Cathodically Depositable Systems Based on Epoxy Resin and Blocked Isocyanates with Cardanol*

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Synopsis

Cathodically electrodepositable binders based on the reaction products of epoxy amine adduct and various proportions of partially blocked isocyanates with cardanol were prepared. Paints were formulated from the above binders using rutile titanium dioxide as pigment in the pigment volume concentration, ranging from 0–50%. A comparative study has been made on the physicochemical properties and electrodepositable characteristics of binders and the paints.

INTRODUCTION

In recent years, there is a trend of replacing many of the conventional solvent-based coatings by watersoluble systems due to the increased price of petroleum solvents and their toxicity and inflammability, leading to health and fire hazards. In addition, these systems have the added advantage of their application by electrodeposition either by anodic or cathodic processes.[1-4] The cathodic electrodeposition is gaining importance in recent years over the anodic electrodeposition mainly due to the passivation of metal substrate, thereby offering better protection against corrosion.[5-7] Very few cathodic electrodepositable binders have been reported, which are mostly in the form of patents.[8,9] The use of cardanol, a naturally occurring phenol, with side alkyl chain of 15-carbon atoms, varying in degree of unsaturation, as a binder for electrodeposition purposes has come into existence only in recent years.[10-12]

The present paper deals with the preparation of cathodically electrodepositable binders based on the reaction product of epoxy amine adduct and various proportions of partially blocked isocyanates of cardanol, a naturally occurring phenol. The physicochemical properties of these systems were determined. From this study, the best combination was selected for formulating paints with different pigment volume concentrations (PVCs) ranging from 0–50% using utile titanium dioxide as pigment. The physicochemical properties of these systems have been studied.

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EXPERIMENTAL

Materials

The epoxy resin used was Araldite 6071 (CIBA-GEIGY). Cardanol was obtained by distillation of cashewnut shell liquid (CNSL) at 240°C under 3–4 mm pressure. The major constituent is cardanol (90%), which is a meta-substituted phenol with an alkyl chain of 15-carbon atoms, varying in degree of unsaturation; the other constituent is cardol (10%), which is a dihydroxy meta-substituted phenol with alkyl chain of 15-carbon atoms, varying in degree of unsaturation. Glacial acetic acid, toluene diisocyanate, and butyl cellosolve are of L.R. grade reagents. Titanium dioxide was of pigment grade. Mild steel discs of diameter 32 mm, mild steel panels of 150 × 100 mm and 100 × 25 mm of gauge 20 (0.9 mm), and mild steel rods of size 100 × 5 mm diameter were abraded with emery paper of increasing order of fineness in white spirit medium and swabbed with xylene and butyl cellosolve. The mild steel discs were further degreased with methyl ethyl ketone for 2 h. The residual solvent from the degreased specimen was removed *in vacuo*. Tin panels 150 × 100 mm were cut from electrolitically tinned mild steel (0.315 mm). The tin panels were lightly abraded with a fine emery paper and swabbed with xylene and finally with butyl cellosolve.

Procedures

Preparation of Epoxy Amine Adduct (EAA)

The adduct of low amine content was prepared by reacting epoxy resin (400.00 g) with a calculated amount of diethanol amine (105.00 g) at 180 ± 5°C for 10 h under constant stirring/refluxing in the presence of ethoxy ethyl acetate as solvent. The completion of the reaction was confirmed by testing the sample for its infinite dilutability in acidified water with 2% acetic acid.

Preparation of Partially Blocked Isocyanates with Cardanol (PBIC)

Partially blocked isocyanates with cardanol was prepared by reacting cardanol and toluene diisocyanate taken in 1 : 1 mole ratio at 60°C and reaction was monitored by TLC and also by IR (Fig. 1). The absorption band in the IR of the product at 2285 cm^{-1} indicated the presence of NCO group.

Preparation of Electrodepositable Binders

The binders suitable for electrodeposition were prepared by reacting the epoxyamine adduct with partially blocked isocyanate at 80°C in the mole ratios of EAA and PBIC, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 and the products obtained were designated as A, B, C, and D, respectively. The completion of the reaction was followed by testing periodically the product for infinite dilutability in acidified water (2% acetic acid) and also monitoring by IR (Fig. 1), which indicated the completion of the reaction by the disappearance of absorption band at 2,285 cm^{-1}. In the preparation of the binder "D," extreme precaution was taken as toluene diisocyanate concentration was higher, leading to possible gellation during the experiment.

