

# Organic Deposits on Precious Metal Contacts

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(Manuscript received December 12, 1957)

*An amorphous brownish organic deposit has been found on non-arcing palladium contacts. It is shown that this material is produced when a number of metals, notably those of the palladium and platinum groups, are rubbed together in the presence of low concentrations of organic vapors. The deposit is given by a very wide variety of organic materials, and is thought first to involve chemisorption of the vapor on the metal, followed by frictional activation and polymerization of the chemisorbed layers to form the visible accumulation. The use of a gold alloy overlay on the palladium to minimize the troublesome effects of the polymer on contact performance is discussed.*

## I. HISTORICAL REVIEW

The reliability of telephone switching and the quality of speech transmission are vitally dependent on the effective performance of the hundreds of electrical relay contacts employed in the completion of a call. Despite all reasonable efforts to maintain clean operating conditions, the function of a contact may be impaired by a variety of contaminants, the sources of which are often far from obvious. The discovery and control of such contaminants has been a continuing task at the Laboratories for many years. In 1947, however, a new approach was made to the problem, with the employment of the plastic replica technique as a micro-analytical tool.<sup>1</sup> Briefly, the method consists of pressing the warmed contact into a clear thermoplastic sheet material such as Vinylite. When cooled, the resulting imprint reproduces faithfully all surface details of the contact. Even more important, foreign deposits are transferred in their original configuration to the transparent medium for microchemical study.

Through this medium of sampling and analysis, a systematic study was made of contact contamination as it occurs under the conditions

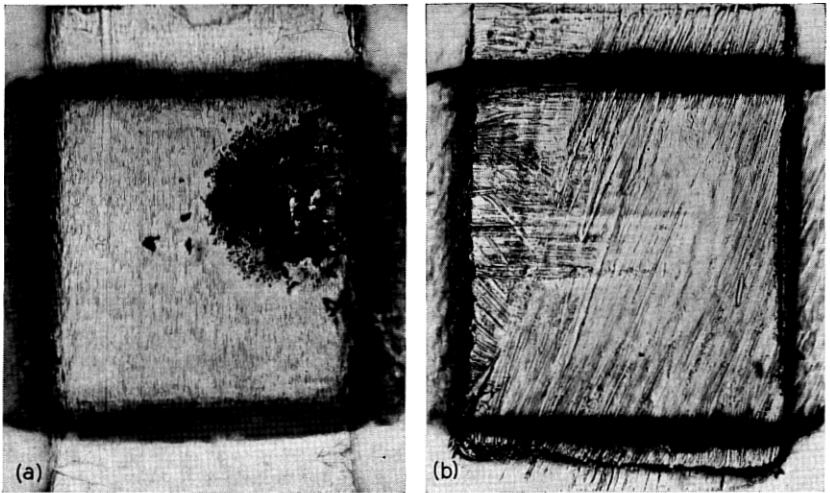


Fig. 1 — (a) Vinylite replica of a palladium relay contact, showing organic deposit formed from vapors of organic structural parts after  $10^6$  closures; (b) replica of a silver relay contact after  $10^6$  closures, showing complete absence of organic deposit. (Both magnified 75 times.)

of manufacture, installation and switchroom operation. This study led to the discovery of a wholly unexpected source of contamination, which appears to explain many of the mysterious transient "opens" frequently encountered in switching. It was found that a dark brownish, structureless deposit was invariably present on non-arcing palladium but never on silver contacts. Under the microscope, the deposit was always observed to accumulate around the area of contact impact and slide. Fig. 1(a) shows a Vinylite replica of a palladium relay contact contaminated with the brown deposit produced by about one million closures. Fig. 1(b) shows a replica of a silver contact operated under the same conditions. In a typical case, most of the deposit is found considerably outside the contact area as a dark powdery mass. Closer to the area of slide may be seen thin translucent films which transmit a yellow to red light. These films are formed by impaction and smearing of the somewhat plastic deposit.

This contaminant could not be traced to any known atmospheric or shop source. Moreover, its quantity was undiminished on palladium contacts operating in the cleanest environments, virtually free from all air-borne contaminants. Significantly, too, this material was found on unwired contacts of operating relays but never on contacts which had not been subject to operation or vibration.

To summarize, 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.

These peculiar circumstances led to the view that the deposit must be a frictional product, involving either palladium and dust-free air or palladium and some vapor derived from the relay structure. Microchemical studies made on replicas taken in the field failed to disclose more than traces of palladium in the deposits. Thus, although not easily acceptable, the evidence pointed strongly to vapors emanating from the relay structure as the source of the frictional product.

To test this view, new relays with carefully cleaned palladium contacts were enclosed in sealed glass chambers, with the contacts unwired. The magnet coils were energized at one-second intervals. At the end of several hundred thousand operations, the chamber was opened and replicas were made of the contacts. A brown deposit, identical in all respects to that observed in the field, was found around the frictional areas of the contacts. Similar experiments with silver contacts produced no deposit.

A relay with palladium contacts was then constructed in which all organic components were replaced by glass in sheet or fibrous form. As an additional precaution, this relay was solvent-extracted and out-gassed by repeated baking and evacuation. When it was operated as before in the sealed container, no deposit appeared on the contacts (see Fig. 2). However, when pieces of phenol fiber such as are used in the normal relay were introduced into this container, a deposit again appeared when the relay was operated. Likewise, deposits were obtained when this inorganic relay was operated in the presence of pure vapors such as benzene or hexane (see Fig. 3). The conclusion thus was inescapable that the brown deposit is formed by traces of organic vapors emanating from the insulating materials of the relay structure.

