

# Developments in Platinum Electroplating: P & Q Salt Solution Optimization

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Processing conditions for the ‘P’ and ‘Q’ salt baths (containing platinum as diamminodinitrate) have been studied using electrochemical methods with a view to improving cathodic efficiency while maintaining adequate current density. The mechanism of electrodeposition is discussed in terms of the competing behavior, and simple calculations based on potential shifts have supported this approach.

The platinum group metals have extremely noble characteristics and consequently pose special problems for electrodeposition process development, notably the difficulty of establishing a good soluble form of the metal. A further preference is to avoid the use of organic solvents or fused salts, although the latter are advantageous sometimes (*e.g.*, production of platinized titanium). Any metal complex needs to be relatively cheap, appropriately stable, environmentally acceptable and easy to make and maintain. Four fit into these categories:

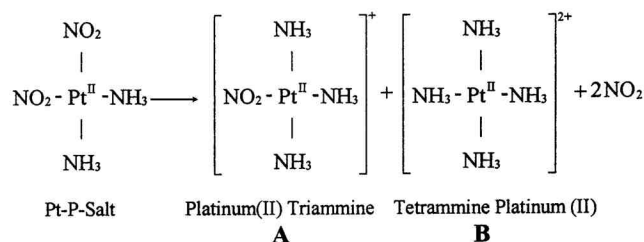
- amines
- nitrito
- hydroxy
- acid chloride

Each has well-recorded formulations from the 1940-1970 period.<sup>1</sup> For example, chloroplatinic acid has been shown to give softer, more ductile deposits that can be used to produce platinized platinum surfaces.<sup>2</sup> Platinum may be used in both the II and IV valence states for commercially viable processes:

- Pt(II) phosphate-based ‘P’ salts
- Pt(IV) hexahydroxyplatinatate or tetrachloride solutions including ‘Q’ salts

A recent continuing study by Pletcher, *et al.*<sup>3-8</sup> has addressed several options, especially those based on ‘Q’ salt or  $\text{Pt}(\text{NH}_3)_4^{2+}$  in a phosphate buffer that can be considered a newer version of the older ‘P’ salt or diamminodinitrate,  $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ .

This investigation has considered the most common commercial solutions based on P and Q salts as well as the common solution composition



**Table 1**  
**Dinitrodiammine Platinum ‘P’**  
**Salt Solution Composition**

		Dinitrodiammine Platinum
Pt 10 g/L	$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$	16.5 g/L
Ammonium Nitrate	$\text{NH}_4\text{NO}_3$	100 g/L
Sodium Nitrite	$\text{NaNO}_2$	10 g/L
Ammonia (28% solution)	$\text{NH}_4\text{OH}$	50 mL/L
Anodes	Platinum	

**Table 2**  
**Sodium Hexahydroxyplatinate ‘Q’**  
**Salt Solution Composition**

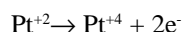
Sodium Hexahydroxyplatinate	
Sodium Platinate	20 g/L
Sodium Hydroxide	5.6 g/L
Sodium Oxalate	5.6 g/L
Sodium Sulfate	33.7 g/L

adjustments that can be made with phosphate and pH to maximize cathodic efficiency in the context of overlay coating for aero-engine parts such as turbine blades. Preliminary work has been reported elsewhere<sup>9,10</sup> and has dealt with the use of phosphates in the ‘P’ salt formulations and the use of pulsed current. In these studies, the avoidance of high-temperature processes has been a consideration, it having been recognized that commercial formulations have recommended the use of temperatures greater than 90 °C and pH greater than 10.<sup>11</sup>

In the ideal solution, it is normal for platinum metal ion additions to be the only maintenance required. For such solutions, using ‘P’ salt, ‘Q’ salt etc., the compositions used in this study are shown in Tables 1 and 2.

