

POLYPHENYLENE OXIDES AS SURFACE COATING MATERIALS

M VIJAYAN, S PITCHUMANI AND V KRISHNAN

Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

The electrosynthetic route of preparing polyphenylene oxide is proved to generate uniform coating on Fe anodes. The course of polymer coating is monitored to assess the possibility of obtaining a dense and uniform coating of desired thickness. Such a method also helps to electrocoat more number of plates from a single electrolytic bath. These polymeric coatings are found to resist corrosive atmosphere to a higher degree.

Key Words: surface coatings, electropolymerisation, polyphenylene oxide

INTRODUCTION

Synthetic polymers serve as potential basic materials in many of the surface coating formulations [1,2] which play a vital role for protection against corrosion of metal sheets utilized for structures such as car bodies, panels for electric household appliances, etc. Polyphenylene oxides belong to a novel class of coating materials that can be synthesised both chemically [3] and electrochemically [4]. The technique of electrosynthesis is quite attractive for generating polymers in the desired form, as it offers ease of preparation and precise control over the processing conditions [5]. Such a technique provides a one stage preparation of the polymer in the desired form, its spreading over the substrate and possibility of its crosslinking to form insoluble network. These advantages make it more attractive than electrophoretic deposition of the polymer which suffers from the disadvantages such as use of higher voltage, necessity of prepolymer formation, separate curing stage and poor adhesion of the polymer to the substrate.

Electropolymerization of catechol [3], resorcinol [3] and o-cresol [5] have been found to give corresponding polyphenylene oxide type polymers either as thick deposit or as an adherent film of varying thickness on iron anodes through anodic oxidative coupling reaction. The process is found to be highly facile in the presence of an amine which helps the resultant polyphenylene oxide to grow as an adherent coating on the electrode surface. The role of amine is to prevent the formation of passive metallic oxides thus helping the smooth growth of polymer. Further, adsorbed amine is believed to help the passage of current to be smooth until a total insulation occurs on the electrode surface. This is confirmed by carrying out electropolymerization runs both with and without amine. The runs with the amine give a more adherent, smooth and homogeneous coating than the runs without amine which is in accordance with earlier findings [8]. Such a growth of polymer coating through in-situ electropolymerization is very much influenced by various synthetic conditions, which can be used to monitor the coating to the desired level.

This paper aims at demonstrating the utility of such an electrosynthetic route to generate useful coatings of polyphenylene oxides based on phenolic monomers.

EXPERIMENTAL

Materials

Catechol (AR), resorcinol (AR), sodium hydroxide (GR), ethylene diamine

(AR), allylamine (AR) and β phenylethylamine (CECRI knowhow) were all used as such without any further purification. o-Cresol (Ranbaxy) was distilled and used in all the runs.

Preparation of electrodes

Stainless steel and mild steel plates were cut into proper dimensions, cleaned and buffed as per the standard procedure. Just prior to use, electrodes were rewashed and degreased either with benzene or trichloroethylene.

Electrogeneration of polyphenylene oxide (PPO) coatings

Polyphenylene oxide coatings were generated on mild steel/stainless anode through in-situ electropolymerization technique, from catechol, resorcinol, o-cresol as described before [4,6]. The electrogeneration of the coating was achieved both in a single compartment cell and in H-type cell as well. The electrolytic bath consisted of either of the monomer, aqueous NaOH and an amine in fixed proportions. The coatings were generated under different experimental conditions.

Characterization of polymer coating

The polymer coating thus generated was scrapped from the electrode surface, made into a pellet by mixing with KBr and IR spectrum was recorded with Perkin-Elmer Infrared Spectrophotometer.

Test for corrosion resistance

The polymer coatings were subjected to salt-spray test in a NaCl atmosphere as described elsewhere [7].

RESULTS AND DISCUSSION

Observations are presented in Figs. 1-10. Parameters for PPO coating formation Fig. 1 shows the polymer yields with time of polymerization for systems under consideration at a fixed proportion of all the ingredients. It can be seen that the growth of polymer as coating is linearly time dependent and thus one can program the growth of the coating to the desired thickness for a given set of conditions. In the case of o-cresol, the formation of polymer coating is found to be faster than catechol and resorcinol (data not included) and occurs in a few minutes. This indicates the possibility

of obtaining a flash coating on iron anodes from the latter system.

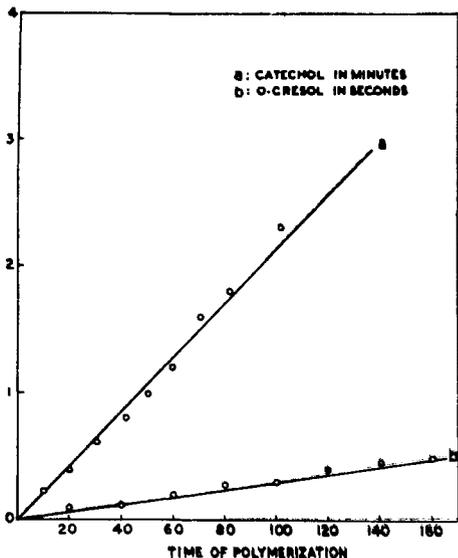


Fig. 1. Polymer yields VS Time of Polymerization

Fig. 2 refers to polymer yields obtained for different number of plates that can be coated from the same electrolyte. It may be seen that there

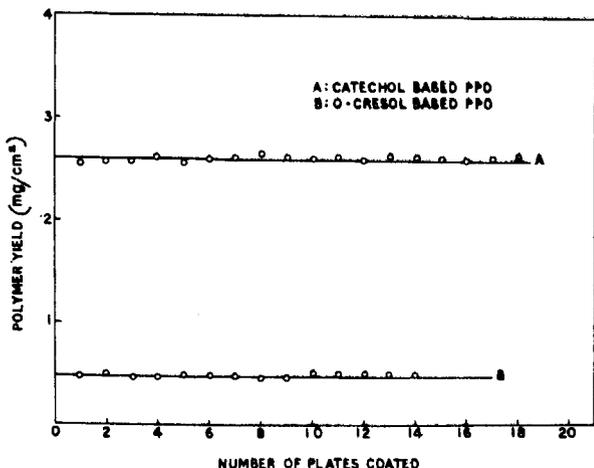


FIG. 2

is no significant change in polymer yields. This indicates the possibility of coating large number of plates industrially with possible economy [9].

The uniformity and completion of coating was assessed by monitoring the drop in current with respect to time of electrolysis under different experimental conditions for all systems. In all the cases, sharp drop in current was observed as the coating formation proceeded. In the case of catechol and o-cresol, the current drop was more significant than resorcinol. It indicates that the PPO coating formed is more uniform, complete and adherent.

Further the influence of conditions over the PPO coating formation has pronounced effect on the drop in current, as can be seen from the following figures.

Fig. 3 shows the characteristic feature of PPO coating based on catechol for the different amines employed. It can be seen that there is a sharp

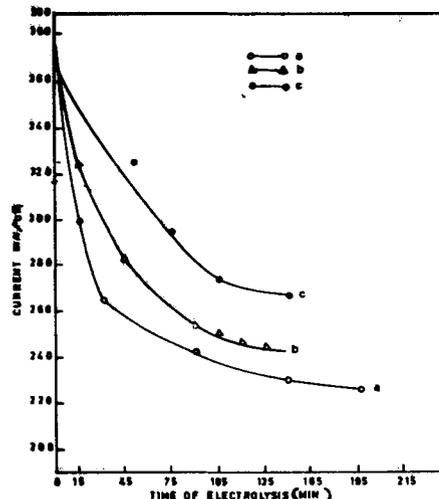


Fig. 3. Drop in Current VS Time of Electrolysis (Catechol)

