The Corrosion Behaviour of Objects Electroplated with Platinum

IMPORTANT INFLUENCE OF INTERMEDIATE LAYERS

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If base metals are thinly coated with platinum from an aqueous electrolyte the deposit is likely to be porous, thus enhancing the susceptibility of the substrate metal to corrosion and the surface to discolouration in certain environments. This paper considers the processes involved and shows that the application of a suitable intermediate layer can effectively prevent this, so enabling the inherent properties of platinum to be utilised for a greater number of functional and decorative applications.

Thin layers of metallic platinum can be produced in a variety of ways: by electrolytic deposition from aqueous electrolytes or salt melts, by thermal evaporation or cathodic sputtering (the physical vapour deposition or PVD processes) or by firing printed pastes. Depending on the deposition process and the parameters involved, the properties of the coating can vary considerably. Those deposited from aqueous electrolytes at thicknesses of a few microns or less are highly stressed and porous, although bright, hard and wear resistant. Deposits from molten salts are generally more than $1\mu m$ thick; they are low stressed and have low porosity, being semi-bright in appearance, soft and highly ductile. Layers produced by the PVD processes are generally in the thickness range of $0.1\mu m$ or less, and therefore rather porous. Fired ceramic pastes often form thick layers with internal porosity. These processes may compete for technical applications, for example coatings produced from aqueous electrolytes or by the PVD processes are used for decorative and functional applications by the electronics industry, on razor blade edges and on spectacle frames. Deposits from salt melts are found in the electronic, chemical and glass industries; fired platinum-containing pastes form decorative and functional coatings in similar areas.

With the exception of coatings deposited from salt melts, platinum layers a few microns thick are generally quite porous, which makes them difficult to use for the protection of less noble substrate materials. Where porosity in the platinum coating exposes a base metal surface, and in the presence of an electrolyte, the electrochemical nobility of platinum makes these regions very susceptible to dissolution of the base metal, discolouration of the platinum surface by corrosion products and changes in the chemical or mechanical behaviour which may result in premature failure of the coated object.

During the course of a research programme undertaken at our institute on the properties of platinum and platinum alloy layers deposited from aqueous electrolytes we found that even a thin intermediate layer could have a profound influence on the corrosion behaviour of nickel or copper alloy substrates coated with thin porous platinum coatings.

Electrochemical Considerations

If two metals of different electrochemical potentials are in direct contact in an electrically conductive aqueous solution then "contact corrosion" may occur. In this case an intermediate potential forms with a value between those of the two individual metals. Thus the

more noble metal is cathodically and the less noble metal anodically polarised, with the result that the corrosion rate of the latter is increased while that of the nobler metal is decreased. Such combinations frequently occur, for example cracked or porous layers of platinum, rhodium, gold or silver may overlay brass, bronze, copper or nickel. In many instances also a bright sulphur-containing nickel deposit is applied as an intermediate coating beneath rhodium or gold layers (1).

As a first approximation, the "normal potential" of metals and alloys can be used to predict the corrosion behaviour of certain metal combinations (2). However caution is essential as many factors not taken into account when establishing these "normal potentials" have a significant effect on corrosion taking place under practical conditions; such factors include for example solution composition (3). Table I shows the potentials of selected metals in a sodium chloride-containing solution and in artificial perspiration, as measured on suitably prepared samples with a Knick millivoltmeter.

In order for contact corrosion to occur, a potential difference must exist between the two metals and they must be in electrical contact. It is also necessary to consider their interaction

Fig. 1 The principle of a contact corrosion localised couple is shown, as it occurs when a crack through the platinum plating brings electrolyte into contact with the platinum and the copper substrate

Table I

Potential of Various Metals as Observed in Sodium Chloride Solution and Artificial Perspiration

Metal	Potential [a]	
	Sodium chloride solution [b]	Artificial perspiration [c]
Platinum	400	420
Gold	240	250
Palladium	190	230
Miralloy [d]	140	150
Silver	140	220
Nickel 99.6	50	65
Bright nickel	40	45
Copper	10	15