The purely organic nature of the deposit was confirmed by microchemical tests. The product was found to be combustible at red heat, leaving no residue. On the replicas, the material quickly disappeared in a drop of concentrated sulphuric acid containing chromic acid, with the formation of bubbles, presumably  $\text{CO}_2$ .

The electrical behavior of the brown deposit on the contacts was studied by the use of microprobes. The nonconducting nature of the

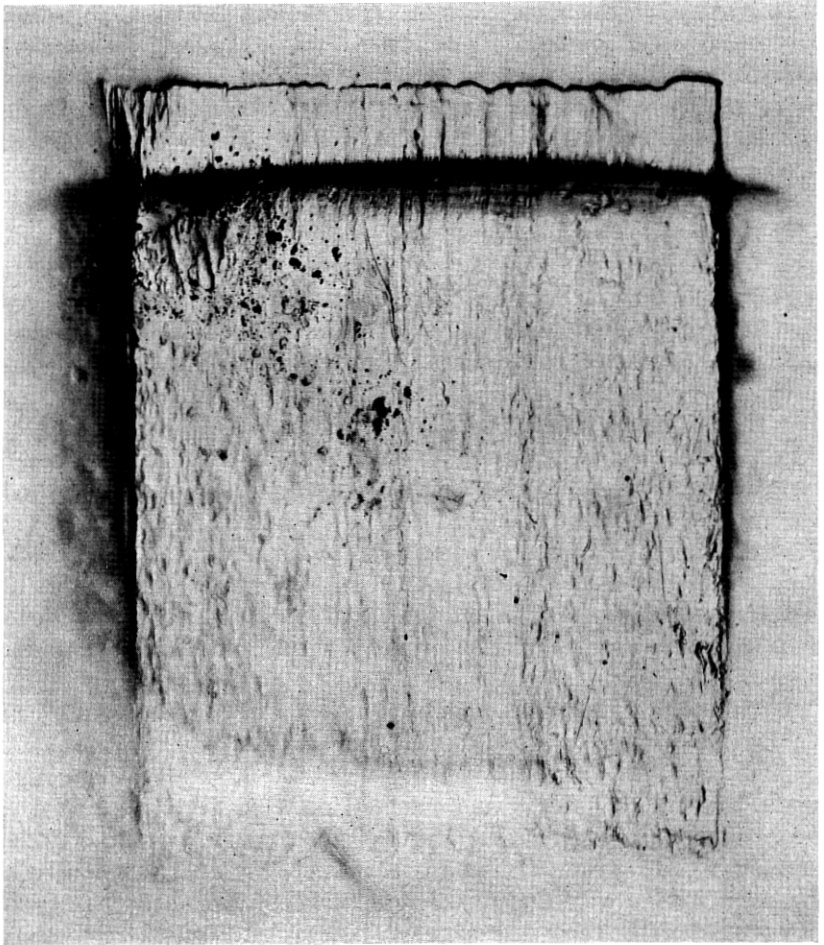


Fig. 2 — Replica of a palladium contact after  $10^6$  closures on a relay with all inorganic parts, showing only metallic wear particles. (Magnified 75 times.)

material was confirmed, but it was found that the deposits were quite fragile compared with fibers and other particles to which most persistent opens on operating equipment have been traced. Nevertheless, it was believed that many transient effects might be explained by this contaminant.

Confirmation of these suspected transient effects was obtained when an extensive laboratory study was made to compare relay performance with and without dust-excluding enclosures.<sup>2</sup> Test circuits were employed

in this study which were designed to detect all opens, even those of short duration. Despite the absence of dust, the relays in the tightest enclosures showed the most opens, and the only contaminant found on these contacts was the characteristic brown organic deposit. Enclosure of the relays evidently had trapped their organic vapors, accelerating the formation of the deposit.

## II. PRODUCTION OF THE DEPOSIT IN LABORATORY DEVICES

Attention was next directed to reproducing the brown deposit in the laboratory by a simplified mechanism which would provide for

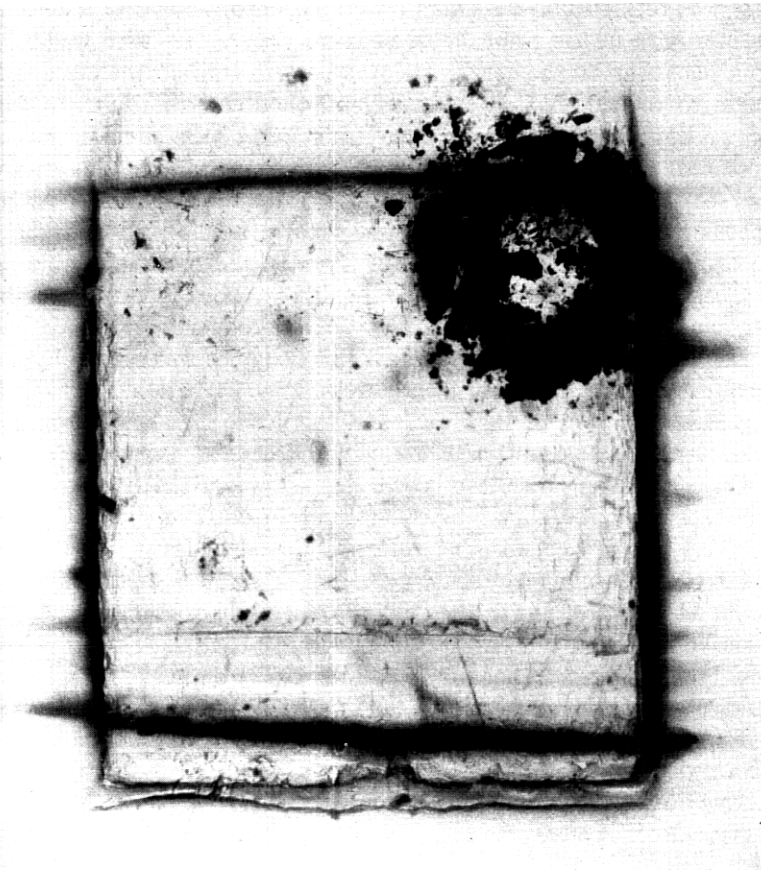


Fig. 3 — Replica of a palladium contact with all inorganic components, showing organic deposit from hexane vapors after  $10^6$  closures. (Magnified 75 times.)

