

The effect of the additive cetyl trimethyl ammonium bromide on the electrodeposition of lead dioxide

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The electrodeposition of lead dioxide on graphite substrates was studied earlier. In this work rotation or oscillation of the anode was employed to get a smooth and adherent deposit, free from pinholes. The influence of the addition of cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, to the bath during the electrodeposition of lead dioxide has been studied in the present work.

It has been found that the addition of the surfactant not only gives a smooth and adherent deposit free from pinholes under stationary condition but also permits the use of higher current densities during deposition.

The throwing power, conductivity and surface tension of the bath have been measured. The internal stress in the electrodeposit and anode potential measurements in the presence of CTAB are also reported.

Studies on the effect of other quaternary ammonium surfactants like tetradecyl and dodecyl trimethyl ammonium bromides on the deposition of lead dioxide are also incorporated.

1. Introduction

Recent developments of the various means of depositing lead dioxide successfully on different substrates, with a view to obtaining suitable-sized anodes, have increasingly stimulated their use for the production of several important inorganic chemicals [1]. The anodic deposition of lead dioxide from the nitrate bath [2-9] has been widely studied and a detailed description of the method of depositing lead dioxide on graphite and/or carbon substrates was reported earlier [2-4].

In order to obtain deposits free from pinholes or pores, different techniques such as rotation of the anode for rods [2, 3], the oscillation of the anode for plates [2, 3] and the movement of inert particles in the electrolyte (fluidized bed technique, [10, 11] were employed and the operating conditions established. Several means of avoiding pinholes by the addition of both ionic and non-ionic surface active agents, have been described. These include small amounts of hydrophilic colloid [12], gelatin [13], hexaethylene oxide lauryl ether [14], p-toluene sulphonamide [15],

alkylaryloxy polyoxy ethylene ethanol surfactant [9, 16], Teepol, Monoxal O.T. [17] and Tergitol NP 35 [18] (a high molecular weight form of sodium alkyl sulphate).

Cetyl trimethyl ammonium bromide (CTAB) [$C_{16}H_{33}(CH_3)_3.NBr$], a cationic surface active agent, was found to improve the finish in copper polishing and this was further substantiated with evidence which indicated that this cationic surface active agent was adsorbed at both the anode surface and on the walls of oxygen bubbles [19]. It was also reported that the use of CTAB had a beneficial effect on the cathodic deposition of metals [20].

In the course of measuring the stress in electrodeposited lead dioxide, the authors found that the addition of CTAB not only lowered the stress but also facilitated the deposition of lead dioxide free from pinholes both under stationary and rotating conditions [21]. Hence systematic studies were undertaken to examine the effect of the addition of CTAB during the deposition of lead dioxide on graphite substrates and the results are presented in this paper.

2. Experimental

2.1. Electrodeposition of lead dioxide

2.1.1. Cell assembly. A 1 litre Pyrex beaker, fitted with a PVC cover containing suitable holes to introduce the anode, the cathode and the thermometer, acted as a cell container. Two rectangular stainless steel plates ($14 \times 3 \times 0.1$ cm each) and a graphite rod (1 cm diameter \times 15 cm long), which was pretreated as described earlier [2], were used as cathode and anode respectively. When the experiments were carried out to obtain thicker deposits of lead dioxide, a 2 l Pyrex beaker containing a cylindrical stainless steel cathode was used. The cell was placed in an outer vessel containing water and the temperature of the cell was maintained at desired levels either by heating or cooling the water kept in the outer vessel.

2.1.2. Electrolyte. This was an aqueous solution of lead nitrate ($350 \pm 10 \text{ g l}^{-1}$) and copper nitrate ($25 \pm 2 \text{ g l}^{-1}$) to which different concentrations of cetyl trimethyl ammonium bromide (CTAB) were added. The concentrations of lead nitrate and copper nitrate were estimated by the EDTA method [22] and the iodometric method [23] respectively.

2.1.3. Electrolysis. 850 ml of this solution (with an initial pH of 4) was used. Both electrodes were kept stationary during electrolysis. The weight of the anode was measured before and after electrolysis. Direct current was supplied from a selenium rectifier (0–12 V and 50 A). The electrolysis was carried out for a definite time depending on the thickness of deposit required. During electrolysis calculated quantities of lead monoxide or lead carbonate and copper carbonate were added to neutralize the nitric acid formed.

