Study of Epoxy – Isocyanate Coating System for High Performance Application in Chemical Industries

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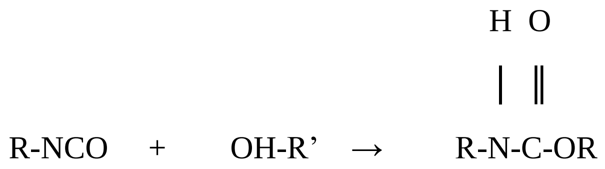
Abstract

The versatility of epoxy resins has been long exploited in the paint industry to give various applications to fulfil the growing demand for industrial maintenance coatings for its corrosion protection and high chemical resistance. Combined to this fact is also the attractive market segment for polyurethane coatings for its excellent durability and high abrasion resistance. In view of the above stated facts, a paint system combining the above two resins was chosen. The combined properties of epoxy and polyurethane are expected to have the advantage of both the resins and perform like a high-performance paint system. The paint system was found to have the exterior durability of polyurethane and better chemical resistance of epoxy resins which is an ideal combination for protection of equipment and structures in chemical industries.

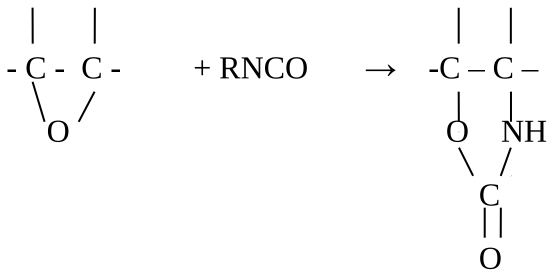
Key words*: Polyurethane coating, Epoxy coating, Polyamide, Toluidine Di-diisocyanate.*

Introduction

Epoxy resins are one of the important classes of synthetic resins available to manufacture industrial maintenance coatings. The broad interest in epoxy resins originates from the extreme wide variety of chemical resistance material that can be used for the coating. Epoxy resins from bis-phenol A and epichlorohydrine constitute the most useful resins. The outstanding performance characteristics of these resins are impacted by the bis-phenol A moiety (toughness, rigidity, and low temperature performance), the ether linkage (chemical resistance) the hydroxyl group and epoxy group (adhesive property and reactivity with a wide variety of chemical curing agents) [1] The epoxy resin can be characterised by the presence of one or more 1, 2 epoxy group per molecule. This group lie within the body of molecule but is usually terminal. The main reactions arising from epoxy resins are polyaddition resulting from reaction with compounds containing liable hydrogen atoms such as polyamines, polyacids, polyphenols etc. The use of isocyanate to cure epoxy group results in the formation of polyurethane [2]. As the isocyanate reacts primarily with the hydroxyl group, the higher molecular weight solid resins (in which the hydroxyl group predominates) are used in isocyanate cured compositions.



Film forming compositions based on this approach are cross-linked via the urethane linkages formed by the isocyanate/ hydroxyl reaction. The higher molecular weight solid resins (in the 2000 – 4000 WPE range) have been found useful in these systems due to their hydroxyl functionality. Then the simultaneous reaction between epoxide rings with isocyanate groups to form heterocyclic oxazolidone rings [3] and this general curing reaction is given below



The polyurethane and epoxy resins are joined both by physical penetration of the chain (entanglement) and the chemical binding which has a significant influence on the properties of the product. The ambient cure two component paint involving the reaction of epoxy hardener with isocyanate system expected to produce high performance coating for a variety of application including underground pipelines, structures and equipment in chemical industries [4]. The present study is to prepare a coating system combining polymeric toluidine diisocyanate with high molecular weight epoxy resins in the stoichiometric ratio of 1:1 (OH/NCO ratio) based on the solid content of hydroxyl equivalent weight of epoxy and NCO equivalent weight of TDI to get a pot life of eight hours. The test solution were thoroughly mixed and applied on mild steel panel. The films were allowed to cure at ambient conditions (Room temperature at 30^0 C and relative humidity of approximately 50-60%). The present study is to prepare a coating system combining polymeric toluidine diisocyanate with high molecular weight epoxy resins in the stoichiometric ratio to get a pot life of eight hours. The mixed coating were applied on mild steel panel and their physical, mechanical, durability & corrosion protection properties were tested and compared with conventional epoxy polyamide system.