better observation and more quantitative control. It was particularly desired to examine the behavior of metals other than palladium, and to produce a sufficient quantity of the organic material from known vapor sources to permit further study of its properties.

Closure of relay contacts involves both impact and slide. It was believed that impact played no part in producing the deposit, and this matter was settled by adjusting the springs of a relay so that the contacts slid over each other but never opened. The brown deposit was still produced in about the same quantity, indicating slide to be the essential motion.

This conclusion was verified by a simple device in which a palladium disc was rotated under a small ball fused onto the end of a 30-mil palladium wire in the presence of benzene vapor. The wire was soldered to a phosphor bronze spring and was bent to trail on the disc, at a low angle to reduce chatter. After several thousand rotations, a ridge of brown deposit was observable on either side of the circular track. The best results were obtained when the wiping speed did not exceed 10 cm/sec and the contact force was not greater than 35 gms. With higher speeds and contact load, wear was greatly accelerated and the yield of organic deposit fell off rapidly. Even at the most favorable speeds and loads, this device behaved erratically, at times producing the brown organic material copiously and at times producing mostly palladium wear products. It was believed that this behavior was caused by a high-frequency chatter inherent in the particular construction. It was interesting to note, however, that wear and the production of the organic deposit tended to be mutually exclusive effects.

On the rotating disc, the brown deposit was distributed over a long track, making it difficult to collect and to observe. Perfection of the rotating-disc device was therefore abandoned in favor of the development of one using reciprocating motion of small enough amplitude to confine the entire slide to the field of a microscope. The feature most attractive in such a device was the possibility that the rubbing elements could be so mounted that they could be readily detached for microscopic study, weighing and chemical examination of the friction product.

Exploratory devices of this type gave a fairly reproducible yield of brown deposit when the wipe velocity was held below about 10 cm/sec. Above this velocity, wear was again noticeable, with erratic and diminishing yields of brown product, just as had been found on the rotating-disc device.

Two machines using reciprocating motion were evolved. One is driven magnetically using 60-cycle alternating current which produces two

magnetic pulses per cycle and hence 120 oscillations per second of the slider (240 wipes per second). The other machine employs a motor-driven cam and lever arrangement for actuating the slider. Figs. 4, 5(a) and 5(b) show the general features of the magnetically driven device. The fixed friction member is a small plate, 0.5 cm  $\times$  1.0 cm, which may be recessed for retention of the friction products. This plate is held in a vise attached to the frame of the machine. The slider is a 30-mil wire, the end of which is bent sharply back on itself to provide a rounded sliding surface. The slider is clamped at the end of a phosphor bronze spring so that its tip is in line with the axis of the spring. The spring, which may be adjusted to the desired tension, is mounted on the end of the driving rod. No special finish was needed on either the slider or plate to obtain reproducible results, although polishing with levigated alumina facilitated microscopic study of the track by eliminating confusing scratches and other surface irregularities.

The driving rod is suspended in the frame by two beryllium-copper cantilever springs which provide the restoring force against the pull of the magnet. Early experiments showed that support of the driving rod in sleeve bearings was undesirable because of a tendency for it to wear and bind, even when lubricated with graphite. The driving rod terminates in a disc-shaped soft iron armature which is actuated by an E-shaped electro-magnet. The magnet assembly is attached to the frame in a sleeve clamp which permits adjustment of the armature gap. By this means and by regulation of the current, the stroke amplitude is controlled.

The frictional parts of the machine are enclosed in a tight-fitting cylindrical glass shell. A thin copper diaphragm is placed between the magnet and the armature, sealing off the rear of this chamber. Thus, the coil, the only part containing organic material, is on the outside. All parts enclosed by the chamber, except the actual friction members, are gold-plated to reduce reactivity to vapors of a chemically corrosive nature. Vapors to be tested may be passed through the chamber with any desired diluting gas, and inlet and outlet tubes for this purpose are provided. Alternately, liquids or solids to be vaporized may be placed inside the chamber in glass capsules.

