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The influence of ultrasonics on the electrodeposition of lead dioxide

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The influence of an ultrasonic field on the deposition of lead dioxide on to a graphite substrate from an aqueous solution of lead nitrate and copper nitrate has been investigated. In general, the deposits were smooth, adherent and free from pinholes at anode current densities up to 10 A dm^{-2}.

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1. Introduction

The use of electrodeposited lead dioxide on a suitable substrate like graphite for the commercial production of a number of inorganic chemicals e.g. chlorate, perchlorate, bromate etc., is well known. A smooth and adherent deposit of lead dioxide free from pinholes is necessary for this purpose. Several techniques have been reported for obtaining smooth and adherent deposits of lead dioxide free from pinholes. Among them, rotation of the cathode [1, 2], rotation of the anode [3–7], and fluidized bed techniques [8–10], have been applied. Different addition agents were also tried by various authors [11–20] in order to obtain good pore-free deposits.

In recent years, one more technique, ultrasonics, has been applied with considerable success in many fields of engineering and chemistry and in particular in the electroplating industry. Ultrasonics is being used very commonly for cleaning operations before electroplating. The effect of the ultrasonic vibrations on the anodic polarization process on smooth lead plates anodized with a constant current density of 0·5 mA cm^{-2} in 6·7 N sulphuric acid was studied at 25 ± 3° C by Kukoz and Skalozybov [21]. No reference has been found in the literature on the use of ultrasonics in the deposition of lead dioxide from its soluble salts on suitable substrates. Its influence on the deposition of lead dioxide on a graphite substrate is presented in this paper.

2. Experimental

2.1. *Cell Assembly*

A 400 ml pyrex tall-form beaker fitted with a PVC cover containing suitable holes to introduce the anode, cathode and thermometer, acted as the cell container. A graphite rod and a cylindrical stainless steel plate were used as the anode and cathode respectively. This cell assembly was suspended in an ultrasonic tank (45 KHz and 0–400 W supplied by M/s Vibronics Private Ltd., Bombay) in such a way that the cell was not resting on the bottom of the tank. The tank was filled with water up to three-quarters of its capacity and its temperature maintained by passing ice cold water or cold water through stainless steel coils kept in the tank.

2.2. *Anode*

A graphite rod (1 cm diam. × 15 cm long) with the lower end rounded off served as the anode. Before electrolysis the graphite rod was cleaned by making it the anode in 10% (W/V) sodium hydroxide solution and electrolysing at a current density of 10 A dm^{-2} for 10–15 min. Later it was washed well with water and then dipped in dilute nitric acid (10% V/V) for 5 min and washed well with distilled water. The diameter and weight of the anode before and after electrolysis were measured.

Table 1. Effect of anode current density on the deposition of lead dioxide under the influence of an ultrasonic field

S.No.	*Anode current density* $A\,dm^{-2}$	*Cell voltage* *V*	*Quantity of electricity passed* *A.h.*	*Weight of lead dioxide deposited* *g.*	*Nature of deposit*
1	1·0	1·3–1·35	3·2	13·14	Smooth, adherent and pore-free deposit
2	2·0	1·4–1·5	3·2	14·11	–do–
3	3·0	1·55–1·7	3·2	14·78	–do–
4	5·0	1·9–2·0	3·2	14·25	Smooth, velvety deposit, free from pinholes
5	10·0	2·5	3·16	14·02	Smooth, adherent and pore-free deposit
6	15·0	2·9–3·0	3·65	16·77	Adherent deposit with rough surfaces and free from pinholes
7	20·0	3·3–3·4	3·35	15·17	Rough deposit. Bottom chipped off. In some places, buckling is observed

Electrolyte: Lead nitrate 350 ± 10 g l^{-1} and copper nitrate 25 ± 2 g l^{-1}; Initial pH 4, Temperature 30 ± 5° C; Ultrasonic field 45 KHz (fixed).

2.3. *Cathode*

A perforated stainless steel (6·0 cm diam. x 9·5 cm height) cylinder was used as the cathode.

2.4. *Electrolyte*

The electrolyte was an aqueous solution of lead nitrate (350 ± 10 g l^{-1}, Analar) and copper nitrate (25 ± 2 g l^{-1}, Analar). The concentrations of lead and copper in the electrolyte were estimated by the EDTA method [22] and iodometric method [23] respectively.

2.5. *Electrolysis*

The pH of the electrolyte before starting the deposition was measured and it was found to be 4. 350 ml of the electrolyte were then added to the cell which was suspended from the cover placed on the top of the ultrasonic cleaning tank. The cathode and anode were introduced into the cell. Direct current was supplied from a selenium rectifier (0–18 V, 50 A).

The intensity of ultrasonic cavitation varies at different heights of liquid. So in all the experiments the water level in the ultrasonic cleaner tank was kept at the same height and the power also kept constant.

An electrolysis was carried out by passing a definite quantity of electricity. Calculated quantities of lead carbonate and copper carbonate were added to the electrolyte to neutralize the nitric acid formed during the electrolysis.

2.6. *Photomicrographs*

Photomicrographs of the lead dioxide deposited on a graphite substrate under the influence of the ultrasonic field were taken with the help of a metallurgical microscope (C. Reihert, M.F. Microscope) under a magnification of x 100. Fig. 2 (a–m) shows the surface structures of the deposit obtained under various conditions.

3. Results and discussion

3.1. *Effect of anode current density*

The results are given in Table 1. The deposits obtained were smooth, adherent and free from pinholes for anode current densities from 1–10 A dm^{-2}. At higher current densities (15 and 20 A dm^{-2}), rough surfaces and pinholes were observed. As in the case of anode rotation [4], it may be expected that the gas bubbles on the surface of the anode will be dislodged during deposition. A deposition on a stationary anode in the absence of an ultrasonic field will always have a lot of pinholes under these conditions.

3.2. *Effect of temperature*

The results of the effect of temperature are given in Table 2.

Table 2. Effect of temperature on the deposition of lead dioxide under the influence of an ultrasonic field

S.No.	*Temperature* °*C*	*Anode current density* *A dm*$^{-2}$	*Cell voltage* *V*	*Quantity of electricity passed* *A.h.*	*Weight of lead dioxide deposited* *g*	*Nature of deposit*
1	30	5	1·9–2·0	3·2	14·25	Smooth, velvety adherent deposit and free from pinholes
2	30	10	2·5	3·16	14·02	Adherent and pore-free deposit
3	40	5	1·8–1·9	3·14	14·6	Smooth, adherent and pore-free deposit
4	40	10	2·35	3·16	14·17	Adherent and pore-free deposit
5	50	5	1·8	3·18	14·23	Smooth adherent and pore-free deposit. Grey in colour
6	50	10	2·3	3·19	14·23	Rough, adherent and with pin-holes
7	60	5	1·75	3·10	13·84	Smooth, adherent and free from pinholes
8	60	10	2·2	3·15	14·0	Rough, adherent and with pin-holes

Electrolyte: Same as in *Table 1*.
Initial pH 4, Ultrasonic field 45 KHz (fixed)

The deposit of lead dioxide was smooth, adherent and free from pinholes at temperatures ranging from 30 to 60° C at an anode current density of 5 A dm^{-2}. A similar deposit, but with a rough surface, was observed for the deposit of lead dioxide obtained at temperature of 40° C at a current density of 10 A dm^{-2}. However, at higher temperatures, namely 50 and 60° C, and at an anode current density of 10 A dm^{-2}, the deposits had pinholes even under the influence of the ultrasonic field.

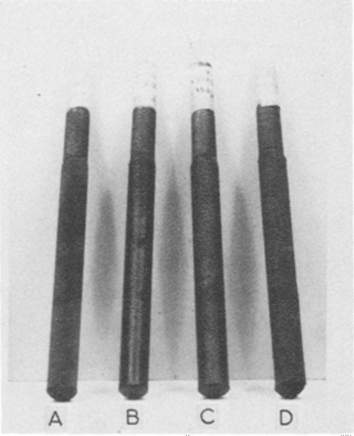

Fig. 1. Photographs of lead dioxide obtained on graphite rods under the influence of an ultrasonic field
A = 5 A dm^{-2}; B = 10 A dm^{-2}; C = 15 A dm^{-2}; D = 20 A dm^{-2}.

3.3. *Photographs and photomicrographs of the lead dioxide deposit*

The photographs of the lead dioxide deposit obtained at different anode current densities ranging from 5–20 A dm^{-2} at a temperature of 30° C are shown in Fig. 1. It can be seen that smooth, adherent and pore-free deposits were obtained at current densities of 5 and 10 A dm^{-2}.

The photomicrographs (x 100) of the lead dioxide deposits obtained under the influence of the ultrasonic field at different current densities and temperatures are shown in Fig. 2 (a–m). The photomicrographs of the deposits of lead dioxide obtained on rotating and stationary graphite anodes at an anode current density of 5 A dm^{-2} and temperatures of 30 and 60° C are shown in Figs. 3a and b and 4a and b, respectively, for comparison. It can be seen that the deposits obtained under the influence of the ultrasonic field at an anode current density of 5 A dm^{-2} and temperature of 30, 40, 50 and 60° C [see Figs. 2d, h, j, and l] are uniformly smooth, whereas at the anode current density of 10 A dm^{-2} and at all temperatures (other than 30° C) indicated above, the deposits are rough and with lumps and nodules [see Figs. 2e, i, k and m]. At lower current densities, viz. 1, 2 and 3 A dm^{-2}, the deposits are smooth [see Figs. 2a, b and c].

