

Cathodically Electrodepositable Novel Coating System from Castor Oil*

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SYNOPSIS

A novel polyol synthesised from castor oil by aminolysis and a partially blocked toluene-diisocyanate blocked with *N,N'*-diethyl lactamide was used to prepare an urethane. This was used in different weight proportions to modify epoxy amine adduct to give binders suitable for cathodic electro-deposition. The pigmented composition of these binders based on the iron oxide (natural) and titanium dioxide (rutile) gave coatings with improved performance.

INTRODUCTION

Water-soluble paints are gaining industrial importance in recent years over the conventional paints formulated with petroleum-based solvents, because the former systems cause minimum atmospheric pollution, prevent health and fire hazards, and facilitate the cleaning of the manufacturing and application equipments with ease. These binders and paints also have the additional advantage over the conventional paint in their ease with which they can be electrodeposited either by anodic¹⁻⁴ or cathodic⁵⁻⁷ process. Of late the cathodically electro-depositable coatings are coming into prominence as they are more effective in preventing corrosion of metals by their passivation of the substrates than the conventional coatings. Most of the information regarding the synthesis of cathodically electrode-depositable coatings and parameters for their electro-deposition is contained in patents.⁸⁻¹⁰

The present paper deals with the utilization of castor oil in the preparation of a binder suitable for formulating cathodically electrodepositable paint.

EXPERIMENTAL

Materials

The following raw materials were used in the synthesis of the binder: Castor oil used had an iodine

value 87 cg I₂/g and hydroxyl value 166.0 mg KOH/g, and epoxy resin used was of commercial grade (Araldite 6071), with molecular weight ranging from 900 to 1000 and with an epoxy equivalent of 450.

Lactic acid, *N,N'*-diethyl amine, diethanolamine, toluenediisocyanate (TDI), glacial acetic acid, 2-ethoxy ethyl acetate, toluene, xylene, butanol, and white spirit were all of pure IR grade.

Iron oxide (natural) with a specific gravity of 5.17 and surface area 8 m²/g as determined by BET technique and titanium dioxide (rutile) with a specific gravity 4.2 and surface area 12 m²/g as determined by BET technique were both of pigment grade were used for preparing the paints.

Cobalt naphthenate and lead naphthenate were used as driers as solutions in butyl cellosolve.

Stainless steel panel and mild steel panels (M.S. Panels) of size 2.5 × 7.5 cm. were used as substrates.

Synthesis of Binder

The cathodically electrodepositable binder ricinoleic bis(2-hydroxy ethyl) amide urethane was prepared by the following procedure.

Synthesis of Ricinoleic Bis(2-Hydroxy Ethyl)amide (RBHEA)

Castor oil (1 mol) was taken in a flask equipped with mechanical stirrer, reflux condenser, dropping funnel, and a thermometer. Diethanolamine (3 mol) was added dropwise to the castor oil in the course of 30 min. The reaction was carried out in presence of lead monoxide (0.01 g/100 g oil) as the catalyst, at a temperature of 115 ± 5°C for 1 h under constant

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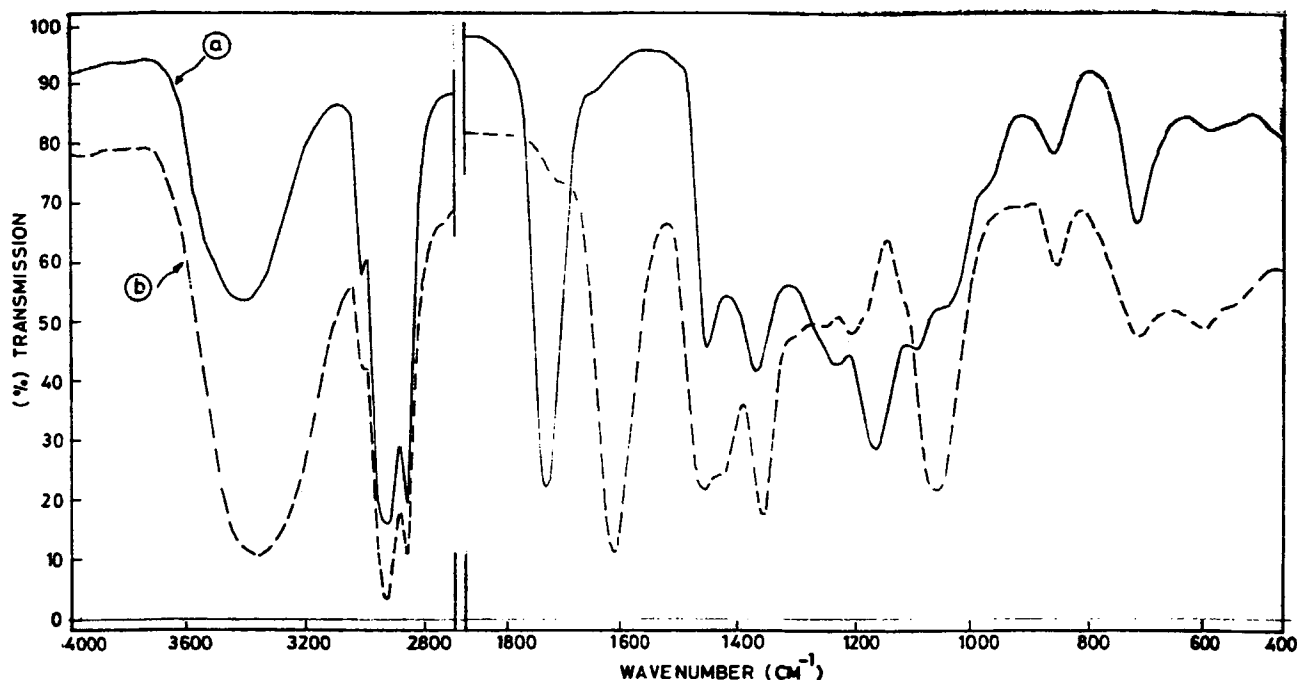