The motion of the slider is simple harmonic, making 120 oscillations per second on the fixed plate, or 240 wipes. The average wipe velocity therefore will be  $S \times N$ , where  $S$  is the amplitude and  $N$  the number of wipes per second. The stroke amplitude is measured microscopically, with the travel of a fine scratch on the spring being observed. The actual velocity in simple harmonic motion will, of course, vary from zero at

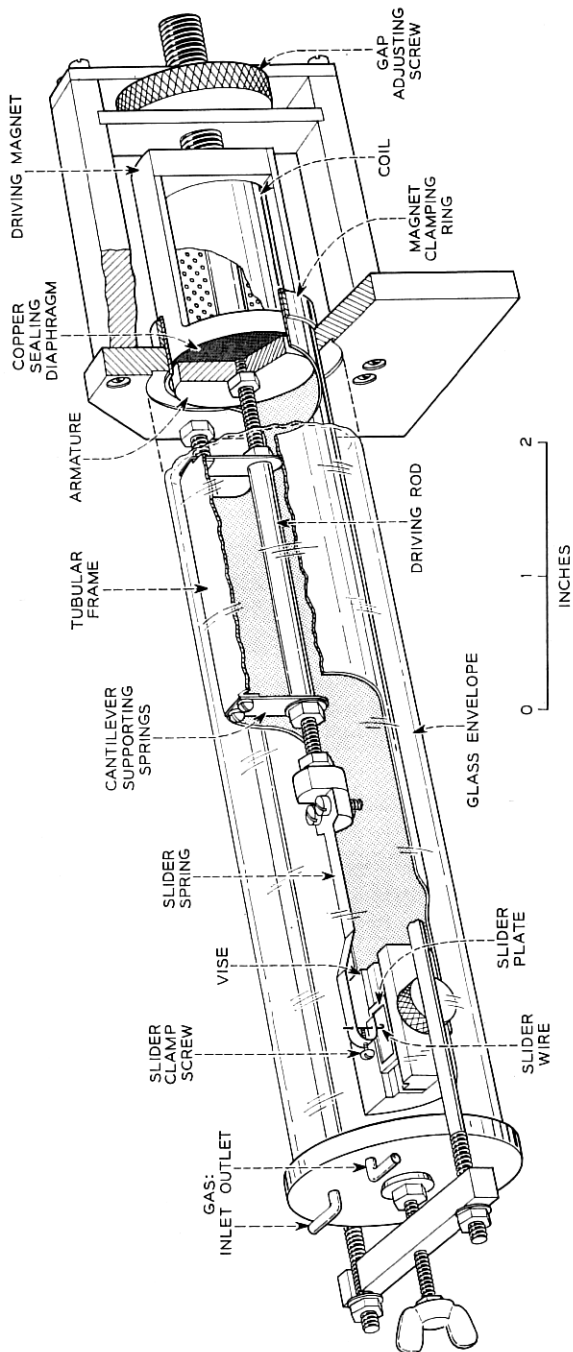


Fig. 4 — Electromagnetically driven friction device.



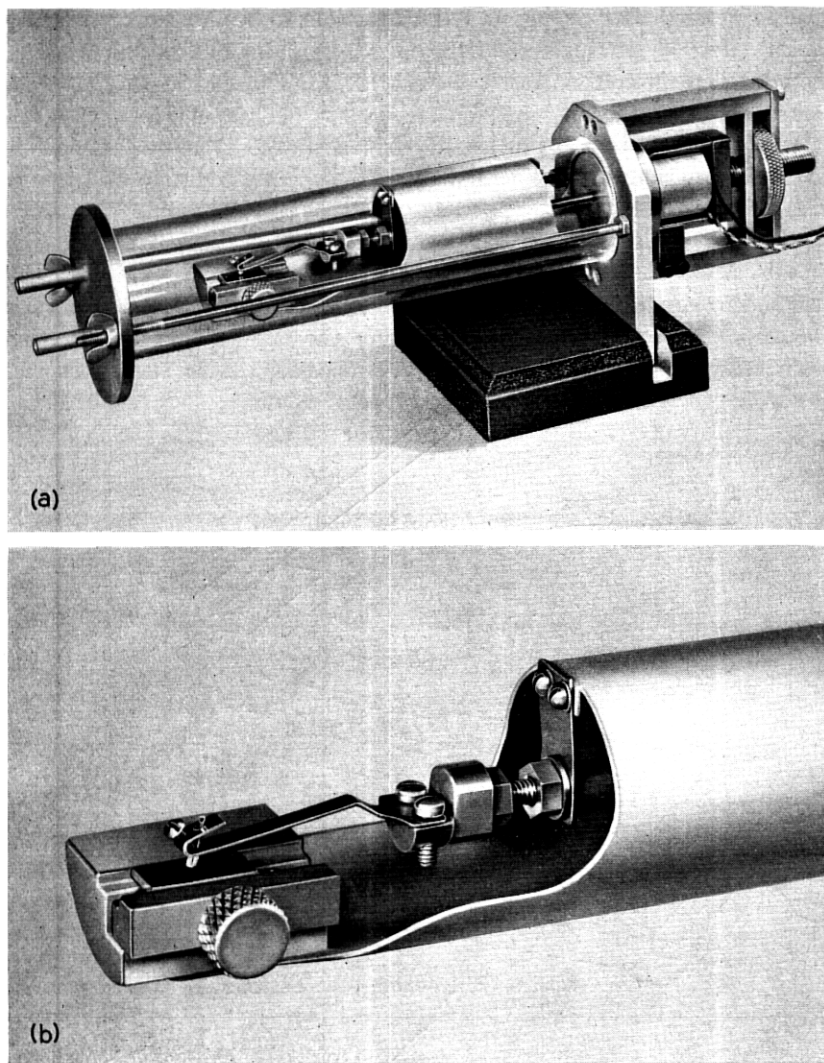


Fig. 5 — Close-up views of electromagnetically driven friction device.

the ends of the stroke to a maximum, given by  $\pi/2 (S \times N)$  or  $1.57 (S \times N)$ , at the midpoint. Thus, with the amplitude of 170 microns commonly used, the maximum wipe velocity would be 6.41 cm/sec.

To measure yields of organic deposit, the plate and slider wire are weighed together on a microbalance before and after each run. The

gain in weight, after drying at  $100^{\circ}\text{C}$ , is taken to be the organic product yield. After the products are removed, the plate and slider are cleaned in redistilled methyl alcohol and again dried. The loss in weight is the wear.

