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# High speed platinum deposition from a sulphamate formulation

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## Abstract

A sulphamate based bath was identified as being suitable for high-speed platinum plating. The bath offers current efficiency approaching 70–80% and the deposits are bright in appearance. SEM examination showed that the grains are fine and XRD analysis indicates their grain size to be at the nano level. Cyclic voltammetric studies of the deposits indicate increased surface area. The properties of deposits obtained from sulphate and sulphamate formulations are compared.

## 1. Introduction

Platinum is extensively electroplated on to, for example, some aviation components, turbine blades, electrodes, electronic components and jewelry to improve their properties and appearance [1]. Raub et al. [2] reviewed the common electroplating baths for platinum and Skinner [3] described a new bath suitable for high rate of deposition of thick layers of platinum. This solution was based on a tetrammineplatinum with a buffer operating in the pH range 10.0–10.6 and temperature range 364–368 K. The current efficiency claimed was 60% when the bath temperature was above 361 K. Hadian et al. [4, 5] developed a phosphate buffer based P salt bath claiming around 20% efficiency with 5 g $l^{-1}$ platinum in solution. Electrodeposition of platinum from an alkaline electrolyte [6] of undisclosed composition has been claimed to yield 87% efficiency.

Of all the reported formulations, the P salt bath [1], Q salt [4–9] and the dinitritosulphatoplatinous acid bath (DNS) [9] have been commercially proven. P salt formulation, prepared from $Pt(NH_3)_2(NO_2)_2$, allows a maximum current density of 5.0 A $dm^{-2}$ and operates above 343–363 K. This electrolyte causes inconsistency in plating due to frequent changes in nitrite concentration and hence demands continuous monitoring of its constituents. The Q bath formulation, prepared from $Pt(NH_3)_4^{2+}$ complex, dissolved in an aqueous buffer of pH $\sim$ 10, offers the required current efficiency only above 366 K, which limits the choice of substrate materials in addition to the associated operational and maintenance problems [7]. These limitations led to the development of an alternative bath based on a solution of $Pt(H_2O)_4^{2+}$ in 1 M acid which allows a high rate of deposition at room temperature [8]. The difficulty in preparation of $Pt(H_2O)_4^{2+}$ was experienced as a major drawback. Preparations based on the addition of $Ag^+$ salt to $PtCl_4^{2-}$ are expensive and difficult to control [5, 9–11].

An electroplating bath containing Platinum as $H_2Pt(NO_2)_2(SO_4)$ complex prepared from P-salt has been reported and adopted commercially [12–16]. The advantages of the DNS bath are (i) capability to operate between 300 and 340 K (ii) low susceptibility to metallic contamination (iii) non-demanding nature for continuous stirring (iv) consistency (v) long life and (vi) stability. However, it normally offers a current efficiency of 15–20% only. Though this low rate of deposition, weighing the merits, does not have serious implications while plating thin layers, it is a serious problem during heavy deposition. Pletcher et al., in a series of papers on various platinum plating electrolytes [4–8], have studied the voltammetric behavior of platinum solutions containing methane sulphonic acid [8]. They have reported that complete conversion of $Pt(NO2)_4^{2-}$ to $Pt(H_2O)_4^{2+}$ is not essential to the production of an acceptable electroplating bath. They have also discussed the sulphamate bath. The sulphamate based platinum electrolyte has been recommended for deposition of platinum at high current densities [17]. In our pursuit of improved current efficiency of the DNS bath and to make it competitive for high speed plating lines, we decided that a modified sulphamate formulation would be a suitable choice.