- a. ETHYLENE DI AMINE
- b. ALLYL AMINE
- c. B-PHENYL ETHYL AMINE

drop in current for ethylene diamine based bath than that of the baths containing allylamine and β -phenylethylamine, indicating a faster growth and greater homogeneity of the coating from the former. Thus the order of preference in the use of amine for the catechol based PPO coating generation is:

ethylene diamine > allyl amine > β -phenyl ethylamine

The concentration of amines was also found to have a profound influence over PPO coating generation and it can be predicted from the curve that higher concentration of ethylene diamine produces more homogeneous coating, as is evident from sharp drop in current (Fig. 4).

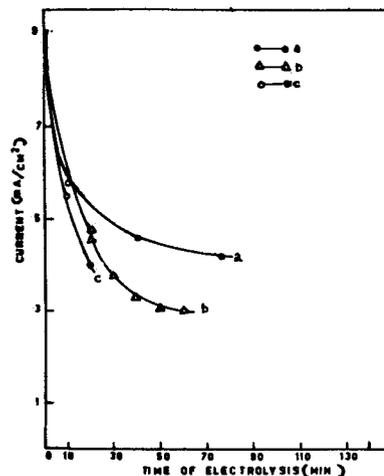


Fig. 4. Drop in Current VS Time of Electrolysis (Catechol)
 a. 0.1M Ethylene di Amine
 b. 0.2M Ethylene DI Amine
 c. 0.3M Ethylene DI Amine

In the case of allyl amine too (Fig. 5), the effect over PPO coating generation is similar.

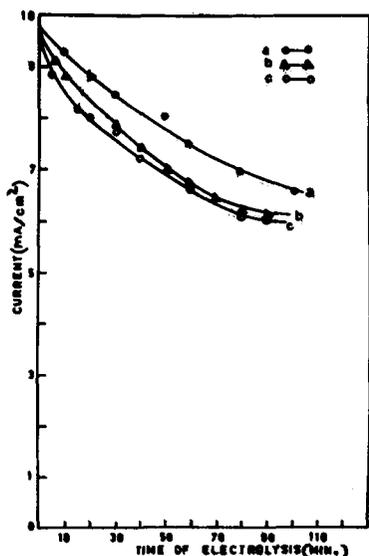


Fig. 5 Drop in Current vs Time of Electrolysis
 a. 0.1M Allylamine
 b. 0.2M Allylamine
 c. 0.3M Allylamine

The current drop for the coating formation is not significant for the bath containing β -phenyl ethylamine (Fig. 3) possibly due to the inferior type of coating that has been encountered in different runs.

Figs. 6 and 7 represent the PPO coating generation based on resorcinol.

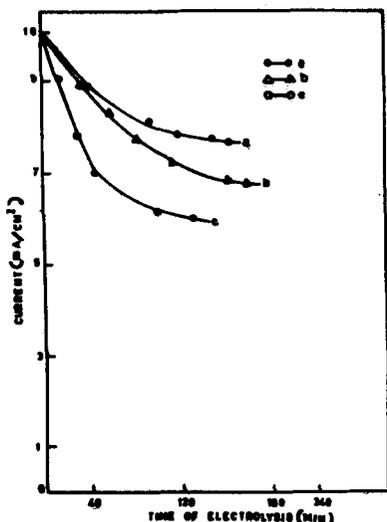


FIG. 6. Drop in Current vs Time of Electrolysis (Resorcinol)
 a. 0.1M Ethylene Diamine
 b. 0.2M Ethylene Diamine
 c. 0.3M Ethylene Diamine