2.2. Throwing power of the bath

The throwing power of the lead nitrate-copper nitrate bath for the anodic deposition of lead dioxide was reported earlier by Narasimham *et al.* [24]. In the present work the throwing power was measured for the lead nitrate-copper nitrate bath both with and without the addition

of CTAB, using a Haring-Blum cell [25] [$12 \text{ cm (l)} \times 2 \text{ cm (b)} \times 2 \text{ cm (h)}$] at a linear ratio of 1:5.

2.3. Specific conductance of the bath

The conductance of the electrolyte was measured at $60 \pm 1^\circ \text{C}$, using a Philips conductivity bridge type GM 4144. Owing to the large quantities of dissolved electrolytes employed, the specific conductance was $0.06 \Omega^{-1} \text{ cm}^{-1}$. Addition of $2 \pm 0.05 \text{ g l}^{-1}$ of CTAB did not affect this value.

2.4. Anode potential measurement

A smaller (400 ml) pyrex beaker was used as the cell for this part of the work. Deposition was carried out on a pretreated graphite rod (0.38 cm diameter \times 5 cm long). Only a 1 cm length of the anode was left exposed and the rest stopped off using 'Amarico' lacquer. Two thin strips of copper (2.5 cm width \times 8 cm long) were used as cathodes. A Luggin capillary was introduced in such a way that the tip of the capillary just touched the anode. Another limb of the bridge was introduced into another glass vessel containing ammonium nitrate. Connections were made to the saturated calomel electrode (SCE) immersed in a saturated potassium chloride solution through another bridge. Direct current was supplied from a constant current generator exhibiting less than 1% a.c. ripple. Anode potential measurements as a function of applied current were carried out in baths with and without CTAB and with reference to a saturated calomel electrode, employing a Philips d.c. Vacuum Tube Voltmeter (Type GM 6020). The readings were taken after equilibrium was attained at each stage.

2.5. Internal stress

The internal stress of the lead dioxide electro-deposited from a lead nitrate-copper nitrate bath has been reported earlier [21]. In the present investigation internal stress was measured by means of a 'Hoar-Arrowsmith balance' [26, 27].

A 400 ml Pyrex beaker constituted the cell. Nickel strips, cold rolled to 200–250 μm thick, were used as substrates on which to deposit lead dioxide. A thin copper strip (9 cm long \times 2 cm wide) was used as the cathode. Deposition was

carried out for 3 min from the bath containing 2 g l^{-1} of CTAB at $60 \pm 2^\circ \text{C}$.

3. Effect of other quaternary ammonium surfactants on the deposition of lead dioxide

In order to investigate the effects of other cationic quaternary ammonium surfactants, the electro-deposition of lead dioxide was carried out on graphite substrates from lead nitrate-copper nitrate baths containing (1) tetradecyl trimethyl ammonium bromide ($\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{NBr}$) and (2) dodecyl trimethyl ammonium bromide ($\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{NBr}$) in a similar way to that reported for CTAB.

4. Results and discussions

4.1. Electrodeposition of lead dioxide

4.1.1. *Effect of concentration of CTAB.* It can be seen from Table 1 that even quite small quantities of CTAB are sufficient to obtain a deposit which is adherent, smooth and free from pinholes. The solubility of CTAB at room temperature is about 50 mg l^{-1} . However, on heating the electrolyte, the solubility increases. It was found that a concentration between 1 and 2 g l^{-1} of CTAB gave the desired results. Due to the non-stoichiometry

of lead dioxide, the yield efficiency was more than 100% in some cases.