Mechanically, this magnetically driven device is more susceptible to small variations in stroke amplitude than the more rugged and precise cam-driven machine. It was devised to obtain workable quantities of deposit quickly from various combinations of known vapors and metals. Molecules of the organic vapor reach the metal surface by diffusion through the diluting gas. This process is relatively slow when the vapor concentrations are low, as in the case of those emanating from relay components. Therefore it is possible, with the short rest

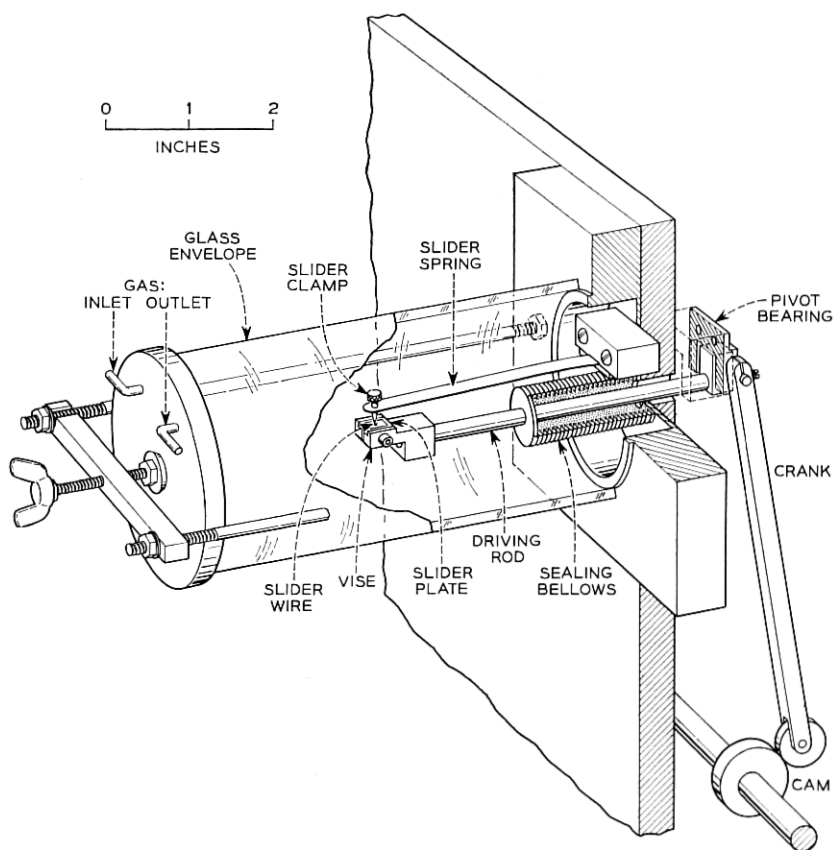


Fig. 6 — Cam-driven friction device.

period afforded by 120 oscillations per second and a low vapor concentration, that not enough adsorption will take place between each wipe to produce the needed film and little or no deposit may result. For this reason, the experiments with the magnetic device are made using high vapor concentrations. A sufficient supply of vapor molecules for rapid saturation even at high operation rates thus is assured.

The cam-driven machine, on the other hand, operates at frequencies up to 6 cycles per second and thus comes within the range of relay test cycling. It is intended for more precise studies, particularly those involving low vapor concentrations. It has been used, for example, to evaluate deposits formed from vapors emanating from materials used in relays and associated equipment and their proposed substitutes.

Fig. 6 shows the details of the cam machine. The friction elements are essentially the same as in the magnetic device, and are likewise enclosed in a glass envelope. In this case, however, the plate vise is mounted on a stiff rod which pivots at the back of the machine. The rod is moved by a lever arm and is spring-loaded against a motor-driven cam. The opening in the back plate through which the rod passes is sealed off by a metal bellows which surrounds the rod. In operation, the rod oscillates through a small vertical arc determined by the cam eccentricity and the length of the lever arm.

The slider, again a 30-mil looped wire, is held in a small chuck at the end of a nickel-silver cantilever spring mounted on the back plate and above the driving rod. As the rod moves up and down against this spring, slip occurs between the plate and slider in much the same manner as between the contacts of a relay. The motion is still essentially simple harmonic, but there will be a difference in contact force between the top and bottom positions of the rod. On the device in use, the force at the bottom of the stroke is about 70 per cent of that at the top. The stroke is set for 170 microns and the slide velocity will therefore depend on the frequency of operation. At 6 cycles per second the average velocity is 0.2 cm per second.

### III. INITIAL EXPERIMENTS WITH BENZENE VAPOR

Benzene was used as the vapor source for the first series of observations for several reasons: (1) the deposit formed from it resembled closely the one found on contacts of relays in the field; (2) the benzene ring is a characteristic part of the structure of most of the vapors given off by relay components; (3) pure benzene is easily obtained; (4) its high vapor pressure permits a wide range of vapor concentrations by dilution of benzene saturated air.

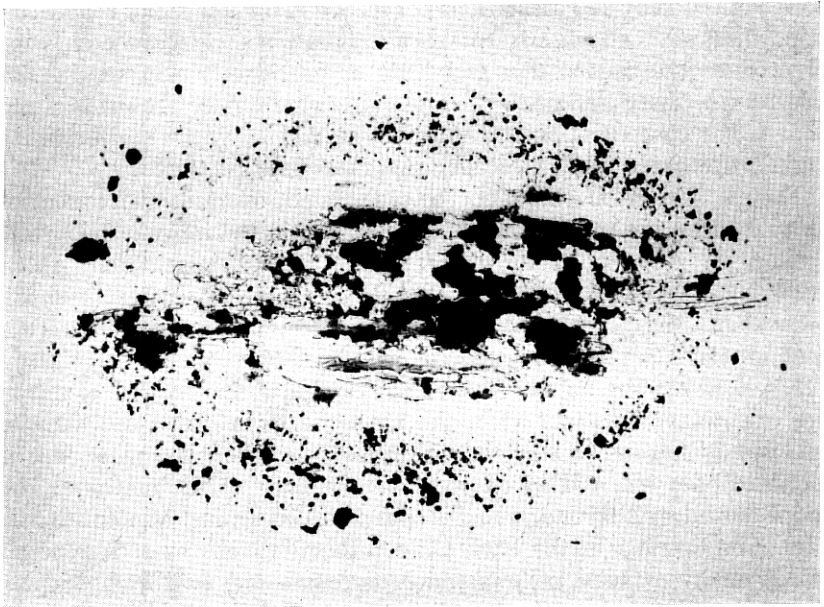


Fig. 7 — Replica of palladium plate, showing organic deposit formed after one minute in benzene vapor with 120-cycle machine. (Magnified 400 times.)

Air was first passed through a column of benzene by means of a fritted glass bubbler, then through the 120-cycle magnetic device with the stroke adjusted to 170 microns. The sliding elements were palladium and the spring force was 30 grams. At the end of ten seconds (2400 wipes) a replica of the plate was made and examined microscopically. A shallow wear area was found to contain numerous furrows and scratches, obviously the composite pattern formed by lateral variations in the slider position. Palladium wear fragments were scattered in and around the wear area, together with amber to dark brown translucent flakes of organic materials. At the bottom of many of the furrows there was a thin, continuous film of organic deposit. After one minute (Fig. 7), the wear had not increased appreciably, but the low areas were now almost filled with the organic material. From this point on, successive observations disclosed no further wear, the organic friction product apparently providing effective lubrication. At the end of five hours (4,320,000 wipes) the product had accumulated around the slide area as a brown powdery pile. The yield amounted to about 35 micrograms.

Another run was started, but after five minutes the machine was

stopped and the wear products were removed without disturbing the slider. It was started again and operated for five hours, after which all of the friction product was removed and ashed. Only a trace (less than 0.1 microgram) of palladium was found, confirming the belief that wear is negligible once an appreciable organic film is formed.

In view of the marked suppression of wear attending generation of the organic product, a comparison was made of the amount of wear produced in the absence of organic vapors under the same conditions. Figs. 8(a) and 8(b) show the result after 4,320,000 wipes. A deep pit has worn in the plate, with a voluminous pile of finely divided palladium surrounding it. Figs. 9(a) and 9(b) show the result of the benzene vapor run with the organic deposit surrounding the track, and with this deposit removed to show the small wear area.

Table I compares quantitatively the wear obtained on three benzene

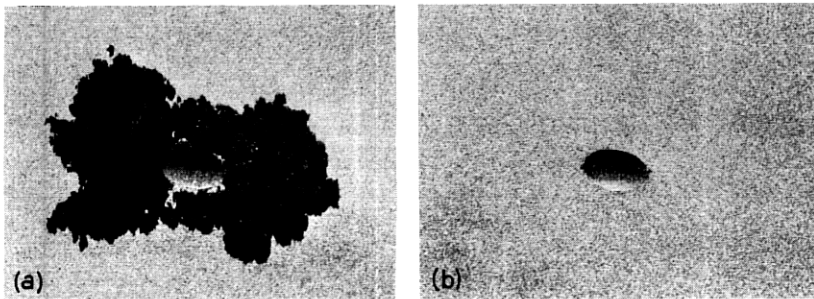


Fig. 8 — (a) Palladium wear products generated in the absence of organic vapors after about  $4 \times 10^6$  wipes; (b) deposit removed, showing deep pit in absence of lubrication by the organic deposit. (Magnified 25 times.)

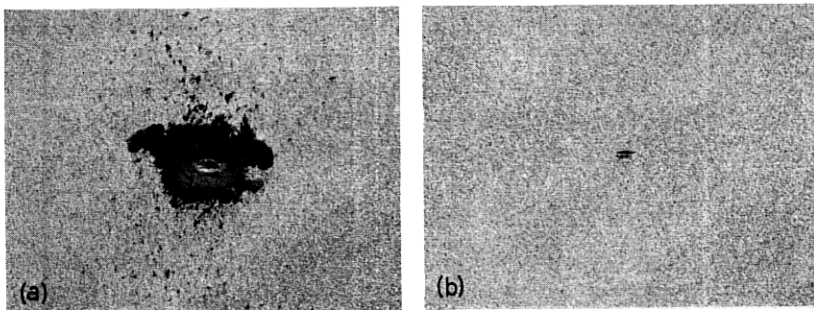


Fig. 9 — (a) Organic deposit formed from benzene vapors after  $4 \times 10^6$  wipes; (b) deposit removed, showing greatly reduced wear due to lubrication by the vapors and deposit. (Magnified 25 times.)