Figure 1 IR spectrum of: (a) castor oil; (b) ricinoleic bis(2-hydroxy ethyl) amide (RBHEA).

stirring. The progress of the reaction was monitored by micro-TLC.

After the completion of the reaction, for the purpose of characterization of the product formed, a

portion of the product was extracted with ether and washed successively with 15% sodium chloride solution to remove the glycerol formed. The product was then dried over anhydrous sodium sulfate for about 24 h and recovered. It was subjected to column chromatography using silica gel (60–120 mesh) and eluted with hexane and ethyl ether solution (60/40, v/v) to isolate the ricinoleic bis(2-hydroxy ethyl) amide. This product was characterized by IR and NMR (Figs. 1(a) and (b), 2, and Table I) and the

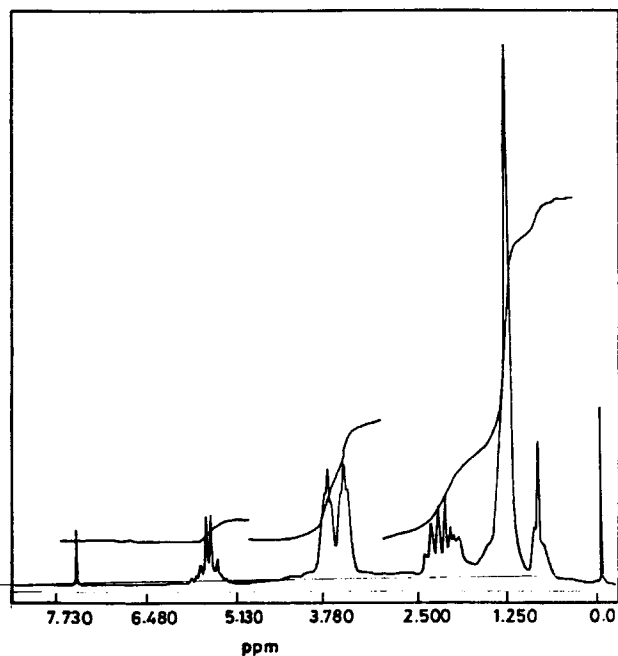


Figure 2 NMR spectrum of ricinoleic bis(2-hydroxy ethyl) amide (80 MHz, CDCl_3).

Table I PMR Spectral Assignments of Ricinoleic Bis(2-Hydroxy Ethyl)amide (CDCl_3 , 80 MHz)^a

δ (ppm)	No. of Protons by Integration	Assignments
0.87(T)	3 H	— CH_3
1.34(S)	20 H	— CH_2
1.93–2.43(m)	7 H	— CH_2 , OH — CH —
3.50(T)	6 H	— NCH_2 — CH_2
3.68(T)	5 H	—OH (Identified by D_2O exchange)
5.0–5.56(q)	2 H	— $\text{CH}=\text{}$

^a T = triplet, S = singlet, m = multiplet, q = quartet.