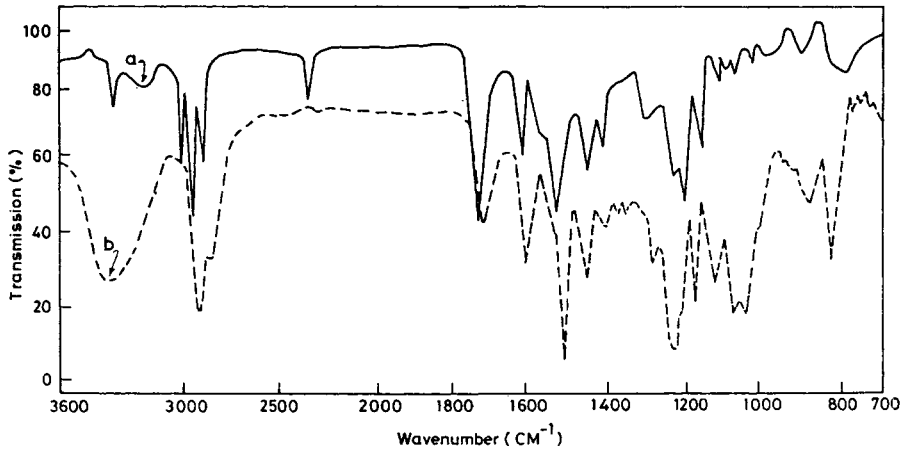

Fig. 1. (a) IR spectrum of partially blocked isocyanate of TDI with cardanol; (b) modified amine adduct with partially blocked isocyanate.

Cathodic Electrodeposition of Binders

The watersoluble media required for cathodic electrodeposition were prepared by making 10% solution of binder in acidified water–pH made up to 6.

The electrodeposition of the binders was carried out at different Voltages 10, 20, 30, and 40, and for different periods of timing 1, 2, 3, and 4 min. The cathodically deposited films were taken out of the bath, washed with running water to remove loosely adhering binder, and baked at 150 ± 5°C for 30 min. The baked coatings were examined for uniformity of coating, dry film thickness, and resistance to chemicals and solvents. Table I shows the effect of variation of different voltages at constant time on the thickness of the electrodeposited coatings after baking. Timings less than 3 min yielded one-side coatings, and greater than 3 min, orange peel surfaces.

20 V and 3 min dip time were chosen as electrodeposition parameters for coatings to carry out evaluation of physicochemical properties. Table II lists the mechanical properties and resistance to chemicals/solvents.

TABLE I
Effect of Variation of Voltages on Film Thickness of Binder at Constant Dip Time of 3 min

Serial no.	Voltage	Dry film thickness (microns) of binders[a]	
		C	D
1	10	20	20
2	20	25	22
3	30	23	18
4	40	22	17
5	45	20	16

[a] C, mole ratio: epoxy amine adduct : blocked isocyanate with cardanol = 1 : 3; D, mole ratio: epoxy amine adduct : blocked isocyanate with cardanol = 1 : 4.

TABLE II
Physicochemical Properties of Water Soluble Binders of Different Mole Ratios

Serial no.	Tests carried out	Binder with OH/NCO ratio[a] C (1/3)	D (1/4)
1	Resistance to water (48 h)	P	P
2	Resistance to 2% H_2SO_4 (16 h)	SB	SB
3	Resistance to 5% Na_2CO_3 (4 h)	P	P
4	Resistance to 1% NaOH (4 h)	P	P
5	Resistance to white spirit (4 h)	P	P
6	Resistance to *n*-butanol (4 h)	P	P
7	Resistance to xylene (4 h)	P	P
8	Flexibility ($\frac{1}{4}$" mandrel)	P	P
9	Impact resistance		
	Direct	P	P
	Indirect	F	F

[a] P, pass; SB, slight blushing; F, fail. Conditions for cathodic deposition: Voltage 20, time 3 min.

The coatings from binders A and B were found to be nonuniform and hence dry film thickness of coatings could not be controlled. These binders were not used for formulating paints. Similarly, binder D, although it gave uniform film, could not be considered for paint formulation because of the difficulties involved in the preparation of the binder.

Preparation of Paint

Aqueous binder solution of "C" at ball mill consistency was selected for preparing cathodically depositable paints, using titanium dioxide as pigment with PVCs ranging from 0–50% and grinding it to 7–8 Hegmann gauge scale in a laboratory ball mill and diluting it to 20% solids before carrying out electrodeposition.

