

# Stress in Electrodeposited Rhodium

## EFFECTS OF CONTAMINATION BY ORGANIC COMPOUNDS

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*In the electrodeposition of rhodium from the sulphate bath normally employed highly stressed deposits are produced. In this paper the author describes an investigation of the effects of contamination by organic compounds contained in masking paints on these stresses, and shows that the results of earlier studies on internal stress may have been vitiated by the employment of a method relying on such paints for masking one side of the cathode. An apparatus completely avoiding the use of paint was designed in the course of the present investigation, and an improved paint, giving markedly less contamination and lower stresses in the deposit, was formulated for use in commercial rhodium plating practice.*

The complete resistance to tarnish and the extreme hardness of electrodeposited rhodium has led to its widespread use in electrical contact applications. For rhodium to be used successfully in these and other applications, the electrodeposit must be free from cracks caused by high internal stresses, but a fairly high level of stress is characteristic of such deposits.

Except where very thin deposits are applied, it is economically necessary to confine rhodium to those areas where it is required. This is usually done by coating with a masking paint those areas where rhodium is not needed.

Observations in commercial rhodium plating practice show that stress cracking

often appears to originate at the boundary of the rhodium and the masking paint, suggesting that contamination of the electrolyte has occurred at this point. A study was therefore made of the effect of this contamination on the internal stress in the deposit.

Stress in electrodeposits is usually calculated from a measurement of the deflection of a thin cathode which has been plated on one side only. Soderburg and Graham (1) have described the simple variant of this method, where an initially straight strip is allowed to bend. The radius of curvature is then calculated from a measurement of chord height taken on a travelling microscope. Hoar and Arrowsmith (2) used a measured electromagnetic force to oppose the stress, and the strip was thus held straight. The Brenner and Senderoff (3) contractometer is a more robust instrument, which measures the twisting of a spiral cathode. Kushner (4) measured the variation of hydraulic pressure behind a thin disc cathode. Reid (5, 6) has measured the variation of stress in deposits of rhodium deposited from solutions at various temperatures, using a bending strip technique.

In all these methods some means of blanking off one side of the cathode was used. With the exception of the method of Kushner this blanking off was effected by means of stopping-off paint or lacquer. Thus none of these techniques could be used without some modification to study the effect of paint on rhodium solutions.

Weisner and Meers (7) have reported considerable variation of internal stress in deposits taken from similar but distinct

batches of rhodium solution. For this reason all the experimental work was performed on solutions diluted from one batch of rhodium sulphate concentrate.

## Experimental Details

The basic electrolyte used was as follows:

Rhodium, as rhodium sulphate	8.0 g/l
Sulphuric acid	30.0 g/l

The standard plating procedure was 5 amp/sq. ft for thirty minutes at 40°C unless otherwise stated.

A plating jig which completely eliminates the use of stopping-off lacquers was designed and is shown in exploded view in Fig. 1. The beryllium-copper strip is clamped against a stainless steel backing plate, using P.T.F.E. as an insulator.

The strips were made from one batch of Mallory 73 beryllium-copper strip, 0.375 × 0.005 inch. The strip was stretch-straightened

and then cropped into 3.5 inch lengths. At this stage the metal was in the cold rolled condition and it was then given the standard heat treatment in air at 350°C for two hours. This treatment was carried out in a clamp which held the strips flat.

The strips were measured for the zero curvature in a modified Soderburg and Graham apparatus shown in Fig. 2 and weighed before mounting in the plating jig.

Degreasing of the strip in cold trichorethylene which was ultrasonically agitated was followed by cathodic cleaning for ninety seconds. After rinsing the strips were transferred to a 1.5 per cent phosphoric acid solution and anodically etched for forty seconds at 7 amp/sq. ft. After a thorough rinse the strip was ready for plating.

After plating, the jig was rinsed in a drag-out tank and dismantled. The strip was dried and weighed. Three readings of the curvature were taken, the strip being

moved along each time so that an average value of the chord height was obtained.

Internal stress was calculated by use of the equation:

$$S = \frac{I}{d} \frac{h}{bxt} \frac{4E_B}{(t + xRd)}, \text{ where}$$

S = internal stress

d = deposit thickness, calculated from the increase in weight

$E_B$  = Young's modulus for the basis metal

b = width of the strip

$x = \frac{\text{width of deposit}}{\text{width of strip}}$

t = thickness of basis strip

h = height of chord measured by Soderburg and Graham apparatus

$R = \frac{\text{Young's modulus of deposit}}{\text{Young's modulus of strip}}$

I = moment of inertia about the neutral axis, given by

$$I = bt^3 \left\{ \frac{xRd}{4} \left[ \frac{d+t}{dxR+t} \right] + \frac{T}{I_2} \right\}$$

For all experiments the values of  $E_B$ , b, t and R were regarded as constant.

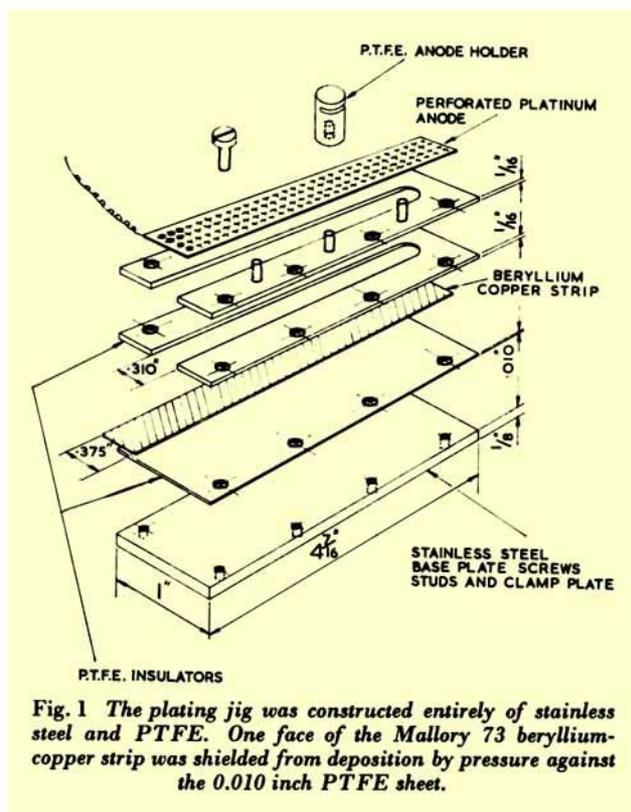


Fig. 1 The plating jig was constructed entirely of stainless steel and PTFE. One face of the Mallory 73 beryllium-copper strip was shielded from deposition by pressure against the 0.010 inch PTFE sheet.

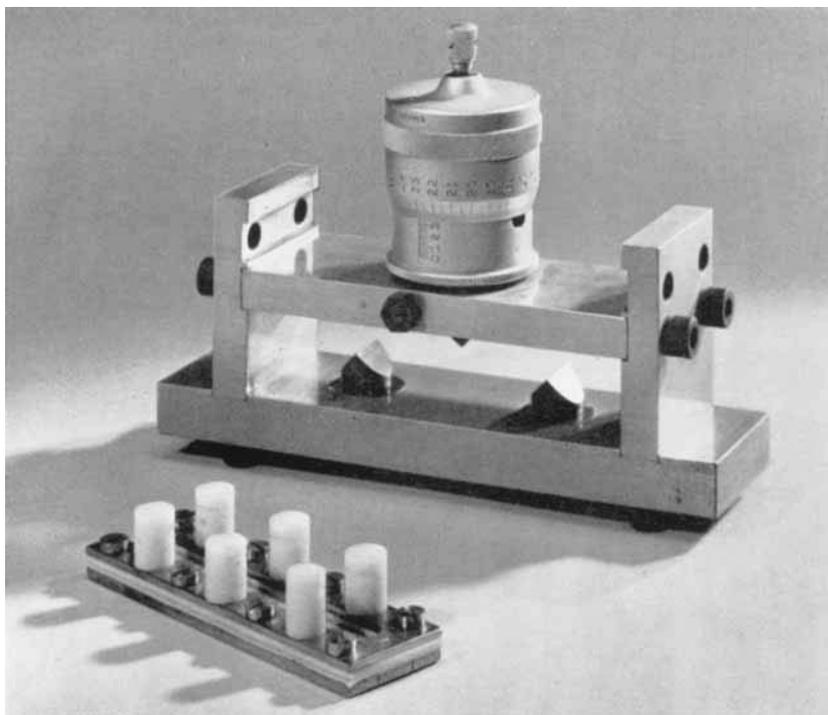


Fig. 2 *The plating jig and the micrometer device used for measuring curvatures. During measurements the strips were set up between the knife edges, and the point of contact with the micrometer point adjusted using an eye glass.*

In the case where a paint was being studied, a copper panel  $2 \times 1$  inches was first coated with the paint and air dried for twenty-four hours. This panel was immersed in 200 ml of the rhodium solution at the temperature under consideration for thirty minutes, and then removed. The solution was thoroughly stirred and the stress measurement made.

Where a paint solvent or other water insoluble substance was being studied, 1 g of the substance was introduced into 200 ml of rhodium solution, at the temperature under consideration, and stirred for thirty minutes. The solution was filtered and the stress measurement made.

## Results

Curve A of Fig. 3 shows the results obtained by varying the temperature of the standard rhodium solution. Curve B shows the stress against temperature when a

commonly used stopping-off paint, Detel CRP, had been in contact with the solution. It will be noted that the rate of contamination rises sharply with temperature. Electrographic tests revealed that the deposits produced at  $30^{\circ}\text{C}$  from both solutions were cracked, while all other deposits were crack free.

The organic constituents of a paint of this type can be divided into three groups,

- resins
- plasticisers
- solvents

The resin used in this paint is a chlorinated rubber, and a rhodium solution treated with this substance gave a value of stress of 111,000 lb/sq. in. showing no change compared with the pure rhodium solution.

The plasticisers used in commercial paints vary considerably, but tests carried out on two typical examples showed that rhodium solution saturated with dibutyl phthalate and

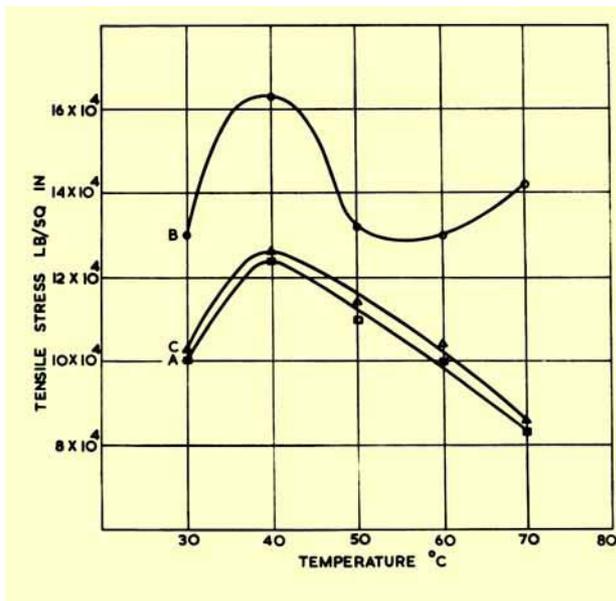


Fig. 3 Variation of stress with temperature. Curve A gives the values obtained with the rhodium sulphate electrolyte alone, Curve B with the use of the older Detel CRP masking paint, and Curve C with the new formulation, Detel RHP. The low values obtained at 30°C are the result of relief of stress by cracking of the deposits.

with Aroclor 1248 (a chlorinated diphenyl from Monsanto Chemicals Limited) gave values of 114,000 and 110,000 lb/sq. in. respectively, again very similar to those from the pure solution. For this reason no further tests were carried out on other plasticisers.

The solvents used are often commercial grades of solvent naphtha and stress measurements made on rhodium solutions treated with various samples of these solvents showed considerable variation. These were shown to agree closely with variations in the sulphur content of the solvent as seen in Table I.

