

ORGANIC COATING BY ELECTROPOLYMERIZATION OF O-CRESOL*S AZIM and S GURUVIAH*

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ABSTRACT

In electropolymerization, as in electrodeposition use is made of electrodes, an electrolyte, and a source of electric power. Oxidation or reduction can take place at the electrode and radicals may be formed. These radicals can react with unsaturated monomers in the electrolyte and polymerization can take place on one of the electrodes with formation of a coating.

The electrochemical oxidation by phenol function in this case of substituted phenol derivatives leads to polymer films of polyphenylene oxide. The electrochemical polymerization of o-cresol was carried out in alkaline medium using mild steel as anode and stainless steel as cathode. Various concentrations of monomer with various additives were studied. The polymer film formed has an average thickness of 10-12 μ . The polymer film was subjected to IR Spectra for confirmation and the properties of the coated mild steel substrate were evaluated.

Key words: Electropolymerisation, organic coating, o-cresol

INTRODUCTION

In electropolymerization, oxidation or reduction can take place at the electrodes and radicals may be formed. These radicals can react with monomers in the electrolyte and polymerization can take place on one of the electrodes resulting in a coating. The electrochemical oxidation of phenol and its derivatives had led [1] to different products depending upon the conditions employed. It was established [2] that two anodic reactions were possible with simple phenol: (i) a two electron loss from the unionized phenol to give phenoxium ion and (ii) the removal of one electron from phenoxide to give phenoxy radical. The latter is highly possible in the presence of a strong base. This paper describes the controlled polymerization of o-cresol in sodium hydroxide, where a uniform coating on mild steel substrate was obtained and the properties were evaluated.

EXPERIMENTAL**Preparation of bath**

O-cresol (LR), sodium hydroxide (LR Merck) and sodium nitrite were used as such. The bath composition and additive used in the study are given in Table I below;

Table I: Composition of baths studied

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| 1. O-cresol 0.1 M + NaOH 0.1 M + No additive |
| 2. O-cresol 0.1 M + NaOH 0.1 M + NaNO ₃ 50 ppm |
| 3. O-cresol 0.1 M + NaOH 0.1 M + NaNO ₃ 100 ppm |
| 4. O-cresol 0.1 M + NaOH 0.1 M + NaNO ₃ 150 ppm |
| 5. O-cresol 0.1 M + NaOH 0.2 M + NaNO ₃ 100 ppm |
| 6. O-cresol 0.2 M + NaOH 0.2 M + NaNO ₃ 100 ppm |
| 7. O-cresol 0.2 M + NaOH 0.3 M + NaNO ₃ 100 ppm |
| 8. O-cresol 0.3 M + NaOH 0.3 M + NaNO ₃ 100 ppm |

Experimental procedure

A 3-electrode cell was used for the anodic oxidation. This cell consisted of a working electrode, auxiliary platinum electrode and a reference SCE

electrode. A mild steel electrode of 1 sq. cm. was polished to 4/0 emery and cleaned with trichloroethylene. Various bath compositions indicated above were taken in the cell and the mild steel electrode was immersed into the solution. A potential sweep from its O.C.P. to +2V was applied to the electrode at rate of 20 mV/sec. and the resulting current was recorded with the help of an X-Y recorder. All potentials were measured with respect to SCE.

Bulk deposition of the polymer was carried out in a beaker with proper enclosure. Stainless steel panel of 5 x 6 cm. size was used as cathode and mild steel panels of the same size were used as anodes. The mild steel specimens were polished, degreased with trichloroethylene, cleaned cathodically for 2 minutes in a solution containing 35 g/l sodium hydroxide and 25 g/l sodium carbonate, and washed well with distilled water. A DC rectifier was used to power the cell. The deposition was carried out till the current comes close to zero. Large numbers of panels were coated and were used for investigations.

Determination of physical properties of the coating

The coated panels were airdried and the following properties were determined.

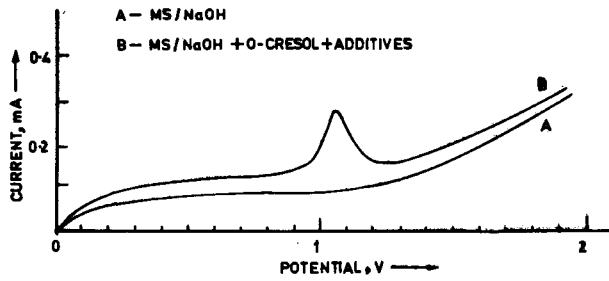
- i) Drying time - by visual observation
- ii) Thickness of the coating - by Elcometer
- iii) Adhesion by scotch tape method
- iv) Hardness - with pencil hardness tester
- v) Infrared spectra of the polymer film for determination of structure

Corrosion-resistance properties*i) Salt spray test*

Canning salt spray chamber was used for the evaluation of the coating in 3% sodium chloride solution. Triplicate panels of size 5 cm x 6 cm were exposed for 5 days.

ii) Anodic polarisation

1 sq.cm. mild steel specimens were used. Both the coated and uncoated specimens were polarized up to +500 mV in 3% sodium chloride at a scan rate of 1 mV/sec.



iii) Capacitance, resistance measurements:

'WAYNEKERR' Universal bridge B224 was used for these tests. The measurements were carried out at 1000 Hz in 3% NaCl. Three areas were used for the measurements and the average values were reported.

