

Comparative Study of Polyol with Varying Hydroxyl Values in Polyurethane Coatings

J Manivannan^(1*), S Kalaiselvan⁽²⁾ & N Velmani⁽³⁾

^(1 & 2)Department of Chemistry, SNS College of Technology, Coimbatore, Tamil Nadu, India

⁽³⁾Department of Chemistry, PG and Research Centre, Government Arts College, Coimbatore, Tamil Nadu, India

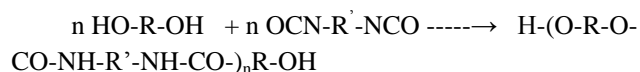
Corresponding author-Email:manijv@gmail.com

Abstract -The polyurethane coatings have been one of the fastest growing sectors of the coating industries. Though high cost, excellent durability, flexibility, resistant to corrosion and abrasion, resistant to chemicals make urethane coatings suitable for high performance applications. The recent type of product in refinish industry is based on hydroxyl function acrylic resins in association with polyisocyanate second component. Varying degree of hydroxyl value of acrylic polyols combined with polymeric Toludine di-isocyanate were manufactured and evaluated for its performance properties. It was found that the coating system which contains lower hydroxyl value exhibited better performance in flexibility test and corrosion protection compared to the system with polyol of higher hydroxyl value. However the coating system with polyol of higher hydroxyl value showed better performance in all other properties.

Keywords: Polyurethane coating, TDI Polymer, Acrylic Polyol, Coating System,

I. INTRODUCTION

The commercial development of polyurethane paint has been long exploited in paint industry to give various applications to fulfil the ever growing demand for high performance coatings such as automotive finishes, vehicle refinishes, floor coatings, marine coatings etc. Polyurethane coatings are reaction product of poly isocyanate with hydroxyl functional resins such as Alkyd, Polyester, Epoxy, and Acrylics. These polymers are characterised by presence of urethane groups in their repeating unit (-O-CO-NH). This structure has some sort of similarity with polyamides because both linkages contain -CO-NH- groups; however polyurethane contains one more oxygen. The additional oxygen provides flexibility to materials. The polyaddition reaction between diisocyanates and polyol gives polyurethane



The two component system contains polyol and polyisocyanates. It has been reported that the reaction of polyisocyanate with polyols has a great impact on the properties of the coating film [1]. It is found that the interaction of polyol with polyisocyanate gives greater cross linking density and increases the hardness, abrasion resistance and chemical resistance. There is a lot of scope to vary diisocyanates as well as diols (polyols) to suit tailor made properties.

The performance properties of coating system with the combination of different polyisocyanates and polyols have been studied by S.Desai et al[2]. These two cross linking materials are supplied in two different packages. Part A contains polyol, pigments and additives and second component contains polyisocyanate derivative, also called as hardener. Solvents are added to both the parts to give the desired viscosity for application and to obtain the mixing ratio of part A and part B. The two components are mixed together before application and applied within prescribed period (pot life). P Suchitra et al studied the performance properties of the polyurethane paints made from aliphatic isocyanate and acrylic polyol[3]. Due to higher cost of aliphatic isocyanates, aromatic isocyanates have the largest market share. They are used where oxidative discolouration due to exposure to UV radiation is not a problem. Aromatic diisocyanates are more reactive than aliphatic under similar conditions[4]. The polymeric aromatic toluidine diisocyanates (TDI) has been taken as cross linker. The term polyisocyanate is used to describe derivative of diisocyanate with at least two (usually three) NCO groups. They are used because they provide higher cross linking density[5] and are safer to handle as they have reduced vapour pressure due to increased molecular weight. Hydroxylated acrylic resins have been used for cross linking by isocyanate for two component polyurethane systems. These are popular due to their properties like rapid curing, good gloss etc.,. In our study two acrylic polyols with different hydroxyl values were taken as resin with pigments dispersed along with suitable solvents and

additives, manufactured in lab scale pot mill. The prepared base is cured with polymeric tolueneisocyanate as hardener with mixing ratio of NCO: OH = 1:1. The polyurethane coatings prepared were applied on mild steel panel and their physical, mechanical, chemical resistance and durability properties were compared.

