# Contacts/1984

## REPORT ON GOLD-RELATED PAPERS READ AT TWO RECENT CONFERENCES

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*Research on gold for electronic contacts was a central theme of papers presented in September 1984 at the 12th International Conference on Electrical Contact Phenomena held concurrently with the 30th Holm Conference on Electric Contacts in Chicago. New findings in sliding wear and the migration of corrosion films across gold surfaces show how to optimize the properties of gold finishes by controlling the plating process, upgrading contact design, and improving methods for environmental testing in the laboratory.*

Gold is the premier contact material for low voltage, low current electrical contact applications. Its nobility ensures that corrosion films which can degrade contact resistance do not form — low and stable resistance values being the primary requirement of a contact material. Since gold normally is used as a thin coating on a conductive substrate, its resistance to wear-through in sliding is a prime characteristic for application in electronic connectors, instrument slip rings, light duty switches and other devices.

Much research has been devoted to understanding the mechanisms of wear (1) and to improving the durability of gold coatings by modification of the plating process, optimization of substrate and topographic features, and by the use of contact lubricants. Nevertheless, studies of wear continue to be pursued diligently, this topic being the focus of several papers on gold that were presented at the recent 12th International Conference on Electrical Contact Phenomena held concurrently with the 30th Holm Conference on Electrical Contacts (2).

### Wear of Hard Gold Electrodeposits

In 'Wear Properties of High Speed Gold Electrodeposits', K.J. Whitlaw of Lea Ronal, Buxton, and J.W. Souter, I.S. Wright and M. Nottingham of the Plessey Company, Northampton, England, found that the wear resistance of a gold deposit depends critically on the operating conditions and composition of the solution from which it is plated. The performances of deposits obtained from cobalt, nickel, or iron-hardened acid formulations of potassium gold cyanide baths that are coming into commercial use in selective plating processes, which are operated at high current density and with vigorous agitation, have sometimes been found to be unacceptable. Sliding may occur with high friction, metal transfer, and the formation of loose debris. The authors conducted a comprehensive analysis of the wear of deposits from three acid gold cyanide solutions, two of which contained cobalt with different chelating agents, and one that was doped with nickel. Plating was carried out at current densities from 10 to 60 A/dm$^2$, at fixed temperature and pH, and the alloying element content of the plating solution was varied between wide limits. A typical phosphor bronze connector contact and a mating polished brass plaque were coated; substrate effects were minimized by depositing the gold to 5 µm thickness.

Plated layers were analyzed for hardening element content and potassium in the near-surface region with an electron microprobe. Potassium is believed to be present in codeposited compounds which also contain a portion of the hardener element and complexed carbon, nitrogen, and oxygen. Sliding was effected at a contact normal load of 150 g for 500 cycles repeatedly in the same track. The extent of surface damage of the plaque was determined qualitatively by visual inspection. 'Good' wear was synonymous with coefficients of friction of 0.26 or less, and 'bad' wear with larger values. Both bright and dull deposits were obtained. 'Good' wear was associated more with bright than dull deposits; however, not all of the bright deposits were wear-resistant.

Data from experiments with the two cobalt-doped gold solutions are given in Figures 1 and 2 (weakly chelated 'HV' process) and Figures 3 and 4 (strongly chelated 'MRC' process). The lines on the surfaces within which the crosses lie delineate the good wear regions, and numerical values of coefficient of friction are given in Figures 2 and 4. It is clear that only within certain levels of bath hardener and current density will satisfactory results be obtained with deposits from a given process. Also, the HV and MRC solutions can produce finishes at the same current density having different properties. The range of conditions for satisfactory deposits from the MRC process is larger than that for the HV process; furthermore, the much higher cobalt content of the MRC solution may facilitate bath maintenance, since replenishment with hardener need not be as precise. Another finding is that although the presence of some cobalt in solution is necessary to obtain good deposits, excessive cobalt gives unacceptable results, especially from the HV bath. In addition, there is no simple relationship between the cobalt and potassium contents of a deposit, for corresponding surfaces in the 3-dimensional graphs obtained from the two solutions (Figures 1 and 3; Figures 2 and 4) are quite different. Results from the strongly chelated nickel bath (not shown) were similar to those from the MRC solution.

