

Synthesis and Characterization of Mannich Bases from Cardbisphenol*

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Synopsis

Water-soluble Mannich bases were synthesized from cardbisphenol by Mannich reaction and were characterized by ¹H-NMR and ¹³C-NMR spectroscopic methods. The effect of electrodeposition parameters on the film formation from binders and from the pigmented composition were studied. The polymers gave uniform coatings with good mechanical properties and the pigmented systems exhibited high resistance to organic solvents and excellent corrosion resistance properties.

INTRODUCTION

Ecological and economic pressures have led to the advancement of water-soluble coating technology in the 1970s, resulting in the use of water-soluble polymers in the place of costly and hazardous petroleum-based solvents, especially in industrial coating sector. Their application by conventional as well as by electrodeposition methods, have been the other reason for their popularity.

Preparation of a Mannich base (MB) from condensed phenols is one of the methods of introducing nitrogen atom in a polymeric molecule and converting it after neutralization with acidified water into a cathodically electrodepositable system. The patents literature¹⁻⁴ describes polymer systems suitable for cathodic electrodeposition which are Mannich bases derived from the reaction of condensed phenolic compounds with hydroxyl containing secondary amine and formaldehyde. These are reported to have the advantage of deposition at a pH range of 7-9.

In the previous publication,⁵ the synthesis and characterization of cardbisphenol were reported. The aim of the present work is to synthesize Mannich bases from cardbisphenol, characterize them by ¹H-NMR and ¹³C-NMR spectral data, and evaluate their suitability as water-soluble polymers for cathodic electrodeposition.