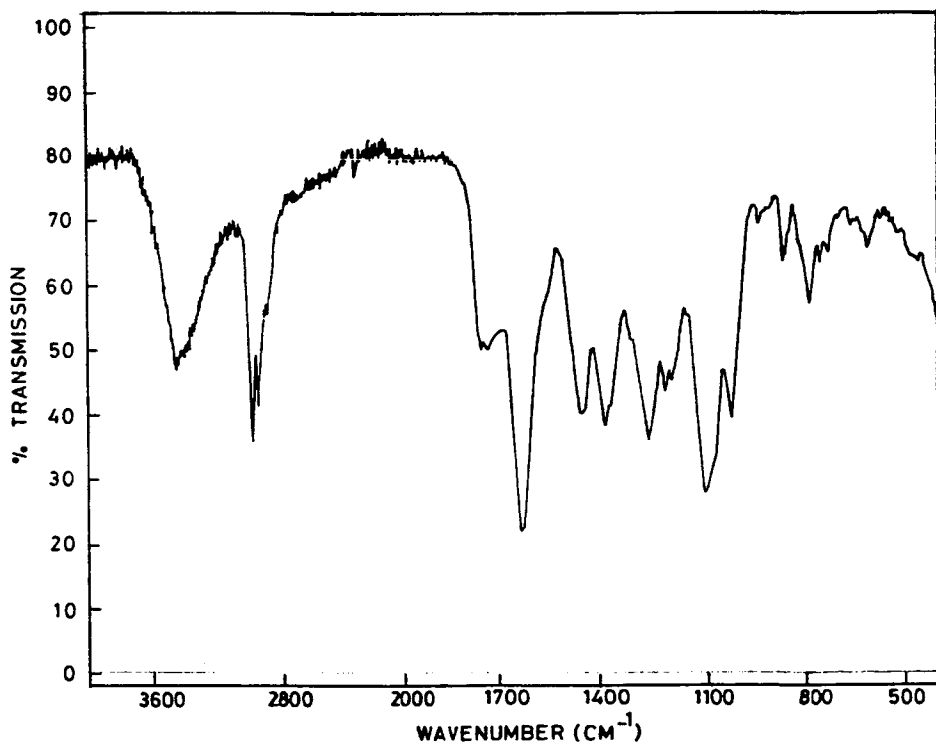


Figure 3 (a) IR spectrum of *N,N'*-diethyl lactamide.

molecular weight determined by vapor pressure osmometry using carbontetrachloride as the solvent and found to be 400.0 (theoretical value 385.0).

Synthesis of *N,N'*-Diethyl Lactamide

Lactic acid (1 mol) was taken in a flask equipped with a mechanical stirrer, a condenser, a Dean-Stark accessory, a dropping funnel, and a thermometer. *N,N'*-diethylamine (1 mol) was added dropwise under constant stirring at $60 \pm 2^\circ\text{C}$ over a period of 30 min. After the complete addition of the amine, the temperature of the reactants was raised to 110°C and maintained for 30 min and then cooled to 95°C . A calculated amount of toluene (5% by weight based on the total weight of the reaction product) was added and the reaction temperature was raised again to $110 \pm 2^\circ\text{C}$, to remove azeotropically water formed during the reaction. The amount of water collected was 16 mL (theoretical amount = 18 mL). The residual toluene and the unreacted amine were stripped off under vacuum at 160°C . The product was analyzed by micro-TLC and IR (Fig. 3).

Synthesis of Epoxyamine Adduct

The adduct of low amine content was prepared by reacting epoxy resin (1 mol) with diethanolamine

(2 mol) using 2-ethoxy ethyl acetate as solvent (5% on the weight of the total reaction products) at $180 \pm 5^\circ\text{C}$ for about 10 h with constant stirring and refluxing. The resultant epoxy amine adduct was characterized by IR [Fig. 4(b)] [for comparison Fig. 4(a) gives the spectrum of epoxy resin]. The solubility in acidified water (2% acetic acid solution) also confirms the formation of adduct.

Preparation of Partially Blocked Isocyanates of *N,N'*-Diethyl Lactamide

Toluenediisocyanate (1 mol) in 2-ethoxy ethyl acetate as solvent was taken in a flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer. *N,N'*-diethyl lactamide was added dropwise in about 30 min into the flask with the reaction mixture kept under constant stirring. The temperature of the reactants was not allowed to exceed 35°C . After the complete addition of the amide, the reaction temperature was raised to 45°C and kept for 4 h under constant stirring in an inert atmosphere of nitrogen. Catalyst dibutyl tin dilaurate (0.1 g/100 g total reaction product) was then added to enhance the reaction rate and stirring was continued for 3 more hours. The progress of the reaction was monitored by determining