## 2. Experimental details

The bath was prepared using chloroplatinic acid (0.38–0.4% Pt, supplied by M/s. Arora Matthey Ltd, Calcutta) as the starting material. Sulphate and sulphamate formulations were prepared via the P salt route [18]. The P-salt was dissolved in the required quantity of sulphuric/sulphamic acid, boiled at around 368 K for 1 hour, cooled, pH adjusted electrometrically and used for deposition. The solution color was straw yellow though it passed through a series of colors ranging from green, blue and yellow while boiling with the acid. Experiments were performed on sand blasted titanium substrates (ASTM Grade II) after prior etching in a solution containing hydrochloric acid and hydrofluoric acid [19–21]. The pretreatments were carried out under identical conditions such that the substrate roughness was almost equal. The effective geometric plating area was $2 \times 1$ cm$^2$. The thickness of the deposits was determined by X-ray fluorescence spectroscopy (CMI, XRX series, USA) and the measurements were accurate to $\pm$ 0.0001 $\mu$m. The microstructure of the deposits was examined using Scanning Electron Microscopy (Hitachi, Model No. S-3000 H) and XRD spectra were recorded using a JEOL, JDX-8030 machine with Cu-K$\alpha$ radiation. Grain size was calculated from the formula, $0.9\lambda/\beta \cos\theta$.

Cyclic voltammetry was performed using platinum electrodes in a three-necked H-type cell with a saturated calomel (SCE) reference electrode using a potentiostat (Wenking, Model 81, Germany) connected to a function generator (Wenking, Model SG 79) and a X-Y-t recorder. Potential scanning was carried out between $-0.240$ V and $-1.25$ V at a scan rate of 100 mV s$^{-1}$. Experiments were conducted in the plating baths to study the nature of deposition and the deposits prepared were tested in a solution of 1 M sulphuric acid to estimate the surface area.

## 3. Results

As observed by Pletcher et al. [8], the solution prepared at room temperature without boiling while mixing the P-salt and acid did not yield a platinum deposit. After boiling, and pH adjustment, the deposits obtained from the sulphamate bath appeared more white and compact than those obtained from the sulphate bath. The Cathode Current Efficiency (CCE) obtained from the sulphamate bath was appreciably higher than that from the sulphate bath under certain operating conditions.

Figure 1 compares the effect of metal content in the solution on the cathode efficiency of platinum deposition from the two electrolytes. The sulphate formulation yielded maximum cathode efficiency of 22% at 5 g l$^{-1}$ platinum concentration in the bath and further increase in its concentration caused only marginal change. In the sulphamate formulation, on the other hand, the CCE rose almost linearly from 22 to 82% when the platinum concentration was increased from 10 to 25 g l$^{-1}$.

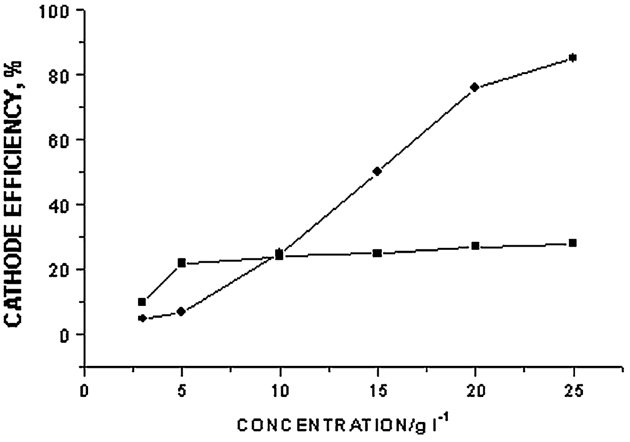

*Fig. 1.* Effect of Pt concentration on CCE of deposition 0.5 A dm$^{-2}$; –■– sulphate bath (pH 1.8); –•– sulphamate bath (pH 1.0); 303 K.

Platinum deposition from the above electrolytes is highly pH sensitive. With 10 g l$^{-1}$ platinum, the CCE of the sulphate bath was less than 10% up to pH 1.5, rose to 22% at pH 1.8 and decreased at pH 2. The sulphamate bath performed better yielding 26% efficiency at pH 1.0 which decreased linearly to 8% at pH 2.0. Thus, while the former shows maximum CCE at pH 1.8, the latter has a maximum at pH 1.0

Figures 2 and 3 show the effect of current density on the cathode efficiency at different pH values. The maximum efficiency of 75% is obtained from the solution containing 20 g l$^{-1}$ platinum at pH 1.0 and at 0.5 A dm$^{-2}$. CCE was 25% at 10 g l$^{-1}$ and 5% at 5 g l$^{-1}$ platinum concentrations at the above current density and pH. It was also observed that the bath containing 5 g l$^{-1}$ platinum yields high efficiency of 12% at pH 1.8 against pH 1.0 at higher concentrations.