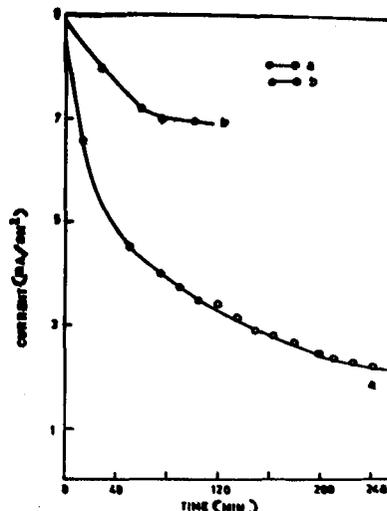


FIG. 7. Drop in Current vs Time of Electrolysis (Resorcinol)
 a. β -Phenyl Ethylamine
 b. Ethylene Diamine

It can be seen that there is a sharper drop in current for the bath containing β -phenylethylamine than the baths containing ethylene diamine. This indicates that better homogeneity and adherence for PPO coating is achieved in β -phenylethylamine based bath. Increase in amine concentration enhances the rate of PPO coating generation as is evident from lower current values with respect to time (Fig. 6). For resorcinol based PPO coating generation, the order of preference in the utility of amine is β -phenyl ethylamine > ethylene diamine > allylamine

The use of the allylamine for resorcinol based baths did not produce PPO coating uniformly over the iron electrode surface.

Figs. 8, 9 and 10 represent the characteristic features of current drop for o-cresol based baths with different amines.

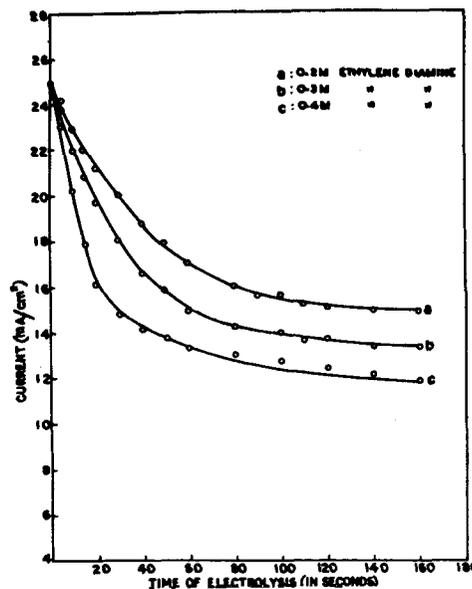


FIG. 8. Drop in Current vs Time of Electrolysis (O-Cresol)

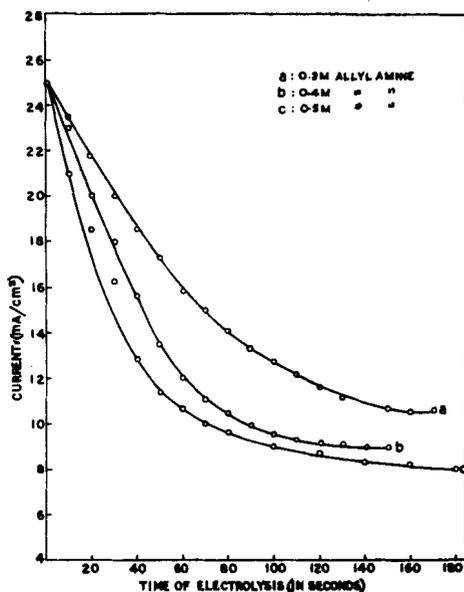


FIG. 9. Drop in Current vs Time of Electrolysis (O-Cresol)

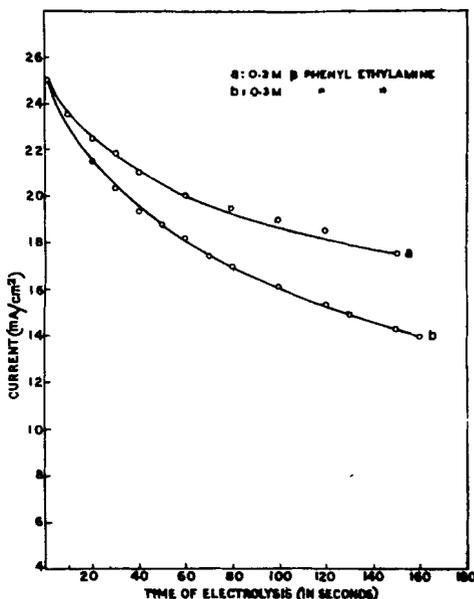


FIG. 10. Drop in Current vs Time of Electrolysis (O-Cresol)