2 Experimental

2.1 Materials

The raw materials 1) Epoxy resin (Epoxy Equivalent weight 2000-3000) and 2) Epoxy resin (Epoxy equivalent 450-500), Polymeric Toluidine Diisocyanate (TDI) were procured from M/s Resins & Plastics Ltd., Mumbai, M/s Synthetic Polymers Ltd Mumbai and Polyamide resin was obtained from M/s Ciba Atul Industries, Mumbai.

Table 1 Epoxy Resin Specification

Sample	Specific gravity at 25^0 C	Epoxide equivalent	Viscosity (poise)	Non-Volatile Content
Epoxy resin (A)	1.1 - 1.2	2000-3000	65 (40% solution in carbitol at 30^0 C)	60
Epoxy resin (B)	1.08 – 1.10	450-500	60 at 30^0 C	75

Table 2 Specification of Toluidine Diisocyanate

Sample	% NVM Content	Equivalent weight	Viscosity at 25^0C	Monomeric diisocyanate
Polymeric Toluidine Diisocyanate	13.5	32.3	15 poise	Less than 0.5

Table 3 Specification of Polyamide solution

Sample	Colour on Gardner Scale	Amine value (mg KOH per gram)	Viscosity
Polyamide Resin	11	290-320	80-120 poise (40^0 C)

2.2 Manufacture of Epoxy Isocyanate Paint System

The solid epoxy resin (A) is ground into fine powder and made into solution with the solvent in a laboratory high speed stirrer. In the two-pack epoxy isocyanate systems the epoxy resin solution (A) and the isocyanate hardener were mixed in the stoichiometric proportion and similarly in epoxy polyamide system, the liquid epoxy resin (B) and polyamide hardener were mixed in the required weight percentage [5] and these samples were kept for fifteen minutes for maturation before they were applied on mild steel panels for further study.

2.3 Method for characterisation of film properties

Both the coating systems were evaluated for their mechanical properties such as scratch hardness, adhesion and flexibility, chemical resistance properties and corrosion resistance properties.

2.3.1 Determination of mechanical properties

Hardness: Hardness is the resistance of material to indentation of scratching. The most widely used hardness test for coatings is scratch hardness. It was measured by using scratch hardness tester. The panels were loaded with different weights until a clear scratch showing the bare metal surface was seen.

Adhesion: Adhesion was determined by using crosscut hatch adhesion tester on the paint film on mild steel panel. In this test a die with number of close set parallel blades were pressed in to the film in both the direction perpendicular to each other to give a pattern of squares. A strip of self-adhesive tape was placed over the pattern and firmly pressed with fingertip. The taps is then removed sharply and the adhesion of the film is assessed from the amount of coating removed

Flexibility: Flexibility of coating films was determined by bending the panels. Tin strips of specified size were prepared and the paints applied. The panel was air dried for 48 hours. The strip was then placed in conical mandrel and bent through 180^0 in one second .The film at the bend is examined for detachment or cracking

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2.3.2 Determination of chemical resistance properties

The chemical resistance properties of coating films were determined by exposing them to various solvents, acids, alkalis, and water. The coated panels were sealed from three sides by using molten paraffin wax before dipping in various chemicals.

