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International Classification[4]— C01B 13/14.

Title : A PROCESS FOR THE PREPARATION OF POLYPHENYLENE OXIDE AS AN ADHERENT FILM ON METALLIC SUBSTRATES.

Applicant : COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-110001, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES Act (ACT XXI OF 1860) 1860).

Inventors : MUTHANA THEVER VIJAYAN, SETHURAMAN PITCHUMANI AND VENTAIASUBRAMANIAN. KRISHNAN.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by Muthana Thevar Vijayan, Sethuraman Pitchumani and Venkatasubramanian Krishnan, all of Central Electrochemical Research Institute, Karaikudi - 623006 (TN), India and all Indian citizens and relates to an in-situ electropolymerization process for the preparation of polyphenylene oxide.

The polyphenylene oxide is formed as an adherent film (coating). The polymer film prepared by the process of the present invention can be used for protective application and in the fabricatioon of capacitor.

The process of the present invention broadly consists of the following procedure.

An electrolchemical undivided cell is fabricated with PVC lid which helps proper positioning of electrodes, stirrer and thermometer. The aqueous electrolyte medium is composed of the monomer which may be catechol., O. Cresol etc. and sodium hydroxide with ethylene diamine as an addition agent. The concentration of the monomer may range from 0.1M - 0.3M and that of NaOH 0.3M. The concentration of ethylene diammine may be 0.3M. The polymerization is triggered by impressing a fixed current at the initial stage and the process proceeds by oxidative coupling mechanism. An anodic current density ranging rom 0.25A/dm^2 to 0.98A/dm^2 may be employed. The temperature range at which the electrodeposition is effected may be from 25^{0}C to 30^{0}C. To avoid any pores, nitrogen gas is bubbled. The growth of polymer can be seen as an adherant film on the anodic surface which has been pretreated by etching or sand blasting. The thickness of adherant film can conveniently be varied by

varying the monomer concentration for a given set of conditions. The adherant film of polyphenylene oxide can continuously be obtained by replacing the anodes soon after the commpletion of the desired thickness of the film. Thus the process can be continuous and films of various thickness can conveniently be obtained on different anodes from single electrolytic bath, an unique advantage of the process of this invention.

Following are the advantages:

1. The process opens up new possibilities of electrosynthesis to obtain the polymer as adherant film directly on metallic substrate.
2. Degree of polymerization can be controlled by controlling the potential
3. The rate of polymerization can be monitored to control the current density.
4. Materials involved are cheaper in this process and are available in plenty indigenously.

Dated this 27th day of June 1986.

N R Subbaram

(N.R. SUBBARAM)
JOINT ADVISER (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

16845

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

Title : A PROCESS FOR THE PREPARATION OF POLYPHENYLENE OXIDE AS AN ADHERENT FILM ON METALLIC SUBSTRATES.

Applicant : COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (ActXXI of 1860).

Inventors : MUTHANA THEVER VIJAYAN, SETHURAMAN PITCHUMANI & VENTATASUBRAMANIAN KRISHNAN.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

.This rel N D P opolymerization process for the prepara de.

The main objective of this invention is to provide an electropolymerization process for the preparation of polyphenylene oxide film on metallic surfaces.

The polymer film produced in the process of the invention can be used for protective application and in the fabrication of capacitor. No method has so far been known for the preparation of the polymer film.

This invention relates to the preparation of polyphenylene oxide as an adherent film on metallic substrates such as mild steel, copper etc. in an alkaline medium.

An electrochemical undivided cell is fabricated with PVC lid which helps proper positions of electrodes, and thermometer. The aqueous electrolyte medium is composed of the monomer, which may be catechol, O.cresol etc and the alkaline medium which may be sodium hydroxide. The electrolyte may contain an addition agent such as ethylene diamine. Preferably the concentration of the monomer may range from 0.1M-0.3M and that of the alkali 0.3M. The concentration of the addition agent in the electrolyte may be 0.3M. The polymerization is triggered by impressing a fixed current at the initial stage and the process proceeds by oxidative coupling mechanism. An anodic current density ranging from 2.5 mA/cm^2 to 9.8 mA/cm^2 may be employed and the temperature may range from 25^{o}-30^{o}C. To avoid any pores, the nitrogen gas is bubbled. The growth of polymer can be seen as an adherent film

on the anodic surface which has been pretreated by etching or sand blasting and electrochemical cleaning using surfactants. The thicknes of the adherent film can conveniently be varied by varying the monomer concentration for a given set of conditions. The adherent film of polyphenylene oxide can continuously be obtained by replacing the anodes soon after the completion of the desired thickness of the film. Thus the process can be continuous and films of various thickness can conveniently be obtained on different anodes from single electrolytic bath, an unique advantage of the described technique.