The mechanisms by which the codeposited elements control wear are unknown. Deposit physical properties and structure as well as deposit composition are presumed to depend on the process. Nevertheless, these data can be used for plating process control, since they define the operating window of solution cobalt and current density which yields deposits having satisfactory sliding characteristics.

The sliding performance of plated connector contacts was

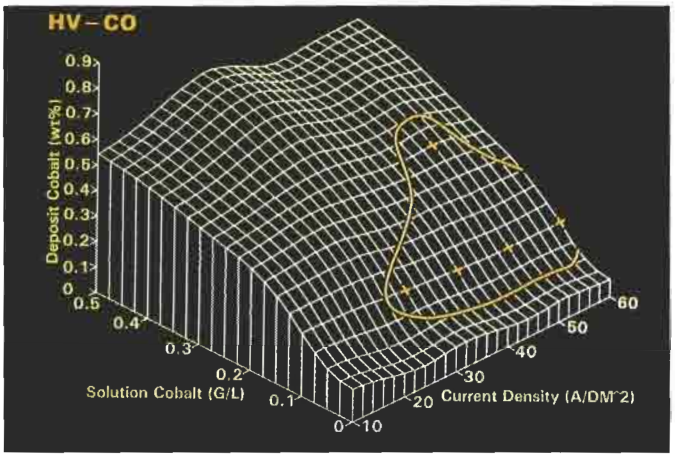

Fig. 1 Relationship between cobalt content of a gold deposit and concentration of the solution from which it was plated over a wide range of current densities. Cobalt from weakly chelated complex. The crosses on the surface signify the experimental runs which gave good wear

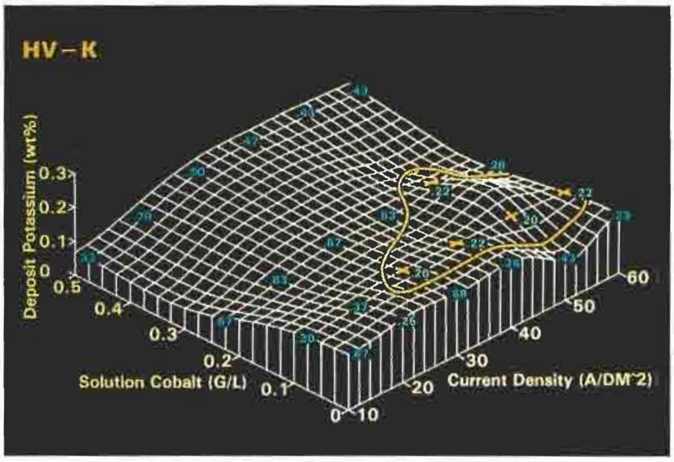

Fig. 2 Relationship between potassium content of the gold deposit in Fig. 1 to cobalt concentration in the solution and to plating current density. The numbers are the coefficients of sliding friction from the experimental runs

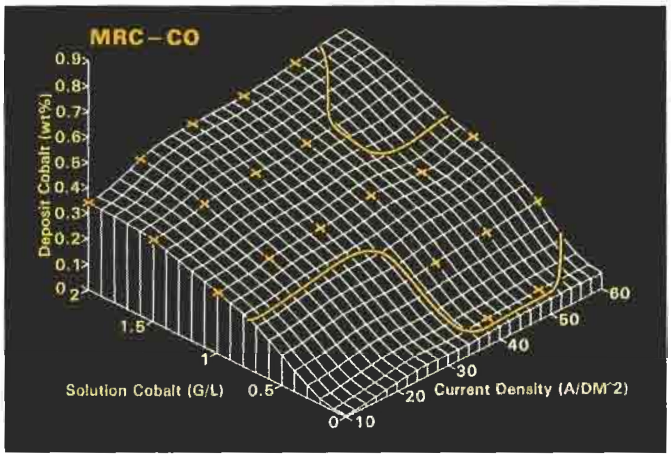

Fig. 3 Relationship of deposit cobalt content to plating parameters for a solution in which the hardener is strongly chelated

