<技術解說>

THE ELECTRODEPOSITION OF RHODIUM

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The platinum group of metals consists of platinum, palladium, rhodium, ruthenium and osmium. These metals, together with gold, are unique in their resistance to corrosion and the formation of surface films.

Of the six platinum, only platinum, palladium and rhodium have been used to any great extent for commercial electroplating. Of these three rhodium has been much more widely used. It has been estimated that the relative consumption of rhodium for plating purposes, as compared to platinum or palladium was 100 : 1.

The reasons for this are well founded. Not only have more reliable electrolytes been available for the deposition of rhodium but also the unique combination of its properties in the electrodeposited condition have made it outstanding. The hardness in the plated condition is in the range of 900-1000 vickers which makes it one of the hardest of the electrodeposited metals, comparable to hard chromium plating. Coupled with this it has an extremely high wear resistance. Electrolytes can be prepared without the addition of complex brightener systems which give fully bright deposits. The reflectivity of rhodium through the visible spectrum range is not only very high (80-90% of freshly polished silver) but it is uniform. This means, therefore, that is has a pure white colour, like silver, but unlike silver it does not tarnish. The density of rhodium is only just over half that of platinum so although it is more expensive weight for weight, the cost for a specified thickness of rhodium is lower than that of platinum. The high hardness and wear resistance also means that only very small thicknesses are required for long lasting protection.

For the above reasons rhodium has long been used for plating very thin deposits for decorative purposes. For these uses the control of electrodeposition processes is not very critical. In recent years, however, the rapid development of the electronics industry has created a demand for long lasting contact surfaces of very low and stable contact resistance. Modern electronic devices employing solid state components (transistors, integrated circuits etc.,) operate on much lower voltages and currents. A change in the resistance of contacts in the circuit due to the formation of surface films can upset the function of a complete electronic instrument.

For this reason it became necessary to produce thicker deposits whose properties could be closely controlled.

The chemistry of the platinum group metals is extremely complex. In all types of solutions which are suitable for electrolytes for electrodeposition the metal is present in the form of an anionic or cationic complex e. g. $Pd[NH_3]^{++}$, $Pt(OH)_6^{++}$. These complexes vary widely in their stability. Small changes in conditions of preparation can result in the formation of a different complex. In general complexes of intermediate stability make the best plating solutions. Although they are amongst the most noble of metals contrary to expectations, they are not always easy to electroplate. This is due to their high activation over potentials for metal deposition and generally results in fine grained deposits and low cathode efficiencies. For example ruthenium cannot normally be deposited from aqueous solutions at cathode efficiencies above 30% even at elevated temperatures.

Although many alternative electrolytes have been proposed for the electrodeposition of rhodium, most plating today utilises acid electrolytes based on rhodium sulphate, rhodium phosphate or a combination of the two.

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The use of the term rhodium sulphate and rhodium phosphate suggests a simple compound. This is not the case. In the case of sulphate the rhodium is probably present partly as a hydrated cation Rh$(H_2O)_6^{+++}$, partly as an anion $Rh(SO_4)_3^{---}$ and probably also as $Rh(OH)^{++}$, $Rh(OH)_2^{+}$.

The isolation of a simple sulphate is extremely difficult and is not attempted commercially. Both the phosphate and sulphate are normally prepared as a syrup containing 100 g/l rhodium, water and some free acid.

The first step in the preparation of a syrup is to get the rhodium into solution. This is not easy as rhodium is completely unattacked by most chemicals in the massive state. This involves the preparation of very fine rhodium powder referred to as rhodium black. Three methods are frequently used

1. The fusing of rhodium powder with lead and the extraction of the lead with 1 : 4 nitric acid.
2. The reduction of rhodium chloride solution with alkaline sodium formate.
3. The low temperature reduction of insoluable rhodium chloride with hydrogen.

The second step is to dissolve the black in boiling concentrated sulphuric acid.

This sulphate solution is then diluted and rhodium hydroxide is precipitated by raising the pH to 6.5 with ammonium hydroxide. If excess ammonium hydroxide is added the rhodium will redissolve as an amine complex.

The hydrated hydroxide is filtered and carefully washed, care being taken to see that the hydroxide does not dry out. If this is allowed to happen it becomes insoluable at the next stage.

The moist hydroxide is then dissolved in either sulphuric acid or phosphoric and the concentration adjusted to 100 g/l to make the appropriate syrup.