Accordingly, the present invention provides a process for the preparation of polyphenylene oxide as an adherent film on metallic substrates as herein described, which comprises electropolymerization of an aqueous electrolyte which consists of a phenolic monomer, alkali and addition agent such as herein described, using mild steel, stainless steel or copper as anode and stainless steel as cathode at a temperature ranging from 25-30°C for 10 to 45 minutes employing voltage and current density ranging from 2 to 2.5 V and 1.0 to 15 mA/cm^2. In this process the polymerization and coating formation on metal substrates take place simultaneously. The polymer film with desired thickness can be achieved in this method.

The invention is further illustrated by the following Examples which should not be construed to limit the scope of this invention.

Example 1

In situ electropolymerization of catechol to polyphenylene oxide.

Anode	:	Mild steel/stainless steel
Cathode	:	Stainless steel
Electrolyte	:	0.3M sodium hydroxide of 200 ml
Concentration of monomer(catechol)	:	0.1M
Concentration of ethylene diamine	:	0.3M
Cell voltage	:	2V
Anodic current density	:	15 mA/cm^2
Temperature	:	25-30°C
Anode area	:	40 cm^2
Thickness of film	:	10-15 micron
Time of polymerization	:	45 minutes
Characteristics of the product	:	A dark brown coherent, adherent and homogeneous polymer/film is obtained on the sand blasted surface of the anode.

Example 2.

In-situ electropolymerization of O-cresol to polyphenylene oxide.

Anode	:	Mild steel/stainless steel/copper
Cathode	:	Stainless steel
Electrolyte	:	Aqueous 0.3M NaOH of 200 ml
Concentration of monomer(O-cresol)	:	0.1M
Concentration of ethylene diamine	:	0.3M
Cell voltage	:	2.5V
Anodic current density	:	15 mA/cm^2
Temperature	:	25-30°C

Anode area	:	40 cm^2
Time of polymerization	:	10-15 minutes
Thickness of film	:	5-10 micran
Characteristics	:	A brown coherent, adherent and homogeneous polymer film is obtained on the sand blasted surface of the anode.

The main advantages of the invention are :-

i) This has opened up new possibilities of electrosynthesis to obtained polymer as an adherent film directly on metallic substrate.

ii) Degree of polymerization can be controlled by controlling the potential.

iii) Controlling the current density helps to monitor the rate of polymerization.

iv) Material involved are cheaper in this technique and available plenty indigenously.

We claim

168451

1. A process for the preparation of polyphenylene oxide as an adherent film on metallic substrates as herein described, which comprises electropolymerization of an aqueous electrolyte which consists of a phenolic monomer, alkali and addition agent such as herein described, using mild steel, stainless steel or copper as anode and stainless steel as cathode at a temperature ranging from 25-30°C for 10 to 45 minutes employing voltage and current density ranging from 2 to 2.5 V and 1.0 to 15 mA/cm^2.

2. A process as claimed in claim 1 wherein the phenolic monomer employed is selected from catechol, o-cresol.

3. A process as claimed in claims 1 and 2 wherein the alkali is sodium hydroxide.

4. A process as claimed in claim 1-3 wherein the addition agent is ethylene diamine.

5. A process a claimed in claims 1-4 wherein the concentration of addition agent in the electrolyte is 0.3M.

6. A process as claimed in claims 1-5 wherein nitrogen gas is bubbled through the electrolyte to avoid any pores in the film.

7. A process as claimed in claims 1-6 wherein the said electrolyte has concentration of 0.1M-0.3M of the phenolic monomer and 0.3M of sodium hydroxide.

8. A process as claimed in claims 1-7 wherein an anodic current density ranges 2.5 mA/cm^2 to 9.8 mA/cm^2 is employed.

9. A process for the preparation of polyphenylene oxide as an adherent film on metallic substrates substantially as herein described with reference to the Examples.

Dated this 26th day of May 1987

SCIENTIST (PATENTS)
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH