STUDIES ON ANODIC POLYMERIZATION OF CERTAIN POLYHYDRIC PHENOLS

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The electrochemcal oxidation of phenols and its derivatives were extensively studied [1]. However all these studies have been carried out in acid medium and the products were mainly oxidised compounds. In the present investigation we report a comparative anodic oxidative studies on catechol, resorcinol and hydroquinone in alkaline conditions using stainless steel electrodes. In recent years electrochemical polymerisation reactions have gained importance due to its applications in the preparation of polymer coated metal sheets. The present work is an extension of the earlier work on electrochemical polymerization of catechol [2].

EXPERIMENTAL

Catechol, Resorcinol and hydroquinone (Aldrich Chemicals, USA), Sodium hydroxide (LR.E.Merck) and ethylene diamine (LR.E.Merck) were used as such. The electrolytic oxidation was performed in an undivided electrochemical cell consisting of a cylindrical glass vessel with an ebonite lid through which electrodes were inserted conveniently. Stainless steel was used both as anode and cathode. Calculated quantities of these phenols and sodium hydroxide were first dissolved in double distilled water and fed into the electrolytic cell. A required amount of amine was added as an addition agent. A definite amount of current was then passed through the electrolytic solution from a dc power source and the polymerization was monitered by the actual current flowing through the current meter in the circuit. The amount of polymer formed was calculated from the difference in weights of electrode before and after electropolymerization.

Characterisation of Electropolymerization

Polarization studies were extended to the best electrolytic composition consisting of calculated amounts of phenols, sodium hydroxide solution and ethylene diamine in the electrolytic cell. The reference electrode Hg/HgO was prepared based on standard procedure [3] using AR grade HgO.

TABLE 1

YIELD UNDER DIFFERENT CURRENT DENSITIES

Electrode area: 0.01175 dm^2, Phenols; 0.1 M, NaOH: 0.3 M, amine: 0.1 M

No.	Current density amp/dm2	Yield % of Polymer		
		Catechol	Resorcinol	Hydro-quinone
1.	2.550	5%	3%	4%
2.	3.404	4%	1%	3%
3.	6.810	1%	1%	2%

TABLE 2

NATURE OF POLYMER AT DIFFERENT pH

Current density 2.55 A/dm^2

No.	pH	Nature of deposit
1.	9	Fine powder
2.	7-8	Copious precipitate
3.	7-8	Copious precipitate

The IR spectra was run for the polymer using Perkin Elmer IR spectrometer, using Nujol mull

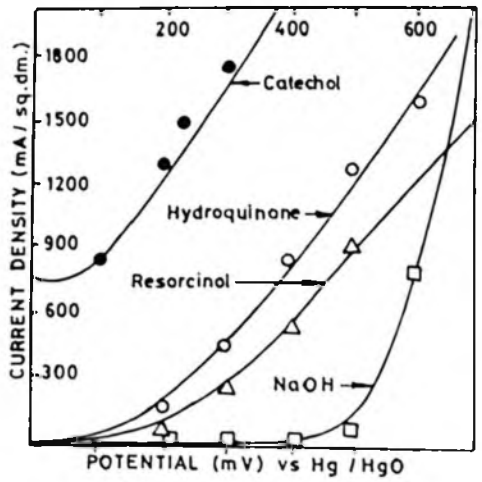
Experiments were conducted under different conditions of alkalinity, both in the presence and in the absence of NaOH.

RESULTS AND DISCUSSION

The result of various experiments are shown in the tables.

It is interesting to note (Table 1) that the catechol gives the better yield of the polymer. This is also indicated in the polarisation curves for the catechol (Fig 1). It was reported [4] that two anodic reaction are possible with simple phenol:(i) a two electron loss from the unionized phenol to give a phenoxonium ion and (ii) the removal of one electron from phenoxide to give a phenoxy radical. The fine coating of the polymer was observed when the experiment was carried out in the absence of NaOH. (Even in this medium pH is > 7 and phenol is expected to be in the anionic form. The amine is an important ingradient and it helps in the growth of polymer coating leading to a strong deposit by preventing the anodic formation of passivating

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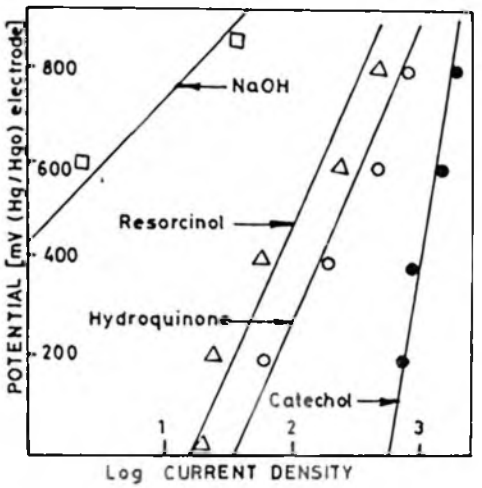


Fig. 1 & 1a Polarisation curves

metal oxides. The amine also enters into polymerization with phenols as shown in IR spectral studies.

The polarization curves show the efficiency of depolarization is in the order Catechol > Hydroquinone > Resorcinol which may possibly be due to stereochemical factors. From the graph (Fig 1a) it is seen that there is a good depolarization at lower current density.

The product on examination through IR spectral data indicates the characteristic absorption peak of -C-O-C linkage at 1380 cm^{-1}. The broad break observed in the range of 3500-3000 cm^{-1} can be attributed to NH group present in the polymer [6]. These results clearly show the formation of a phenoxy radical and the build up of polymer chain.

It was also observed that the substituted mono hydric phenols like p-nitro phenol, p-chloro phenol and p-cresol did not give the polymerized product.

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