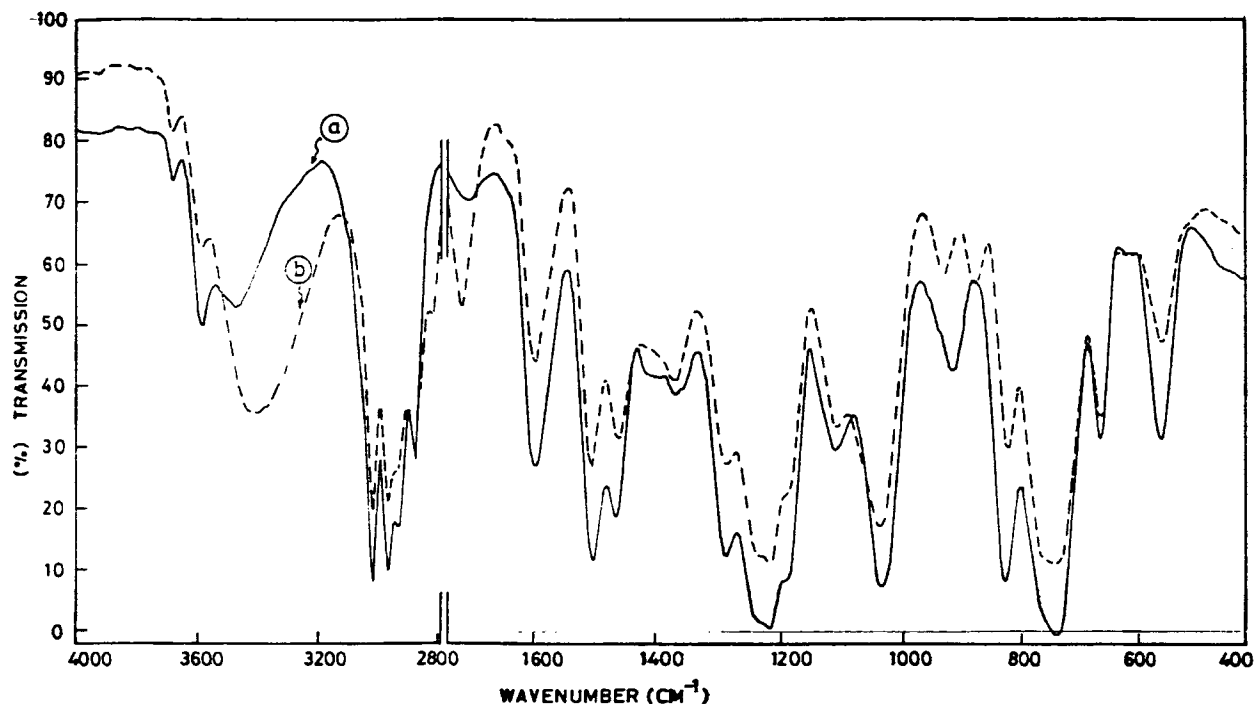


Figure 4 IR spectrum of: (a) epoxy resin; (b) epoxy amine adduct.

the free isocyanate content in the reaction product,¹¹ and the reaction was allowed to proceed till the isocyanate content reached a value of 9.8 (theoretical value 13.17). The final product was analyzed by IR (Fig. 5).

Synthesis of Ricinoleic Bis(2-Hydroxy Ethyl)amide-Urethanes (RBHEA-Urethanes)

RBHEA (0.3 mol) was added to the partially blocked isocyanate (1.0 mol) at 45°C. The reaction temper-