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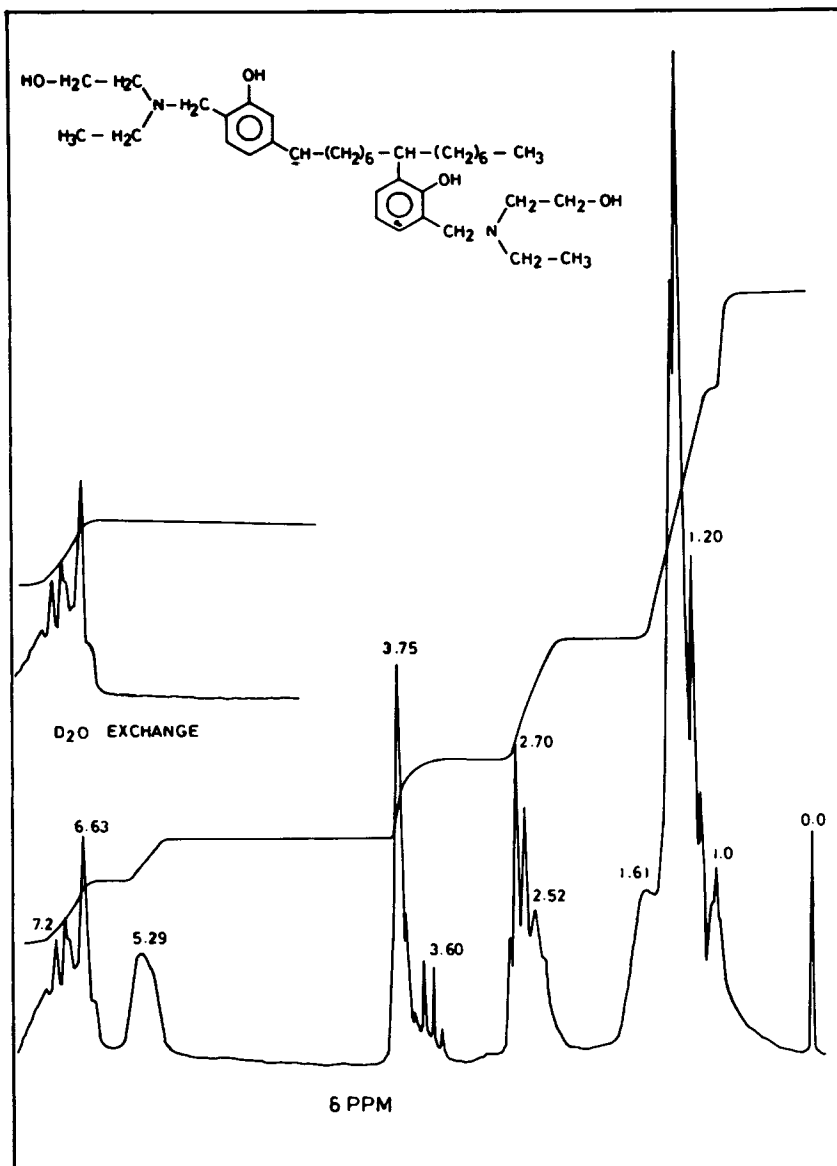
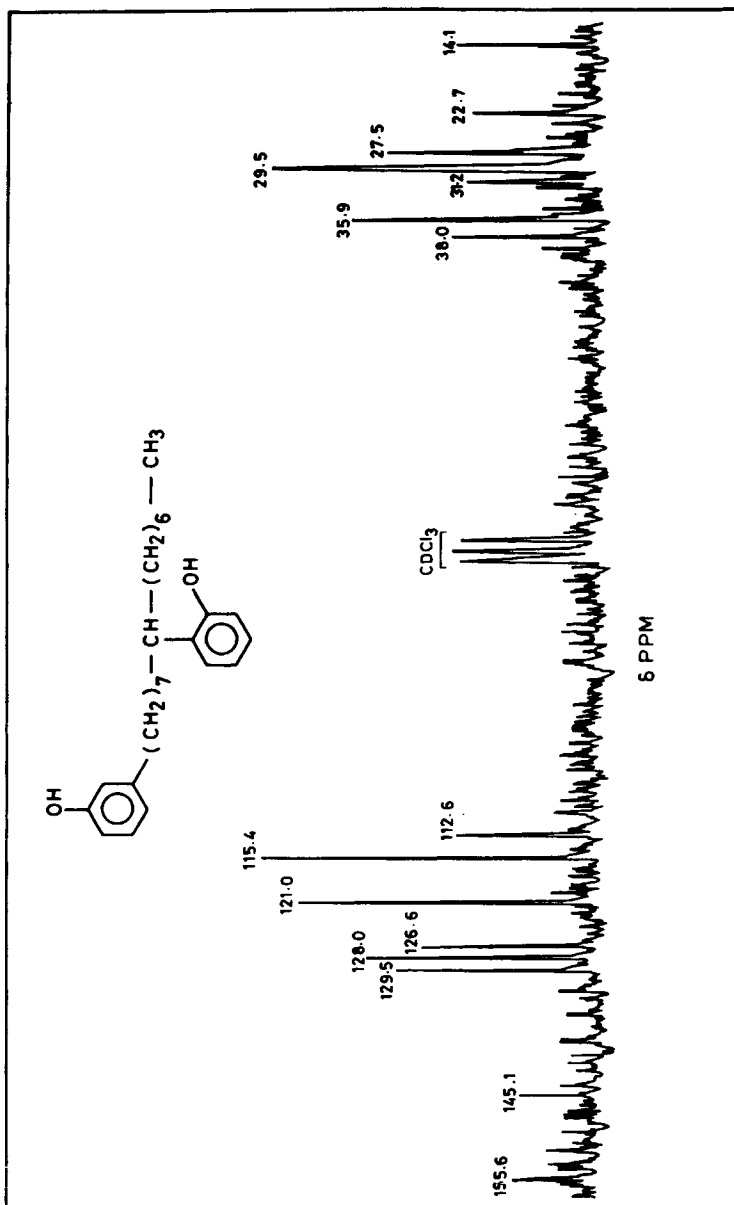


Fig. 1(a). ¹H-NMR spectrum of Mannich base (MB₁).

The products MB₁ and MB₂ were characterized by ¹H-NMR and ¹³C-NMR spectra. NMR spectra were recorded in deuterated chloroform on Jeol FX 90Q spectrophotometer operating at 89 MHz. The chemical shifts are given in δ ppm downfield from internal TMS standard. The ¹H-NMR spectrum of MB₁ and ¹³C-NMR spectra of CB and MB₁ are represented in Figures 1(a), 1(b), and 1(c), respectively. The chemical shifts for various protons present in CB, MB₁, and MB₂ and their assignment are tabulated in Table I, and their physical properties are given in Table II.

Fig. 1(b). ^{13}C -NMR spectrum of cardbisphenol (CB).