(a) As measured against a silver/silver chloride electrode
(b) According to DIN 50905, pH 7.5, 20°C
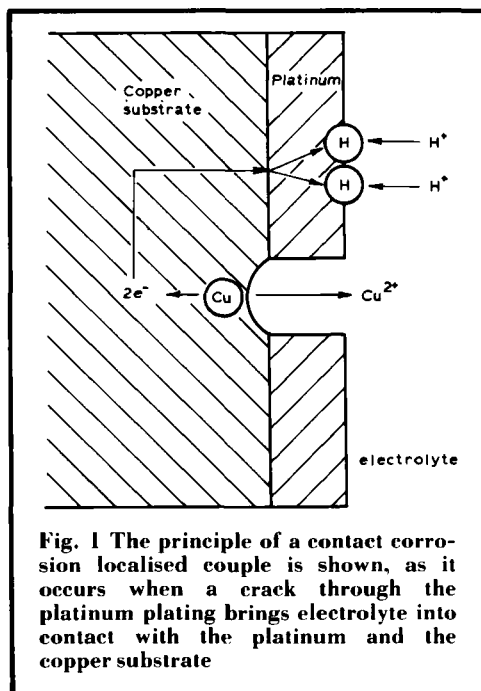(c) According to DIN 6424/1
(d) 50 copper–50 tin

with water and its constituents, that is with the H^+ ions, the OH^- hydroxyl ions and the dissolved oxygen. The principles of contact corrosion as it may occur at a crack in a platinum layer on a copper substrate are shown in Figure 1.

The dissolution of the anode is determined by Faraday's law, and from it the weight loss, ΔG, can be established:

$$\Delta G = \frac{Mt}{nF}.I$$

where G = weight loss (grams), t = time (seconds), F = Faraday constant (96,500 coulombs), M = atomic weight, n = valence of the ions formed, and I = galvanic current (amperes). The current I depends on the difference between the cathodic and anodic areas, and obeys Ohm's law, the electrical resistance being made up of the resistance between the corrosion partners (internal resistance) and that within the electrolyte (external resistance). Reaction schemes 1, 2, 5 and 6 apply. If the anode is insoluble Reactions 3 and 4 take place. The cathodic reactions may
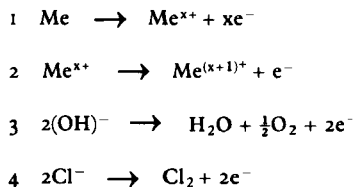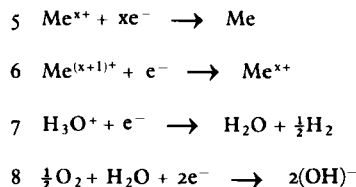
be just the anodic reactions reversed. If no metal ions are present—especially in acid solutions—protons or H^+ ions may be discharged, if hydrogen overvoltage permits.

In the considered copper/platinum system, copper is dissolved anodically below defects in the platinum layer. At the cathodic platinum coating, either H^+ ions are discharged as hydrogen or dissolved oxygen is reduced to OH^- ions, depending on the conditions in the electrolyte (Reactions 7 and 8 apply). The dissolved copper ions migrate over the platinum surface discolouring it around the defects.

Test Procedures

Using copper substrates the corrosion protection provided by platinum layers deposited from a commercial electrolyte onto the intermediate layers listed in Table II was studied. The test procedures used were immersion in artificial perspiration (ISO/DIS 6424/I), the salts spray test DIN 50021 and the sulphur dioxide-containing Kesternich test (DIN 50018). All tests were terminated after 48 hours. During the Kesternich test the samples were examined after 1, 2 and 5 cycles. The criterion considered was the visual appearance of a typical part of the surface after testing compared with that of an as-prepared sample; exceptional areas such as those showing edge corrosion were disregarded. The samples measured 2cm × 2.5cm and the thickness of the intermediate layers varied between 1 and 12 μm. The thickness of the platinum coating, which was deposited from a sulphuric acid-based commercial bath (Platinbad K, DEGUSSA AG), was determined by X-ray fluorescence.