Figure 4 shows the effect of electrolyte temperature on the deposition efficiency at two different concentrations. It is clear that increasing bath temperature improves the bath efficiency in 5 g l$^{-1}$ platinum. But with 10 g l$^{-1}$ a reduction in CCE was observed at pH 1.0 compared to that observed at room temperature and maximum efficiency was shifted to pH 1.8. With 5 g l$^{-1}$ platinum,

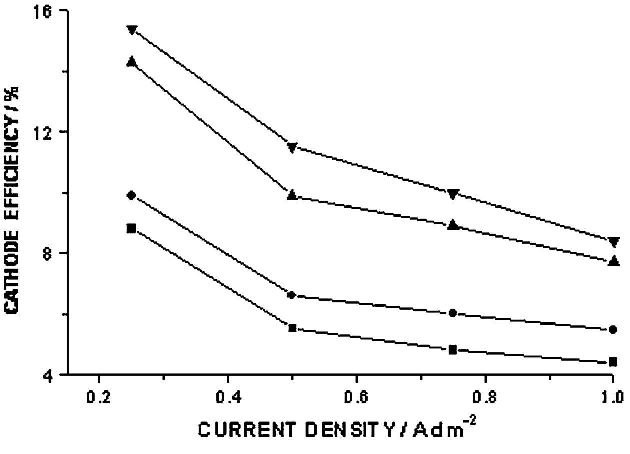

*Fig. 2.* Effect of cathode current density on CCE of deposition at different pH values 5 g l$^{-1}$ Pt in solution; 303 K pH –■– 1.0; –•– 1.5; –▼–1.8; –▲– 2.0.

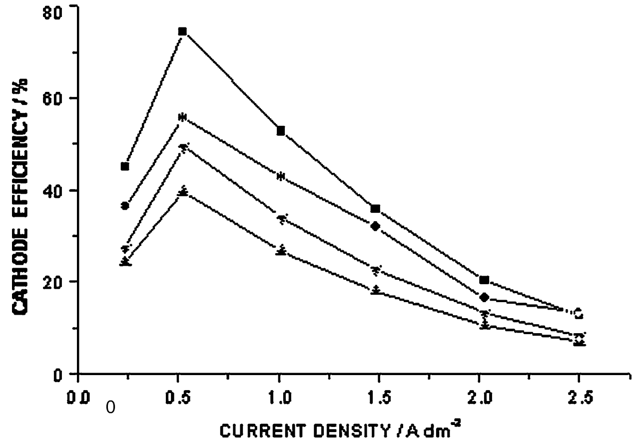

*Fig. 3.* Effect of cathode current density on CCE of deposition at different pH values 20 g l$^{-1}$ Pt in solution; 303 K pH -■- 1.0; -•- 1.5; -▼- 1.8; -▲-2.0.

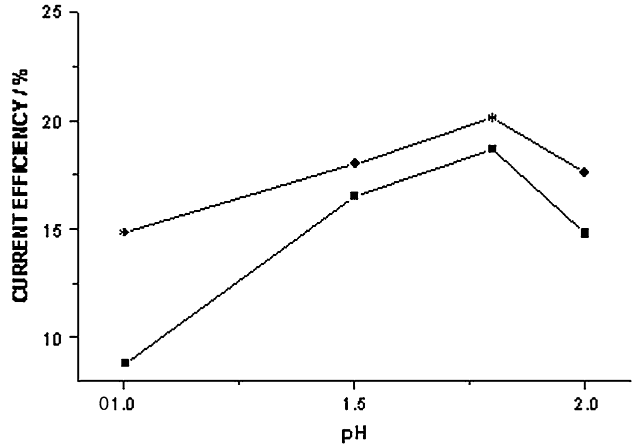

*Fig. 4.* Effect of bath temperature on CCE of deposition, Temperature 323 K; Pt concentration: -■-5 g l$^{-1}$; -•-10 g l$^{-1}$.

the sulphate bath yielded bright white deposits only up to 1 $\mu$m thickness. The deposites then turned darker, whereas in the sulphamate solution they remained bright white, even above 3 $\mu$m thickness.