4.1.2. *Effect of current density.* Table 2 shows the effect of current density on the deposition of lead dioxide from a nitrate bath containing different concentrations of CTAB. It was possible to employ an anode current density as high as 30 A dm^{-2} when 0.5 to 2 g l^{-1} of CTAB were added to the electrolyte. This is different from the results reported earlier [2, 3]. If the deposition was carried out for a long duration at high current densities (10 – 20 A dm^{-2}), it was possible to get smooth and thicker deposits. Even with rotation of the anode and without the addition of CTAB to the bath, it was found that the maximum current density for obtaining an adherent deposit free from pores [2, 3] was only 5 A dm^{-2} . Thus the addition of CTAB to the electrolyte not only led to a smooth deposit with a stationary anode but also enabled a higher current density to be employed, thereby reducing the duration of the deposition for a particular thickness.

4.1.3. *Effect of temperature.* At low concentrations of CTAB (0.5 – 1.0 g l^{-1}) the deposits obtained were smooth but contained pinholes when prepared at 30°C . With 2 g l^{-1} of CTAB, the deposit developed cracks at anode current

Table 1. Effect of concentration of CTAB on lead dioxide deposition

Sl. No.	CTAB added g l^{-1}	Quantity of electricity passed (Ah)	Weight of lead dioxide (g)	Yield efficiency (%)	Nature of deposit
1	0.05	3.2	14.31	101	Smooth, adherent, coherent deposit with velvety appearance. Free from pinholes and lumps.
2	0.1	3.2	14.37	101	
3	0.2	3.2	14.33	101	
4(a)	0.5	3.2	14.27	100	Lumps formed; a few pinholes observed.
(b)	0.5	17.4	79.00	101	
5(a)	1.0	3.2	14.29	100	Velvety smooth adherent deposit.
(b)	1.0	17.4	77.00	99	Lumps formed; free from pinholes.
6	2.0	17.4	77.80	100	Coarse grained adherent deposit free from pinholes.

Electrolyte: lead nitrate $350 \pm 10 \text{ g l}^{-1}$; copper nitrate $25 \pm 2 \text{ g l}^{-1}$; initial pH: 4; temperature: $60 \pm 2^\circ \text{C}$; anode current density: 10 A dm^{-2} ; current: 3.0 – 3.2 A ; cell voltage: 2.8 – 3.1 V .

Table 2. Effect of anode current density on lead dioxide deposition

Sl. No.	CTAB added (g l^{-1})	Anode current density (A dm^{-2})	Cell voltage (V)	Current (A)	Quantity of electricity passed (Ah)	Weight of lead dioxide (g)	Yield efficiency (%)	Nature of deposit
1	0.5	10	2.8-3.2	3.0-3.1	17.4	79.0	101	Slightly coarse, adherent deposit.
2	0.5	20	3.7-4.1	6.0-6.1	17.4	73.6	94.8	Lumps formed and pinholes found.
3	0.5	30	3.8-4.3	9.0-9.2	19.0	81	95.5	More lumps and pinholes observed.
4	1.0	10	3.0-3.3	3.0-3.1	4.1	17.7	100	Adherent, smooth deposit free from pinholes and lumps. Velvety appearance.
5	1.0	15	3.1-3.3	4.5-4.7	4.1	17.8	101	
6	1.0	20	3.7-4.1	6.0-6.1	4.1	17.7	100	
7	1.0	30	3.7-4.3	9.0-9.2	17.0	72.8	96	
8	2.0	10	2.8-3.2	3.0-3.1	17.4	78.0	100	Fine grained adherent deposit.
9	2.0	20	3.7-4.1	6.0-6.1	19.1	80.6	94.6	Fine grained adherent deposit.
10	2.0	30	3.8-4.3	9.0-9.2	18.2	79.4	97.0	Lumps formed; a few pinholes observed.

Electrolyte: lead nitrate $350 \pm 10 \text{ g l}^{-1}$; copper nitrate $25 \pm 2 \text{ g l}^{-1}$; initial pH: 4; temperature: $60 \pm 2^\circ \text{C}$.

densities of $5\text{--}10 \text{ A dm}^{-2}$. The use of higher temperatures facilitated the addition of more CTAB and the results in Table 3 indicate that satisfactory deposits could thus be obtained at higher temperatures i.e. 60°C .

4.2. Photographs and photomicrographs of lead dioxide

Fig. 1 shows the photograph of lead dioxide obtained from a lead nitrate ($350 \pm 10 \text{ g l}^{-1}$) and copper nitrate ($25 \pm 2 \text{ g l}^{-1}$) bath containing CTAB (2 g l^{-1}) at current densities of 5 and 10 A dm^{-2} and a temperature of 60°C . It is seen that the deposit is smooth, adherent and free from pinholes.