Preparation of reagents

Acids: The acids were diluted by taking the required quantity of water and acids on a volume basis to achieve the desired concentration. The acids were added slowly in the water to make dilute acids. The following concentrations of various acids were used: Sulphuric acid (10 per cent), hydrochloric acid (10 per cent), acetic acid (15 per cent) and phosphoric acid (50 per cent)

Alkalis and Solvents: Sodium hydroxide was dissolved in water to make solutions of 50 per cent concentration and also 50% solutions of ammonium hydroxide were also taken for evaluation. These reagents, along with other solvents such as xylene, ethanol, petrol, lubricating oil were used to determine the chemical resistance of the cured epoxy coating films. The panels were observed for a visible change in the condition of the films at regular intervals when immersed in these chemicals at an ambient temperature for the prescribed period of time.

2.3.3 Determination of corrosion resistance properties

Durability test for corrosion protection: It is defined as the capacity of the paint to remain unchanged by environments and events. Salt spray test were conducted using 5% NaCl solution and the test panels are exposed to the salt mist for duration of 500 hours. Then the panels are removed and examined for any sign of deterioration at the diagonal cut and observed the travel of rust. It is also examined for blistering and adhesion.

Another set of painted panels after air drying for 48 hours kept in outdoor environment at an angle of 45^0 facing south. The test panels were exposed for a period of 90 days. Then the panels were examined for any sign of deterioration and blistering. The test results examined were reported in table 8.

To confirm the results obtained by salt spray test and the exposure test, and to study the coating behavior mechanism in more details, electrochemical impedance spectroscopy was performed. The three electrodes electrochemical cell was used in this study. A platinum electrode acted as a counter electrode, a saturated calomel electrode (SCE) as reference and the sample A & B coated MS steel panel as the working electrode with the contact surface equal to 10 cm^2. Electrochemical data were obtained at open circuit potential (OCP) by Metro Ohm Auto Lab Instrument with NOVA software in the frequency range of 10 kHz to 0.01 Hz with amplitude of 10 mV. The cell assembly was open to air and analysis done at room temperature (303K) and in 3.5% NaCl solution.

3 Results and Discussion

Application of Coating.

The two coating system, epoxy isocyanate and epoxy polyamide samples were applied on mild steel panels by brush and cured to get a film thickness of 50-60 microns. The mild steel panels were cleaned, dried, are free from rust & mill scale before they were applied with the coating systems. The coated panels were tested for physical, mechanical, stability and durability properties. All the tests were conducted as per the Indian Standard IS101.

3.1 Presence of residual isocyanate groups

The successful formulation should eliminate the free isocyanate group from epoxy isocyanate coating to ensure free from any toxicity**.**IR study was carried out to check the completion of the curing reaction i.e.) the gradual decrease of the NCO groups which gets converted to NH-COO group. The residual NCO groups are those which absorb the radiation at 2270 cm^{-1} and hence the absorbance of the cured film at this frequency gives the amount of NCO left unreacted

The percentage of isocyanate absorbance peak at 2270 cm^{-1} decreases with the passage of time which reflects the decrease in the amount of NCO group. In order to check the presence of NCO group in the complete cured film, the gelled material was scanned which showed the complete disappearance of the NCO peak at 2270cm^{-}. Hence it is inferred that there is no residual isocyanate present in the completely cured film.

3.2 Physical properties- Drying characteristics

The coating system applied on mild steel panel were analysed for dry times at 30^0C and relative humidity 65±5%.

Table 4 Drying Characteristics

Sample	Surface Dry	Through Dry	Recoat (min)
Epoxy Isocyanate system	2 hours	4 hours	3 hours
Epoxy Polyamide system	3 hours	8 hours	6 hours

It is seen from the table that epoxy isocyanate system produces coating with shorter drying time at the specified environmental condition. The shorter cure time of epoxy isocyanate system is attributed to the faster reaction between the isocyanate group and the hydroxyl group of the epoxy resin [7]. However the system showed blooming when the temperature was below 5^0C and the relative humidity was above 85%.