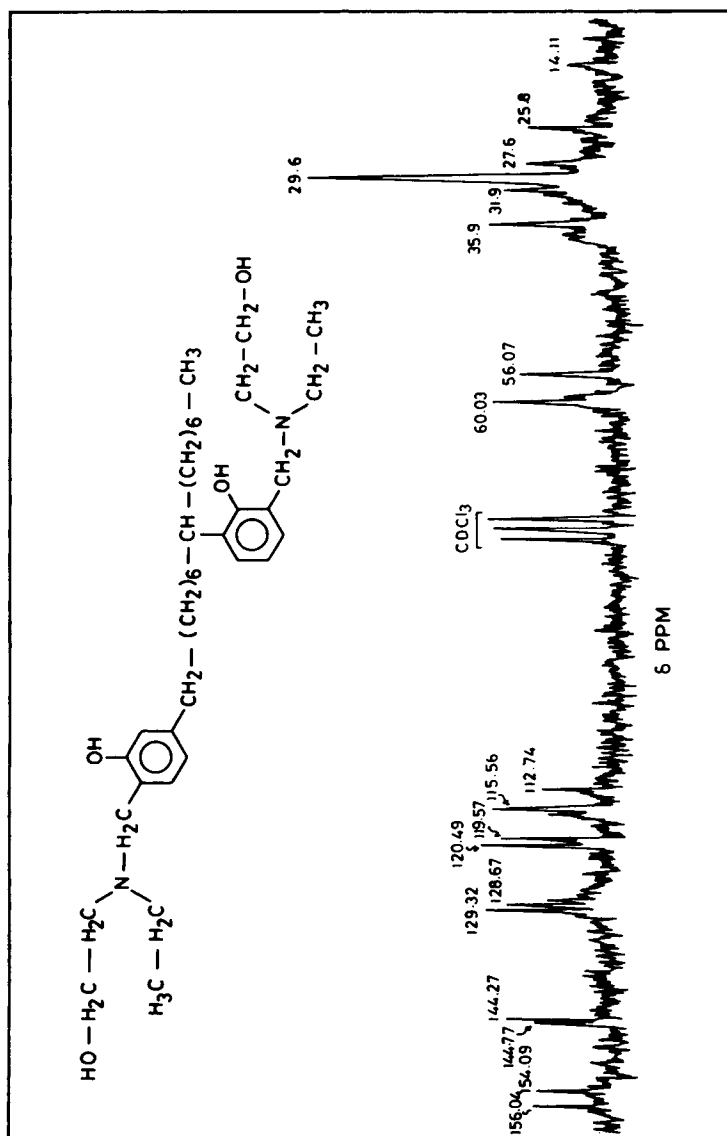
Fig. 1(c). ¹³C-NMR spectrum of Mannich base (MB₁).

TABLE I
¹H-NMR Spectral Data for Cardbisphenol (CB) and the Mannich Bases MB₁ and MB₂^a

Chemical shifts (δ ppm)			
CB	MB ₁	MB ₂	Assignment
0.84 (dt, 3 H)	1.00 (dt, 9 H)	1.00 (dt, 3 H)	— CH ₃
1.20–1.55 (brm, 24 H)	1.20–1.61 (brm, 24 H)	1.20–1.62 (brm, 24 H)	 — CH ₂
2.52 (t, 2 H)	2.52–2.70 (brm, 11 H)	2.52–2.72 (brm, 11 H)	Ar — CH ₂ — CH ₂ — H ₃ C — CH ₂ — N —
2.59–2.87 (m, 1 H)			— CH — Ar
—	3.60–3.75 (m, 8 H)	3.65–3.77 (brm, 12 H)	R ₂ N — CH ₂ — Ar HO — CH ₂ — CH ₂ —
4.67–4.79 (brS, 2 H)	5.29 (brS, 4 H)	4.78 (brS, 6 H)	Phenolic — OH — H ₂ C — OH
6.65–7.20 (m, 8 H)	6.63–7.20 (m, 6 H)	6.63–7.20 (m, 6 H)	— HC = CH — Ar

^adt: distorted triplet, t: triplet, S: singlet, brm: broad multiplet, m: multiplet, brs: broad singlet, Ar: aromatic.