II. EXPERIMENTAL

2.1 Materials

The raw materials ie) polyols and polyisocyanate needed for the work was obtained from M/s Resins and Plastics Ltd., Mumbai, India

2.2 Acrylic Polyol Specifications

Table 1: Specification of Acrylic Polyol

Sample	%NVM	OH Value	Viscosity at 25°C	Acid Value (mgs of KOH/g)
A	55.5	52.5	20 poise	8
B	61	92	32 poise	6

Table 2: Specification of Hardener* (Toluidine diisocyanate)

Sample	%NVM Content	Equivalent weight	Viscosity at 25°C	Monomeric diisocyanate
Polymeric TDI	13.5	32.5	15 poise	< 0.5

(Note: * Approximately 75% in Ethyl acetate)

2.3 Manufacture of Polyurethane Paint Systems:

The two acrylic polyols 'A' and 'B' were taken and the pigments were dispersed along with solvents and additives in a laboratory pot mill and the base was prepared. The isocyanate content of polymeric Toluene Diisocyanate and the hydroxyl value of acrylic polyols were provided by the original manufacturers. The base and the hardeners were mixed to give 1:1 ratio of NCO: OH prior to application on mild steel panels. The two coating systems were applied on mild steel substrates and the specified properties were evaluated.

2.4 Application of coating

The two types of acrylic isocyanate polyurethane coatings were applied on mild steel panels as per the requirement of IS101 to give a dry film thickness of 50-70 microns. The cured panels were tested for physical, mechanical, stability and durability properties. All the tests were conducted as per the Indian Standards IS101.

2.5 Testing:

2.5.1 Determination of Drying Time

The mild steel panels were used to determine the drying time of both the coatings. The surface dry time was noted

by moving the finger on the film without applying any pressure and if impression of fingerprint is not observed on the film, it is considered as 'surface dried'. When the thumb is pressed on the film and moved and if there is no thumb impression on the film it is said to be 'tack free'.

2.5.2 Mechanical Properties

The mechanical properties like Scratch hardness, Cross cut adhesion and Flexibility were tested for the two coating systems.

Hardness: Scratch hardness of the coated samples was measured with specified pointed load indenter and the result was tabulated.

Flexibility: 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° in one second. The film at the bend is examined for detachment or cracking.

Adhesion: The Cross cut test was done 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 tape is then removed sharply and the adhesion of the film is assessed from the amount of coating removed.

2.5.3 Chemical resistance test:

The painted panels were air dried for 48 hours and they were immersed in acid, alkali, solvents, petrol, lubricating oil for a specified period and the panels are examined for the percentage retention of original gloss and shade and the corresponding readings are tabulated.

2.5.4 Durability test: 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 panels were kept suspended in a humidifying chamber at 100% relative humidity level at a temperature cycle of 42-48° C and exposed for 7 days. The panels were observed for any sign of deterioration and also examined for blistering and adhesion failure.

The painted panels were after air drying for 48 hours kept in outdoor environment at an angle of 45° 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.

III. RESULTS AND DISCUSSION:

3.1 Physical properties

The paint systems applied on MS Panel were analysed for surface dry, tack free and pot life. It was observed that as the hydroxyl value of polyol increases there is increase in the surface dry time and tack free duration. This could be due to increase in the number of hydroxyl groups per mg of sample increases and hence curing takes more time to get cross linked with the increased hydroxyl groups of the polyol.

Table 3: Physical properties of PU Paint systems

Sample	Surface Dry	Tack Free	Pot Life
A	10 min	2 Hours	6 Hrs 30 min
B	12 min	3 Hrs 30 min	8 Hrs

3.2 Mechanical Properties

The mechanical properties of the two polyurethane paints were evaluated as shown in table 4. PU paint system with higher hydroxyl value of polyol gives hard coating compared to the other with low hydroxyl polyol[6]. It is seen from the result that the coating with sample B with polyol of higher hydroxyl value formed marginal damages in flexibility test. Higher hydroxyl value indicates that the resin reacts with isocyanate making more three dimensional networks and the resultant film will be harder and brittle[7]. The system which contains polyol of lower hydroxyl value shows more flexibility & elongation.