Depending on whether methods 1, 2 or 3 are used at the first stage the properties of the electrolyte vary. This is shown mainly by the hardness of deposits produced. Some results are shown in table 1.

Table 1. The effect of method of "black" preparation on the hardness of rhodium deposits(thickness; 12.5 microns).

Method	Hardness (D. P. N.) Sulphate electrolyte	Phosphate-sulphate electrolyte
1.	910	850
2.	945	870
3.	998	930

The temperature reached during the dissolution of the hydroxide in the acid also affects the properties of the electrolyte. High solution temperatures result in harder, brighter, more stressed deposits, and for fixed operating conditions, in lower cathode efficiencies.

The stress can vary from 20,000 to 120,000 p. s. i. It has also been noted that the stablity of the complex produced, varies. Rhodium sulphate or phosphate in the trivalent state Rh^{+++} is yellow, red-brown in colour depending on the concentration. Solutions of the Rh^{++++} ion are, however, green and it is reported those of Rh^{++++++} are blue.

Low temperatures at the hydroxide solution stage produce an electrolyte which turns green during plating due to anodic oxidation of Rh^{+++} to Rh^{++++}. These generally speaking are the best solutions as the cathode efficiency is high, the hardness sufficiently high and the stress relatively low. The higher stress deposits crack spontaneously even at quite small thicknesses similar to chromium plating.

Solution Formulations and Operating Conditions.

For decorative deposits and where non-tarnishing and good appearance are the required properties thicknesses are usually below 1 micron. In this case either all sulphate or sulphate phosphate electrolytes are used. A typical solution is:—

Rhodium (as sulphate or phosphate syrup)	2 g/l
Sulphuric acid	20 ml/l
Temperature	35-40 degrees C.
Current density	1-4 A/dm^2

If the work being plated is susceptible to acidic attack an all phosphate bath can be used where phosphoric acid is substituted for sulphuric acid. The cathode efficiency is, however, lower. The phosphate-sulphate solution is claimed to give whiter deposits with a slightly higher reflectivity. For heavy deposits (as used in the electronics industry) which, where rhodium is concerned, refers to coatings of minimum thickness 2 microns, more concentrated

Table 2. Formulations of rhodium sulphate electrolytes

Date	Author	Range of deposit thickness (ins.)	Rhodium content (g/*l*)	Sulphuric acid content (m*l*/*l*)	Temp. (°C)	Current density A/sq. dm.	Cathode efficiency	Agitation	Ref.
1950	Schumpelt	'Heavy'(0.001 in.)	10	100	50	0.5	90	—	11
1954	Laister	General purpose	4	?	35	1.0	—	None	1
1952	Wiesner	0.0002	10	25	50	2	90	Vigorous	9
1955	Parker	Up to 0.0001	3.7	17	40-50	1-5	60-70	Yes	10
		0.0001-0.0005	5.3	15	40-50	1-3	80	Yes	—
1956	Fischer Leonhard	0.0001→	10	'Lowest possible'	70-80*	0.5-1.0	60-70	Vigorous	12
1956	Wiesner Meers	0.0001-0.0002	10	30	50	1.5	85-98	Yes	8
1956	Reid	0.001-0.002	20	50	50	1-2	—	Yes	7
		0.0001-0.0005	10	100	50	1-2	—	Yes	—
1961	DTD 931	0.000015-0.000025	2	20	30-50	1-2	—	—	—
		0.0001-0.0002	4	20	30-50	1-2	—	—	—
		0.0004-0.0008	10	50	30-50	1-2	—	—	—

* Bright deposits 0.0004-0.0008 in. thick

solutions are used. A list of recommendations by various authorities is geven in table 2.

For these deposits, all sulphate solutions are preferred because of the lower stress, greater hardness and perhaps more important the higher cathode efficiencies. They have the added advantage in that the efficiency is little affected by increase in acid concentration which is in contrast with the phosphate sulphate electrolyte (See fig. 1). This is important as all rhodium solutions use inert platinum or platinised titanium anodes and metal replenishment is effected by addition of the same 100 g/*l* syrup used to prepare the electrolyte. As the syrup must contain some free acid and the rhodium is present as a sulphate complex this results in the continual build up of sulphuric acid in the solution. Usually in practice the acid content stabilises itself at around 100 ml/*l* when the rate of addition is ballanced by dragout losses.