Preparation of Polymer Solutions for Electrodeposition

Aqueous solutions for electrodeposition were prepared by neutralizing the Mannich bases with acetic acid and diluting with sufficient quantity of deionized water to provide 12% solids content maintaining the pH of the solutions between 6.5 and 7.0.

Preparation of Paint

The paint was prepared with the acidified aqueous solution of MB₂ and natural iron oxide pigment (α iron oxide, specific gravity 5.2) at 5% pigment

TABLE II
 Physical Properties of Polymers^a

Physical property	Results		
	CB	MB ₁	MB ₂
Color			
10% solution in xylene at 36°C	15R, 42Y	10R, 31Y	15.1R, 30Y
Viscosity,			
50% solution in xylene at 35°C (Cps)	13.0	40	72
Refractive index [36n _D]	1.523	1.524	1.529
Solubility,			
in 5% aq. solution of acetic acid	Insoluble	Soluble, clear transparent solution	Soluble, clear transparent solution

^aCB = cardbisphenol and MB = Mannich base

TABLE III
Physico chemical Properties of Electrodeposited Films of Mannich Bases and Paint^a

Film property	Results		
	MB ₁	MB ₂	Paint
Mechanical properties			
Maximum dry film thickness (μm)	10	10	15
Scratch hardness (g)	2200	2400	2700
Flexibility (1/4 in. mandrel) IS: 101-1964	P	P	P
Impact resistance: DEF: 1053 (17), 10.5 lb, 23 in.			
Direct	P	P	P
Indirect	P	P	P
Adhesion strength (kg/sq cm)	240.7	256.5	317.8
Durability tests*			
Salt spray test: IS:2074-1062	NE	NE	NE
(h)	(480)	(480)	(576)
Humidity corrosion test: IS: 101-1964	NE	NE	NE
(h)	(720)	(720)	(960)

^a Voltage = 50 Volts, time of deposition = 120 s.

Note: *The films are resistant to distilled water; white spirit; IS: 101-1964; H₂SO₄ (2%) IS: 2932-1964; NaOH(1%); butanol and xylene. P = pass: no visual cracks and coating is intact even on gentle rubbing. MB₁ = Mannich base from 2-ethylaminoethanol. MB₂ = Mannich base from diethanol amine. NE = no effect.

volume concentration (PVC). The paint at 50% solids level was ground to a fineness of grind 7–8 on Hegman gauge in the Red Devil paint grinding unit, and was strained through a fine muslin cloth and stored in closed bottles for a period of 2 days. Then it was thinned down to 12% solids with requisite quantity of deionized water and used for electrodeposition.

Electrodeposition

Electrodeposition was carried out using the paint described above on replaceable mild steel panels, rods, and discs as cathodes⁶ and a stainless steel anode under the following conditions: pH of the bath 6.5–7, applied voltage 50 V, immersion time 2 min, current density 3–5 amp/sq ft, temperature 28°C, and pole to pole distance of 6 cm. The coated test pieces were washed with deionized water and baked at 120–130°C for 30 min. The physico chemical properties of electrodeposited films of Mannich bases and paint are listed in Table III.

Pigment Migration Efficiency

Pigment migration efficiency (PME) is the pigment to binder ratio in the cured electrodeposited film divided by the pigment to binder ratio in the bath expressed in percent. The pigment to binder ratio in the deposited film was determined by scraping the film from the metal after washing with water but before submitting it for baking and collecting it in a weighed porcelain crucible. The crucible with its contents were heated to 120°C for 20 min, cooled, and weighed. The cured scrapings were then ashed in the same crucible in a muffle furnace at 500°C and reweighed to determine the percentage of

TABLE IV
Effect of Time on the PVC in Cured Electrodeposited Paint Films^a

Sample no.	Time (s)	PVC of the bath (%)	P/B ratio of the bath	P/B ratio in the cured film	PVC in the cured film (%)	Pigment migration efficiency (%)
1	30	5	0.27	0.22	4.05	81
2	60	5	0.27	0.25	4.50	93
3	90	5	0.27	0.34	5.76	126
4	120	5	0.27	0.40	7.10	148
5	150	5	0.27	0.42	7.42	155
6	180	5	0.27	0.44	7.60	159

^aVoltage = 50 V. Note: PVC = pigment volume concentration; P = pigment; B = binder.

