Organic Deposits on Noble Metal Contacts

AN INVESTIGATION INTO CONTACT CONTAMINATION IN TELEPHONE RELAYS

The complex effects of arcing between the surfaces of electrical contacts are now well appreciated. The local heating is intense enough to melt even the most refractory of metals and to produce pitting and general erosion; in addition it may break down traces of organic molecules in the surrounding atmosphere and give rise to numerous other side effects. In particular, the mechanism by which certain noble metal contact surfaces may be "activated" by carbon deposits derived from organic vapours has been the subject of considerable study.

More recently, a group of investigators working in the Bell Telephone Laboratories have observed that, most unexpectedly, a dark brown amorphous insulating film consistently forms on the surface of palladium contacts in telephone relays when the relays are opened and closed *without interrupting an electrical circuit*. In other words, this film forms in the absence of any arc or spark as a consequence only of the rubbing and rolling actions involved in repeatedly bringing the contact faces together and then separating them. The effect seems allied to that of "fretting corrosion".

In their introduction to a description of a comprehensive programme of work carried out over the last ten years on this phenomenon H. W. Hermance and T. F. Egan write (*Bell System Technical J.*, 1958, 37, (3), May, pp. 739–776) "This mysterious brown deposit appeared on palladium but not on silver contacts. Its occurrence was completely independent of such environmental factors as air-borne dusts and corrosive gases. Its formation required mechanical but not electrical operation of the contacts. It accumulated in the area immediately surrounding the region of contact slide. Arcing electrical discharges appeared to destroy such deposits, completely or in part."

It was found early in the investigation that the deposits never contained more than traces of palladium and were organic in character. Microexamination of the deposits was considerably assisted by a technique which was developed in 1947 involving the transference of the deposit from the contact surfaces to a plastic replica. The contact is warmed and pressed into a clear thermoplastic sheet material such as Vinylite; when cool the resulting imprint faithfully reproduces all surface details of the contact, and foreign deposits are transferred in their original configuration to the transparent medium for micro-chemical study. The evidence of all this work pointed strongly to vapours emanating from the relay structure as the source of the frictional product, and although at first this conclusion was not in the authors' words "easily acceptable", subsequent experimental studies have fully confirmed it.

It was found, for instance, that new relays with carefully cleaned palladium contacts developed a brown deposit after a few hundred thousand operations when enclosed in sealed glass chambers with the contacts unwired. When, however, a special relay was constructed in which all organic components were replaced by glass in sheet or fibrous form, and the relay was then solvent extracted and outgassed by repeated baking and evacuation, no deposits at all appeared on the contacts when operated in the sealed container.

As a final check, pieces of a phenol fibre similar to those used in a normal relay were introduced into the chamber and a deposit again appeared when the relay was operated.

One further general observation needs to be noted. It is known that closure of a relay contact involves both impact and slide. It is believed that impact plays no part in producing the deposit and it was easily shown that sliding motion alone produces the deposit at the rates observed. The springs of a relay can be adjusted so that the contacts slide over each other but never open, and in these conditions the usual brown deposit is produced.

In order to investigate in as much detail as possible the conditions which are responsible for the production of brown films, special equipment was built in which contact metals could be caused to slide over one another under carefully controlled conditions. With this equipment one new interesting feature of the phenomenon was at once disclosed. When a palladium slider was oscillated in contact with a palladium plate in air, a considerable degree of frictional wear was observed. A deep pit was worn on the plate and a voluminous pile of finely divided palladium built up at the sides. When the experiment was repeated in air saturated with benzene vapour, however, wear virtually ceased after operating for about a minute, and afterwards the organic friction product apparently provided most effective lubrication. As sliding was continued, a brown powdery pile of translucent flakes of organic material accumulated around the slide area. Calculations are given which suggest that, as the slider was oscillated over the plate, about one monolayer of benzene was converted to the solid material which constituted the organic deposit at each traverse of the slide.

Considerable efforts were made, as might be expected, to identify the nature of the solid organic material which was formed when palladium contacts were operated in benzene vapour. No solubility was found in any solvent except such strongly organic solutions as ethanolamine and pyridine and even with these solution was never complete. Chromatographic and infra-red measurements have given little conclusive evidence of the constitution of the deposits, but there is some evidence that aromatic rings are present, alkene and carbonyl groups being linked together to form long-chain molecules. Electron diffraction studies indicate an amorphous material of high molecular weight.