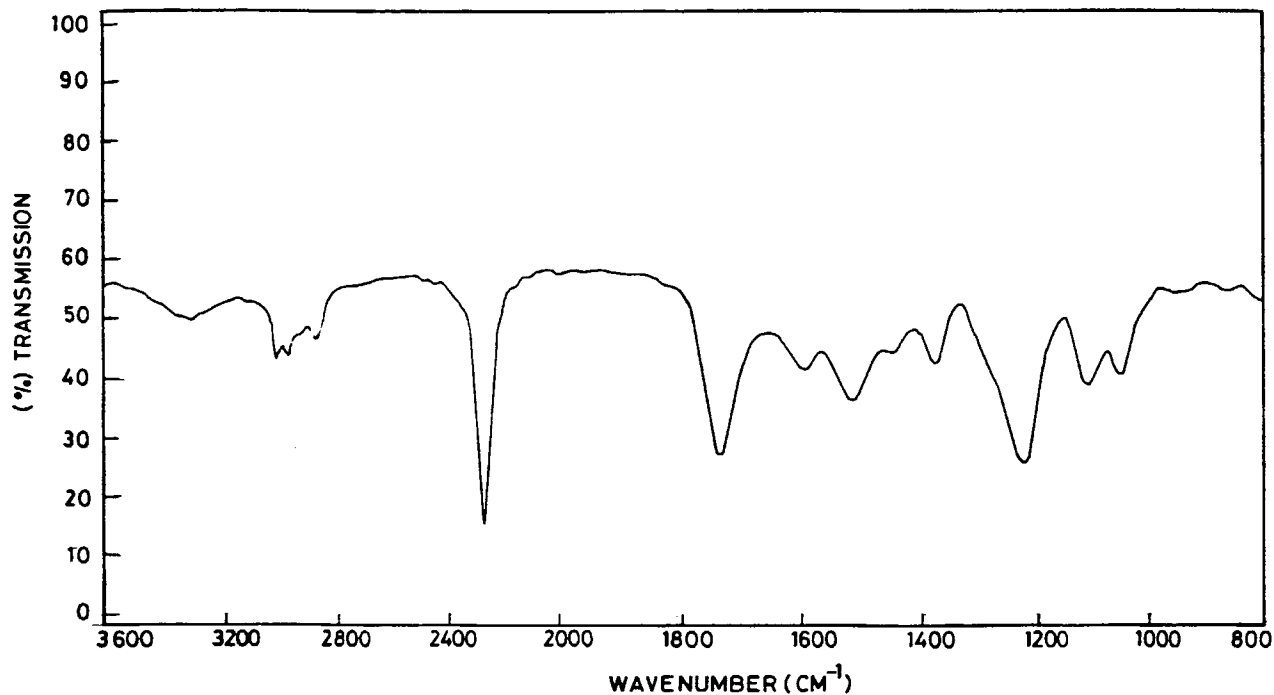


Figure 5 IR spectrum of partially blocked isocyanates of *N,N'*-diethyl lactamide.

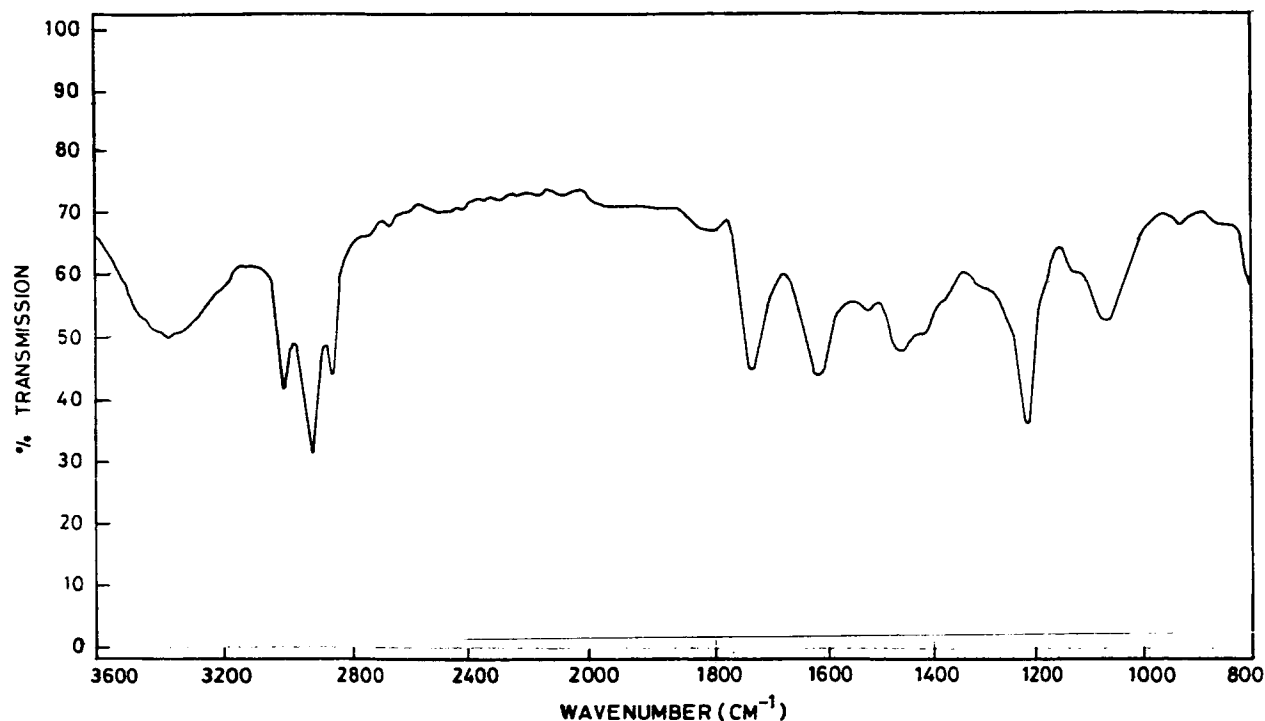


Figure 6 IR spectrum of ricinoleic bis(2-hydroxy ethyl) amide urethane.

ature was raised to 80°C and held for 6 h. The reaction was followed periodically by determining the isocyanate content till it reached a negligible value. The reaction product was characterized by IR (Fig. 6).