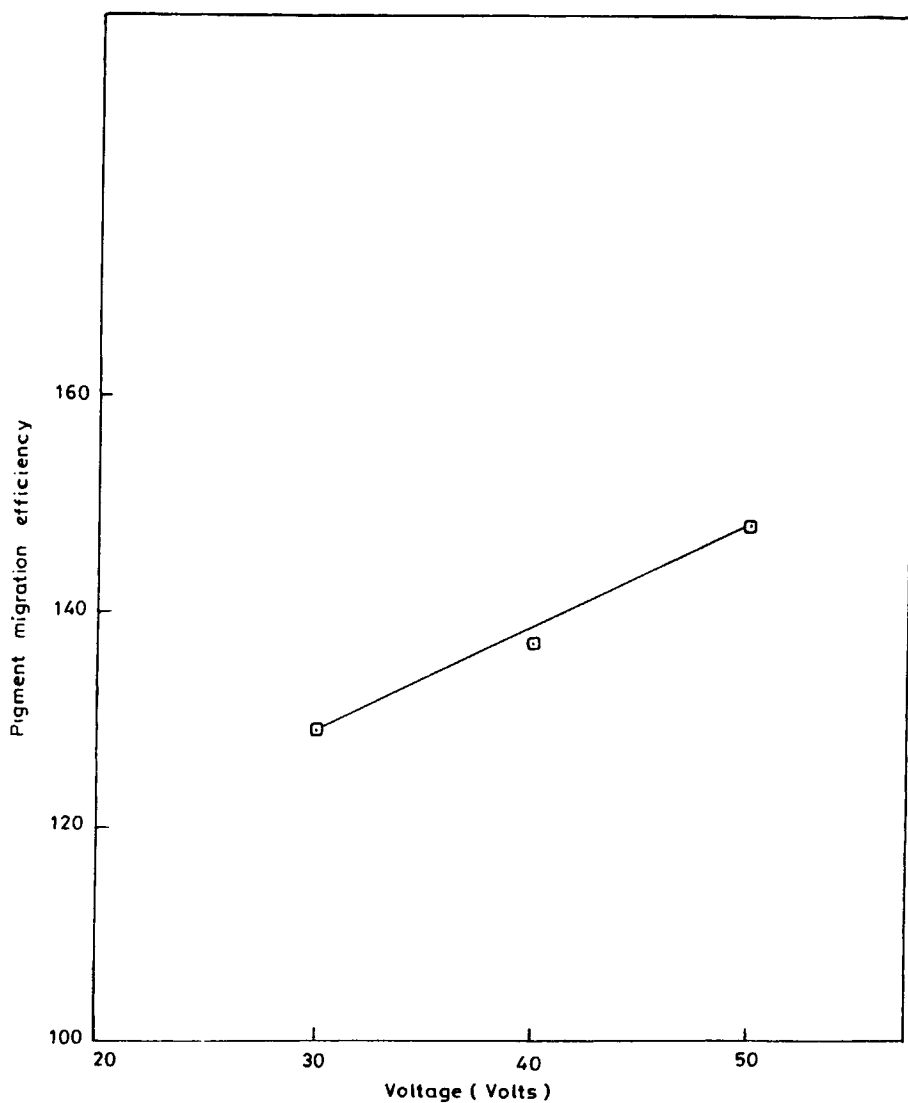


Fig. 2. Effect of voltage on pigment migration efficiency of iron oxide paint at 120 s.

pigment in the cured film. With the help of pigment to binder ratio in the cured film and in the bath, the PME was calculated for the electrodeposited coatings. The PME of the paint was determined at different deposition time intervals ranging from 30–180 s at a constant depositing voltage of 50 V (Table IV) and also at constant voltages ranging from 30 to 50 V at the deposition time of 120 s. In the above determinations separate baths were used for each experiment. The observations made are illustrated in Figure 2.

The percentage PVC in the cured electrodeposited films was calculated from the pigment to binder ratio in the cured films. The results are listed in Table IV.

The effect of variation of deposition time at constant voltage of 50 on dry film thickness, scratch hardness, and adhesion of the paint films was studied. The observations are represented in Figures 3–5.