RESULTS AND DISCUSSIONS

Fig.1 shows the potential-current plot obtained by the anodic oxidation of o-cresol in sodium hydroxide on mild steel at a sweep rate of 20 mV/sec. From this, it may be seen that the oxidation begins at 0.85 V and reaches a maximum at 1.01v (i max = 3.3 mA/cm²) decreases to i mini = 0.37 mA/cm² and remains constant up to +2 V, beyond which a sharp increase in current was observed due to gas evolution. From this, it is evident that o-cresol gets oxidised at 1.01V.

Table II gives the results obtained with various concentrations of o-cresol with sodium hydroxide, sodium nitrate in beaker scale experiments.

Table II: Details of bath composition and operating conditions
Applied voltage: 10 V; Duration: 40 min

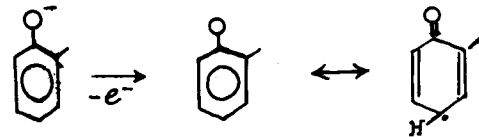
Composition of the bath	Current in mA		Thickness in μm	Remarks
	Initial	Final		
1. O-cresol 0.1 M + NaOH 0.1M	300	40	5	Thin brown coating
2. O-cresol 0.1 M + NaOH 0.1M + NaNO ₃ 50 ppm	320	5	12	Thin brown coating
3. O-cresol 0.1 M + NaOH 0.1M + NaNO ₃ 100 ppm	330	5	12	Brown coating with pores
4. O-cresol 0.1 M + NaOH 0.1M + NaNO ₃ 150 ppm	310	5	12	Black spongy deposit
5. O-cresol 0.1 M + NaOH 0.2M + NaNO ₃ 100 ppm	270	5	13	No uniform coating
6. O-cresol 0.1 M + NaOH 0.2M + NaNO ₃ 100 ppm	330	5	15	Black uniform coating
7. O-cresol 0.2 M + NaOH 0.3M + NaNO ₃ 100 ppm	300	5	12	Black coating with hair line cracks
8. O-cresol 0.3 M + NaOH 0.3M + NaNO ₃ 100 ppm	290	5	13	Thick black coating with cracks

It can be seen that the effective bath composition consists of o-cresol 0.2 M + NaOH 0.2 M and NaNO₃ 100 ppm (bath-5).

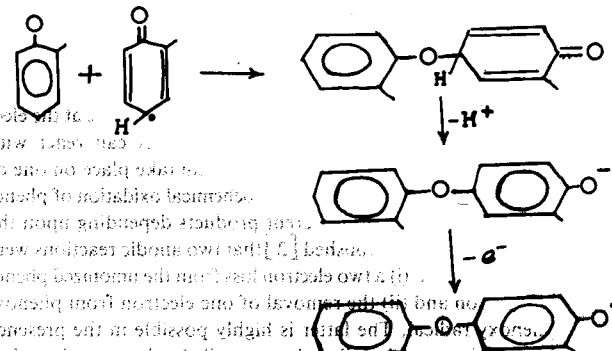
The coating was dried in air and it dried within 5 min. Thickness of the coating obtained was between 12 μm and 15 μm by Elcometer. In adhesion test, the coating did not peel off and it passes the pencil hardness test up to 6H. This shows that the coating has good adhesion with the substrate.

In infrared spectroscopic analysis, the peak at 1200 cm⁻¹ indicated the presence of C-O-C linkage, which is known as polyphenoxide film (PPO film) [3]. The mechanism by which the polymerization occurs to the formation of PPO film was by direct oxidation of the phenol group [4]. A similar mechanism is being proposed for the present study, namely, direct oxidation of phenate ion to phenate radical, which is followed by head to tail coupling with elimination of H⁺ ion and then termination.

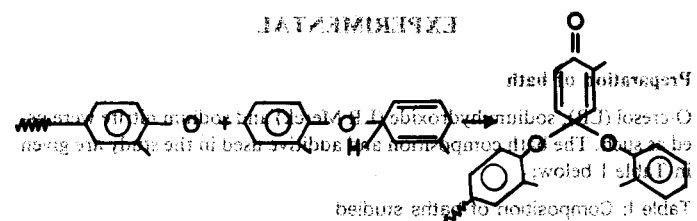
Initiation



Propagation



Termination



The coating resists corrosion up to 48 hrs in 3% NaCl after which the corrosion starts, slightly at some places.

Anodic polarization curves give a lower i_{corr} value for the coated sample i.e. 0.09 mA/cm² than the uncoated one, for which the value is 1.9 mA/cm².

Table III: Resistance and capacitance measurements

Time (hrs)	Capacitance (μF)	Resistance (ohm)
0	2.3	265.2
24	3.5	100.0

Table III shows the capacitance and resistance values of the coated samples. It may be noticed that the values are low. The capacitance increases with time, whereas the resistance decreases with time.

CONCLUSION

The anodic oxidation of o-cresol in basic medium leads to the formation of continuous and adhesive polyphenylene oxide film on the mild steel electrode. The coating ensures protection against corrosion of mild steel to some extent.

REFERENCES

1. N L Weinberg and H R Weinberg, *Chem Rev*, **68** (1968) 449
 2. F J Vermillion Jr and I R Pearl, *J Electrochem Soc*, **111** (1964) 1392
 3. A S Hay, *J Polym Sci*, **58** (1962) 581
 4. F M Barno, M C Phan and J E Dubois, *Electrochim Acta* **22** (1977) 451
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