When tested for porosity by conventional heat treatment in air at 923 K [19, 21–23], deposits obtained from sulphamate bath were less porous at 0.5 $\mu$m thickness compared to those from sulphate solution, which were pore free only above 0.75 $\mu$m.

Cyclic voltammetric curves obtained for the platinum deposition from the two baths are shown in Figures 5 and 6. Figure 5a shows the voltammogram for platinum deposition from the sulphate solution. At pH 1.0 and 1.8 the curves are similar with no peak. At pH 1.0, the voltammogram shifted positively with a higher current. When the bath temperature was increased to 323 K, the curves showed a further shift to more positive potentials and a small hump was visible at about $-0.200$ V.

Figure 5b compares the voltammetric behavior of platinum deposition from sulphate and sulphamate solutions. The voltammogram from the sulphamate bath shows a clear peak at $-0.22$ V in the forward scan whereas that from the sulphate solution shows no peak. The deposition potential ($E_d$, which is taken from the origin of the raising portion of the peaks) for the sulphamate bath occurs at a more negative potential than that for the sulphate bath.

Figure 6a and b compare the voltammograms obtained from sulphamate solutions with 5 and 10 g l$^{-1}$ platinum. Unlike in the sulphate bath, a distinct peak (peaks) is obtained. With 5 g l$^{-1}$ platinum at pH 1.0 and at 305 and 323 K, two peaks were obtained at $-0.24$ and 0.34 V as reported by Pletcher et al. [8]. The voltammogram obtained at pH 1.8 recorded a single plateau with a much lower current and the deposition ($E_d$) started at a more negative potential.

With 10 g l$^{-1}$ Pt in solution the same trend was observed under similar conditions, with a slight increase in the peak current. The second peak in the cathodic sweep is less distinct compared to that observed in the previous case.

Figure 7 shows the voltammogram of platinum deposits of 3 $\mu$m thickness in 1 M sulphuric acid at a scan rate of 100 mV s$^{-1}$. The area of the hydrogen adsorption - desorption region shows a marked increase for deposits obtained from sulphamate bath. The charge $Q^1$ and $Q^{11}$ corresponding to the adsorption and desorption regions and the surface roughness calculated knowing that 210 $\mu$C are required for the monolayer formation of hydrogen on a smooth surface. Table 1 presents the $Q$ values and the surface roughness obtained from the voltammograms.

SEM pictures (Figures 8–9) of the deposits obtained from the two baths at 1 $\mu$m and 3 $\mu$m thickness showed a clear picture of the nucleation and growth of the grains. As the thickness increases progressively, the grains aggregate forming a globular structure. The grains formed from the sulphamate solution are much smaller, of sub micron size, compared to those from sulphate formulation, which are a few microns in size having a globular cauliflower like structure. The smaller grain size should be the reason for the compact nature and relatively pore free nature of the deposits.

The XRD spectra of the platinum deposit obtained from the sulphamate bath is shown in Figure 10. Deposits obtained from both baths showed almost similar patterns. The grain size calculated from the half width of the peak is 20.75 nm

## 4. Discussion

The solution was prepared via the P salt which makes it easy to isolate platinum as $Pt(NH_3)_2(NO_2)_2$ in a fairly pure form devoid of anions, especially chloride ions. This complex, on treatment with either sulphuric acid or sulphamic acid yields the sulphito/sulphamato complex $H_2Pt(NO_2)_2(SO_4)/H_2Pt(NO_2)_2(SO_3NH_2)$ replacing the ammonium ligand.