A study of the various solvent samples by vapour phase chromatography showed that the sulphur compound present was essentially

thiophen. The results of adding this compound directly to the rhodium solution are shown in Table II.

As a result of these findings a paint was formulated in co-operation with Detel Products Limited using solvents of low sulphur content. The stress/temperature results for this paint, designated Detel RHP, are shown as curve C in Fig. 3. It will be seen that the increase of stress compared to the paint-free solution is virtually constant with changes of temperature.

## Discussion

The rhodium sulphate electrolyte will normally produce highly stressed deposits. It has been shown that small additions of

Sulphur g/l	Stress lb/sq. in.	Electrographic test
<0.0005	112,000	crack free
0.0009	114,000	crack free
0.0027	120,000	crack free
0.0175	134,000	crack free
0.3650	75,000	cracked

Thiophen molarity	Stress lb/sq. in.	Electrographic test
0.0001	113,000	crack free
0.0003	137,000	crack free
0.001	62,000	cracked

organic sulphur compounds will markedly increase this stress level.

It appears that previous determination of internal stress in rhodium deposits using a method relying on paints for stopping-off one side of the cathode must be suspect, and only an apparatus completely avoiding the use of paint can be used with confidence.

The contamination from Detel CRP paint has been shown to vary with temperature, becoming considerably greater at the higher temperatures tried. The Detel RHP paint, containing sulphur-free solvents, did not exhibit this effect.

The introduction of this new paint to the plating shop has improved operations on two counts; first, the stress cracking originating at the paint/plating interface is almost eliminated and secondly, the frequency of treatment of the solution with active carbon

in order to remove organic contaminants is much reduced. Whereas with standard paints the plating solution was being treated after every ten days' operation, the interval has now been increased to as long as eight to ten weeks.

The author is indebted to Mr H. A. Slade, of Detel Products Limited, for advice and assistance in the provision of paint samples.

### References

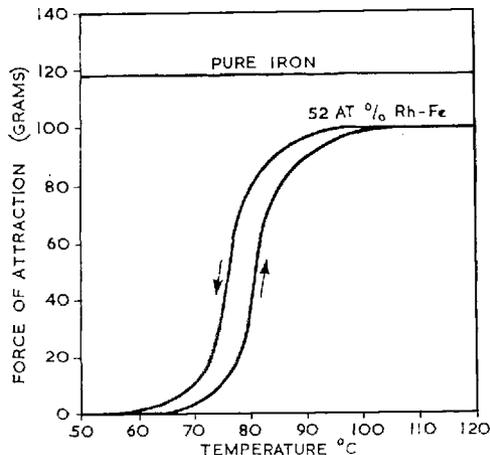
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## Magnetic Transformation in Iron-Rhodium Alloys

### SOME THERMAL SWITCHING POSSIBILITIES

The unusual magnetic properties of iron-rhodium alloys were demonstrated at the Johnson Matthey stand at the 1964 exhibition organised by the Institute of Physics and the Physical Society. Alloys containing approximately equal numbers of atoms of iron and rhodium are non-magnetic at room temperatures and become suddenly ferromagnetic when heated to about 70°C. The apparatus displayed comprised a small cylinder of 52 atomic per cent rhodium alloy suspended in a heating zone. On reaching the critical temperature, it was pulled downwards by a cobalt-platinum alloy magnet, which cooled the specimen until the antiferromagnetic state was attained; the test piece was then released upwards into the heating zone and the cycle repeated.

The curve illustrates the force exerted on an iron-rhodium armature, 0.64 cm in diameter and 2.5 cm long, hung vertically in a field tapering from 1000 to 200 oersteds along its length. The alloy had been previously ordered at 500°C for 20 hours. The force developed in the field became appreciable at 70°C and exceeded 90 g at 90°C. Over the same temperature range a geometrically



identical cylinder of pure iron was attracted uniformly with a force of 118 g. Although the non-uniform field has widened the transition temperature range, the results of this simple study provide a quantitative indication of the actuating forces which an elementary iron-rhodium thermal switch could exert and might possibly help to solve some thermal protection problems.

A. S. D.