3.3 Heat Resistance

The epoxy isocyanate coating system showed temperature resistance of 60^0 C when exposed continuously and 120^0 C dry heats on intermittent heating conditions whereas epoxy polyamide coating system showed temperature resistance of 80^0 C and withstood 150^0C dry heat. There was reduction of gloss level and darkening observed above this temperature. Hence the coating film of epoxy isocyanate system has shown good resistance to temperature however it is lesser compared to epoxy polyamide coating.

3.4 Curing characteristics

The DSC scans were obtained for both the paint systems and both the systems showed exothermic heat flow vs. temperature [10]. Exothermic peaks were obtained in the range of 80 – 200^0C at a scan rate of 10^o C/min. The characteristic temperature at which the reaction started (T_i), attained a maximum (T_p), the cure range and cure time were tabulated.

Table 5 Cure characteristics of epoxy coating systems

Sample	Onset temperature, T_i (^{0} C)	Maximum temperature, T_P (^{0} C)	Completion temperature, T_f (^{0} C)	Cure Range (^{o}C)	Cure time (minutes)
Epoxy isocyanate system	98	130	190	87	12.6
Epoxy polyamide system	78	136	188	106	20

The initial cure temperature for epoxy isocyanate system is higher due to its higher functionality and the cure range and cure time are lesser compared to epoxy polyamide system. It is clear from the data that the reaction and curing of epoxy isocyanate system is faster at ambient temperature.

3.5 Mechanical Properties

The mechanical properties of the two epoxy coating systems were evaluated and are given in the table.

Table 6 Mechanical properties of the epoxy coating systems

Sample	Scratch Hardness	Cross cut Adhesion	Flexibility (Bend Test)
Epoxy isocyanate system	2600 grams	Passes	No crack of paint film
Epoxy polyamide system	2200 grams	Passes	No crack of paint film

It is seen from the table that the epoxy isocyanate paint system form more three dimensional network and as a result the film is harder, extremely tough, higher scratch hardness leads to high abrasion resistant coating[8].

3.6 Chemical Resistance Testing

The two coating systems were exposed to a number of chemicals and the resistance of these systems were tabulated. The data indicates that both the systems have good resistance to splash and spillage of a range of chemicals[9].However, the epoxy isocyanate system has shown higher resistance to mineral acids

Table 7 - Stability properties of the epoxy systems towards chemicals

Chemical	Epoxy Isocyanate	Epoxy polyamide	Rating
Hydrochloric Acid10%)	8	4	Scale from 0 to 10 0-Complete failure 10- No change
Sulphuric Acid (10%)	8	4	
Acetic Acid(5%)	8	3	
Phosphoric Acid(50%)	5	3	
Sodium Hydroxide 50%	8	7	
Ammonium Hydroxide	8	7	
Acetone	4	4	
Ethyl Alcohol	3	3	
Petrol	8	8	
Lubricating Oil	8	8	

3.7 Corrosion Resistance Properties:

Both the coating systems were tested for salts spray test as per the specification of IS 101.The metal panels after curing for 30 days were exposed to salt mist produced by salt spray chamber for 500 hours. The panels were examined for any sign of deterioration by removing paint near the diagonal cut made and observed the travel of rust. Both the coating systems showed good resistance to corrosion under salt spray test. Also the second set of coated panels after air drying for 48 hours kept in outdoor environment at an angle of 45^0 facing south. The test panels were exposed for a period of 90 days. Then the panels were examined for any sign of deterioration and blistering. As this experiment was carried out in ambient temperature and at less severe condition both the systems showed no sign of corrosion and blistering but considerable reduction in the gloss level was observed in epoxy polyamide coating system. Hence it shows that epoxy isocyanate coating system has got better durability when exposed to outdoor environmental condition compared to epoxy polyamide coating system.

