ORGANIC COATING BY ELECTROPOLYMERIZATION OF O-CRESOL

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ABSTRACT

In electopolymerization, as in electrodeposition, 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 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 o-cresol 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: Electrolysis, organic coating, o-cresol

INTRODUCTION

In electopolymerization, 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 phenox 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 1 below:

Table 1: Composition of baths studied

<table>
<thead>
<tr>
<th>No.</th>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O-cresol 0.1 M + NaOH 0.1 M + No additive</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O-cresol 0.1 M + NaOH 0.1 M + NaNO3 50 ppm</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O-cresol 0.1 M + NaOH 0.1 M + NaNO3 100 ppm</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>O-cresol 0.1 M + NaOH 0.1 M + NaNO3 150 ppm</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>O-cresol 0.1 M + NaOH 0.2 M + NaNO3 100 ppm</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>O-cresol 0.2 M + NaOH 0.2 M + NaNO3 100 ppm</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>O-cresol 0.3 M + NaOH 0.3 M + NaNO3 100 ppm</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>O-cresol 0.3 M + NaOH 0.3 M + NaNO3 100 ppm</td>
<td></td>
</tr>
</tbody>
</table>

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 polarization

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

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 pm and 15 pm. 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 takes place in the formation of PPO 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.

FIG. 1

Propagation

Initiation

Termination

TABLE II: Composition and operating conditions

<table>
<thead>
<tr>
<th>Composition of the bath</th>
<th>Current in mA</th>
<th>Thickness of the coating</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-cresol 0.1 M + NaOH 0.1M</td>
<td>300</td>
<td>Thin brown</td>
<td>Initial</td>
</tr>
<tr>
<td>O-cresol 0.1 M + NaOH 0.1M</td>
<td>50 ppm</td>
<td>Thin brown</td>
<td>Final</td>
</tr>
<tr>
<td>1: Sodium hydroxide, sodium nitrate in beaker scale experiments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied voltage: 10 V; Duration: 40 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>Thin brown coating</td>
<td>12 pm</td>
<td>12 pm</td>
<td></td>
</tr>
<tr>
<td>Thik brown coating</td>
<td>12 pm</td>
<td>12 pm</td>
<td></td>
</tr>
<tr>
<td>Black sponge deposit</td>
<td>12 pm</td>
<td>12 pm</td>
<td></td>
</tr>
<tr>
<td>No uniform coating</td>
<td>12 pm</td>
<td>12 pm</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III: Resistance and capacitance measurements

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Capacitance (μF)</th>
<th>Resistance (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.3</td>
<td>263.2</td>
</tr>
<tr>
<td>24</td>
<td>3.5</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Applied voltage: 10 V; Duration: 40 min;%
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

2. F J Vermillion Jr and I R Pearl, J Electrochem Soc, 111 (1964) 1392

ETCHING OF ALUMINIUM FOIL FOR CAPACITORS

Process developed at Central Electrochemical Research Institute, Karaikudi-623 006

(Indian Patent Nos. 130650, 109313, 131900, 139702, 139258)

Etched aluminium foils are used for the manufacture of aluminium polarized electrolytic capacitors. The capacitors of various working voltage and capacitance ratings are used in all types of electronic measuring instruments/equipments, radio, TV sets etc.

Etched aluminium foils are being produced in the country by some firms. However, the entire production is being consumed by them for their own production of capacitors. Obviously, the rest of the electrolytic capacitor manufacturers have to depend on imports for their requirements of etched foil.

Hitherto known practice is to treat the foil anodically in soluble chloride solution using pure A.C. or A.C. superimposed D.C. or square wave or D.C. with various percentage of pulsation. This suffers from the drawback that etching in conventional sodium chloride electrolyte using pure DC does not give etch ratio of more than 12 at 30 volts. AC superimposed DC involves the use of AC having a frequency of more than 130 cycles/second and having a high degree of pulsation. So special generators for AC source as well as suitable filters and chokes are needed. Similarly, special type of equipments are required to produce square wave or pulsating DC. They are costly, and may have to be imported if not available indigenously.

Process developed

A suitable formulation for etching aluminium and aluminium alloy with pure DC to obtain desired high etch ratio in the order of above 38 at 30 volts has been successfully developed. The new process consists of electrochemical etching of aluminium and its alloy in a bath which comprises of a soluble chloride like sodium chloride or hydrochloric acid solution.

The process has been studied on a pilot plant designed to process 4" wide aluminium foil rolls.

Super-pure and commercial grade aluminium foil, etching chemicals (sodium hydroxide, nitric acid, hydrochloric acid) are the main raw materials. Except superpure aluminium foil, all the other raw materials are available indigenously.

Major equipments required are rectifier for etching, DC motor reduction gear for the DC motor, constant speed arrangement, motor with reduction gear, centrifugal pump, contact roller, etched foil drier, silica immersion heater, rectifier for DC motor, de-ionizer unit, copper busbar, cathode mounting assembly, stainless steel tanks, MS tanks, aluminium tanks, polythene tank.