The authors conclude that the organic deposit is a complex mixture of high molecular weight cross-linked materials. There are indications that oxygen enters into combination with the benzene vapour, and they suggest that cross-linkage may be through oxygen containing groups such as aldehyde or carboxyl. The products resemble mixed polymers in their properties and the authors propose that they should be called "frictional polymers".

Since palladium has for many years been the first choice as a contact material for telephone relays in the American Telephone & Telegraph Company's system, attention has been directed particularly to polymer formation on this metal. It was found, however, that similar films form equally readily on platinum, and that ruthenium, molybdenum, tantalum, chromium and many common platinum contact alloys become coated with appreciable quantities of deposit. On the other hand, nickel, copper, iron, tungsten, vanadium and zinc resemble silver in remaining quite free from visible organic films under the conditions of test. It is particularly interesting that even when silver is used against palladium the deposit is negligible, probably because of frictional transfer of silver to the palladium surface at the outset of the experiment. An important observation is that gold contacts produce only a very small quantity of polymer, the nature of which appears identical with that of the deposit formed on palladium.

Considerable effort was naturally expended in endeavouring to find some means of preventing the formation of the polymers. If catalysis is involved in polymer formation it would be reasonable to expect that alloying of small amounts of such materials as arsenic with the palladium might produce a poisoning effect and inhibit film formation. Alloys containing arsenic, lead, antimony, phosphorus, bismuth and mercury were tested but none showed any useful reduction in the quantity of polymer which was produced.

One method of preventing polymer formation would be to eliminate organic vapours completely from the contact enclosure. This was not considered a practicable step by the Bell Telephone Laboratories, and the solution which has finally been adopted has been based on the observation that the polymer films do not form to any serious extent on a gold surface. Gold, unlike silver, is tarnish-resistant, but unfortunately under arcing conditions gold corrodes badly. The scheme adopted by the Bell Telephone Laboratories has been to combine gold and palladium structurally so as to obtain the advantages of both metals. The contacts are made in the form of a bimetal consisting of a relatively thick base of palladium (0.009 inch thick) covered with a thin overlay (0.001 inch thick) of gold alloy. The gold alloy contains 8 per cent of silver which is added to increase the hardness. With this construction the gold alloy overlay serves to prevent polymer from forming when the contacts are operated without the passage of sufficient current to cause arcing. Thus any relay contacts which are only required to operate at infrequent intervals will remain clean enough to allow electrical contact to be made between them whenever the occasion arises. On the other hand, when heavy currents are passed through the contacts, the thin layer of gold will rapidly erode away and expose the erosion-resistant palladium. In these conditions, of course, the arc will burn away any polymer as soon as it is formed between the exposed palladium surfaces.

This construction has been under test since 1953 in large scale contact reliability tests organised by the Bell Telephone Laboratories. The results are described in detail in a further paper by H. J. Keefer and R. H. Gumley (*Bell Telephone System Technical J.*, 1958, **37**, (3), May, pp. 777–814).

These results are particularly valuable in helping to put in perspective the importance of polymer formation on the contacts of relays in telephone switching systems—all operating, it may be noted, on 50 volts. About 75 per cent of the contacts do not arc and on these, if they are made of palladium, polymer accumulates in compacted lumps in amounts which are visible under a hand glass after 100,000 operations. After several hundred thousand operations the compactions are large enough to cause contacting failure by dusting off and falling into the contacting area. Such a contact, having failed, will clean itself on an average in about five relay operations and thereafter it will not be any more likely than other contacts to fail until the deposit has once more built up. Failures due to fibrous dust tend to be much more persistent. Moreover, it was established that polymer failure was significantly reduced by using contacts which are large, well aligned, and having a surface providing the maximum contact area. The remaining 25 per cent of the contacts, which erode in service, show a very low failure rate from dirt or organic films, since the arcing burns away the deposits.

The Bell System have decided that, to improve the performance of the contacts which do not erode, all wire spring relays shall be fitted with contacts having a gold overlay, which need only be thick enough to provide for the expected mechanical wear. With this construction, on contacts which erode, the overlay is quickly worn away and the underlying palladium provides their needed life.

Preliminary reports from the installations so far made indicate that the contact performance of the new relays with gold overlay on the moving contacts has been highly satisfactory.

J. C. C.