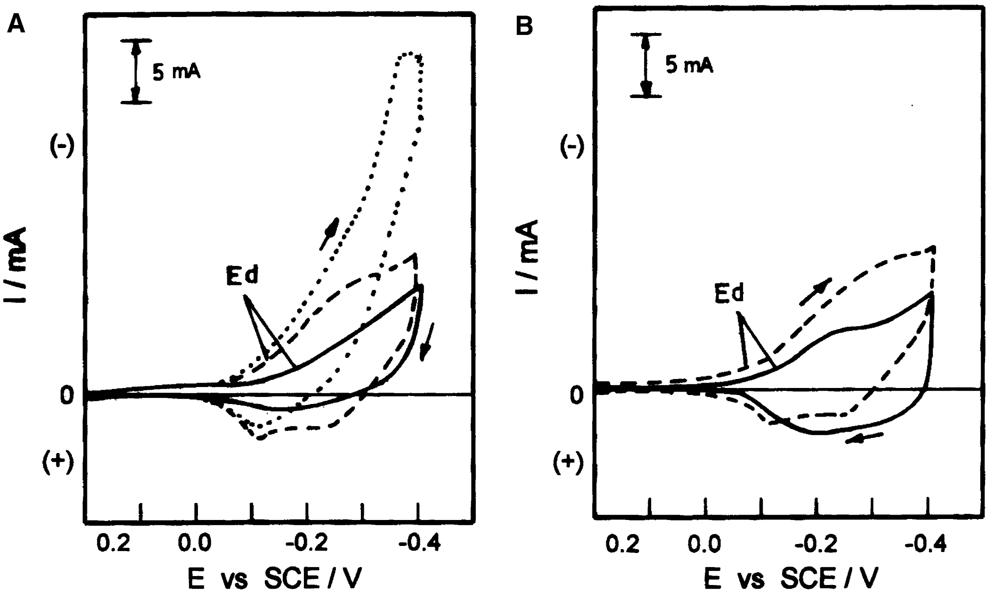

*Fig. 5.* (a) Cyclic voltammogram of platinum deposition from sulphate bath, Scan rate 100 mV s$^{-1}$; 10 g l$^{-1}$ Pt; pH: ——1.8; - - - - - 1.0; ......1.0, 323 K. (b) Cyclic voltammograms of platinum deposition from sulphate bath and sulphamate bath, Scan rate 100 mV s$^{-1}$; 10 g l$^{-1}$ Pt; pH 1.0; —— sulphamate; - - - - - sulphate.