In all the runs, the PPO coating occurs faster in few minutes and steep drop in current is observed for all the baths. It indicates that homogeneous and adherent PPO coating can be formed rapidly from the baths containing any of these amines. The drop in current is found to be more pronounced in the case of allylamine compared to the other amines. An increase in amine concentration enhances the rate of PPO coating generation and thus improves the homogeneity and adherence of the coating.

The saturation level in the above cases indicates the completeness of PPO coating formation on the Fe anode surface.

All the above illustrate clearly that the generation of PPO coating is very much influenced by different ingredients of electrolytic bath and the coating (generation formation) to a desired level is possible by programming the synthetic conditions properly [9].

Characteristics of PPO coatings

i) Appearance

Monomer employed	Colour of PPO coating
Catechol	Pale brown to dark brown
Resorcinol	Reddish brown to dark brown
O-cresol	Pale yellow

In the catechol and resorcinol, coatings of thickness ranging from 10-15 μm can conveniently be obtained by altering the bath compositions. In the case of o-cresol, the maximum thickness that is obtained in this study is of the order 2-3 μm , as the insulation of electrode surface occurs faster due to quick generation of PPO coating. The PPO thus generated is found to be insoluble in all the common organic solvents thus preventing it for characterisation in terms of its molecular weight. This is probably due to crosslinking that might have occurred during the formation of polymer coating.

IR characteristics of coating

IR analysis shows characteristic peaks in the range of 1250-1350 cm^{-1} due to C-O-C linkage, confirming the nature of polymer product.

Corrosion resistant characteristic of PPO coating

All the PPO coatings generated under different conditions resist corrosive NaCl atmosphere to an appreciable extent. This illustrates the protective role of PPO coatings and ranks them as attractive and novel surface coating materials.

CONCLUSION

It can be seen that electrosynthetic route of polymer generation can be used to produce useful polyphenylene oxides (PPO) coatings from phenolic monomers such as catechol, resorcinol and o-cresol. The generation of such PPO coatings can be controlled by different synthetic conditions to produce them to a desired level. Further it is possible to coat a number of iron plates from the same electrolytic bath and a flash coating is possible for o-cresol based PPO. They have protective value indicating the possibility of their use as surface coating material.

REFERENCES

1. A F Payne, *Organic coating technology*, Vol.1, John Wiley & Sons, New York (1964)
2. *Surface coating* - Vol.1. 2nd Edition, Chapman and Hall, London (1983) pp 53-256
3. H L Fiskbeiner, A S Hay and D M White, *Polymerisation Processes, High Polymers* Eds. C E Schildknecht and I S Skeist. Vol.29, John Wiley & Sons, Inc., New York (1977) p 537
4. M Vijayan, S Pitchumani and V Krishnan, *Third International Symp Adv Electrochem Sc Tech, Extended Abstracts* (SAEST, Karaikudi) (1984) p 101
5. M Vijayan, S Pitchumani and V Krishnan, *(to be communicated)*
6. M Vijayan, S Pitchumani and V Krishnan, paper presented in *Nat Con Electrochem* held at Sahupuram during Aug 16-18, 1984 (SAEST Karaikudi)
7. *Methods of Testing Corrosion Resistance by Salt Spray Test*. IS:9844-1981
8. G Mengoli, S Daolio, M M Mustaini, *J Appl Electrochem* 10 (1980) 459
9. M Vijayan, S Pitchumani and V Krishnan (*Processes ready for assignment to NRDC*)