## Factors Affecting Process Performance

According to the usual method of formulation of platinum solutions, plating efficiency of the ‘P’ salt solution tends to decrease with time and use. For an initial make-up, the efficiency should approach 15 percent (*i.e.*, one gram deposited in 15 min); however, this will drop, depending on bath workload and overall age. The reason for the decline in efficiency was initially thought to be caused by oxidation of the platinum, *i.e.*:



Recent NMR (nuclear magnetic resonance) studies have shown, however, that the formation of an electrochemically stable species may hold the key to a steady decline in plating efficiency, as shown below.

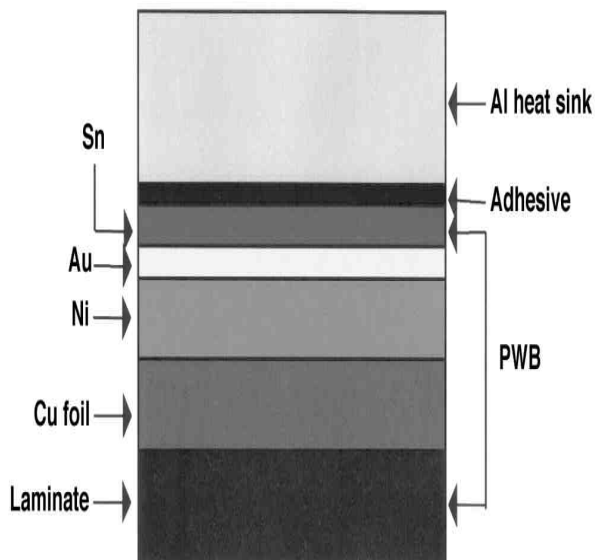


Fig. 1—Cathodic polarization for different solutions: effect of current density.

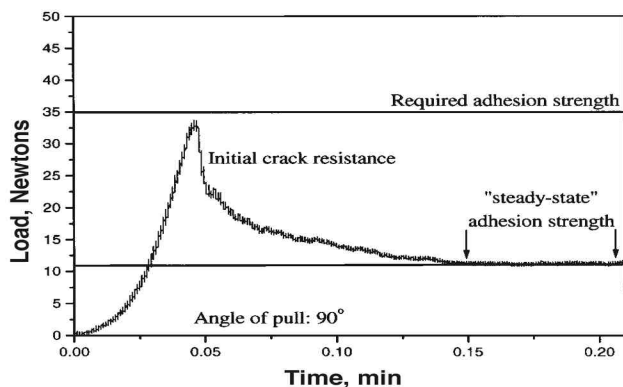
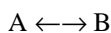


Fig. 2—Cathodic polarization for 'P' and 'Q' salt solutions: effect of current density.

During the dissolution of 'P' salt in aqueous ammonia, two distinct products are formed. In a newly prepared bath, the following equilibrium is formed:



As the bath is worked, the equilibrium slowly drifts toward species B. This shift is speeded by high-current-density plating through preferential depletion of complex A. To reduce this drift, there are two important factors to consider. First, a high excess of ammonia will tend to drive the equilibrium from left to right; accordingly, the bath should be operated at the low end of the pH range. Second, the replenisher stocks should be kept to a minimum to prevent 'long term storage' decomposition.

It is well established that deposition rates of the platinum solution 'Q' salt can be increased by consideration of a number of factors. At a platinum concentration of 5 g/L, 0.6 A/dm<sup>2</sup> was optimal. At 20 g/L Pt, a current density greater than 1 A/dm<sup>2</sup> can be maintained with current efficiency greater than 50 percent. At 30 g/L Pt, still higher current densities are feasible. The bath will operate at a cathode current density between 0.1 and 0.5 A/dm<sup>2</sup>. The optimum current density, however, is 0.25 A/dm<sup>2</sup>, depending upon the metal to be plated.