Synthesis of Binder for Electrodeposition

Several binders were prepared by reacting the epoxy amine adduct with RBHEA-urethane in various weight proportions 1.00 : 1.00, 1.00 : 0.50, 1.00 : 0.25, 1.00 : 0.20, and 1.00 : 0.10, respectively, at $150 \pm 5^\circ\text{C}$ for 30 min. On the basis of the results of the solu-

bility of the products obtained, in acidified water (2% acetic acid solution in distilled water) and their electrodepositable characteristics (Table II), the binder prepared with the weight ratio of 1.00 : 0.20 (epoxy amine adduct to RBHEA-urethane) was found to be the most suitable for electrodeposition and was used for further studies. Further with varying pH (5.0–7.0) electrodeposition experiments were carried out with the chosen medium (Table III), and from the results the pH 6.0–6.5 which was found suitable was chosen for further electrodeposition of medium as well as paints.

Table II Effect of Variation of RBHEA-Urethane on Electrodeposition at Constant Epoxy Amine Adduct

Sample No.	Binder	Epoxy Amine Adduct/RBHEA Urethane (w/w)	Solubility in Acidified Water	Electrodeposition
1	A	1.00 : 1.00	S	No proper deposition
2	B	1.00 : 0.50	S	No proper deposition
3	C	1.00 : 0.25	S	No proper deposition
4	D	1.00 : 0.20	S	Uniform film deposition
5	E	1.00 : 0.10	S	No proper deposition

^a S = soluble.

Table III Effect of pH on Electrodeposition (Binder-D)

Sample No.	pH of Bath	Electrodeposition
1	7.0	No proper deposition
2	6.0–6.5	Uniform deposition
3	5.0	Polymer coalescence/dissolution of the binder

Preparation of Water-Soluble Paint System

Two sets of paints, one with natural iron oxide and the other with rutile variety of titanium dioxide, varying in pigment volume concentrations (0–10%) were prepared using the binder and requisite amounts of driers on the binder. The pigment volume concentration (PVC) is defined as the fraction of pigment volume in paint and given as

$$(i) \text{ PVC} = \frac{V_p}{V_p + V_B}$$

(expressed in terms of volumes)

$$(ii) \text{ PVC} = \frac{W_p/\rho_p}{W_p/\rho_p + W_B/\rho_B}$$

(expressed in terms of weights)

where V_p , W_p , and ρ_p are the volume, weight, and density, respectively, of the pigment and V_B , W_B , and ρ_B are the volume, weight, and density, respectively, of the binder. The studies on the effect of PVC on electrodeposition indicated the pigmentation level at only 3%; in both the cases of pigmentation gave good deposition. Hence, further work was carried out only with 3% PVC paints.

Cathodic Electrodeposition of Media/Paints

The cathodic electrodeposition studies on the above system indicated that only a 10% solution in the case of the binder and 20% solution in the case of pigmented binder were found to give uniform film deposition at a pH 6.0–6.5 with a stainless steel panel as the anode and mild steel panels as replaceable cathodes. The depositions were carried out at different voltages for different intervals of time. The panels with the deposited coatings were taken out of the bath, thoroughly rinsed with deionized water to remove loosely adhering binder/paint, and the coatings were baked at $150 \pm 5^\circ\text{C}$ for 30 min.

The effect of time of deposition at constant volt-

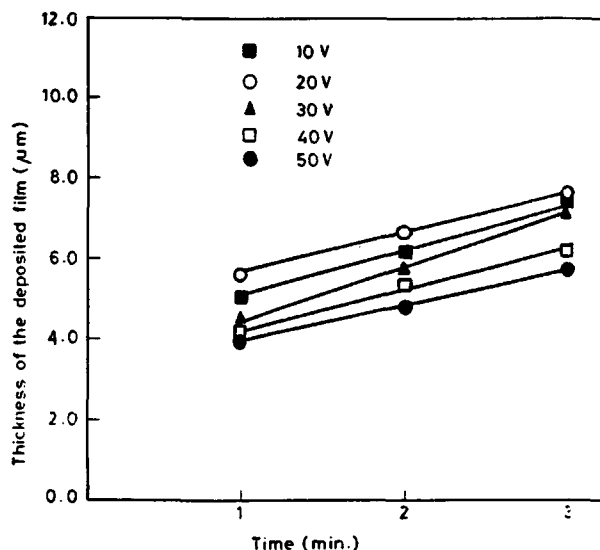


Figure 7 Thickness of the deposited binder film vs. time.

ages on the thickness of the deposited film are given in Figures 7, 8, and 9.