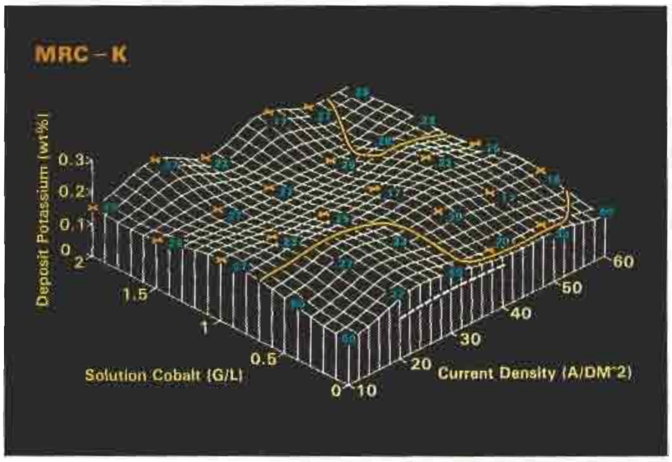

Fig. 4 Dependence of potassium content of the deposit in Fig. 3 on plating solution parameters

described by L-G. Liljestrand, L. Sjögren, L. Révay, and B. Asthner of L.M. Ericsson, Stockholm, Sweden in 'Wear Resistance of Electroplated Nickel-Hardened Gold'. Contact pins were selectively coated with nickel plate and $2\ \mu m$ of nickel-doped gold from three different acidic solutions of potassium gold cyanide, with the levels of dissolved nickel varied from 0.2 to 2.3 g/l. Current densities from 1 to 16 A/dm$^2$ were used. Insertions were simulated with a wear tester in which the mating spring contact was loaded normally at 100 g against the pin contact, much like a hemisphere on a flat, and the pin was moved back and forth 200 times for a short distance. Similar wear results were obtained with connector springs clad either with pure gold or with 69 gold/25 silver/6 copper per cent alloy. This is because wear was determined primarily by the pin material, a result that agrees with the findings of earlier studies (3) in which metal from the member having the larger surface (the plated pin in the present case) was found to transfer and adhere to the smaller surface which results in both contacts having similar interface composition.

Wear damage to the pin could be categorized into four classes: (a) 'mild' which gives a burnished surface; (b) 'severe', or irregular gouging, due to the formation of large adhesive junctions and gross metal transfer; (c) 'brittle' in which cracks appear in the plating at right angle to the direction of sliding; and (d) 'adhesive brittle' where deep scratches in the plating and large loose particles form following gross transfer of pin material to the spring. This last wear process, while relatively uncommon, had earlier been described (3) for a silver-hardened gold deposit from an alkaline cyanide bath.

Figure 5 describes the dependence of the wear process on the nickel content of the three solutions and the current densities used. Figure 6 shows the relationship of coefficient of friction to deposit hardness for deposits obtained at 1 to 4 A/dm$^2$, and delineates the various wear processes. Supplementary determinations of potassium level in the deposits from process C showed this to be relatively independent of current density. X-ray diffraction line broadening tends to increase with increasing nickel content, especially at higher current densities. There were minor differences in surface elemental composition in the sliding track by Auger electron spectroscopy according to the wear process. It is evident that physical properties, deposit structure, and wear behaviour depend in a complex way on bath composition and current density, among other factors. Nevertheless, by careful process control, deposits can be obtained that perform consistently well in practical applications.

## Gold Electrodeposit Thin Film Lubricant

There has been considerable interest in replacing gold on separable connector contacts used in high reliability applications in order to reduce manufacturing expense. Most of the attention has been on palladium which is somewhat less costly than gold on a volume basis. Since more than 90 per cent of electronic contacts in commercial use utilize gold as an electrodeposit, most of these efforts at gold replacement have been directed towards electrodeposited palladium. Alloy electrodeposits of palladium with nickel or silver have recently been developed.