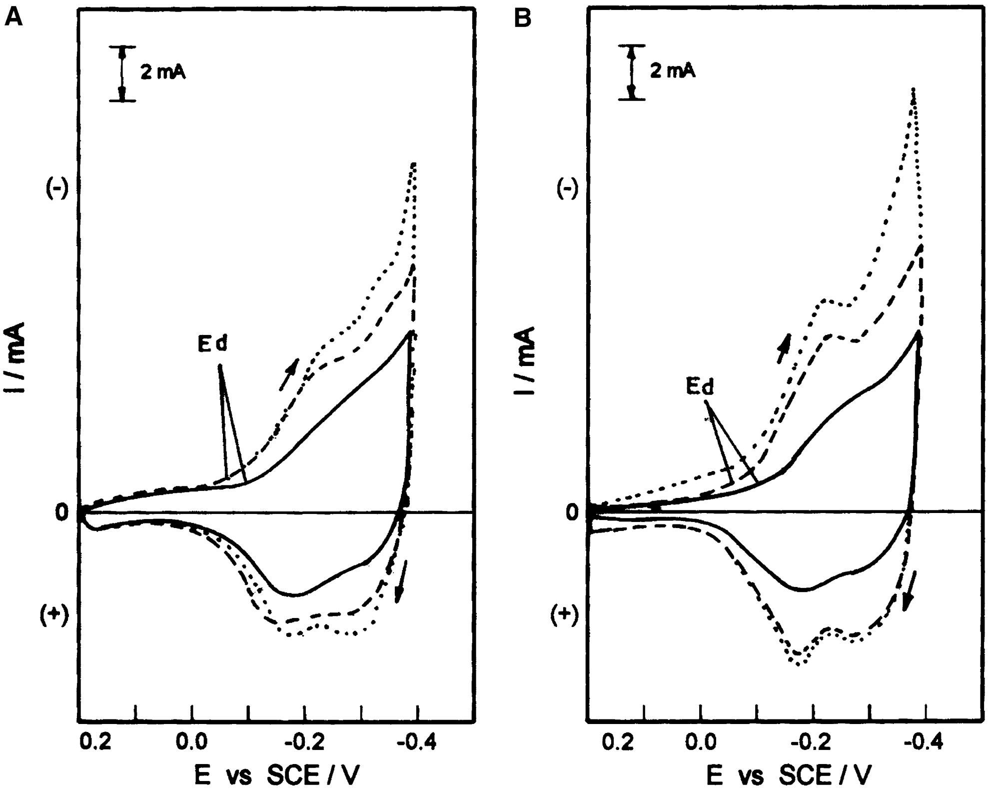

*Fig. 6.* (a) Cyclic voltammograms of platinum deposition from sulphamate bath, Scan rate 100 mV s$^{-1}$; 5 g l$^{-1}$ Pt; pH: —— 1.8; - - - - - 1.0; ......1.0, 323 K. (b) Cyclic voltammograms of platinum deposition from sulphamate bath, Scan rate 100 mV s$^{-1}$; 10 g l$^{-1}$ Pt; pH: —— 1.8; - - - - - 1.0; ......1.0, 323 K.

According to Pletcher et al. [8] deposition of platinum from nitrite complex occurs by stepwise removal of the nitrite ligand with hydroxyl ion on boiling with the acid.

$$Pt(NO_2)_4^{2-} \rightarrow Pt(NO_2)_3(H_2O)^- \rightarrow Pt(NO_2)_2(H_2O)_2$$
$$\rightarrow Pt(NO_2)(H_2O)_3^+ \rightarrow Pt(H_2O)_4^{2+}$$

The absence of platinum deposition from solutions which were not boiled with the acid has been attributed to the presence of large amounts of $Pt(NO_2)_4^{2-}$ along with traces of $Pt(NO_2)_3(H_2O)^-$. Thorough boiling enables stepwise displacement of the nitrite ligand. Since our observations during the preparation of the bath, like the color changes and the effect of boiling etc, are similar

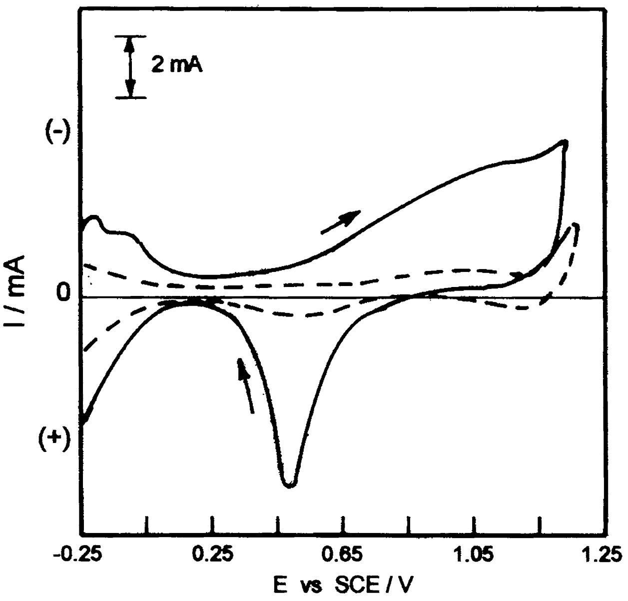

*Fig. 7.* Cyclic voltammograms of platinum deposits in 1.0 M $H_2SO_4$, Scan rate 100 mV $s^{-1}$; Deposits from —— sulphamate bath; - - - - - sulphate bath.