Test Methods

The physicochemical properties of the binder and paint system such as adhesion determined by the crosshatch method,¹² impact resistance by the falling weight method,¹³ flexibility by the mandrel method,¹⁴ and resistance to chemicals and solvents¹⁴ of the coatings were measured on films coated at 10 V, 3 min for binder, 20 V, 3 min for titanium dioxide paint, and 40 V, 2 min for iron oxide paint as these parameters gave good coating. The results are tabulated in Table IV.

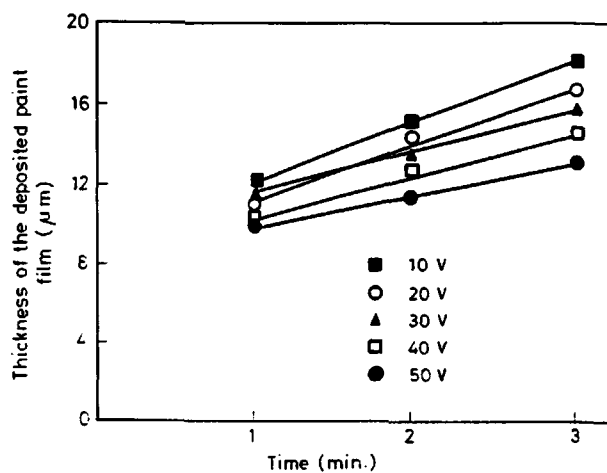


Figure 8 Thickness of the deposited paint film (titanium dioxide) vs. time.

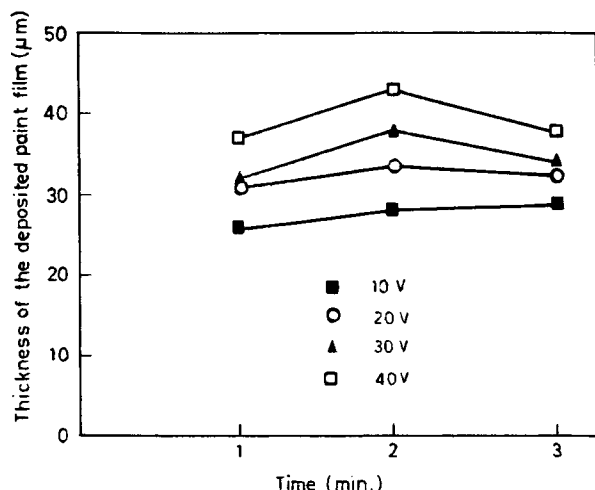
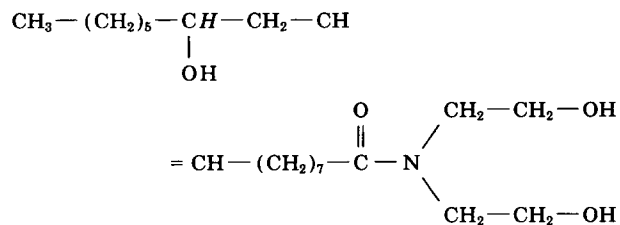


Figure 9 Thickness of the deposited paint film (iron-oxide) vs. time.

RESULTS AND DISCUSSION

The IR spectra (in CHCl_3) of RBHEA [Figs. 1 (a) and (b)] show the disappearance of the ester absorption band at 1740 cm^{-1} of castor oil and the appearance of an amide absorption band at 1620 cm^{-1} , indicating the formation of ricinoleic bis(2-hydroxyethyl)amide. The PMR spectral assignments (Table 1 and Fig. 2) indicate that the isolated product is ricinoleic bis(2-hydroxyethyl)amide, and, based on the spectra, it was assigned the following structure:



The presence of the amide absorption band at 1630 cm^{-1} in Figure 3 and of *N,N'*-diethyl lactamide after removal of unreacted amine and solvent under vacuum indicate the formation of *N,N'*-diethyl lactamide. The appearance of an absorption band at 2335 cm^{-1} in Figure 5 of partially blocked isocyanate of *N,N'*-diethyl lactamide indicates the presence of the isocyanate group. The disappearance of the isocyanate group when it reacted with ricinoleic bis(2-hydroxyethyl) amide shows the formation of urethane linkage in the IR spectrum (Fig. 6) of the final product. The absence of an absorption band at 920 cm^{-1} due to opening of oxirane ring and appearance of hydroxyl and amine band at 3300 cm^{-1} indicate the formation of epoxy amine adduct [Fig. 4(b)]. This has been also confirmed by the dilutability of the product in acidified water.

Among the series of binders prepared by reacting RBHEA-urethane in different weight ratios with epoxy amine adduct, it was found that the binder having the weight ratio 1.00 : 0.20 (epoxy amine adduct to RBHEA-urethane) only gave rise to deposition of uniform film (Table II).