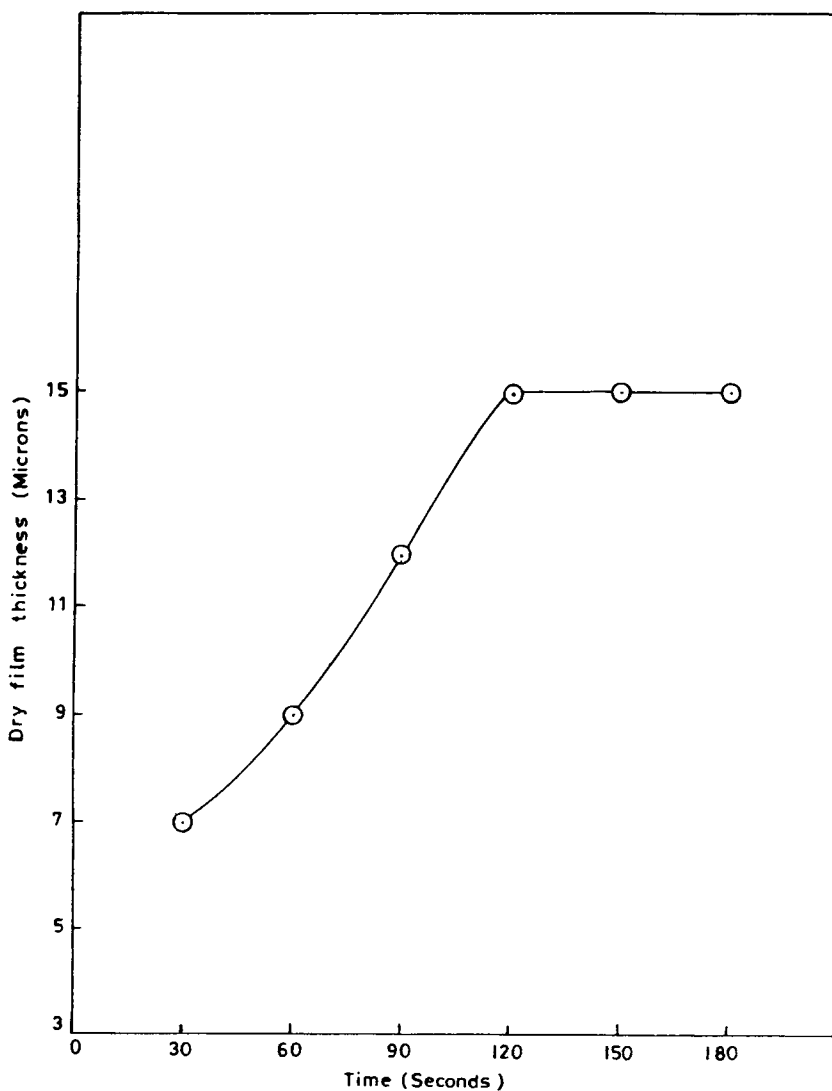


Fig. 3. Effect of time on dry film thickness of iron oxide paint of Mannich base.