Agitation of the solution is required to achieve even distribution of the platinum within the bath. The current efficiency obtained depends on the temperature and current density. Results between 30 and 90 percent have been ob-

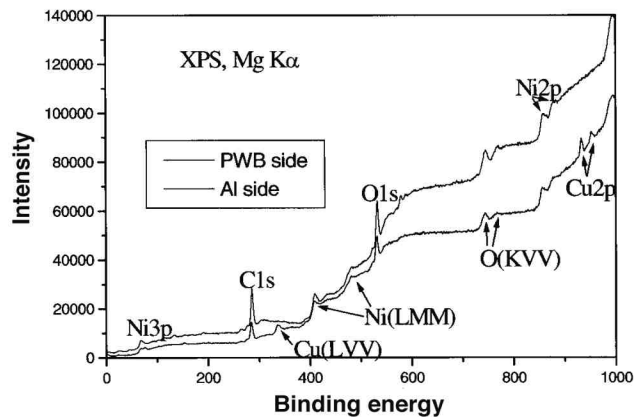


Fig. 3—Cathodic polarization for four different ratio solutions with effect of current density.

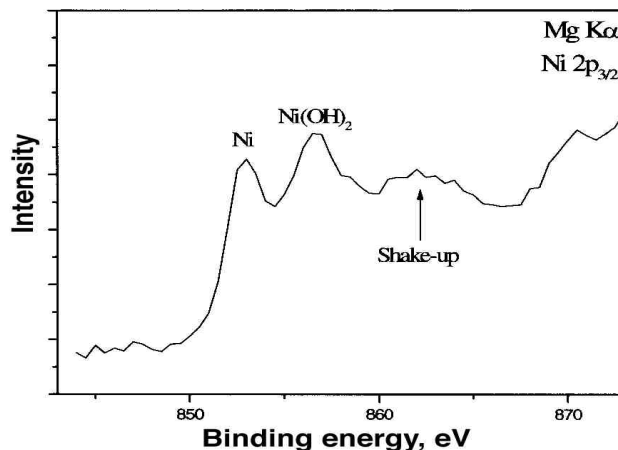


Fig. 4—Cathodic polarization for four different solutions: effects of potential on efficiency.

tained. Optimum results of around 70 percent were obtained at 90 °C and 0.25 A/dm<sup>2</sup>, depending upon factors such as electrode geometry and the substrate, as delineated in Tables 3-6.

Optimization has been reported, based on multivariable experiments, and analysis by statistical diagrams.<sup>11</sup> In this study, polarization characteristics were explored and discussed in the context of the known process performance parameters.

### Experimental Procedure

Normally, addition of platinum metal ions is the only maintenance required, using 'P' or 'Q' salts. Platinum solution compositions are given in Tables 1 and 2. The following processing sequence was employed in the experiments:

1. Ultrasonic vapor degreasing for 30 sec.
2. Cathodic cleaning: 1 min at 600 °C and 40 mA/cm<sup>2</sup>.
3. Demineralized water rinse.
4. 50 v/v hydrochloric acid pickle for 5 min at 500 °C.
5. Demineralized water rinse.
6. Pt 209 for 8 min at 20 mA/cm<sup>2</sup>, 90 °C and pH 8.0 to 9.0.
7. Demineralized water rinse.
8. Pt 'Q' salt deposition for 110 min at 7.5 mA/cm<sup>2</sup>, 80 °C and pH 12.0, yielding 10 μm thickness.
9. Demineralized water rinse, used later to replenish-top Step 8.
10. Demineralized water spray rinse.
11. Dry.

**Table 3**  
Cathode Current Efficiency & pH:  
Solution with 5 g/L Pt at 91 °C.

pH	CCE%
9.9	58
10.0	59
10.1	60
10.2	63.7
10.3	64
10.4	63
10.5	60
10.6	59
10.7	59
10.8	58.8
10.9	57

**Table 4**  
Current Density & Temperature  
Relationship at pH 10.5

CCE%	Temp °C
2	75
5	80
6	83
8	86
10	88
60	90
60	91
60	93
60	97

Polarization was carried out in a 2-L culture vessel with a separate lid that had five openings, thereby facilitating the insertion and removal of various reference and counter electrodes, thermometer and gas bubbler. The lid of the beaker was sealed in position with a gasket and clip.