*Table 1.* Surface roughness calculated from cv data

| Deposits from | Q′/mC $cm^{-2}$ | SR/ $cm^{-2}$ | Q″/mC $cm^{-2}$ | SR/ $cm^{-2}$ | Q‴/mC $cm^{-2}$ |
|---|---|---|---|---|---|
| HDNS | 4.6 | 21.9 | 4.4 | 20.9 | 4.5 |
| CDNS | 1.69 | 3.05 | 1.72 | 8.52 | 1.71 |

Q′ charge in the positive side; Q″ charge in the negative side; Q‴ average charge.

to that reported by Pletcher et al. [8], it is assumed that preparation of the bath through the P salt, also leads to the same mechanism.

From the detailed work on NMR spectra [8] the presence of two reducible species $Pt(NO_2)(H_2O)_3^+$ and $Pt(H_2O)_4^{2+}$ in equilibrium has been reported for a bath duly boiled before plating. As shown in this work it is clear that $H_2Pt(NO_2)_2(SO_4)$, sulphito complex is a misnomer and actually the reaction consists of the formation of the above two species.

Increasing the platinum content in the solution increases efficiency. The low current efficiency is generally attributable to competing electrode reactions like hydrogen evolution. However, the gas evolution observed at the electrode surface was minor compared to that expected to account for the charge not attributed to platinum deposition. The reduction in current efficiency has also been attributed to the reduction of the nitrite ligand parallel to the reaction $Pt^{2+} \rightarrow Pt$. The reduction of nitrite to ammonium ion is a $6e^-$ process and the overall cathodic reaction is,

$$Pt(NO_2)(H_2O)_3^+ + 8H^+ + 8e^- \rightarrow Pt + NH_4^+ + 5H_2O$$

It has also been shown that $Pt(H_2O)_4^{2+}$ is stable at very low pH [9]. Hence, both baths yield metallic deposits below pH 2.0.

The difference in behavior between the two electrolytes can be attributed to the rate of the associated hydrogen evolution reaction. In sulphuric acid medium hydrogen evolution occurs to a higher extent so that no separate peak for platinum reduction is seen in the voltammogram. The reduction peak for platinum has merged with that of hydrogen evolution. The same situation also prevails at high operating temperature, which enhances both the reactions thus resulting in higher current. The hump observed is the platinum reduction peak. The appearance of this reduction peak accounts for the increase in CCE at high operating temperature. Deposition associated with heavy hydrogen evolution in the sulphate bath results in low current efficiency. Since the gas evolution is greater at pH1.0, deposition occurs at a pH of 1.8 i.e. after reaching the most conducive surface pH.

In sulphamic acid hydrogen evolution is relatively low so that the platinum reduction peak is distinct. Good deposits are obtained at pH 1.0 for the same reasons. With 5 g $l^{-1}$ the highest efficiency is obtained only at pH 1.8 and the same trend is observed when the 10 g $l^{-1}$ bath is operated at 323 K. The increased hydrogen evolution at low metal concentration and higher operating temperature delays the onset of conducive surface pH.

In sulphamate bath with 5 g $l^{-1}$ Pt at pH 1.0 at 305 K and 323 K, two peaks are seen. The first two peaks should correspond to $Pt(NO_2)(H_2O)_3^+$ and $Pt(H_2O)_4^{2+}$ reduction followed by hydrogen evolution.