Corrosion in Perspiration

A summary of the corrosion behaviour observed in artificial perspiration is shown in Figure 2. All copper samples plated directly

Fig. 2 The summary of corrosion data, obtained after 48 hours in artificial perspiration (ISO DIS 6424/I) shows the benefit of imposing a thin layer of gold, silver or copper-tin between the platinum coating and the copper substrate
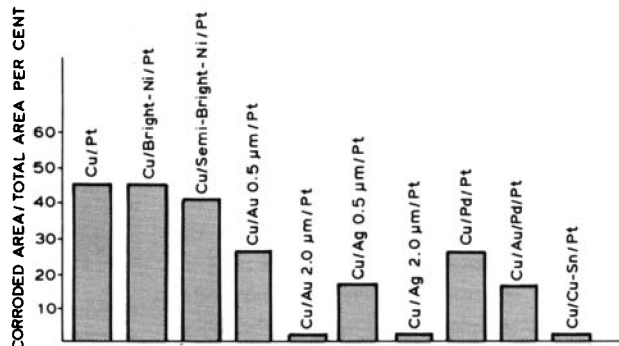
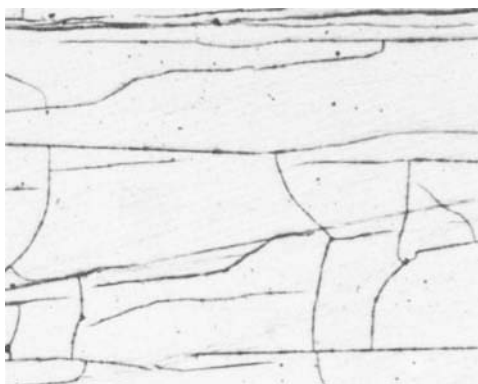| Table II		
Layer Combinations		
Substrate	Intermediate layer*	Outer plating
Copper	None	Platinum
Copper	Bright nickel	Platinum
Copper	Semi-bright nickel	Platinum
Copper	Silver	Platinum
Copper	Gold	Platinum
Copper	Palladium	Platinum
Copper	Palladium on gold	Platinum
Copper	50 copper–50 tin	Platinum
Copper	Gold on silver	Platinum

● In the electroplated form

Fig. 3 The platinum layer 1 micron thick produced from the specified sulphuric acid based commercial electrolyte on a copper substrate was severely cracked ×200

with platinum showed very poor corrosion resistance, with corrosion covering the whole area. Sometimes the coating became separated from the base. The thickness of the platinum layer had no significant influence on this behaviour, since the attack was identical for 0.5 and 1.0μm thick layers. Microscopic investigations showed that it was not possible to produce crack-free deposits at these thicknesses from this electrolyte, see Figure 3. Attempts were therefore made to identify suitable materials for intermediate layers which would prevent cracks and/or porosity penetrating from the platinum surface through to the copper substrate, thus avoiding contact corrosion.

Bright, or semi-bright intermediate nickel layers proved to have no positive effect. Bright nickel coatings between 5 and 10μm were studied. The attack resembled that observed on samples where platinum had been deposited directly onto copper, Figure 4. Bright nickel layers, especially very bright ones with high sulphur contents, are much less noble than semi-bright coatings with considerably less sulphur. The electrochemical potential of semi-bright nickel is closer to that of platinum than is the potential of very bright nickel. It was therefore interesting to see if the use of the former would reduce corrosion. However the corrosion resistance of samples with a 5 to 12μm thick intermediate layer was no better than that of samples with a very bright nickel layer, as can be seen in Figure 5.
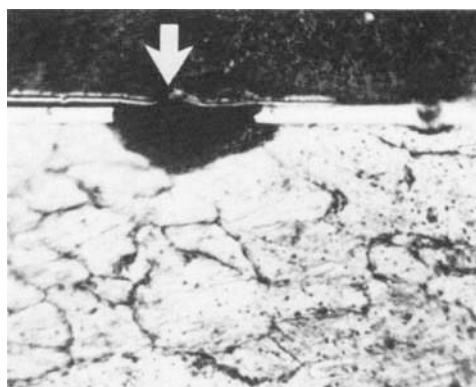

Fig. 4 A crack through the 0.2 micron platinum coating has resulted in localised corrosion of the bright nickel intermediate layer (2μm) and the copper substrate ×1000
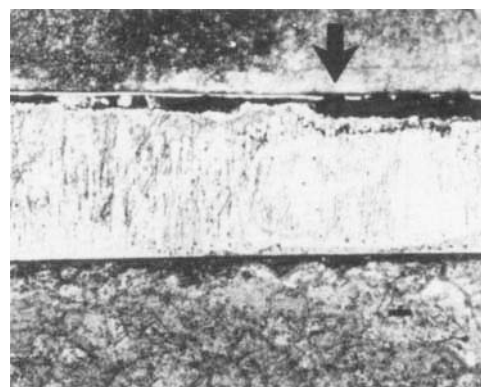

Fig. 5 Defects penetrate the 0.5 micron platinum coating enabling corrosion of the 12 micron thick semi-bright nickel intermediate layer to commence ×500

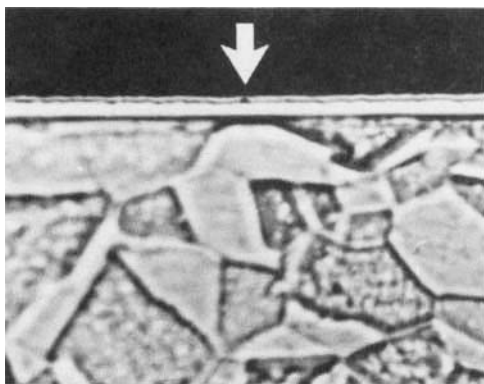Fig. 6 Despite an artificial crack in the platinum layer (arrowed) the presence of the gold intermediate layer (3μm) prevents the occurrence of contact corrosion ×1750

If the copper substrate is plated with silver before the platinum coating is applied a pronounced improvement in the corrosion resistance is observed. Depending on the quality of the substrate surface, for example freedom from defects and low roughness, a 0.5 to 1.0μm thickness of silver is sufficient to completely

prevent corrosion, in the conditions employed. There are two possible explanations for this: [i] If there is no connection between the copper substrate and the platinum, through cracks or pores in the silver, then there can only be contact between silver and platinum. However, the contact potential between these two metals is too small (about 200mV) to cause appreciable damage. [ii] Silver chloride formed during any initial corrosion may block cracks or pores thus preventing any further corrosion.

An intermediate layer of gold with electrochemical potential of 250mV in artificial perspiration gives superb corrosion protection if it is fairly free of pores; a section through such a coating is shown as Figure 6. The porosity of plated layers depends on features such as the quality of the substrate and the electrolyte used, and in the conditions employed here a practically pore free coating was obtained at thicknesses in the range 2 to 3μm. Indeed some samples were free of corrosion when the intermediate gold layer was only one 1μm thick.

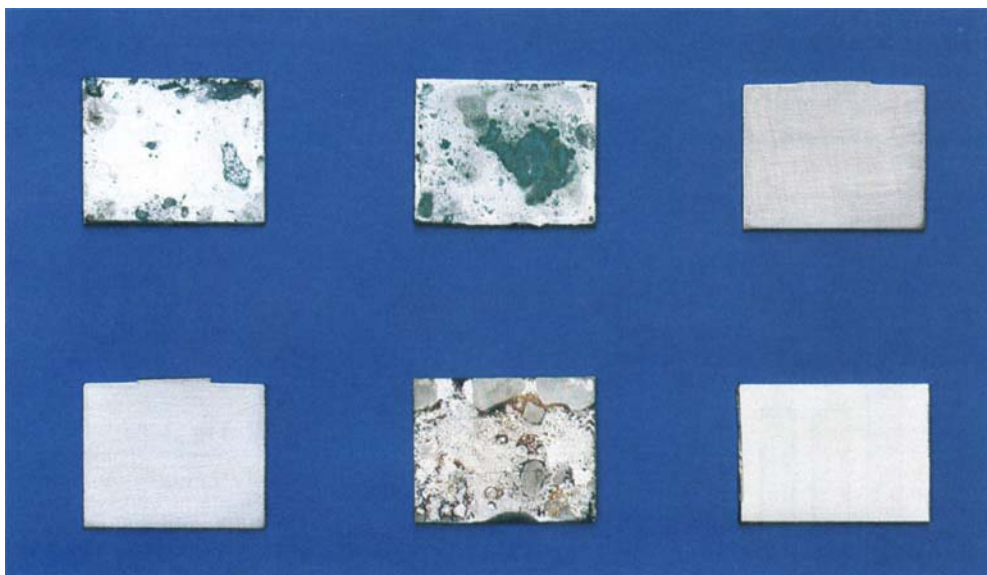Despite the fact that palladium has a slightly

Fig. 7 The corrosion behaviour of platinum plated copper substrates showing the marked effect of the composition of the intermediate layer. Top row, left to right: copper/platinum (0.5μm), copper/semi-bright nickel (12μm)/platinum (0.5μm), copper/silver (1μm)/platinum (0.5μm); bottom row, left to right: copper/gold (3μm)/platinum (0.5μm), copper/palladium (2μm)/platinum (0.5μm), copper/copper-tin (1μm)/platinum (0.5μm)
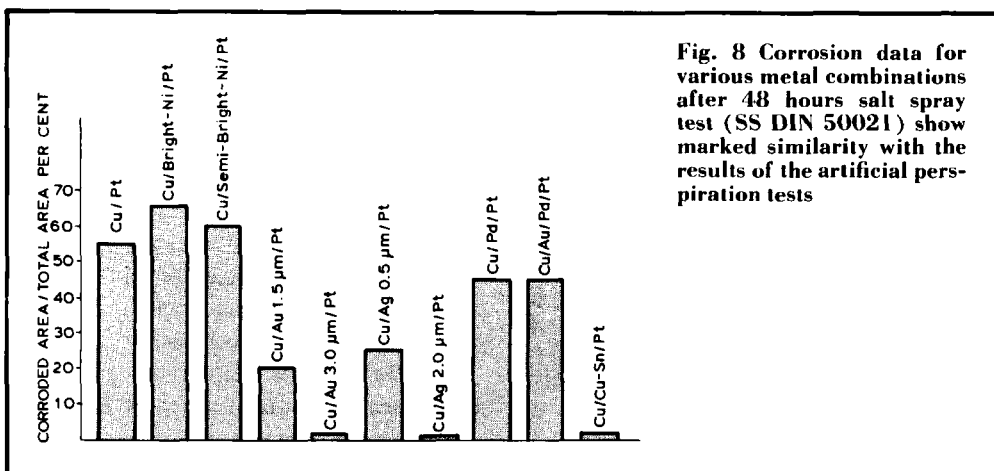
Fig. 8 Corrosion data for various metal combinations after 48 hours salt spray test (SS DIN 50021) show marked similarity with the results of the artificial perspiration tests

higher potential than silver a rather strong contact corrosion is observed when a palladium intermediate layer is tested. Apparently a 2μm thick palladium layer was too porous to prevent contact corrosion effectively. Furthermore the possibility has to be considered that a localised contact couple may have been formed between the palladium intermediate layer and the copper substrate. A gold strike 0.1μm thick between the copper and the palladium had little influence on the corrosion behaviour, as compared with a gold-free sandwich structure.

If a "white bronze" or "speculum" type of electroplated deposit, such as Miralloy is used for the intermediate layer, excellent corrosion resistance can be achieved, Figure 7. A layer about 1μm thick is sufficient to give a behaviour comparable with that of a gold or silver intermediate coating, even if the copper-tin deposit is less ductile. However, if cracks penetrate from the platinum outer surface through to the copper strong corrosive attack is observed.

Corrosion in Artificial Salt Spray

Even when exposure in artificial perspiration enabled us to make detailed statements on the behaviour of the various systems, the standardised salt-spray test (DIN 50021, 48
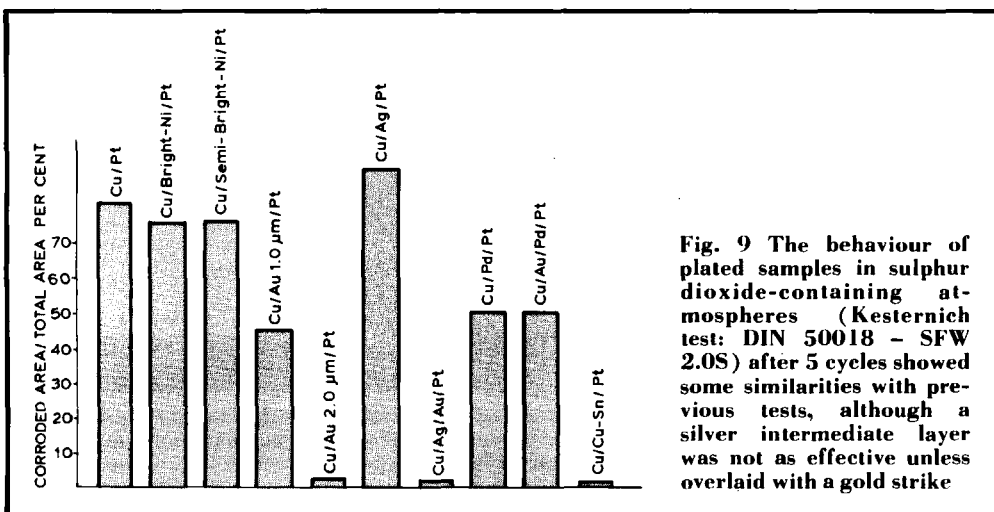

Fig. 9 The behaviour of plated samples in sulphur dioxide-containing atmospheres (Kesternich test: DIN 50018 – SFW 2.0S) after 5 cycles showed some similarities with previous tests, although a silver intermediate layer was not as effective unless overlaid with a gold strike
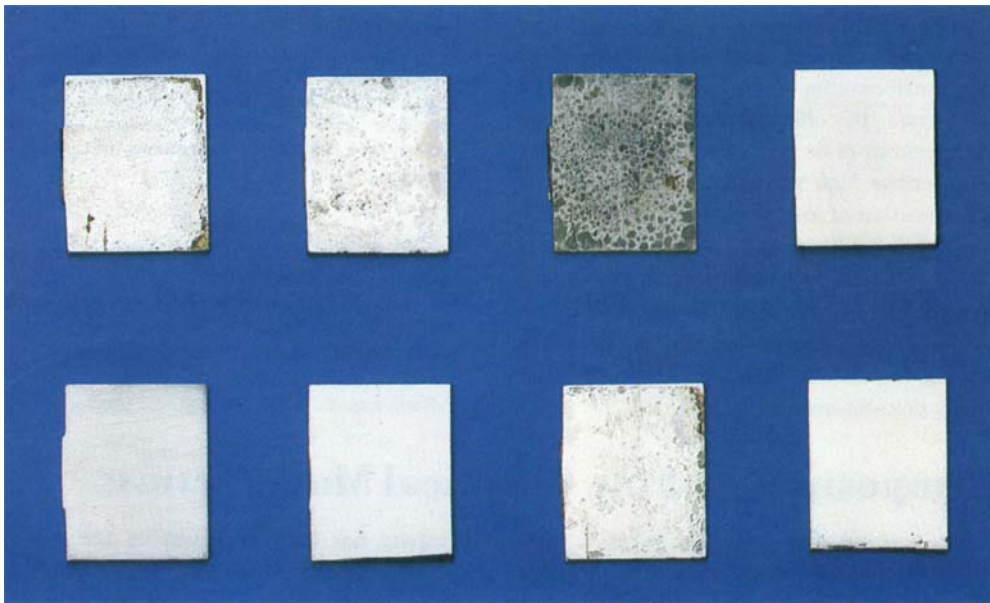
Fig. 10 The appearance of various platinum plated samples after five cycles of the Kesternich test, showing that the use of an appropriate intermediate layer, or layers enables a very satisfactory corrosion-resistant finish to be produced on a copper substrate

hours) was also applied. The results were quite similar, as can be seen by comparing Figures 2 and 8. No corrosion was observed for the combinations using gold, silver or copper-tin intermediate coatings. However, with nickel layers a much stronger attack sometimes occurred, as in artificial perspiration, possibly due to the loss of passivity of the nickel in solutions with a high chlorine concentration.

Sulphur Dioxide Test Results

In order to observe the behaviour of the plated objects during attack by gaseous corrosives we studied their reaction in the Kesternich test (DIN 50018). For combinations without intermediate coatings, or using nickel as an intermediate, the attack resembled that observed in the salt-spray test. A 2μm thick palladium intermediate layer showed no improvement either.

Of the precious metal intermediate layers used a 2μm or more thick gold coating proved very effective in obtaining good corrosion resistance, as can be seen in Figures 9 and 10. Silver layers were not as effective here as in the other tests, which can be explained by the attack of sulphur dioxide on silver and by the formation of fairly soluble silver corrosion products, compared with the rather insoluble silver chloride present in the other tests. However if the silver intermediate layer is given a gold strike below the final platinum deposit, and 0.2μm is an effective thickness, the composite is resistant to the sulphur dioxide atmosphere, see Figure 10. The "speculum" copper-tin alloy again proved to be very effective for corrosion protection in this test, and it appears that it might be a suitable alternative to precious metals for the intermediate layer.

Summary

The inherent properties of platinum make its use as thin electroplated layers interesting for a variety of applications. However as a result of its high chemical nobility there is a danger that localised couples may form between the substrate material and the platinum near any defects in the platinum coating, thus causing high corrosion at these spots. In standard corrosion tests made on samples plated from a

specified sulphuric acid based commercial electrolyte intermediate layers of nickel proved to be ineffective for corrosion protection, as did palladium. In chloride-containing solutions silver proved to be very effective, not only due to its rather high nobility but also because of the formation of insoluble silver chloride corrosion products. Very good corrosion resistance under the test conditions was shown by the layered combination: platinum (outer)/Miralloy copper-50 tin (intermediate)/copper substrate, making this a very satisfactory alternative to totally precious metal systems.

References

1 K. E. Becker, H. Schlegel and A. Kubat, *Metalloberfläche*, 1968, 22, (5), 145
2 G. Kortum, "Lehrbuch der Electrochemie", Verlag Chemie, Weinheim, 1958
3 J. Elze and G. Oelsner, *Metalloberfläche*, 1958, 12, (5), 132
4 E.Raub and W.Pfeiffer,*Gold Bull.*,1980,13,(3),112

Symposium on Fine Chemical Manufacture

Platinum metal catalysts have an increasingly important role to play in producing materials for the healthcare, plant protection and electronics markets. This is a conclusion drawn from the recent symposium entitled "Catalysis in Fine Chemical Manufacture" organised by the Royal Society of Chemistry from 10–12th July, at the University of Birmingham. Of the fourteen papers given, which covered a broad spectrum of catalytic subjects, eight contained references to platinum catalysed reactions, and three drew extensively on platinum metal catalysis to illustrate the importance of matching structure and function in catalysis. These are reviewed here.

Professor P. B. Wells of the University of Hull considered the objectives of catalyst design to be the preparation of catalytically active material in which the chemical and physical properties of the active sites are not degraded during use, and the minimisation of side reactions so that the catalysed reaction results in marketable products. These can be achieved through modification of the active site environment, by surface treatment to give carbonaceous or sulphur deposits, by occlusion of hydrogen during reaction, or by the deliberate choice of a metal-support combination which interacts beneficially under the reaction conditions. With the platinum and titania combination, reduction of the TiO_2 to Ti_2O_3 occurs locally, facilitating the passage of electrons from the metal to the support. With certain supported osmium clusters activity is dependent on the extent of electron transfer. Sintering is linked to metal-support interactions, and the anchoring of small platinum crystallites on silica by Pt-O-Si bonds helps to retard sintering.

Selectivity has been improved by the use of multifunctional systems, for example bifunctional platinum reforming catalysts and polyfunctional zeolite-based catalysts.

In his lecture "Composition and Structure of Catalysts for Vapour Phase Reactions", Professor G. C. Bond of Brunel University described fixed and fluidised bed catalysts. Fixed bed reactors utilise large particles such as pellets, while fluidised bed reactors employ small particles of uniform size. Otherwise the catalysts are very similar, being composed of an active phase (a platinum metal), a support (such as alumina or silica), and a promoter which may alter the texture, electronic structure or poison resistance of the combination – as with the addition of rhenium to a platinum reforming catalyst. In phenol hydrogenations the catalyst is bifunctional, the platinum metal reducing the aromatic ring and the support acid function rearranging the intermediate to give a cyclic ketone. Metal location is important as it affects the mass transport within the pores. This factor is to a large extent determined by the method of preparation; fast absorption from solution gives uniform deposition within the pores while slow absorption allows metal to deposit at pore mouths.

Metal dispersion and location and the effect of these parameters on the activity-selectivity of reactions was the main theme of Mr I. L. Dodgson's lecture. He described the types of palladium on charcoal catalysts manufactured by Johnson Matthey Chemicals for liquid phase reactions, discussed how their physical structure controls their behaviour in selected industrial reactions and recommended appropriate catalysts. A.J.B.