Anodic and cathodic polarization tests were carried out in various platinum solutions as follows:

- (a) Fresh 'P' salt with phosphate buffers.
- (b) Phosphate base solution (*i.e.*, plating bath composition but without platinum).
- (c) Different ratios

of platinum solutions.

- (d) Plating solutions directly from plating Bath A (based on 'P' salt).
- (e) 'Q' salt<sup>b</sup> (Bath D).
- (f) Fresh 'P' salt with sodium buffers.

The platinum solutions were made up from individual chemicals and brighteners. Table 7 shows the standard solution make-up for platinum plating with phosphate buffers, with A being a large tank experiment, and B, C and D consecutive small tank experiments.

### Polarization Results

Cathodic polarization curves for the electrodeposition of platinum are shown in Figs. 1-10. These show polarization curves for the phosphate base solution without addition of 'P' salt. Maximum and minimum currents ( $\text{mA}/\text{cm}^2$ ) were achieved within -1.1 and -0.7 V. They also illustrate polarization curves for Bath A with the same pH value used in a phosphate base solution. Current inflection was more pronounced in the region of  $15 \text{ mA}/\text{cm}^2$  to  $5 \text{ mA}/\text{cm}^2$ , and this was accounted for by the hydrogen evolution reaction. This effect was recorded within a range of -0.65 to -0.7 V. The cathodic polarization curves for phosphate base solution and Bath A show that current drops were observed at -0.6 V, resulting from the effect of hydrogen evolution for both solutions.

Figure 1 also shows polarization curves for Bath A with addition of sodium hydroxide. The data for the platinum solution without addition of NaOH, reveal hydrogen evolution at -0.65 V, including a platinum solution with an addition of 130 mL NaOH for a 2-L solution and the consequent hydrogen evolution effect. The polarization curve for this

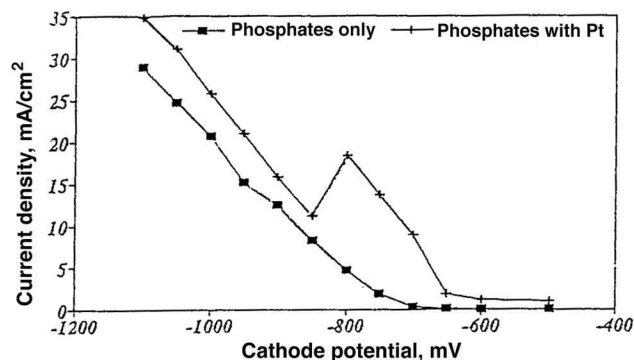


Fig. 5--Cathodic polarization for phosphates and platinum: effect of current density.

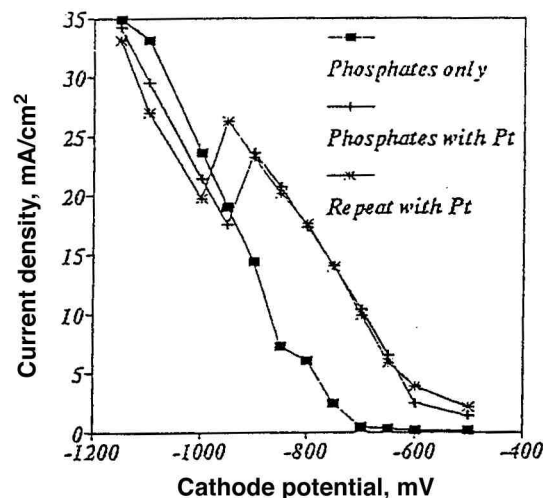


Fig. 6--Cathodic polarization for phosphates and platinum: effects of current density and repeated usage.

case was shifted toward a more negative value. Finally, in the platinum solution with a high addition of 20 g NaOH for a 2-L solution, hydrogen evolution was noted at -0.7 V, for which the polarization curve was also shifted toward a more negative value.