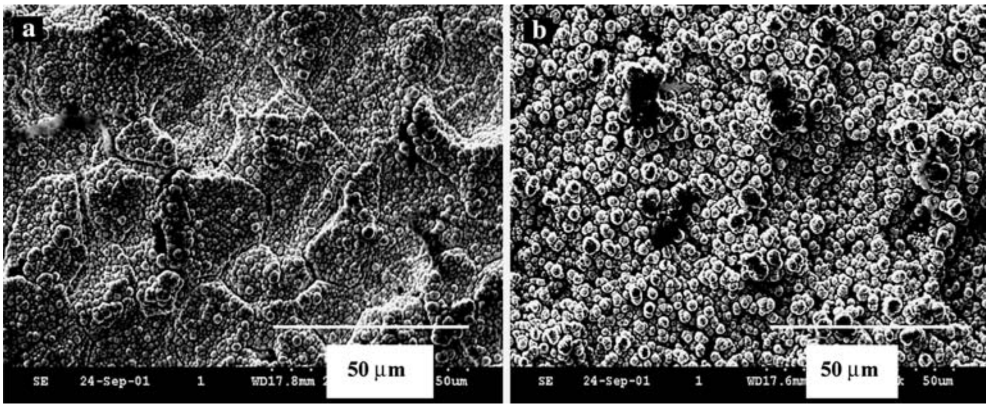

*Fig. 8.* SEM micrograph of platinum deposit obtained from sulphate bath (a) 1 μm thick (b) 3 μm thick.

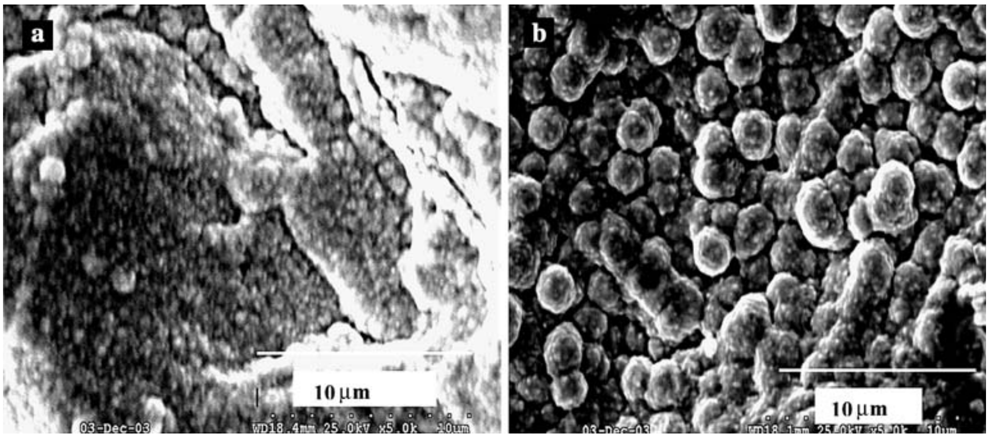

*Fig. 9.* SEM micrograph of platinum deposit obtained from sulphamate bath (a) 1 $\mu$m thick (b) 3 $\mu$m thick.

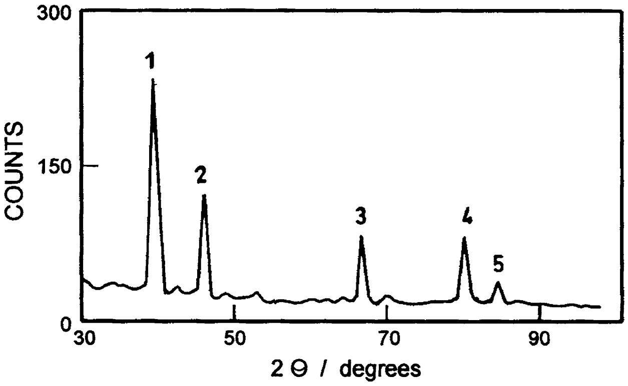

*Fig. 10.* XRD pattern of platinum deposit from sulphamate bath.

Since the peaks are well separated high CCE was obtained. An increase in bath temperature results in the appearance of distinct peaks due to the increased diffusion coefficient of the species. A similar trend is also observed with 10 and 20 g $l^{-1}$ platinum.

## 5. Conclusion

The sulphamate based DNS formulation yields bright smooth adherent and less porous platinum deposits on titanium substrates. The cathode current efficiency of the deposits from this bath is nearly 3 times higher than that from conventional sulphate solution. Cyclic voltammetric studies indicate the presence of two distinct peaks, which represent the reactions associated with platinum deposition from the complex. The SEM micrographs show more fine-grained structure for deposits obtained from the sulphamate bath

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