Electrodeposition of Paints

Electrodeposition of paints were carried out at 20 V for a period of 3 min using a bath concentration of 20% solids. After the said period, coated panels were washed with water to remove loosely adhering paints and they were baked at 150 ± 5°C for a period of 30 min. These were allowed to mature for 48 h before testing the coatings for their physicochemical and mechanical properties. Brief procedures for the various testing methods used are given below.

TEST METHODS

Determination of Adhesion by Sandwich Pulloff Technique

In the present study, the direct pulloff technique based on the use of a Hounsfield Tensometer was used for the reasons put forward by Bullet and Prosser.[13] Bond strengths (practical adhesion values) were determined by the sandwich pulloff technique using a Hounsfield Tensometer.[14,15] Mild steel discs

were coated by electrodeposition process (20 V, 3 min) and stoving at 150 ± 5°C for 30 min. Test doublets were prepared by gluing a painted disc between two stainless steel cylindrical test pieces 2 in (50.8 mm) long and 1 in (25.4 mm) in diameter. The test piece that was stuck to the painted face was turned down to $\frac{3}{4}$ in (18 mm) in diameter so that higher forces could be applied while at the same time obviating the possibility of a break occurring between the coupling test piece and the unpainted side of the disc. For bonding, an adhesive of suitably high bond strength (to the substrate and to the paint surface) was chosen so that failure occurred only at the paint/substrate interface or in the body of the paint film. The adhesive system used for bonding was Araldite AW 106 and Hardner HV 953 U (CIBA-GEIGY Corporation).

During the curing of the adhesive the doublets were kept aligned on parallel rod jigs of the same diameter as the cylinders, with enough pressure being applied to squeeze out the excess adhesive without starving the joints. Great care was exercised in laying the doublets securely on the alignment block for proper alignment of the test specimens. The test doublets were kept under pressure for 48 h to allow the adhesive to cure, the bowing effect of the doublets in the assembly being corrected by suitable clamping arrangements. When curing of the adhesive was complete, the doublets were taken out of the alignment blocks and kept in a vertical position for a further period of 12 h. The doublets were then pulled apart by subjecting them to progressively increasing stress at a constant rate until failure took place. Sagging of the doublet in the Tensometer was prevented by suitable holders. Based on the area of bonded paint surface and the load indicated by the Tensometer at the time of failure, adhesion was expressed as practical adhesion.[16]

Cohesive failure refers to any break in the body of the paint film and adhesive failure describes the break between the paint and the substrate. Classification of the nature and extent of failure was carried out by applying copper sulphate solution to the painted surface of the disc after test, then superimposing a transparent plastic sheet on which squares were engraved and counting the number of squares covering brown deposit. The average practical adhesion value was calculated from the results of 15–20 test specimens.

Determination of Gloss

Gloss was measured at 45°, as prescribed in IS:101–1964, using a Gardner Multiangle Glossmeter.

Determination of Scratch Hardness

Scratch hardness was measured according to IS:101–1964 using a REL automatic power-operated scratch hardness tester.

Determination of Impact Resistance

Impact resistance was measured by a falling weight type instrument using a 2-lb weight at a fixed height of 25 in (DEF 1053 specification).

Determination of Flexibility

Flexibility was measured according to IS:101–1964 by bending the coated panel on cylindrical mandrel ($\frac{1}{4}$ in diameter) and examining the bent portion for cracks or hairline cracks under magnification.

TABLE III
Effect of Dry Film Thickness, Current Density, and Film Resistance on PVC of Binder C[a]

Sample no.	% PVC	Dry film thickness (μm)	Current density (amp/cm^2 $\times$ 10^{-4})	Film resistance V/I (Ohms)
1	10	15.00	75.00	40.00
2	20	20.00	82.00	62.50
3	25	30.00	100.00	66.60
4	30	25.00	93.70	62.50
5	35	20.00	93.10	58.80
6	40	Not uniform	Not uniform	—

[a] Bath conditions: bath concentration, 20% solids; voltage, 20 V; time, 3 min.

Determination of Resistance to Chemicals/Solvents

Chemical/solvent resistance was measured according to IS:101–1964 using distilled water, H_2SO_4 (2%), Na_2CO_3 (5%), xylene, white spirit, and butanol.

