges.

The impedance spectrum of the coating is measured initially and then again at varied intervals during the exposure to a real or simulated aggressive environment. The schematic representation of equivalent circuit presented in the Following Figure - 3.7. Where, \(R_s\) - Resistance of the electrolyte (or) solution resistance, \(R_p\) – Pore resistance due to the electrolyte penetration, \(C_c\)-coating capacitance, \(C_{dl}\) – Electrical double layer capacitance at the metal / solution interface, \(R_t\) – metal charge transfer resistance, \(Z_w\) – Diffusional impedance, normally called Warburg impedance.

The changes in the impedance spectrum with time are related to coating deterioration and disbondment. Attempts have also been made to correlate the electrode impedance with salt-spray \(^{(24)}\) and open circuit electrode potential of the coatings. The impedance spectra can be interpreted through the general model of equivalent electrical circuit with equivcurt software developed by Boukamp \(^{(25)}\). The impedance plots of Nyquist and bode plots are shown in Figure-3. 8 & 3.9.
Figure – 3.7 – Schematic diagrams of the equivalent circuit for coated panels

Figure – 3.8–Schematic representation of impedance – Nyquist plot

Figure – 3.9 – Schematic representation of impedance – Bode plot
In Electrochemical impedance analysis, three different types of plots are commonly used: Nyquist plots (Complex plane, Showing Z'' versus Z') and two different types of bode plots, impedance magnitude versus log frequency, Phase angle versus log frequency (26). The charge transfer resistance (R_t) is obtained (27,28) from the impedance plots, which will give the resistance behavior of the coating. In the Nyquist plot, the value of R_s + R_t correspond to the point where the plot cuts the Z' axis at the low frequency end and R_s correspond to the point where the plot cuts the Z' axis at high frequency region. The difference between the two intercepts gives the R_t value. Then the double layer capacitance, C_{dl} value is obtained by using the following equation,

\[
C_{dl} = \frac{1}{2\pi f_{max} R_t}
\]

Where, \( f_{max} \) – the frequency at which the imaginary part Z'' is maximum, \( R_t \) – charge transfer resistance.

In bode plot, the double layer capacitance C_{dl} can be calculated by extrapolating the line to the log Z axis at \( \omega = 1 \). (log \( \omega = 0, f=0.16\text{Hz(or) }\frac{1}{2} \pi \text{ Hz})

At this frequency, log Z = -log C_{dl} for \( \omega = 1 \), hence,

\[
C_{dl} = \frac{1}{Z}
\]

Where, \( \omega = 2\pi f \) (or) 1
The capacitance values obtained from the plots give an idea about the amount of water absorbed by the coated film. From the capacitance value, some other parameters such as volume percentage of water absorption\(^{(27)}\), relative permittivity and dielectric constant of the coating are calculated.

Estimation of the volume fraction of water\(^{(28)}\) in organic coatings is often made by EIS and according to Brasher-Kingsbury equation\(^{(29)}\).

\[
\log \left( \frac{C_t}{C_0} \right) = \frac{X_v}{100} \log 80
\]

Where, \(X_v\) - volume % of absorbed water, \(C_t\) - Capacitance at time ‘t’, \(C_0\) - Capacitance at zero time, 80 - Constant, the permittivity of the absorbed water.

The dielectric constant can be calculated from the film thickness, coating capacitance and dimension of the sample area by using the equation\(^{(30)}\).

\[
\epsilon_r = \frac{C d}{\epsilon_o A}
\]

Where, \(\epsilon_r\) = Dielectric constant of the coating, \(C\) = Capacitance of the coating, \(d\) = Thickness of the coating (in cm), \(\epsilon_o\) = constant, permittivity of vacuum \([8.87 \times 10^{-14} \text{ F cm}^{-1}]\), \(A\) = Surface area of the coating exposed to the electrolyte (in Sq.cm)
An impedance measurements were carried out with the help of PAR model 6310 EG & G instruments A.C. impedance analyzer was used at a frequency range from 10mHz to 100 KHz. Electrochemical cell used for the study consisted of a coated mild steel panel as the working electrode, a platinum foil as the counter electrode, a saturated calomel electrode as the reference electrode and 3% NaCl solution as the electrolyte. Impedance measurements were carried out at different duration ranging from initial, one day, 10, 20, 30, 40, 50 and 60 days. Values of charge transfer resistance ($R_t$) and the double layer capacitance ($C_{dl}$) evaluated from bode plots for different duration for both coatings reported.
REFERENCES


4. Test method for isocyanate groups in urethane materials or prepolymer—ASTM - D2572-91


6. Gardner,Sward,Paint testing manual (1972) PP 166

7. ASTM Specification – D-1200


10. IS 101- Testing of paints – Part 4 – Optical test Section 4-Gloss
11. IS 101- Testing of paints–Part 5 Mechanical test on paint films–Section 1–Hardness test

12. ASTM Specification: D-3359-23

   PP 480

14. ASTM Specification: G-477

15. British specification: 3900

16. IS 101- Testing of paints – Part 7 – Environment test on paint films, Section 2  
   Resistance to liquids

17. ASTM Specification: B-117


   Ny: Marcel Dekker (1987)