Figure 2 represents Bath D; polarization curves for this bath may be compared with those for Bath A, freshly made solution (Pt 'P' salt) and phosphate only. Although the pH and temperature values are different, allowance can be made by subtraction of  $2 \times 0.059 \text{ mV}$  for pH values for comparison between Baths A and D. Nevertheless, the hydrogen evolution occurred at -1.0 V and the degree of current inflection was low from  $18\text{-}12 \text{ mA}/\text{cm}^2$  when compared with Bath A.

Laboratory and experimental tests resulting from Bath D have shown that the rates of plating, current efficiency and plating time have shown greater improvement. These results indicate that when the polarization shifted toward more negative values, operating difficulties were encountered in the use of all baths. Three electrolytes with different phosphate ratios, but having constant platinum content of 3 g/L, were prepared. The bath composition and operating conditions are given in Tables 1 and 7, and the effect of various potentials upon these electrolytes is shown in Figs. 1-10. The phosphate ratios of 7:1, 4:1 and 1:1 were prepared with a high degree of accuracy; cathode efficiency measurements were made and are listed in Tables 4 and 6.

Cathodic polarization measurements were made, with the results shown in Figs. 1-10. From these results, it can be concluded that the electrolyte with the high ratio (*i.e.*, 7:1) had the highest cathode efficiency, with no hydrogen evolution until the maximum current density was achieved. This

**Table 5**  
**Current Density & Time Required to Deposit 1  $\mu\text{m}$  Pt per  $\text{dm}^2$**

C.D. A/ $\text{dm}^2$	Time in min/ $\text{dm}^2$ with CCE 75 %	Time in min/ $\text{dm}^2$ with CCE 60%	Time in min/ $\text{dm}^2$ with CCE 50%
0.9	5.7	6.8	8
0.8	6.4	7.3	9
0.7	7.3	8.5	10.4
0.6	8.5	10	12.2
0.5	10.2	12	14.4

C.D. A/ $\text{dm}^2$	Time in min/ $\text{dm}^2$ CCE 70%	Time in min/ $\text{dm}^2$ with CCE 60%	Time in min/ $\text{dm}^2$ with CCE 50%
0.5	10	13	15
0.4	13	15	18
0.3	17	20	24
0.2	25	30	35
0.1	51	59	72

9-10, whereas the pH range for Bath A ('P' salt) was 7.0-7.5. This effect generally agrees with the work of Dahms and Croll.<sup>12</sup> Under discharge in these circumstances, according to results shown in Figs. 6-10, hydrogen evolution was delayed or shifted more negatively with a local pH rise.

The main influence on the passivation characteristics of a platinum solution, except 'P' and 'Q' salt solutions, was the pH. In essence, a very low pH value resulted in a high value for  $i_{\text{crit}}$  and, consequently, a high dissolution rate for anodically formed coatings in this type of solution. All groups showed remarkably dissimilar responses at the different values of pH tested: pH 7.0 'P' salt solution curve exhibited high current densities for low overpotentials and generally exhibited a large number of inflections; pH 9.0 solution of 'Q'

corresponds to cathodic polarization having a more negative value and is probably a result of the amount of disodium orthophosphate in solution.

Further tests were carried out with and without phosphates in platinum solutions; results are shown in Fig. 1. It appears from this figure that higher temperatures could raise the current density and lower hydrogen evolution or vice versa. These tests were also carried out using fresh platinum solutions, as shown in Figs. 8 and 9.

Effects on cathodic polarization of high and low pH as well as temperature were investigated and are shown in Figs. 8-10. This study represents the cathodic polarization for platinum baths with high pH and platinum content, compared with low pH and low platinum content.

## Discussion

The cathodic polarization curves plotted for platinum are, in general, of a typical cathodic shape, culminating in the approach to a limiting current, indicating mass-transport-limiting deposition. Dahms and Croll<sup>12</sup> showed that a local pH rise near the electrode surface is favored when  $\text{H}_2$  evolution proceeds simultaneously with deposition, and it seems that sodium hydroxide can be precipitated in the vicinity of the electrode surface. The adsorbed sodium hydroxide permits a high discharge rate of  $\text{Pt}^{+2}$  according to their observations.