Figs. 2a-e give the photomicrographs (magnification $\times 100$) of the surface of lead dioxide deposited from a bath containing CTAB under different conditions. The photomicrographs (same magnification) of the surface of lead dioxide deposited from a lead nitrate-copper nitrate bath without the addition of CTAB, on stationary and

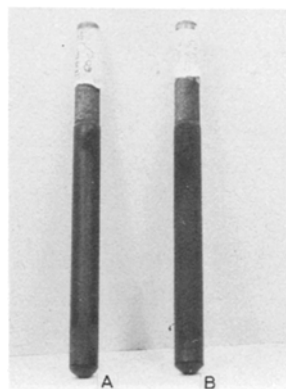


Fig. 1. Photograph of lead dioxide obtained on graphite rods from lead nitrate-copper nitrate electrolyte containing CTAB. (A) 10 A dm^{-2} , 60°C ; (B) 5 A dm^{-2} , 60°C .

rotating anodes, are shown for comparison. (Figs. 3a and b and 4a and b). Figs. 2a to c show that the deposits obtained from a bath containing 2 g l^{-1} of CTAB at a temperature of 60°C and at anode current densities of $5\text{--}20 \text{ A dm}^{-2}$, are smooth. However, the deposits obtained at a temperature of 30°C and at anode current densities of

Table 3. Effect of temperature on lead dioxide deposition

Sl. No.	CTAB added (g l ⁻¹)	Temperature (°C)	Anode current density (A dm ⁻²)	Bath voltage (V)	Current passed (A)	Quantity of electricity passed (Ah)	Weight of lead dioxide (g)	Yield efficiency (%)	Nature of deposit
1	0.5	30	5	2.2-2.8	1.6	3.2	13.9	90	Smooth deposition with pinholes.
2	0.5	60	5	2.2-2.6	1.6	3.2	14.0	92	Smooth and adherent deposit free from pinholes.
3	1.0*	30	5	2.2-2.8	1.6	3.2	14.1	96	Shiny deposit with pinholes.
4	1.0	60	5	2.2-2.6	1.6	3.2	13.9	90	Velvety deposit free from lumps and pinholes.
5	1.0	60	10	2.8-3.0	3.0	4.1	17.7	100	As above.
6	2.0*	30	5	2.2-2.8	1.6	3.2	14.0	92	Coarse, cracks at the bottom.
7	2.0*	30	10	2.8-3.2	3.0	3.2	14.0	92	Coarse, cracks at the top.
8	2.0	45	10	2.8-3.1	3.0	17.4	77.0	99	Shiny deposit free from lumps and pinholes.
9	2.0	60	10	2.8-3.1	3.0	17.4	77.8	100	Fine grained adherent deposit free from pinholes.

* The electrolyte was first heated. Then CTAB was added and the solution cooled. Electrolyte: same as in Table 2; initial pH: 4.