Table 4: Mechanical properties of P.U Paints A & B

Sample	Scratch Hardness	Cross cut Adhesion	Flexibility (Bend Test)
A	1800 gms	Passes	No damage
B	2600 gms	Passes	Slight rough appearance in the bent area

3.3 Stability Properties

3.3.1 Acid/Alkali/ Fuel/Lubricating Oil resistance properties

The two coating systems were evaluated for acid, alkali, petrol and lubricating oil resistance by immersion method. The coating of the system with higher hydroxyl polyol (sample B) showed better resistance compared to the system with lower hydroxyl value

Table 5: Stability properties of the two P.U Paint systems in acidic & alkaline solutions

Sample	6% H ₂ SO ₄ Solution		6% Na ₂ CO ₃ Solution	
	Gloss	Shade	Gloss	Shade
A	15% loss	No change	20% loss	No change
B	10% loss	No change	15% loss	No change

Table 6: Stability properties in Lubricating oil & Petrol

Sample	Lubricating Oil		Petrol	
	Gloss	Shade	Gloss	Shade
A	30 % loss	Slight change	20% loss	No change
B	20% loss	No change	10% loss	No change

The presence of aromatic groups in the cured resin network increases the chemical resistance [8]. In addition the high crosslink densities due to higher hydroxyl value of sample B is the reason for better chemical resistance.

3.3.2 Solvent Resistance

The two coated panels were subjected to solvent resistance test with an aromatic non polar solvent-xylene and a polar solvent- Methyl Ethyl Ketone.

Table 7: Stability in solvents

Sample	Xylene	Methyl Ethyl Ketone
A	No change	slight loss of gloss
B	No change	slight loss of gloss

There is some minor effect of polar solvent on gloss of the film for both the coating systems but there is no considerable difference in loss of gloss between the two samples after 200 cycles of rubbing. Both the coating systems showed good resistance to solvents [9].

3.4 Durability Properties

Both the paint systems were tested for salts spray, resistance to corrosion under conditions of condensation and resistance to outdoor weathering as per the specification of IS 101. The two paint systems showed good resistance to salt spray confirming to IS 101. But the paint system B with polyol of higher hydroxyl value showed mild corrosion under conditions of condensation. The degree to which paint film is permeable to moisture is influenced more by the nature and degree of pigmentation. The blisters produced in the film due to humidity condensation bursts or break if the film is hard and brittle and results in corrosion, whereas in the paint system A,

which has more flexibility, the blisters present does not break and prevent corrosion[10]. In the crucial test for the paints durability or resistance to an environment comprising less humid weather conditions the paint system with higher hydroxyl polyol showed better gloss retention. The experiment which was carried out in ambient temperature and at less severe conditions in the outer exposure test both the systems showed no sign of corrosion

Table 8: Comparison of durability properties

Property Test	Sample A	Sample B
Resistance to Salt Spray (Upto 500 Hrs.)	No sign of corrosion or blistering	No sign of corrosion or blistering
Resistance to corrosion Under conditions of condensation	No sign of corrosion or blistering	Mild corrosion spots observed
Resistance to outdoor exposure	No sign of corrosion. Loss of gloss 20%	No sign of corrosion Loss of gloss 5%

IV. CONCLUSIONS

The polyurethane paints were prepared with acrylic polyol of different hydroxyl value and aromatic TDI based prepolymer. The hydroxyl value of acrylic polyol provides polyurethane coatings with their tailor made properties and performance. The polyol with higher hydroxyl value gives harder coating film and comparatively better mechanical, chemical and gloss retention properties, but poor in flexibility test and also showed mild corrosion under corrosion under condition of condensation test because of comparatively harder and brittle film. The polyurethane

coating system based on acrylic polyol and polymeric aromatic isocyanate is generally useful for undercoats, intermediate and interior coatings. The choice of polyol and the type of isocyanate to be chosen should be based on the desired properties of coating film and its specific area of application

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