The current density-potential curves of these electrolytes show very characteristic behavior in the alkaline pH range. Insofar as the current density increases to a maximum limiting current, it drops to a low value before increasing again, with potential resulting from hydrogen production. How far this kind of 'cathodic passivation' is connected with the hydrogen co-discharge and the adsorption of hydrogen is not yet clear; another explanation might be a sudden change in pH value in the cathodic layer, caused by hydrogen evolution, possibly yielding incipient precipitate films not obviously identified.

The critical current density can be increased by an increase in the concentration of the Pt 'P' salt. Temperature has a decisive influence on the critical current density, while potentials remain nearly constant. Passivation is no longer observed at pH values below 7.0, because hydrogen evolution starts before platinum discharge begins and presumably films are unable to be nucleated. Initial investigations of 'P' and 'Q' salt solutions consisted of electroplating using the most promising solutions from Baths A and D.

The pH of Bath D ('Q' salt) was kept constant at values of

salt exhibited smaller current values for given potentials, also the appearance of less marked inflection phenomena. For all values of pH of 9.0-10.0, 'Q' salt solution currents at given potentials were generally smaller, up to -1.0 V, but gradually increased to 34  $\text{mA}/\text{cm}^2$  at high overpotentials of about -1.7 V.

Surface characteristic features after cathodic polarization were recorded and 'P' salt solutions were observed to yield dark, dull finishes, with silver matte to gray shades being prominent. 'Q' salt samples were generally reflective, bright and less heavily colored.

Broadly categorizing the inflections is difficult because of the scatter of values from individual solutions. There does appear to be some evidence, however, of a trend whereby all hydrogen-evolution analogs seem to produce inflection-type features at the range of values around -700 mV vs SCE for 'P' salt and one also around -1000 mV vs SCE for 'Q' salt. It must be reiterated, however, that these values should be regarded as rather approximate.

As a guide to corrosion resistance, the diffusion coating test was found useful. The results indicate that 'P' salt coatings consistently produced the best performance; 'Q' salt coatings showed larger variations between the duplicate samples tested for each processing condition. This suggests that either the diffusion coating process was producing uneven coating or that the specimens coated under a particular condition were truly variable. 'P' salt coatings were clearly superior to 'Q' salts, producing consistently high levels of uniform coatings and surface platinum corrosion products.

Because of the difficulty in observing the actual commencement of hydrogen evolution in a large-bath operation, it is assumed that the actual onset occurred before these experimental potentials. This suggests that the second inflection (usually strong) on the 'P' salt curve is around -800 mV vs SCE. SEM investigations were carried out on 'P' and 'Q' salt coatings that were subjected to diffusion treatment. This type of processing, however, produced a non-adherent coating from 'Q' salt solutions. On examination, the surface of the specimen from 'P' salt solutions generally appeared to consist of spherical crystals. The 'Q' salt coated surface was made of irregular spherical crystals (some of which exhibited internal cracks) that could possibly be a consequence of post-treatment that resulted in the cracking of the initially-formed film.

Referring to three electrolytes with different phosphate ratios having a constant platinum content of 3 g/L Pt, the bath composition and operating conditions are given in Table 8, and the effect of various potentials upon these electrolytes

**Table 6**  
Influence of Current Density  
& Current Efficiency on Deposition Rates

C.D. A/dm <sup>2</sup>	CCE%	Time to obtain 1.0 μm thickness, min	Thickness/hr μm
0.25	30	47	1.3
	50	28	2.1
	70	20	3.0
0.50	30	24	2.5
	50	14	4.2
	70	10	6.0