TABLE I — COMPARISON OF WEAR — WITH AND WITHOUT  
BENZENE VAPOR  
( $4 \times 10^6$  Wipes, 170-Micron Stroke, 30-gm Force, 120 Cycles/Sec)

| Experiment Number | Gas Phase        | Yield of Organic Friction Products | Average | Yield of Palladium Wear Product | Average |
|-------------------|------------------|------------------------------------|---------|---------------------------------|---------|
|                   |                  | <i>Micrograms</i>                  |         | <i>Micrograms</i>               |         |
| 1                 | air              | —                                  |         | 103                             | 100     |
| 2                 | air              | —                                  |         | 81                              |         |
| 3                 | air              | —                                  |         | 117                             |         |
| 4                 | benzene sat. air | 46                                 | 44      | 4                               | 3.5     |
| 5                 | benzene sat. air | 32                                 |         | 4                               |         |
| 6                 | benzene sat. air | 35                                 |         | 2.5                             |         |

runs with the wear on three "dry" runs. In the benzene runs, no attempt was made to remove the initial wear products and the total wear was obtained by transferring the friction product to a weighed platinum capsule, igniting the organic material and re-weighing to obtain the palladium residue.

A series of runs was made in benzene saturated air on both the magnetic and the cam-driven machines. The results are presented in Table II. The greater reliability of the cam machine is evident. It is interesting, however, that the average yield with these two devices is substantially the same in high benzene concentration, even though one has a slide velocity and frequency twenty times that of the other.

#### IV. YIELD OF DEPOSIT AS A FUNCTION OF SLIDER LOAD

A series of runs was made at several spring loads on the 120-cycle machine with other factors held constant. Fig. 10 shows the results, with yield of deposit plotted against the square root of the slider load.

The yield appears to be proportional to the square root of the load, and the increase in track width due to plastic deformation between the curved slider and the plate would also be proportional to the square root of the load. Hence, it would appear that the load regulates the yield through regulation of the track area.

#### V. MONOLAYERS OF BENZENE TRANSFORMED PER WIPE

If we take 35 micrograms (from Table II) as the average yield of friction product for 4,320,000 wipes, with about 4 micrograms consisting of palladium wear particles, the organic deposit formed per wipe will be about  $(35 - 4)/4 \times 10^6$ , or  $8 \times 10^{-6}$  micrograms.

TABLE II — YIELD REPRODUCIBILITY — MAGNETIC AND  
CAM MACHINES  
( $4 \times 10^6$  Slides, Benzene Saturated Air, 170-Micron Stroke)

| Yield in Micrograms                             |    |   |  |
|---|----|---|--|
| Magnetic — 120 Cycles/Sec<br>30-gm Spring Force |    | Cam — 6 Cycles/Sec<br>20-30-gm Spring Force |  |
| 44  | 40 | 39  |  |
| 46  | 50 | 36  |  |
| 30  | 36 | 29  |  |
| 38  | 36 | 36  |  |
| 30  | 41 | 38  |  |
| 32  | 38 | 30  |  |
| Average = 38.4<br>Average deviation = 4.8       |    | Average = 34.7<br>Average deviation = 3.3   |  |

R. W. Wilson<sup>3</sup> has determined the track width for a gold wire slider on gold. Wilson's data include results of direct microscopic measurements, calculations from contact resistance and values calculated from Hertz and Meyer's equations at 30 grams force. All of these methods agree rather well, giving a track width for annealed gold of  $5 \times 10^{-2}$  mm. From this value, R. L. Barns<sup>4</sup> calculates the track width for work-

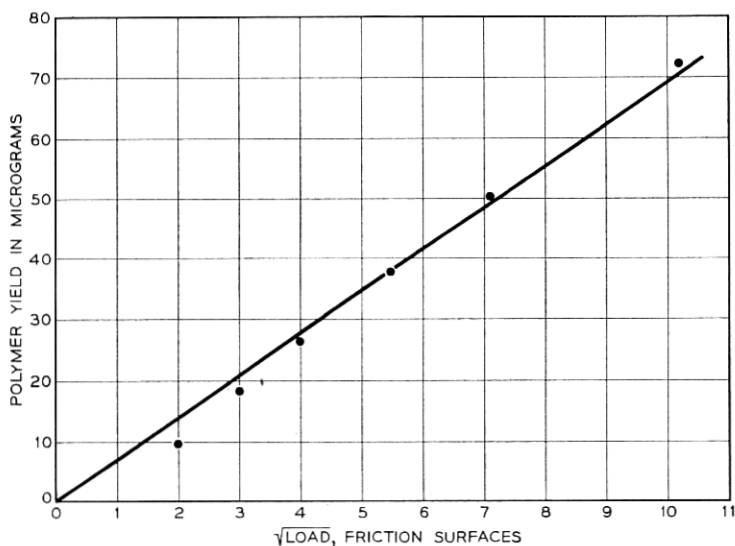


Fig. 10 — Polymer yield versus load. (Palladium on palladium;  $4 \times 10^6$  wipes in benzene-saturated air; 170-micron stroke.)

hardened palladium, using the relation:

$$\frac{d_{\text{Au}}}{d_{\text{Pd}}} = \sqrt{\frac{H_{\text{Pd}}}{H_{\text{Au}}}}$$

where  $d_{\text{Au}}$  and  $d_{\text{Pd}}$  are the track widths, respectively, for gold and palladium and  $H_{\text{Au}}$  and  $H_{\text{Pd}}$  are the hardness values in kg/mm<sup>2</sup> for gold and palladium, respectively. The track width thus obtained for palladium is  $2.4 \times 10^{-3}$  cm. With a 170-micron stroke, the track area will be  $4 \times 10^{-5}$  cm<sup>2</sup>.

The  $8 \times 10^{-5}$  micrograms of deposit formed per wipe corresponds to  $1 \times 10^{-13}$  moles of benzene, which in turn is equivalent to  $6 \times 10^{10}$  molecules of benzene. Dividing this value by twice the wiped area gives about  $7.5 \times 10^{14}$  molecules/cm<sup>2</sup> formed per wipe.