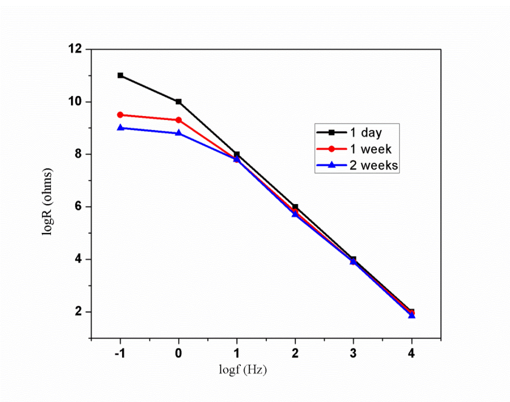
Table 8: Comparison of corrosion resistance properties

Property Test	Epoxy isocyanate system	Epoxy polyamide system
Resistance to Salt Spray (Upto 500 Hrs.)	No sign of corrosion or blistering	No sign of corrosion or blistering
Resistance to outdoor exposure	No sign of corrosion. Loss of gloss 5%	No sign of corrosion Loss of gloss 20%

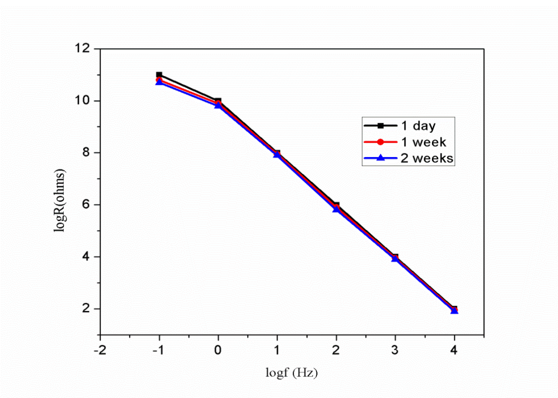
3.7.1. Electrochemical Studies:

In order to confirm the results obtained by salt spray test and testing of corrosion under conditions of condensation, the electrochemical impedance spectroscopy was performed. The results of this method were represented in the form of Nyquist diagrams. These impedance diagrams was a result of MS steel immersed 30 min before each open circuit measurement in the corrosive 3.5% NaCl solution, with respect to the set of matrices. The semicircle diameter which is higher for sample B showed better corrosion resistance of the protective film.

The Bode pattern for the two samples after 30 min immersion in 3.5% NaCl at 298 K was studied. For low frequencies, the high absolute impedance values confirm the greatest protection with both the coating formulations.



Sample A (Epoxy Polyamide System)



Sample B (Epoxy Isocyanate System)

It is known that the impedance values higher than 1×10^7 ohms per cm^2 at low frequencies indicates good protection of the coatings on the substrate. The impedance at the low frequencies gradually decreased with increasing of immersion time for sample A. This phenomenon means the decrease of coating protection property and the initiation of corrosion at the metal/coating interface. After 14 days of immersion, the sample B still maintained very high impedance and the modulus was as high as 1×10^{11} ohms per cm2 at low frequencies whereas for sample A, this has reduced to 1×10^9 ohms per cm2. While, the impedance modulus of both coatings are excellent, the sample B indicates better corrosion protection.

4 Conclusions

As seen from the above studies, the epoxy isocyanate system produces better results in drying characteristics, hardness, mechanical properties and corrosion protection. Further the epoxy isocyanate system is unaffected by broad range of corrosive chemical and industrial environments and showed marked improvement in chemical resistance and particularly acid resistance. The distinguishing superior acid resistance along with better mechanical properties make epoxy isocyanate coating system suitable for the substrates that needs protection against chemical environmental conditions i.e., structures and equipment in chemical industries, fertilizer, petrochemical industries and effluent treatment plants etc. The prevailing environmental condition whether it is sunlight, heat, abrasions, chemicals or other corrosive environments will dictate which coating system is best suited for application. The mechanical properties and anticorrosive properties can be further enhanced through incorporation of nano fillers and corrosion inhibitive materials in the formulation to meet the specific very high protection requirements.

Acknowledgement

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