**Table 7**  
Solution Make-up for Small (A)  
& Large Tanks (B, C, D)

Composition	Weight/Volume	
	170-L Bath	335-L Bath
Pt as 'P' Salt, 28 g/L	425(Pt)	837(Pt)
Disodium Hydrogen Orthophosphate	14.0 kg	27.0 kg
Diammonium Hydrogen Orthophosphate	2.8 kg	5.5 kg

**Table 8**  
Solution Composition  
For Various Constituent Ratios

Composition Ratios	7:1	4:1	1:1
Pt as 'P' salt, 28 g/L	214	214	214
Sodium nitrite, g/L	102	102	102
Disodium hydrogen orthophosphate, g/L	213	187	85.2
Diammonium hydrogen orthophosphate, g/L	39.6	63.4	158
pH	7.65	7.7	7.7
Temperature, °C	84-86	84-86	84-86

shown in Figs. 1-7. Although care was taken to maintain constant experimental conditions, the weight gains obtained during a series of similar deposition runs were subject to considerable variation, indicating large variations in cathode current efficiency. The phosphate ratios of 7:1 and 1:1 were carefully prepared and cathode efficiency values are given. From these results, it is apparent that a ratio of 7:1 gives the highest efficiency and that hydrogen evolution does not commence until the highest current density is achieved. Further tests, with and without phosphates, showed that higher temperatures allowed higher current densities and lower hydrogen evolution.

When the deposition potential lies below the reversible hydrogen potential, there is usually some concomitant hydrogen evolution and possible reduction of other ions; these all lead to lower efficiency and electrical wastage. This statement can be related to the polarization curves. Potential shifts for non-standard conditions can be calculated from the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln \left( \frac{a_M}{a_M^{n+}} \right) \quad (1)$$

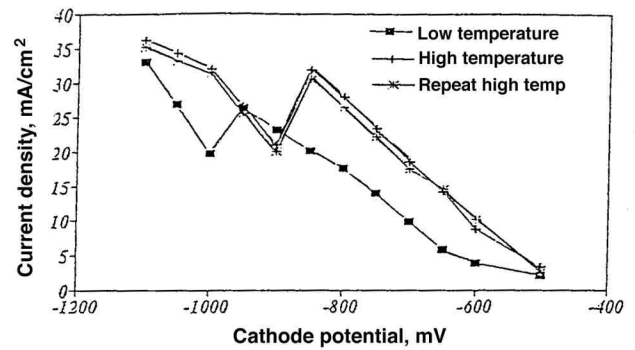


Fig. 7—Cathodic polarization for platinum solutions at high and low temperatures.

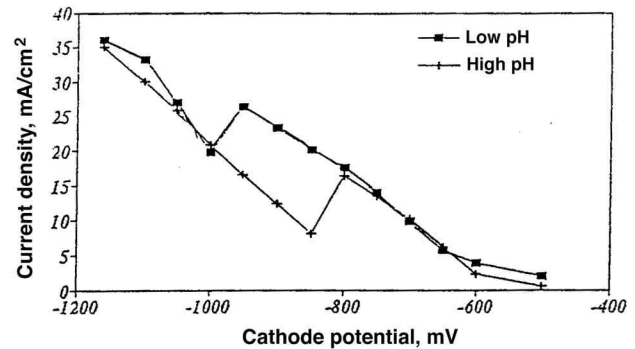


Fig. 8—Cathodic polarization for platinum solutions at high and low pH.

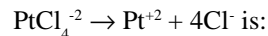
or, at 25 °C, 1 atm. pressure and pure metal:

$$E = E^{\circ} + \frac{RT}{nF} \log(a_M^{n+}) \quad (2)$$

Any potential shift can be expressed as:

$$\Delta E = (E - E^{\circ}) \quad (3)$$

The equilibrium constant for a complex such as



$$\frac{\text{PtCl}_4^{-2}}{\text{Pt}^{+2} \times (\text{Cl}^-)^4} = 10^{-16}$$

Using these equations, the following values are found:

Overpotential (mV)	$a_M^{n+}$
500	$10^{-16.95}$
600	$10^{-20.34}$
650	$10^{-22}$
700	$10^{-23}$
750	$10^{-25.4}$