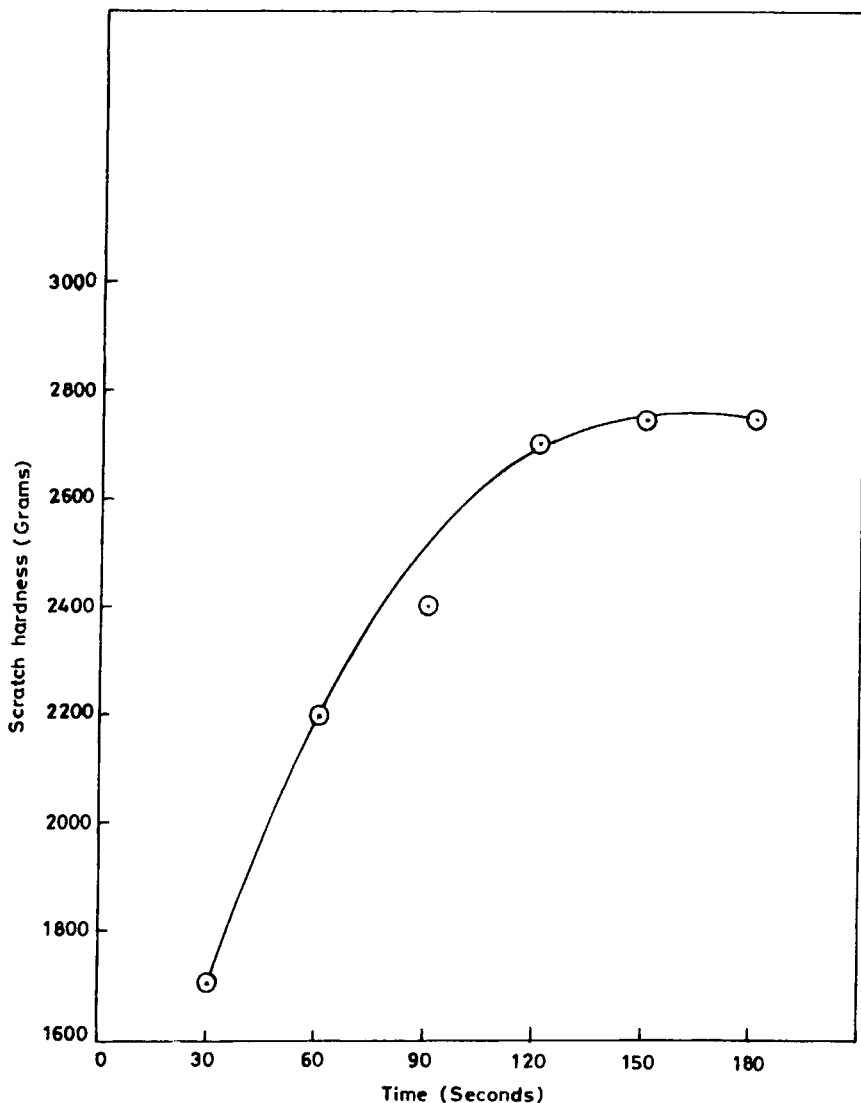


Fig. 4. Effect of time on scratch hardness of iron oxide paint of Mannich base.

RESULTS AND DISCUSSION

The fact that the Mannich bases from carbdisphenol, MB_1 , and MB_2 are soluble in 5% aqueous acetic acid solution indicates the introduction of amine moieties into the carbdisphenol molecule (Table II). This is also indicated in their NMR spectra.

In MB_1 and MB_2 , the methylene protons attached to nitrogen, originating from amine moieties, along with the two methylene and one methine proton present in the starting material (CB), have appeared as a multiplet at δ 2.70. The methylene protons attached to aliphatic-OH, and those between the nitrogen atom and aromatic nucleus, have appeared as a multiplet at δ 3.77, which are absent in the CB [Fig. 1(a), Table I].