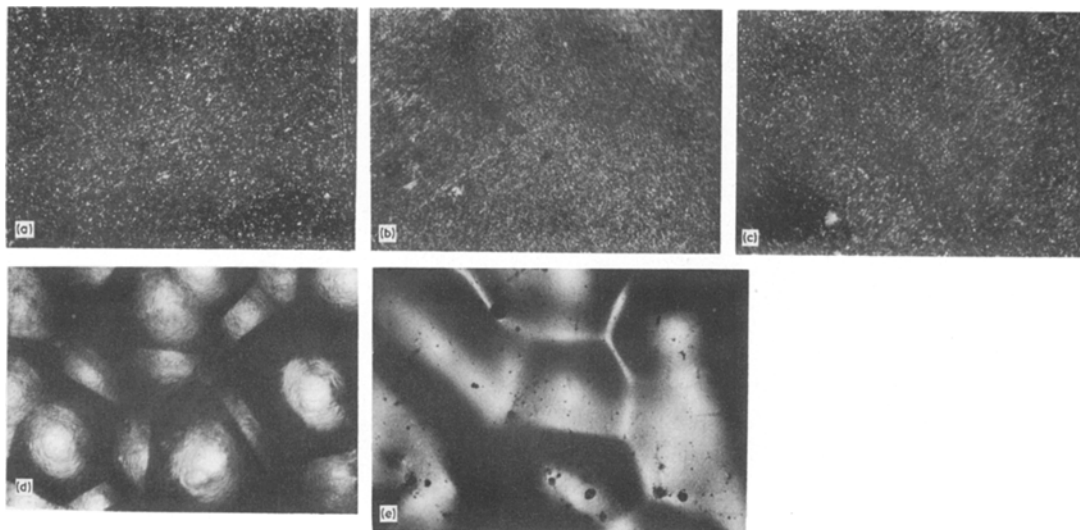


Fig. 2. Photomicrographs of lead dioxide surface obtained from nitrate bath containing CTAB $\times 100$. (a) 5 A dm^{-2} , 60°C ; (b) 10 A dm^{-2} , 60°C ; (c) 20 A dm^{-2} , 60°C ; (d) 5 A dm^{-2} , 30°C ; (e) 10 A dm^{-2} , 30°C .

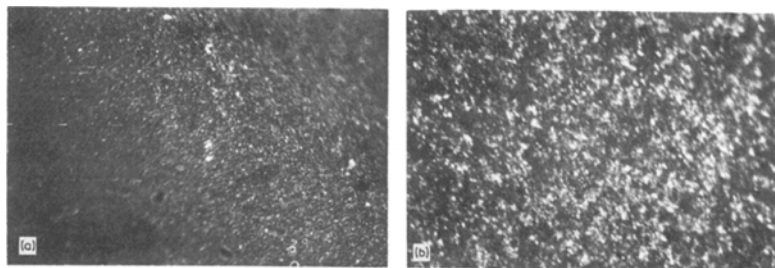


Fig. 3. Photomicrographs of lead dioxide surface obtained from nitrate bath without CTAB using rotation $\times 100$. (a) 5 A dm^{-2} , 30°C ; (b) 5 A dm^{-2} , 60°C .

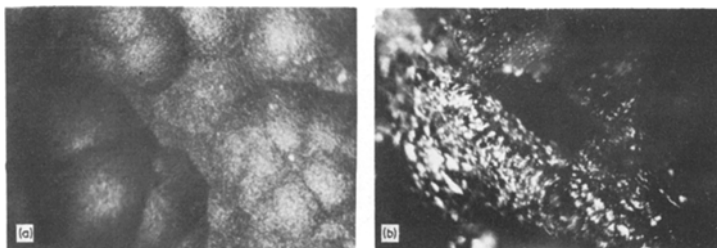


Fig. 4. Photomicrographs of lead dioxide surface obtained from nitrate bath without CTAB using stationary anode $\times 100$. (a) 5 A dm^{-2} , 30°C ; (b) 5 A dm^{-2} , 60°C .

$5\text{--}10 \text{ A dm}^{-2}$ are coarse (Figs. d and e). When the anode is rotated in a bath containing no CTAB, the deposit obtained at an anode current density of 5 A dm^{-2} is smooth both at 30 and 60°C (Figs. 3a and b). On the other hand, rough deposits are obtained on a stationary anode under the same conditions (Figs. 4a and b).

4.3. Throwing power of the bath

It can be seen from Table 4 that the throwing power of the bath is not altered appreciably on adding 2 g of CTAB per 1 under these experimental conditions. The throwing power of the bath is comparable to those for some of the common baths used for the electroplating of metals.