There are, however, limitations in palladium-based materials compared to gold. They include palladium's tendency to degrade by one or more of the following processes: tarnishing in environments that contain certain reactive chlorine compounds, the formation of frictional polymers on the surface of mated contacts which originate in adsorbed organic air pollutants, the generation

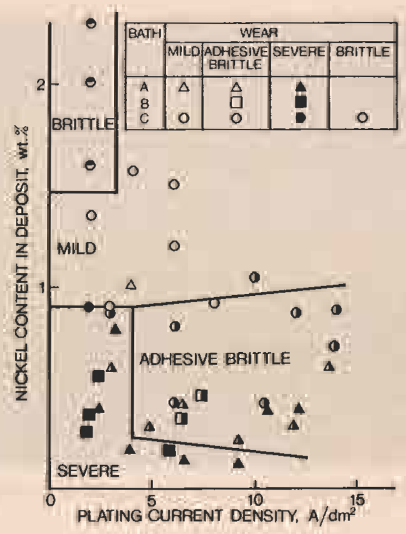

**Fig. 5** Classes of wear for gold deposits from three different solutions as a function of nickel content of the deposit and plating current density

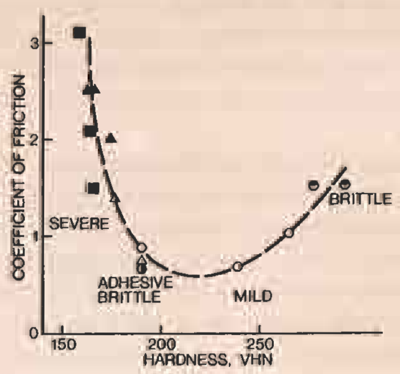

**Fig. 6** Dependence of coefficient of friction on hardness for deposits from various nickel-doped baths described in Fig. 5, plated at 1 to 4 A/dm$^2$

**Table I**
**Sliding Properties of Electrodeposits**

| | Probe | | Flat | | Coefficient of friction | |
|---|---|---|---|---|---|---|
| Test No. | Deposit (μm) | Overplate (μm) | Deposit (μm) | Overplate (μm) | Start | Finish |
| 1 | Au(0.75) | | Au(0.75) | | 0.38 | 0.38 |
| 2 | PdAg(1.9) | | PdAg(1.9) | | 0.53 | 1.3 |
| 3 | PdAg(1.9) | | Au(0.75) | | 0.19 | 0.19 |
| 4 | PdAg(1.9) | Au(0.13) | Au(0.75) | | 0.29 | 0.30 |
| 5 | PdAg(0.9) | Au(0.13) | PdAg(0.9) | Au(0.13) | 0.30 | 0.38 |

of insulating films on palladium-nickel from aging at elevated temperature, and severe wear in sliding applications. Some palladium electroplating processes also tend to give microcracked, porous finishes which can allow accelerated corrosion of a less noble underplate or substrate particularly when the environment is chemically aggressive.

It has been shown that palladium and palladium alloy electrodeposits cannot be mated successfully to themselves in most cases without significant degradation of connector reliability due to wear, by comparison with similar systems of transition metal-hardened gold electroplates. A significant finding, however, was that these alternate materials can be satisfactory provided (a) the opposing contact in a mated pair (preferably the larger surface involved in the connection) is plated with gold, or (b) the palladium contacts themselves are coated with a thin layer of gold, of the order of 0.05-0.2 μm. In some cases, it is also desirable to apply a thin gold preplate, or strike, prior to electrodepositing the palladium. The economics of using multilayer deposits of palladium and gold have been sufficiently attractive to result in their acceptance in some applications.

Three papers at the Conference addressed palladium-gold systems: (a) gold and electrodeposited pure palladium by D. Rühlicke, M. Hageni and H. Kästner of VEB Bergbau und Huttenkombinat (BHK) 'Albert Funk', Freiberg, German Democratic Republic, in 'Electroplated Palladium-Based Sandwich Materials for Electronic Connectors', (b) gold and palladium-nickel deposits by A.H. Graham of E.I. duPont deNemours and Company, Incorporated, Wilmington, Delaware, U.S.A. in 'Wear Resistance Characterization for Plated Connectors', and (c) gold and palladium-silver by F.I. Nobel, Lea Ronal, Incorporated, Freeport, New York, U.S.A. in 'Electroplated Palladium-Silver (60/40 weight per cent) Alloy as a Contact Material'.