From these calculations, it can be concluded that as excess Cl<sup>-</sup> is high, the activity of Pt<sup>+2</sup> is less and therefore Pt<sup>+2</sup> will be less than estimated, so that the calculation is justifiable as a guide. Comparison of the potential shift yields

$$a_{\text{Pt}^{+2}} = 10^{-16}, \Delta E = 500 \text{ mV}$$

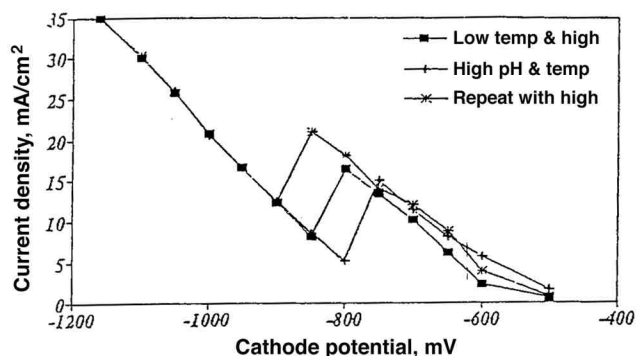


Fig. 9—Cathodic polarization for platinum solutions at high temperature and low pH, compared to low temperature and high pH.

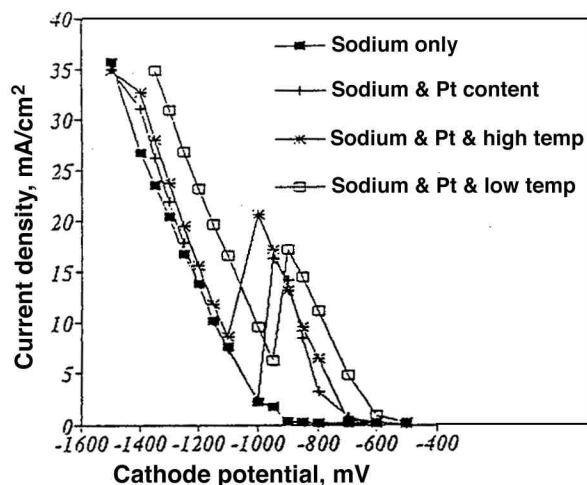


Fig. 10—Cathodic polarization for solutions containing added sodium; added sodium and Pt; sodium with Pt at high temperature; and sodium with Pt at low temperature.

Consequently, it is reasonable to attribute the potential shift primarily to the chloride complexing effect for  $Pt^{+2}$ .

### Summary

The operating conditions for a 'P' salt-based platinum plating solution were been studied and the effects of current density and current efficiency explored in particular.

Electrochemical measurements of potential were related to the solution composition and the resulting data discussed in terms of the complexed nature of the solution and the consequent deposition mechanism.

<sup>a</sup> Available from Johnson-Matthey or Engelhard.

<sup>b</sup> Available from Johnson-Matthey.

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**Table 9**  
Cathode Potentials & Consequent Process Characteristics

	CP mV	WG g	CD mA/cm <sup>2</sup>	CCE %
<b>Ratio 4:1</b>	-600	0.0	0.11	—
	-700	0.012	9.0	6.6 ± 1.2
	-800	0.038	22.0	8.6 ± 1.4
	-900	0.064	20.5	15.8 ± 1.5
<b>Ratio 7:1</b>	-600	0.0	0.083	—
	-700	0.009	7.0	6.2 ± 0.9
	-800	0.04	25.7	8.0 ± 1.2
	-900	0.061	19.4	15.9 ± 2.1
<b>Ratio 1:1</b>	-600	0.0	0.083	—
	-700	0.0	0.7	—
	-800	0.011	10	5.6 ± 1.2
	-900	0.055	24.6	11.3 ± 2.3

CP - Cathode Potential

CD - Current Density

WG - Weight Gain

CCE - Cathode Current Efficiency

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