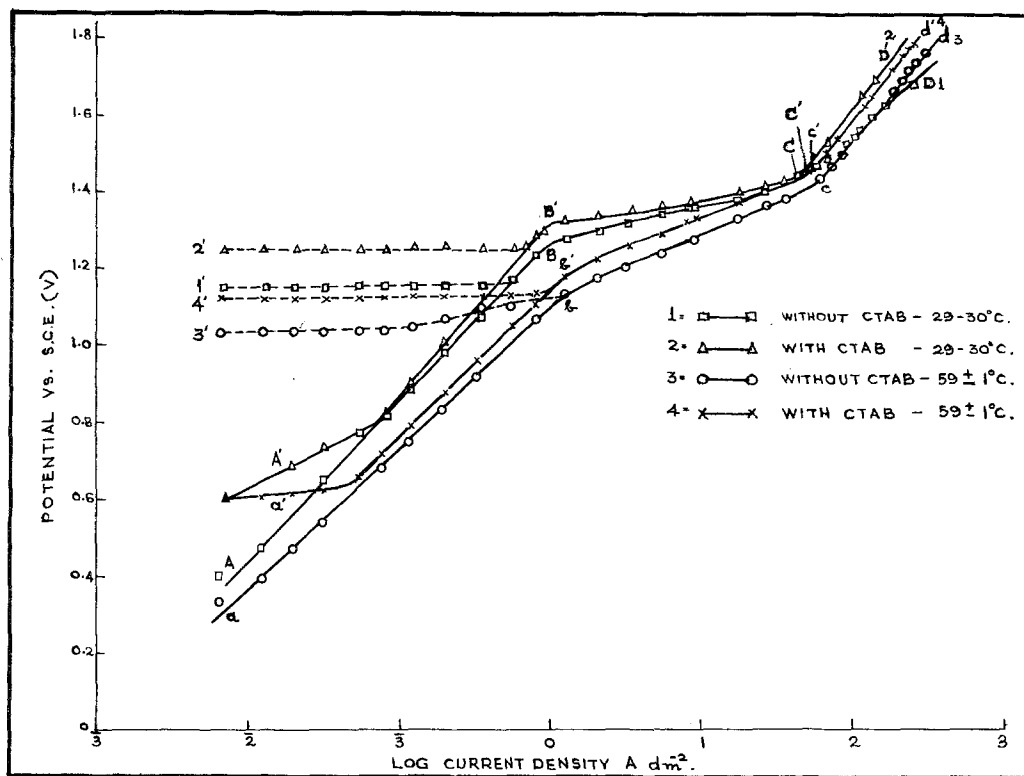


Fig. 5. Variation of anode potential with log current density.

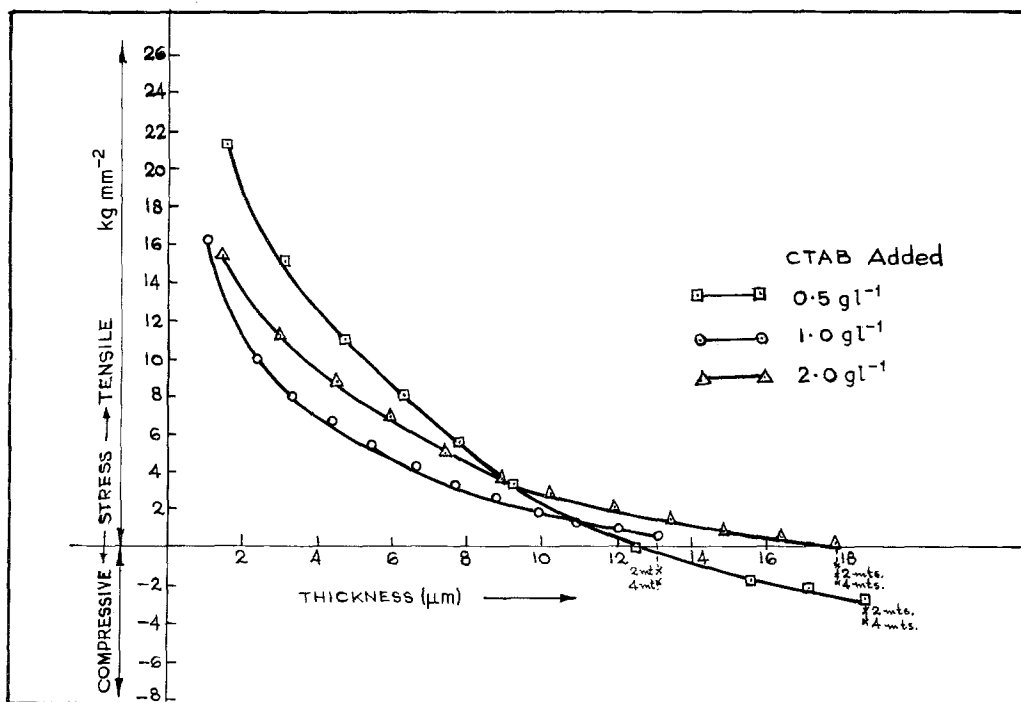


Fig. 6. Variation of internal stress with thickness of lead dioxide at different CTAB concentrations.