Table IV Physicochemical Properties and Resistance to Chemicals/Solvents of Electrodeposited Films

Serial No.	Test Conducted	Binder	Iron Oxide Paint (3% PVC)	Titanium Dioxide Paint (3% PVC)
1	Scratch hardness (N)	3.50	30.00	25.00
2	Adhesion (crosshatch method)	G	VG	G
3	Impact resistance	I	I	I
4	Flexibility ($\frac{1}{4}$ in. mandrel)	ND	ND	ND
5	Resistance to:			
	(a) Water (48 h)	P	P	P
	(b) 2% H_2SO_4 (16 h)	SH	SH	SH
	(c) 5% Na_2CO_3 (4 h)	P	P	P
	(d) 5% NaHCO_3 (4 h)	P	P	P
	(e) 1% NaOH (4 h)	P	P	P
	(f) Xylene (4 h)	P	P	P
	(g) Butanol (4 h)	P	P	P
	(h) White spirit (4 h)	P	P	P

* VG = none of the small squares got detached in the test; G = a few small squares were detached in the test; I = found to have impact resistance of 10.5 lb weight, when allowed to fall through a height of 22.5 in.; ND = no damage such as cracking or detachment of the film when bent through an angle of 180° ; P = serial no. 5 (a-h)—no sign of deterioration in the paint film, gloss, and color; SH = slight haziness.

It was also observed that pH values higher than 6.5 do not lead to uniform film deposition; similarly, deposition at pH values lower than 6.0 give films in which the polymer not only coalesced but also led to the evolution of gas. Thus a very narrow range of pH 6.0–6.5 was found suitable for better film deposition for the above system (Table III).

In the case of binder it is seen that, as the time of deposition increases, the thickness of the deposited binder film increases irrespective of applied voltage up to 20 V, beyond which it decreases (Fig. 7); the maximum film thickness that could be obtained was at 20 V with 3 min of deposition time.

The behavior of titanium dioxide paints (Fig. 8) is very similar to that of binder with respect to the relation between thickness of coating and the time of deposition except that there is a continuous fall in the film thickness with increase in voltage. The maximum film thickness obtained under the experimental condition was at 10 V with 3 min of deposition time. The thickness of the pigmented coatings were always found to be higher than unpigmented systems at all voltages.

However, for iron oxide paints (Fig. 9), with increase in the time deposition, the thickness of the film increased only up to 2 min, and then decreased. This feature has been noticed at all applied voltages. The maximum film thickness was obtained at 40 V with 2 min of deposition time. The film thickness of iron oxide coatings were also found to be higher than that of binder and also found to be higher than that of titanium dioxide coatings at all voltages.

The increase in the thickness in both the coatings could be explained by the fact that there are greater current yields in pigmented systems than in unpigmented system.¹⁵ Also, the current yields for iron oxide coatings appear to be higher than for titanium dioxide coatings. This could be explained by considering the surface area of the pigment particles used in the preparation of paints as measured by surface area measurements by BET technique. The titanium dioxide pigment particles have larger surface area (12 m²/g) when compared with that of iron oxide (8 m²/g). The larger the surface area of pigment particle, the greater will be the quantity of the binder adsorbed on them. From this it could be expected that the deposited films of titanium dioxide paints are likely to have more binder in them than the pigment, thus offering higher electric resistance at a lower thickness. This explains the coatings of lower thickness obtained for titanium dioxide paints and its behavior quite similar to that of the binder.¹⁶

The inflection points noticed at about 2 min of deposition time in the case of iron oxide coatings at

all voltages correspond to the attainment of critical pigment volume concentration (CPVC) in the film. (CPVC is a state of pigmentation where an abrupt change is noticed in the properties of paint film). In the case of titanium dioxide coatings, the CPVC is not reached within the deposition parameters studied. As a result, the film deposited at different voltages are always under pigmented when compared to the iron oxide coatings.

The physicochemical properties of the binder/paints (Table IV) indicate that the films possessed good flexibility, impact resistance, and good adhesion. The scratch hardness was found to be about eight times higher for iron oxide coatings and about six times higher for titanium dioxide coatings over the unpigmented system. This is due to increased amount of binder content in titanium dioxide coatings. The films were found to be resistant to water, alkali, xylene, butanol, and white spirit solvents, but slight haziness developed in 2% sulfuric acid solution.

CONCLUSIONS

1. A suitable cathodic electrodepositable binder was obtained by reacting epoxyamine adduct and RBHEA–urethane in the weight ratio of 1.00:0.20, respectively.
2. A narrow range of pH 6.0–6.5 was found to be suitable for electrodeposition.
3. Titanium dioxide coatings were softer than iron oxide coatings.
4. With increase in concentration of pigment in the coating, iron oxide coatings attained CPVC at an early stage when compared to titanium dioxide coatings.

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