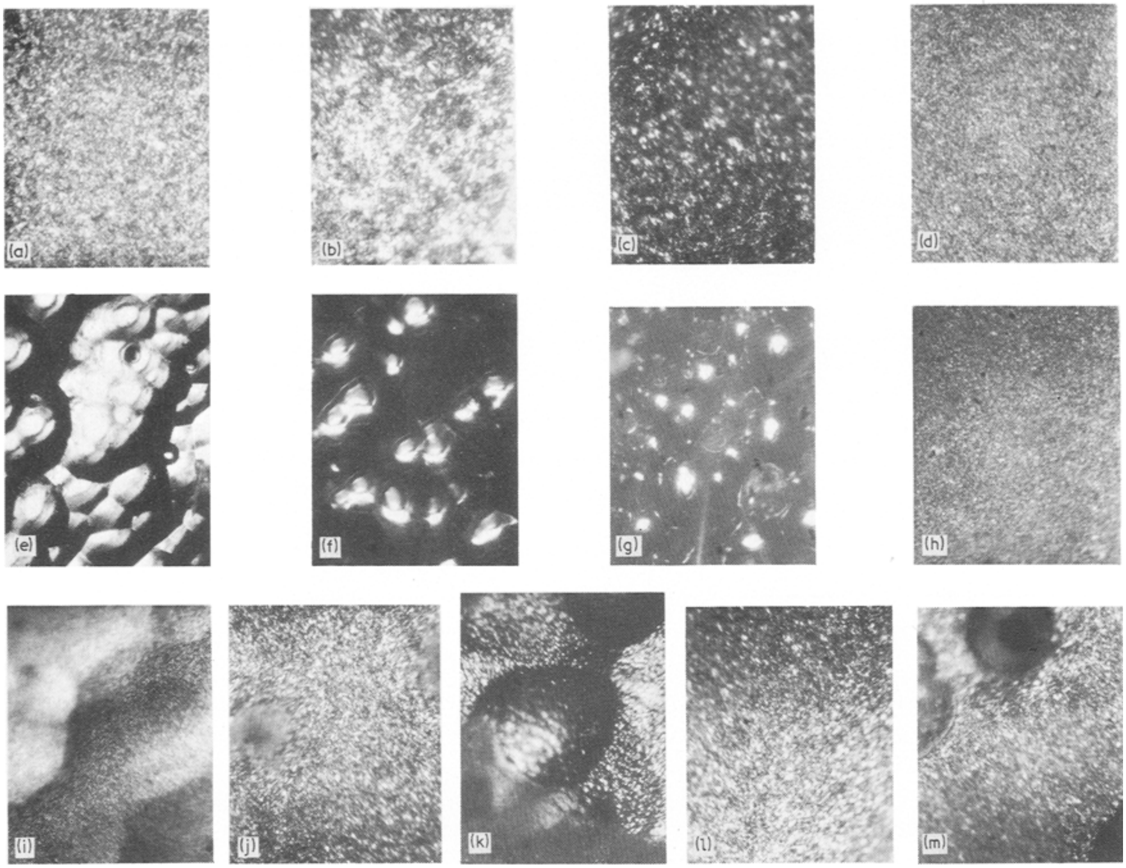

Fig. 2. Photomicrographs of surface of lead dioxide obtained under the influence of an ultrasonic field. (a) 30° C (1 A dm^{-2}); (b) 30° C (2 A dm^{-2}); (c) 30° C (3 A dm^{-2}); (d) 30° C (5 A dm^{-2}); (e) 30° C (10 A dm^{-2}); (f) 30° C (15 A dm^{-2}); (g) 30° C (20 A dm^{-2}); (h) 40° C (5 A dm^{-2}); (i) 40° C (10 A dm^{-2}); (j) 50° C (5 A dm^{-2}); (k) 50° C (10 A dm^{-2}); (l) 60° C (5 A dm^{-2}); (m) 60° C (10 A dm^{-2}).

The deposits obtained at the current densities of 15 and 20 A dm^{-2} are rough with a lot of pinholes [see Figs. 2f and g]. While rotation of the anode gives a smooth deposit, which is free from pinholes, at an anode current density of 5 A dm^{-2} and temperature of 30 and 60° C [see Figs. 3a and b], the deposit obtained on a stationary anode is coarse with pinholes under the same conditions [see Figs. 4a and b]. It is reported [24] that β-type lead dioxide is formed when the deposition of lead dioxide is carried out from acidic baths like lead nitrate. In the present work this has been confirmed by X-ray analysis.

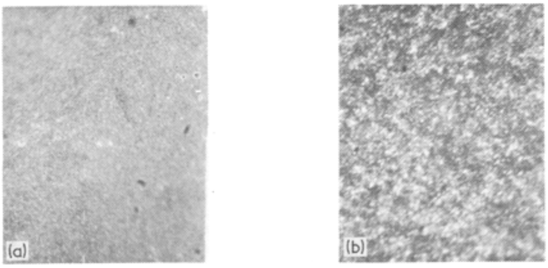

Fig. 3. Photomicrographs of lead dioxide surface obtained from a bath on a rotating anode. (a) 5 A dm^{-2} and 30° C; (b) 5 A dm^{-2} and 60° C.

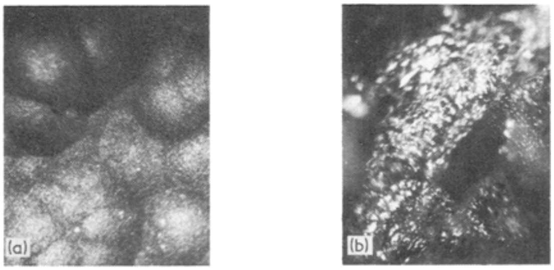

Fig. 4. Photomicrographs of lead dioxide surface obtained from a bath on stationary anode. (a) 5 A dm^{-2} and 30° C; (b) 5 A dm^{-2} and 60° C.

4. Conclusion

The electrodeposition of lead dioxide on graphite rods from a nitrate bath can be carried out under the influence of an ultrasonic field to obtain smooth, adherent, pore-free deposits. This also allows the use of higher anode current densities (up to 10 A dm^{-2}), at temperatures of 30 and 40° C. The photomicrographs of the surface of lead dioxide obtained under different conditions under the influence of the ultrasonic field show that the deposits obtained at an anode current density of 5 A dm^{-2} and at all temperatures between 30 and 60° C are uniformly smooth.

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