Table 4. Throwing power of the lead nitrate-copper nitrate bath

Sl.	Bath composition (g l ⁻¹)	Linear ratio L	Lead dioxide ratio M	Throwing power (%)
				$\frac{L - M}{L + M - 2} \times 100$
1	Lead nitrate 350 ± 10 and copper nitrate 25 ± 2	5	4.4	+ 7.5
2	Lead nitrate 350 ± 10, copper nitrate 25 ± 2 and CTAB 2.0 ± 0.01	5	5.0	0

Anode: nickel plated mild steel; cathode: copper gauze; temperature: 60 ± 1°C;
initial pH: 4.0; current: 0.5 A; duration: 10 min.

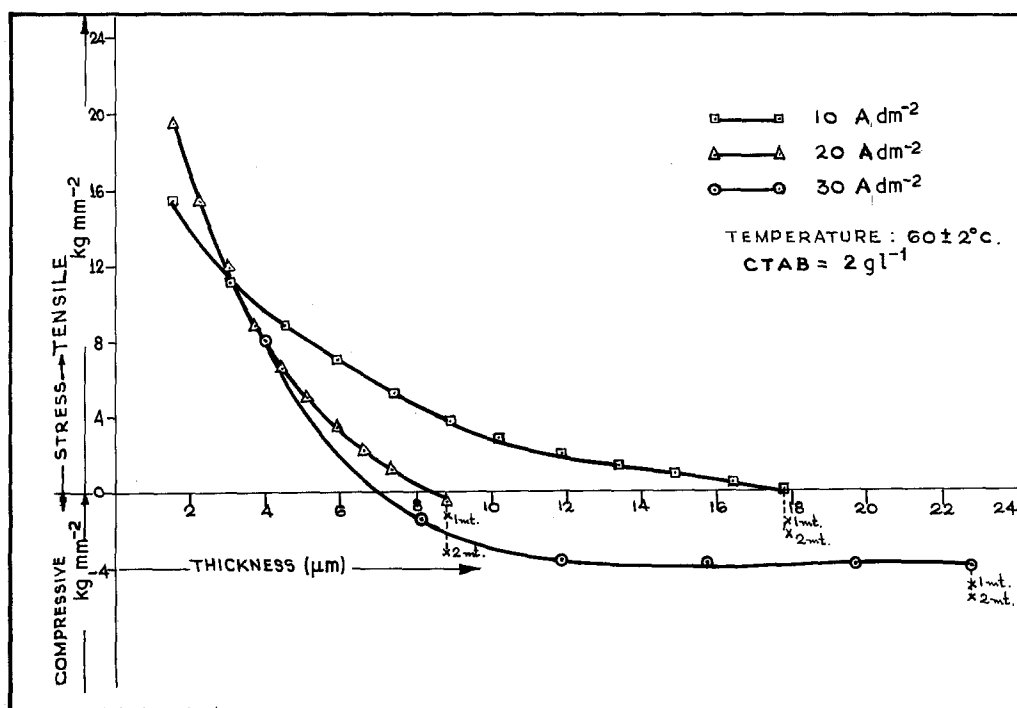


Fig. 7. Variation of internal stress with thickness of lead dioxide at different current densities.

4.4. Anode potential measurements

Fig. 5 is the plot of log c.d. versus anode potential (versus SCE). Curve 1 (ABCD) corresponds to the curve obtained for a bath without CTAB, at 30°C. The addition of 1 g l⁻¹ of CTAB, shifts the anode potential to slightly more positive values (A'B'C'D' (curve 2)). The curves 3 (abcd) and 4 (a'b'c'd') correspond to those obtained at 59 ± 1°C, without and with CTAB respectively; the potentials in these cases are less positive than those at 30°C. It is well known that the potential

decreases with increase in temperature, and this is observed here. The increase in anode potential in the presence of CTAB may be attributed to the adsorption of the additive.