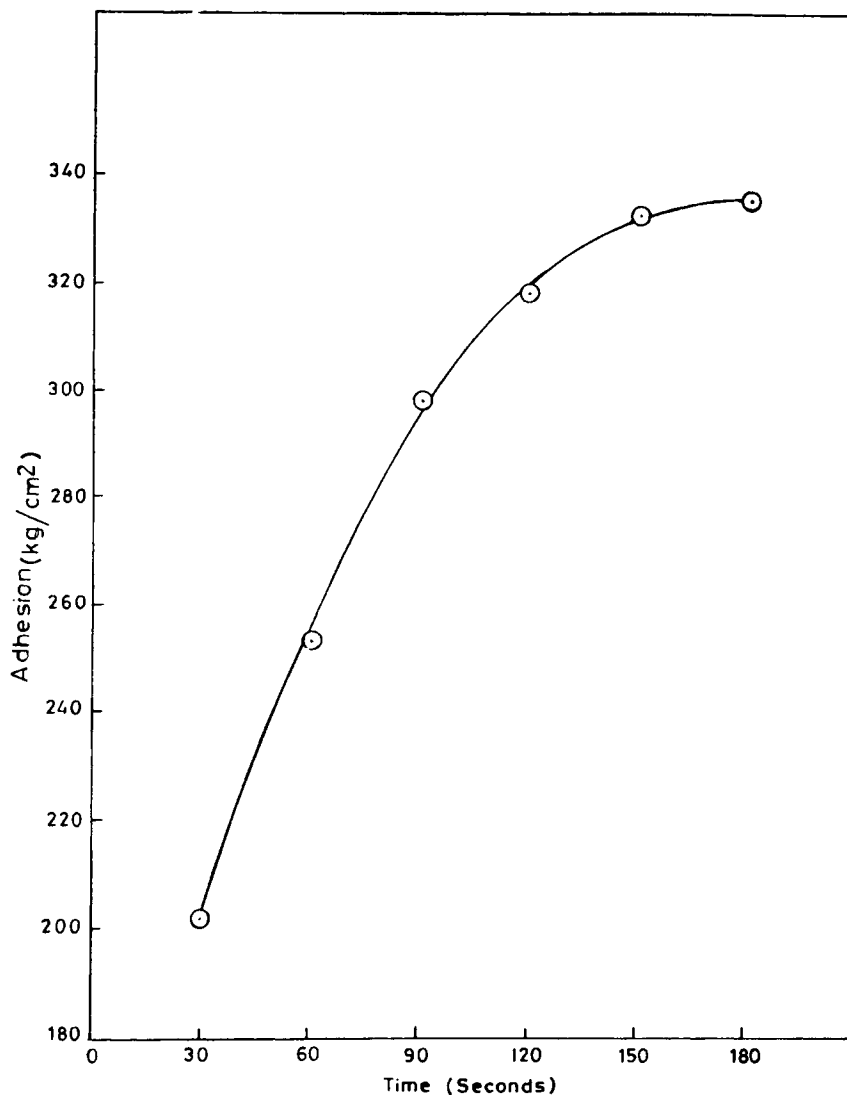


Fig. 5. Effect of time on adhesion of iron oxide paint of Mannich base.

The above observations confirm the introduction of amine moieties into the cardbisphenol molecule. This was further confirmed by ¹³C-NMR spectrum [Fig. 1(c)], which showed peaks at δ 56.07 and δ 60.03 corresponding to the carbons attached to nitrogen and oxygen atoms, respectively, which were not present in the ¹³C-NMR spectrum of the starting material [Fig. 1(b)]. Further, from the integration of ¹H-NMR spectra of MB₁ and MB₂, it can be concluded that two amine moieties have entered into the cardbisphenol molecule in both cases.

Both the Mannich bases MB₁ and MB₂ in aqueous acid solution gave better films when the electrodeposition was carried out at 50 V for 2 min. The binders showed similar performance in many properties except in scratch hardness and adhesion where the values for films obtained from MB₂ are

marginally higher than those from MB₁ (Table III). The increase in scratch hardness and adhesion for the films obtained from MB₂ could be attributed to greater crosslinking, resulting in ether linkages and presence of more polar groups, in the polymer backbone. Because of better properties, MB₂ was chosen for preparing pigmented compositions.

The deposition time (at 50 V) also affected the dry film thickness, scratch hardness, and adhesion of the deposited paint films (Figs. 3–5). With increase in deposition time, the dry film thickness goes on increasing (Fig. 3) reaching a maximum of 15 μm at 120 s and then is almost constant with increasing deposition time. A similar trend was observed in the case of scratch hardness (Fig. 4) and adhesion (Fig. 5).

The physicochemical and anticorrosive properties of the pigmented polymeric films showed an improvement over those of the binder (Table III). The pigment migration efficiency was found to be influenced by deposition parameters, viz., applied voltage (Fig. 2) and time as seen from the values listed in Table IV. The PME increased with deposition time (Table IV) and voltage (Fig. 2).

At 60 s and 50 V, the pigment volume concentration (PVC) of the cured film and of the bath appear to be almost equal (Table IV). However, maximum values of thickness, scratch hardness, and adhesion were observed for electrodeposited coatings when the percentage of PVC in the coatings was 7.1, which was obtained by carrying out the deposition for 120 s.

CONCLUSIONS

The Mannich base from carbisphenol and diethanolamine exhibited higher values for adhesion and scratch hardness when compared to the one from 2-ethylaminoethanol due to the presence of more polar groups in the polymer backbone of the former. The pigment migration efficiency increased with increase in deposition time and applied voltage. The time of deposition affected the film thickness, scratch hardness, and adhesion of the deposited paint films. The values increased with increase in deposition time up to 120 s; thereafter they appear to become steady.

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