There is general agreement that for thicker deposits (5 microns to 25 microns) a rhodium content of 10 g/*l* is required. Laister has claimed that higher metal contents give softer deposits and recommends a solution containing only 4 g/*l* of metal. This is not borne out by experience. Deposits of 900 V.P.N. and above have been obtained from solutions containing as much as 50 g/*l* of rhodium.

At this acid concentration it can be seen from fig. 1 that the loss in cathode efficiency is only small and not serious. Because efficiencies are higher at lower acid concentrations and because it increases during operation there is an urge to keep the initial acid concentration as low as possible. A certain minimum amount of acid is required to prevent hydrolysis and precipitation of the rhodium salts in the solution. Above this level, however, the effect of acid concentration is suprisingly small and is not a very significant factor. It has been reported, however, that with the more concentrated solutions (10 g/*l* and above) high acidity is desirable (up to 100 m/*l*) to reduce pitting and striation of deposits and to minimise cracking. The validity of this, however, appears to be doubtful.

The effect of current density on cathode efficiency is shown in figure 1. Rhodium is remarkably free from burning effects but above a current density of 2.0 A/dm^2 the increased evolution of hydrogen tends to cause excessive pitting. There is little to be gained in speed of deposition by using high current densities as the fall in cathode efficiency approximately ballances out the expected increased plating rate resulting in constant rate of deposition almost independent of current density. For heavy deposits current densities of from 0.5 to 1.0 A/dm^2 are considered best. Pitting and streaky deposits due to adhesion of hydrogen bubbles can cause problems. The highly acidic electrolyte has a high surface tension which

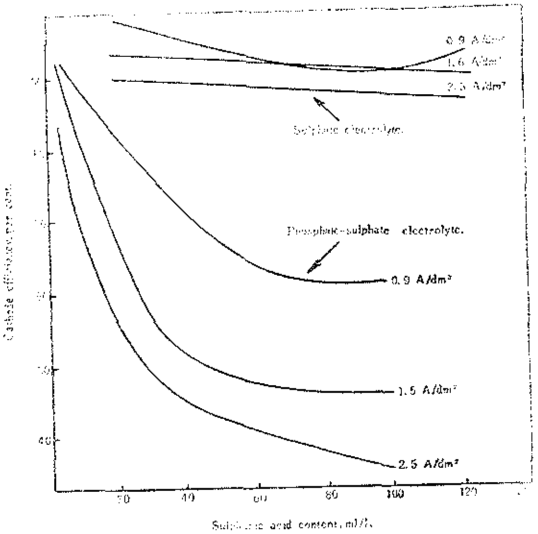

Fig 1. Variation of cathode efficiency with sulphuric acid concentration and current density in rhodium sulphate and phosphate electrolytes.

tends to make hydrogen bubbles adhere to the catnode surface. Up to the present time no wetting (or anti pit) agents have been discovered which are fully compatible with the electrolyte.

Agitation of the solution does result in some improvement of cathode efficiency and mechanical stirring, solution circulation, compressed air and cathode movement have all been used successfully. This agitation serves the additional function of helping to remove hydrogen bubbles from the cathode surface but probably the most effective method is by lifting and dropping the cathode bar at approximately one second intervals to provide a definite "jolting" action.

The optimum operating temperature is 50 degrees C. There are a number of good reasons for choosing this figure. Firstly, there is a marked increase in cathode efficiency between room temperature and 50 degress C, but with usual current densities, little further increase above this temperature. Secondly, the internal stress of deposits falls rapidly with increase in temperature but tends to a minimum at 50 degrees C (See figure 2). The use of higher temperatures is undesireable. Not only does the highly acidic electrolyte beome more corrosive and, therefore, increase the chances of contamination but also there is considerable evidence that changes occur in the electrolyte resulting in higher internal stress and a permanent lowering of cathode efficiency.

Deposits from decorative electrolytes retain brightness up to only 0.25 microns if the solution is free from impurities. The limiting thickness of bright deposits can be extended up to 5 microns if small ammounts of metallic impurities are present.

Under the usual operating conditions, an electrolyte for the plating of heavy deposits (10 g/l sulphate solution), produces smooth milky bright deposits up to 2.5 microns but brightness is progressively lost with increasing thickness and at 12.5 microns deposits are smooth but grey. The internal stess is high (in the order of 20-40 tons/sq inch) and this normally results in the cracking of deposits above 3 microns. This cracking is fine and not normally visible to the naked eye but may readily be observed under a microscope or by electrographic testing.

The thickness at which cracking begins depends on the substrate, particularly on the ductility of the underlying metal and hence its ability to absorb stress. In addition the preparation of the basis metal has a considerable effect. In general lightly etched surfaces are much preferred to highly polished surfaces.

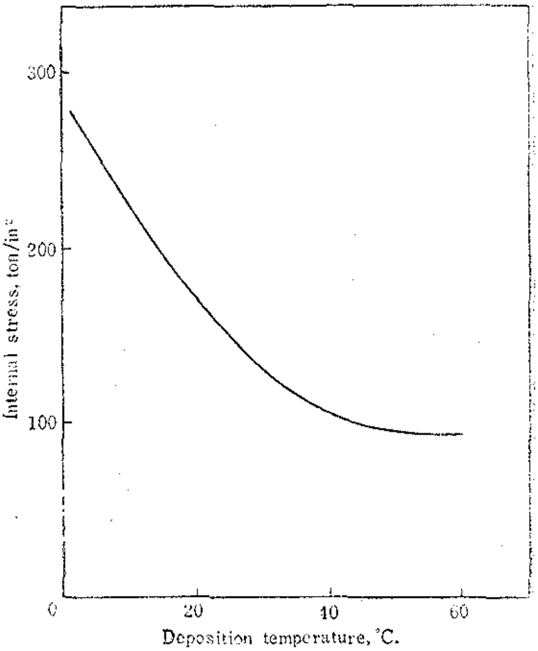

Fig. 2 The effect of deposition temperature on stress in rhodium deposits from a phosphate-sulphate electrolyte

The Effects of Contaminants in Rhodium Plating Electrolytes

The effects of impurities depend to a large extent on the rhodium content of the solution. Effects are, therefore, best considered as they apply to decorative and heavy plating solutions separately.

Table 3 lists some results obtained by Reid at the International Nickel Research Laboratories. It can be seen that iron and nickel do not cause problems in concentrations up to 1. 0 g/*l*. For practical contaminant concentrations e. g. . 0. 1 g/*l* copper and beryllium in phosphate and phosphate-sulphate solutions containing 2 g/*l* rhodium have no ill effects. Parker has, however, reported that copper in concentrations above 0. 005 g/*l* produced milky and increasingly matt deposits from a 4 g/*l* solution. Bismuth and silver in very small concentrations(0. 01 g/*l*) act as brighteners but at higher concentrations produce dark streaks and finally loose spongy deposits; mercury produces similar results. The addition of lead (or lead plus iron) has been used as a brightener. As the solubility of lead is low in phosphate-sulphate solutions there is little danger of over addition.

Results for 10 g/*l* sulphate solutions are shown in Table 4. For these solutions brightness and reflectivity of the deposit are not important, the major facors being surface smoothness, internal stress, cracking and hardness.

Again nickel and iron are without bad effects up to 1. 0 g/*l* and even higher concentrations. Copper up to 0. 4 g/*l* gives an increase in brightness but at higher concentrations produces coppery streaks and severe cracking. Silver in all but the lowest concentrations produces rough, dark grey and finally spongy non-coherent deposits. Mercury has a similar effect.

Addition of aluminium and magnesium result in a reduction in stress and uncracked deposits have been produced at 12. 5 microns. There is, however, a tendancy to greater roughness.

The effects of acid radicals have not been so widely investigated. In 2 g/*l* electrolytes Laister and Benham report that concentrations of 1 ml/*l* of hydrochloric or nitric acids had no effect and Dorner and Froels reported a similar result for concentrations of hydrochloric acid as high as 12 ml/*l*.

According to Weisner, the chloride ion has a marked effect on the properties of deposits from the 10 g/*l* sulphate solution. Deposits become increasingly matt and rough at concentrations from 0. 1 to 1. 0 g/*l* but at the same time there is a reduction in internal stress. This appears to have no practical use as the effect is too critical for practical control. Persulphates are not harmful and as Reid found that electrolytes based on fluoborates were similar to sulphate electrolytes this should have no ill effects as a contaminant. Additions of sulphamate appear to improve the plating rate and reduce cracking of deposits.

The use of ferrocyanide has been recommended by Brenner and Olson for the removal of metallic impurities from electrolytes, but Reid and Wiesner have reported a fall in cathode efficiency to zero in the presence of ferrocyanide.

The general effect of organic materials is to produce darker deposits in the case of the dilute decorative electrolytes while in the 10 g/*l* solution, small circular pits are produced and at higher concentrations, cracking and a scale like appearance of the deposits. Removal is usually effected by treatment with acid washed activated charcoal or alumina. The effect of organic contamination is important now that many printed circuits are processed in rhodium solutions. Melamine resins present special difficulties and if possible the use of this material in laminates for processing in rhodium solutions should be avoided.

Low Stress Electrolytes.

Even though deposits produced from the sulphate electrolyte show a network of fine cracks at thicknesses above 2. 5 microns, with correct plating techniques and the proper choice of substrates, these coatings meet most, if not all requirements for electrical contacts. The presence of cracks in a noble metal coating is, however, undesireable and many efforts have been made to develop solutions which would produce low stress or stress free deposits.

A number of solutions have been produced and are the subjects of patents. One of these is based on quite large additions of magnesium as the sulphate

Table 3. Effect of Impurities in Bright Rhodium Plating Solutions (Phosphate-sulphate)

Electrolyte composition	Rhodium(as phosphate solution)	2 g/l
	Sulphuric acid	10 ml/l
	Current density	4 A/sq. dm.
	Room temperature	

Impurity	Concentration gms/l	Reflectivity of deposit (% Sterling Silver)	Limiting thickness of bright deposit (ins. $\times 10^{-6}$)
Nil	—	81	10
Nickel	0.1	83	10
	0.2	87	10
Nickel+Lead	0.2, 0.005	87	45
Silver	0.1	—	Severe dark streaks
	0.01	86	42
Copper	0.1	83	125(73)
Iron (Ⅱ)	0.1	85	10
Iron (Ⅲ)	0.1	86	10
Iron (Ⅱ)+Lead	0.1, 0.005	85	275
Iron (Ⅲ)+Lead	0.1, 0.005	84	205
Tin (Ⅱ)	0.1	—	Very low efficiency
	0.01	87	10
Tin Ⅱ +Lead	0.01, 0.005	84	47
Lead	0.005-0.01	85	35
Bismuth	0.1	—	Severe dark streaks
	0.025	86	40
Zinc	0.1	70	36(60)
	0.01	83	35(79)
Beryllium	0.1	86	10
Beryllium+Lead	0.1, 0.005	86	98

* Figure in brackets is reflectivity of thickest deposit when this differed significantly from figure in column 3.

or sulphamate to a rhodium sulphate electrolyte. It is claimed that deposits, from this solution can be removed from a substrate in one piece and even flexed.

A typical formula is

Rhodium	5 g/l
Sulphuric Acid	10 g/l
Magnesium sulphamate	30 g/l
Magnesium Sulphate.	10 g/l

The solution is operated at 20-50 degrees C. at a current density of 0.4-2 A/dm^2

It has also been reported that aluminium has a similar effect.

Another type of electrolyte is based on additions of selenic acid to a sulphate solution.

A typical formula is

Rhodium (as sulphate syrup)	10 /l
Selenic Acid	0.4 g/l
Sulphuric acid	50 ml/l
Temperature	50-60 degrees C.
Current Density	1-2 A/dm^2

Deposits from this electrolyte are almost fully bright even at thicknesses of 25 microns. This is at variance with the general observation that brightness is an indication of high stress. Reference to figure 3

Table 4. Effect of Metallic Impurities in Heavy Rhodium Plating

Electrolyte composition	Rhodium (as sulphate)	10 g/l
	Sulphuric acid	50 ml/l
Current density		2 A/sq. dm.
Temperature		40°C
Deposit thickness		0. 0005 in.

Addition	Concn. (gm/l)	Cathode efficiency (%)	Hardness of deposit (D. P. N.)	Appearance of deposit
Nil	—	65	963	Very smooth, light grey-cracked
Copper	0. 1	63. 9	938	Light grey, slightly rough-cracked
	0. 4	64. 4	808	Smooth, slightly milky-cracked
	4. 0	64. 7	339	Bright copper-coloured-severely cracked
Nickel	0. 1	61. 6	914	Smooth light grey-cracked
	1. 0	64. 5	932	Smooth light grey-slight cracking
Iron (Ⅱ)	0. 1	55. 0	827	〃 〃 〃 〃
	1. 0	65. 6	808	Smooth, milky bright-cracked
	5. 0	58. 2	788	〃 〃 〃 〃
Iron (Ⅲ)	0. 1	62. 1	902	Smooth, light grey-slight cracking
	1. 0	60. 9	932	Smooth, milky bright-slight cracking
	5. 0	52. 6	770	Smooth, light grey-cracked
Silver	0. 01	63. 3	695	Smooth light grey-very slight cracking
	0. 05	62. 5	752	〃 〃 〃 〃
	0. 1	53. 0	752	Light grey, rough at edges-very slight cracking
	0. 15	39. 7	—	Some deposit loose, mainly very slight cracking, rough grey-
	1. 0	—	—	Loose black
Zinc	0. 1	65. 9	672	Light grey, slight rough-slight cracking
	1. 0	64. 1	752	Light grey, slight rough-severe cracking
Ammonium	1. 0	62. 6	808	Smooth, light grey, slight cracking
Ammonium + Aluminium	1. 0, 1. 0	69. 9	702	Smooth, light grey, very slight cracking
	1. 0, 5. 0	62. 3	725	Very smooth, light grey very slight cracking
	1. 0, 20. 0	54. 3	—	Smooth mat grey-uncracked
Indium	0. 1	57. 9	—	Smooth light grey-slight cracking
	1. 0	57. 3	—	Smooth light grey-slight cracking
	18. 0	55. 1	—	'Frosted'-severe cracking
Tin (Ⅱ)	0. 1	60. 0	—	Milky bright deposit-slight cracking
	1. 0	53. 1	—	Smooth light grey-uncracked
	2. 0	52. 7	—	Milky bright-very slight cracking
Lead	0. 05	62. 4	—	Smooth light grey-slight cracking

(Time deflection curves for beryllium copper strips plated on one side only in a reference sulphate electrolyte before and after addition of selenic acid) shows, however, that the initial stress is slightly higher. Relief of stress occurs at point A by the formation of a network of extremely fine cracks.

These are barely visible under the microscope(See fig 4) and are not revealed by electrographic testing. Results of corrosion tests in such media as nitric acid ferric chloride seem to indicate that what is observed are filled cracks. The effects of selenic acid in chromium plating solutions are somewhat similar. This and other similarities *suggests a close similarity in the deposition mechanisms* involved for these two metals which also have marked resemblances in the electrodeposited state.

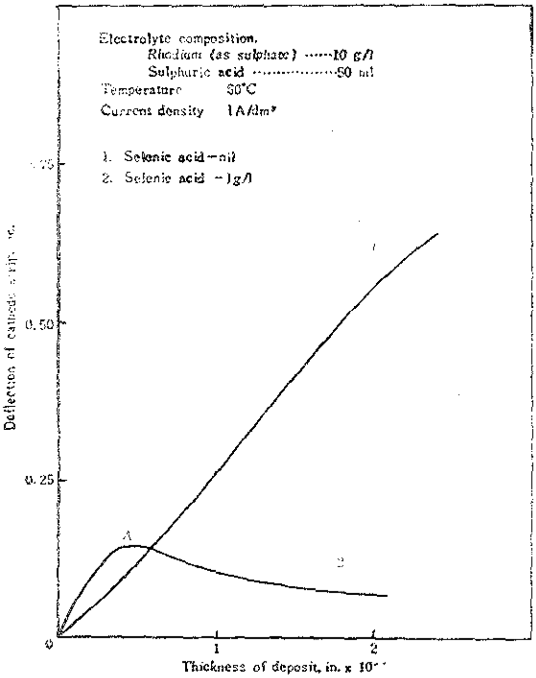

Fig. 3 The effect of selenic acid addition to a rhodium sulphate electrolyte.

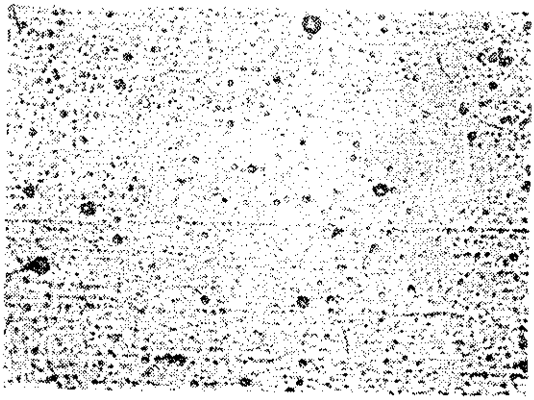

Fig. 4 As-plated surface of rhodium deposit from sulphate electrolyte with selenic acid addition (×300)