Tables III and IV and Figure 2 give the various test results of binder C–TiO_2 paint for different pigment volume concentrations.

Binder C–TiO_2 paints with PVCs ranging from 10–35 resisted all the solvents/chemicals, i.e., water (48 h), 2% sulphuric acid (16 h), 5% sodium carbonate (4 h), 1% sodium hydroxide (4 h), xylene (4 h), butanol (4 h), and white spirit (4 h), except the formulation with 30 PVC and 35 PVC, which developed slight blisters in the case of 2% sulphuric acid.

DISCUSSIONS AND CONCLUSIONS

By examining Table I, the binder based on the reaction product of epoxy amine adduct and various proportions of partially blocked isocyanates with

TABLE IV
Mechanical Properties of Binder C–TiO_2 Paints at Different PVCs[a]

Sample no.	% PVC	Gloss at 45° (Std. 52)	Scratch hardness (g)	Flexibility $\frac{1}{4}''$ mandrel	Impact resistance	Practical adhesion[b] (kg/cm^2)
1	10	45	561	P	P	213.00 (66 AF)
2	20	42	969	P	P	214.00 (78 AF)
3	25	40	1071	P	P	223.50 (98 AF)
4	30	40	663	P	P	210.53 (97 AF)
5	35	40	561	P	P	202.80 (72 AF)

[a] Conditions: bath concentration, 20% solids; voltage, 20 V; time, 3 min.
[b] AF denotes percent adhesive failure.

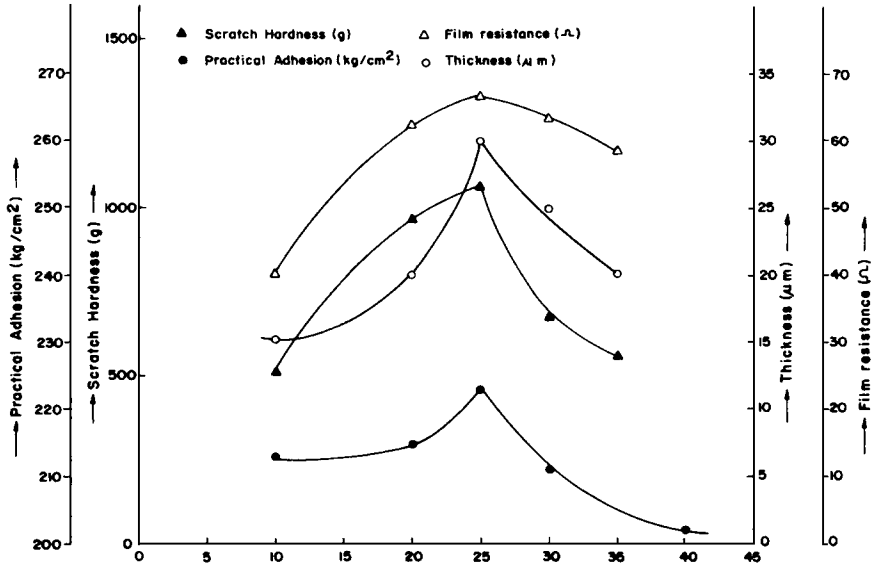

Fig. 2. Physicochemical properties vs. pigment volume concentration of binder 'C'-TiO_2 paints.

cardanol, it is seen that the highest dry film thickness was obtained with cathodic electrodeposition bath conditions: concentration 10% solids, 20 V, and 3 min; 10 V and 3 min also give reasonably good film thickness. By considering Table II, the physicochemical properties of binders with mole ratios 1 : 3 and 1 : 4 of binders C and D, respectively, pass all the tests except in the tests of resistance to 2% H_2SO_4 and also in the indirect impact resistance.

The solubility of binder C in acidified water was found to be infinite. Hence, paints were prepared using binder C and TiO_2 as pigment at different PVCs ranging from 10–50%.

Table III gives the dry film thickness, current density, and film resistance for the TiO_2–binder C paint at different pigment volume concentrations. Twenty-five percent PVC was found to yield better film thickness, current density, and film resistance with bath conditions of 20% solids, 20 V, and a dip time of 3 min. The same trend was observed while considering their physicochemical properties (Table IV). By observing the overall properties, it is noticed that 25% pigment volume concentration paint system exhibited better film properties and was found to be the critical pigment volume concentration (CPVC) for TiO_2–binder C paint system (Fig. 2).

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