The paper by Nobel describes the properties of 60 palladium/40 silver per cent deposits from a new process. Wear testing was conducted with electrodeposits on hemispherically-ended probes and flat coupons that were slid for 500 cycles at 200 g loading to simulate a typical connector. Tests included palladium-silver on itself, palladium-silver against gold, both members with gold coated palladium-silver, and gold plated palladium-silver versus gold. The substrates were copper coupons and brass probes. All finishes had a 2.5 μm thick nickel underplate, as is usual in commercial connectors.

Table I lists coefficients of friction at the beginning and end of the runs. Friction and wear correlated well, the extent of surface damage increasing with rising friction. From these results, it is clear that the 60 palladium/40 silver per cent alloy cannot be slid on itself without unacceptably high friction and wear (Table I, Test 2). All other combinations of finishes involving gold and palladium-silver were much better; indeed, palladium-silver versus gold (Table I, Test 3) showed a lower coefficient of friction at both start and finish of the test than the all-gold pair (Table I, Test 1).

Supplementary determinations were made of the variability of contact resistance in a fretting test using printed circuit boards and card edge connectors with contacts having various finishes. Gold coated palladium-silver mated to itself was found to be good and equivalent to gold versus gold, the gold flash on palladium-silver remaining intact during the test. Gold coated palladium-nickel had unstable contact resistance, and palladium showed significant frictional polymer formation by the end of the run.

The paper given by Graham concerned the wear of palladium-nickel plating in a commercial connector with a contact pin that is inserted into a box receptacle. Both copper alloy contacts in the couple had the same deposits. Three finishes were examined: 0.8 μm of cobalt-hardened gold, 0.8 μm of a palladium-nickel alloy, and 0.8 μm of palladium-nickel with a gold flash. The composition of the palladium-nickel alloy was not given. A 1.3 μm thick nickel underplate was used in all cases. Up to 25 000 insertions were obtained using an automatic tester at a normal load of 300 g.

Electrical performance was monitored after wear testing by exposing the contacts to moist air containing hydrogen sulphide. If any substrate copper alloy had been exposed locally as a result of insertion, insulating films would have formed, spread on the noble metal surface, and tended to degrade contact resistance. Figure 7 shows the results of the test. Contact resistance instability, signifying

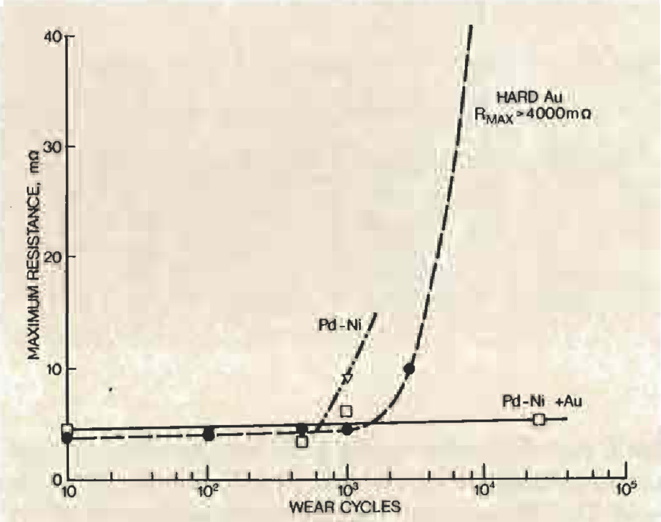

Fig. 7 (top) Maximum values of contact resistance after exposure to a corrosive atmosphere for worn contacts plated with cobalt-hardened gold, palladium-nickel and palladium-nickel with a gold flash

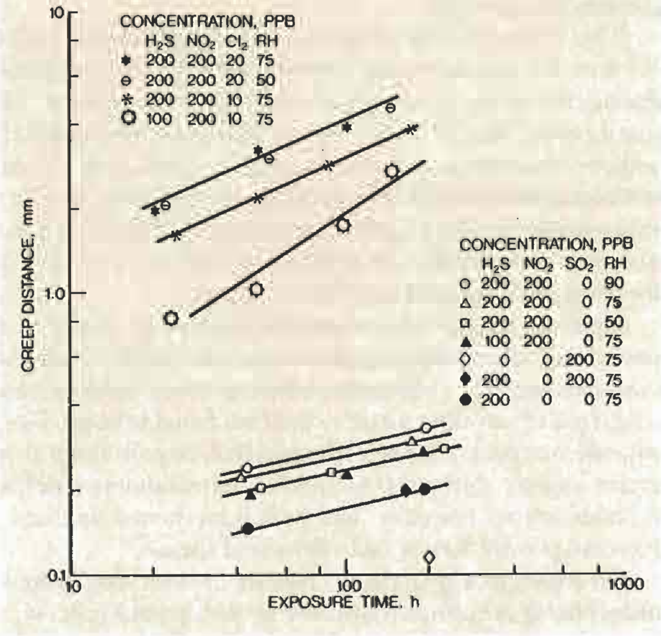

Fig. 8 (bottom) Distances of creep of tarnish films over cobalt-doped gold electroplates for various exposure times. Laboratory chamber test atmospheres contained various air pollutants at controlled relative humidity

the end of useful life, occurred first for the all-palladium-nickel pair, then for hard gold plate mated to itself, and finally for palladium-nickel with the gold overplate. Detailed microscopic and other physical studies of worn surfaces confirmed the high durability of gold flashed palladium-nickel, the gold being little damaged at the end of test. The author concluded that gold flashed palladium-nickel was the most wear resistant finish at the conditions of his test.

The paper by Rühlicke, *et al.*, described palladium plating methods for connector contacts used in the German Democratic Republic. Processes that involve the selective plating of prestamped strip contacts and continuous reel-to-reel plating are employed. Palladium that is 2 to 3 μm thick with 0.2 μm gold flash is the combination that is used. An interesting practice is the application of 0.1 μm gold strike between the nickel underplate and palladium layers in strip plating. This strike promotes adhesion of the palladium, provides corrosion protection to the substrate during palladium plating, and is a soldering aid. In addition, it is believed that the gold strike improves the corrosion resistance of the finish in corrosion testing above 65 per cent relative humidity in hydrogen sulphide- and sulphur dioxide-containing environments when there is some intrinsic porosity in the gold and palladium layers.

The finding that a very thin gold coating on palladium and palladium alloy deposits improves sliding behaviour is consistent with traditional wear theory. This view teaches that composite systems involving a surface layer that shears easily and which is supported by a hard backing will have low sliding friction and be durable. It is obvious, therefore, that pure soft gold would be successful. However, transition metal-hardened gold coatings also work well, for the adhesive junctions which their asperities make under load with an opposing surface have low shear strength due to their brittleness.

The excellent performance of the gold flashed palladium metal system used by Graham may be attributed to the high hardness of the palladium alloy plating, 580 kg/mm$^2$, in contrast to pure palladium and the 60 palladium/40 silver per cent alloy, the hardnesses of which were in the range, 250-300 kg/mm$^2$. The palladium and palladium alloy deposits when slid in the absence of gold fail by severe adhesive wear due to their marked tendency to cold weld. Finally, the success of the systems exhibiting good wear that involve palladium and palladium alloys without a gold overcoat, which are mated to contacts plated with hard gold, is attributable to transfer to the palladium surface of an adherent thin layer of gold in the early stages of sliding. Both members then become identical, hard gold versus hard gold, with resulting low wear and friction.

## Creep of Corrosion Films Across Gold Surfaces

One of the processes by which gold contacts can become contaminated in polluted atmospheres is creep of corrosion films from adjacent base metal surfaces or from intrinsic pores in the finish. For example, copper sulphide, $Cu_2S$, has been found to migrate several millimetres over gold in only a few months in some severely polluted industrial atmospheres. Such films are insulating and can significantly increase contact resistance. The development of selective plating procedures and the growing acceptance of clad inlays, in which the gold is confined only to the actual mating region of a contact structure, has increased the incidence of creep corrosion in separable connectors and other devices with exposed contacts. It has been suggested that in between 15 to 20 per cent of field environments, creep may be the dominant contact failure process.

W.H. Abbott of Battelle Laboratories, Columbus, Ohio, in 'The Effect of Test Environment on the Creep of Surface Films Over Gold', explored materials factors involved in creep, and described methods by which it can be realistically simulated in the laboratory. Older test methods involve exposure to high concentrations of reduced sulphur compounds, such as hydrogen sulphide or flowers of sulphur. However, such procedures give creep kinetics that are too low to be of practical use for laboratory test acceleration and which, incidentally, do not reproduce the composition of corrosion and tarnish films that occut in real environments on other metals, such as silver and palladium. A significant finding is that synergistic effects occur among pollutants. As little as 10 parts per billion of chlorine will accelerate the creep rate of films on gold by an order of magnitude. The composition of the film is still predominantly $Cu_2S$. The mechanism by which chlorine affects creep is unknown; chloride corrosion products themselves do not spread. Other major air pollutants, sulphur dioxide and nitrogen dioxide, have little effect on this process. Variation in relative humidity between 50 and 90 per cent also does not markedly change creep rate.

Figure 8 summarizes the results of tests with a variety of laboratory atmospheres. The specimens were polished coupons of a copper-nickel-tin alloy, CA 725, that is widely used in connectors and which had been selectively plated with a cobalt-hardened gold. Creep values are the distances of farthest advance over gold of the sulphide films as assessed by visual observations. The author believes that realistic creep determinations can be made with low concentration mixtures of hydrogen sulphide and chlorine.

Additional experiments showed the creep of $Cu_2S$ over wrought pure gold to be several times faster than over cobalt-hardened gold. This suggests that very thin films which form spontaneously on the electroplate, e.g. by thermal diffusion to the surface of the hardener element which then oxidizes, has an inhibiting effect on $Cu_2S$ creep. Such oxide films are too thin to affect contact resistance. The postulate of contamination inhibition is consistent with the finding that creep over metals that are more reactive than pure gold, such as palladium and tin plate, occurs at still smaller rates. Also, sulphide creep from brass (30 per cent zinc) is less than that from CA 725, because brass has a lesser tendency to form $Cu_2S$.

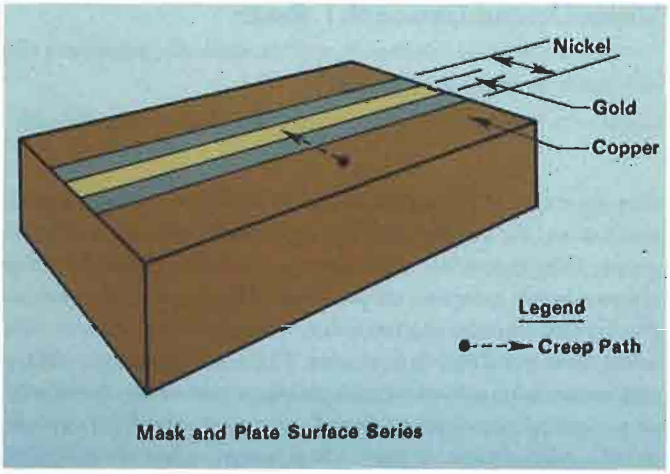

Fig. 9 Configuration of copper alloy coupon selectively plated with nickel and gold. Creep of tarnish film from copper alloy during exposure to a mixed gas atmosphere containing $H_2S$, $NO_2$, and $Cl_2$ occurs as shown. When the width of the nickel stripes is 125 μm or greater, creep does not extend to the gold surface

Finally, experiments were conducted to determine the effects on creep of an intermediate nickel layer between CA 725 and gold plate. Nickel corrosion films spread very little, and it seemed possible that nickel could serve as a barrier. Exposure to an $H_2S$-$NO_2$-$Cl_2$ environment of edge-cut gold plated samples with and without nickel underplate showed little difference in $Cu_2S$ creep rate with a range of nickel layers having thicknesses up to 5 μm, which is as much as is used in commercial practice. This work was extended using larger nickel barriers with samples of the configuration shown in Figure 9, and which were fabricated by mask-plating methods. Provided the width of the nickel stripe was 125 μm or greater, creep on gold was effectively stopped. It is not difficult to use nickel barriers in many connector structures. Contact springs are produced commercially in which nickel is plated over the entire part, and which is then selectively coated with gold on the engineering surface.

### Acknowledgement

J.W. Souter provided Figures 1-4 which are based on data given in his Conference paper, and W.H. Abbott contributed Figure 9.

### References

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