In every case there are three definite slopes. However, when the potential measurements were carried out using a lead dioxide coated graphite rod, only two slopes were observed at first. (See curves 1', 2', 3' and 4') and the initial potential itself became more positive than that observed with graphite.

The first slope (AB or A'B' or ab or a'b') may

Table 5. Effect of other quaternary ammonium surfactants on the deposition of lead dioxide

S.No.	Addition agent added (g l ⁻¹)	Weight of lead dioxide (g)	Yield efficiency (%)	Nature of deposit
(i) Tetradecyl trimethyl ammonium bromide				
1	0.1	14.2	97	Smooth, adherent deposit free from pinholes.
2	0.5	14.15	96	Smooth, adherent deposit free from pinholes.
3	1.0	14.24	98	Smooth, adherent deposit free from pinholes.
4	2.0	14.30	100	Smooth, adherent deposit free from pinholes.
(ii) Dodecyl trimethyl ammonium bromide				
1	0.1	14.15	96	Smooth, adherent deposit free from pinholes.
2	0.5	14.21	97.5	Smooth, adherent deposit free from pinholes.
3	1.0	14.23	98	Smooth, adherent deposit free from pinholes.
4	2.0	14.3	100	Smooth, adherent deposit free from pinholes.

Electrolyte: same as in Table 1; initial pH: 4; anode current density: 10 A dm⁻²; temperature: 60 ± 1°C, current: 3.3 A; cell voltage: 3.2–3.4 V; quantity of electricity: 3.2 Ah.

correspond to the mixed potential of graphite and lead dioxide since initially at very low current densities the surface coverage of graphite will not take place completely. This is further substantiated by the curves obtained initially with a lead dioxide coated graphite rod, in which case this slope is not obtained. The slopes BC or B'C' or bc or b'c' correspond to the potential of lead dioxide deposition. The other slopes CD or C'D' or cd or c'd' correspond to the potential for oxygen evolution. Similar slopes were obtained by Vasundara *et al.* [28] during the deposition of lead dioxide from the nitrate bath containing lead acetate.

4.5. Internal stress

It was reported earlier by the authors [21] that the presence of CTAB in the electrolyte prevented the stress from becoming compressive, during and after deposition. It can be seen from Fig. 6 that the peak stress is higher with the solution containing 0.5 g l⁻¹ CTAB and also the stress is becoming compressive. However with 1 g l⁻¹ and 2 g l⁻¹ CTAB, the stress remains tensile. From Fig. 7 it can be seen that the peak stress is lower at 10 A dm⁻² than at 20 and 30 A dm⁻². This is mainly due to the low epitaxial stress at low current density. At a current density of 10 A dm⁻², the mean stress remains tensile up to a thickness of 18 µm. At higher current densities, the mean stress becomes rapidly compressive even

at a thickness of 6–7 µm. The steep fall in the mean stress value is due to the growing compressive stress, at higher current densities. The compressive after-effect also is slightly increased as the current density increases.

4.6. Effect of other quaternary ammonium surfactants

Table 5 shows that the other cationic quaternary ammonium surfactants like tetradecyl and dodecyl trimethyl ammonium bromides, which are also straight chain alkyl ammonium compounds but which contain less carbon atoms, also behave similarly to CTAB. The lead dioxide deposits obtained from the bath containing these quaternary ammonium surfactants are smooth, adherent and free from pinholes.

5. Conclusion

The addition of 0.1 g l⁻¹ of the surfactant decreases the surface tension of the electrolyte from about 75 dynes per cm to about 30 dynes per cm at 60 ± 2°C. This lowering of interfacial tension facilitates the easy release of the gas bubbles from the anode surface.

The beneficial effect of the cationic surface active agents like CTAB on the anodic deposition of lead dioxide may be due to the adsorption of the surfactant. The adsorption of cationic

surfactants on anodes is not uncommon since Lorking [19] also observed similar effects during the electropolishing of copper.

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