Twice the wiped area is taken on the assumption that the surfaces of both the slider and the plate generate equal quantities of polymer. This would be the case if the relatively small active area of the slider were instantaneously regenerated as it traverses the plate.

A monolayer of benzene on palladium contains about  $7 \times 10^{14}$  molecules/cm<sup>2</sup>. Hence, there has been converted one monolayer per wipe on each surface.

## VI. VAPOR CONCENTRATION VERSUS YIELD OF PRODUCT

As discussed previously, high concentrations of vapors are used in the laboratory to insure a maximum yield of product. Under practical conditions, however, the vapor concentration producing deposits on relay contacts is probably very low. An attempt was made, therefore, to find the critical concentration of benzene below which no deposit would be formed on the palladium sliding surfaces at 6 and 120 cycles per second.

For obtaining measured dilutions of the benzene-saturated air, the technique shown in Fig. 11 was devised. A glass cell of about 50 cc capacity with platinum electrodes sealed into the bottom is connected to the metered air supply line by means of a 10-cm capillary tube of about 0.2-mm bore. The electrodes are covered with dilute sulphuric acid and over this is placed a layer of benzene. The two liquids occupy about half the volume of the cell.

The free space in the cell will be saturated with benzene vapor and its transport into the air supply through the fine capillary will be negligible until gas pressure is generated in the cell by electrolysis of the dilute sulphuric acid. By this means, the small required amount of



benzene vapor is forced continuously through the capillary into the main air supply stream. The volume of vapor is thus metered by the current supplied, in accordance with Faraday's Law. The minute amount of hydrogen introduced into the air stream has no effect on the production of the organic deposit, and the rate of removal of the vapor from the cell is so slow that benzene saturation in the cell is essentially maintained.

Runs were made at 6 and 120 cycles per second using 30 grams spring force and  $4 \times 10^6$  slides at several concentrations. The yields of deposit were plotted against the vapor concentration at the two slide frequencies and are shown in Fig. 12. The values near the critical concentrations are approximations, since estimation of these low yields is subject to considerable error and the cut-off point must be judged from microscopic evidence alone. The latter observation is aided, however, by the abrupt increase in wear and change in the track texture as the organic product disappears. Even with these limitations, it seems clear that with the lower wipe frequency the critical concentration is lowered. At 240 wipes per second, a concentration of about 35 parts per million is re-

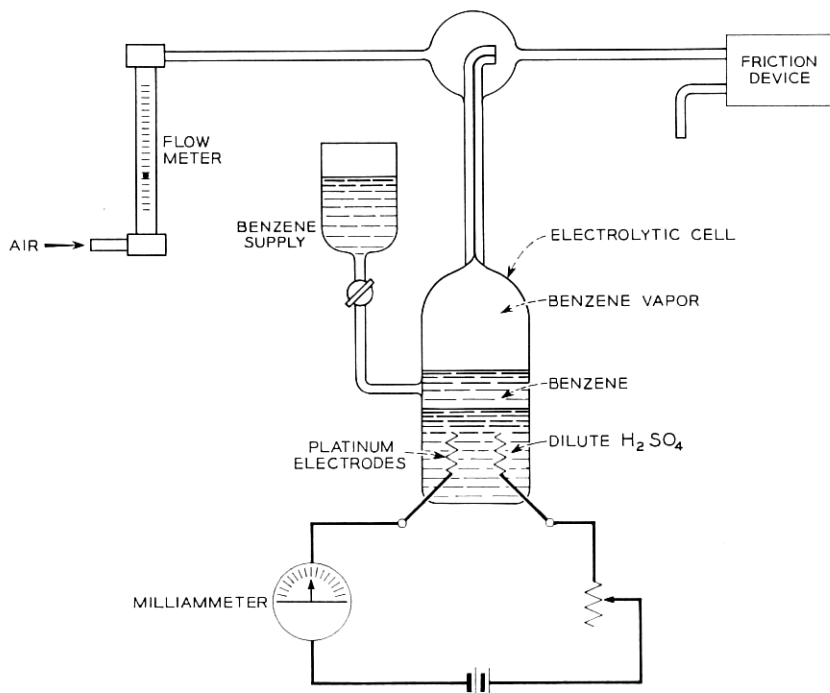


Fig. 11 — Device for obtaining metered dilutions of benzene vapor.

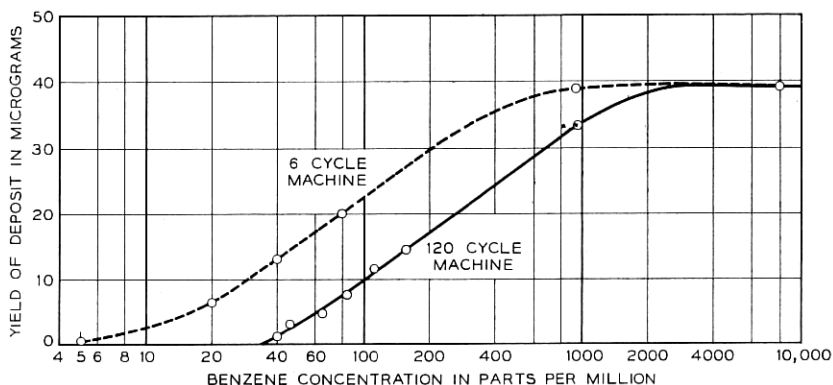


Fig. 12 — Yield of benzene deposit as a function of vapor concentration and wipe frequency.

quired for the appearance of the deposit. At 12 wipes per second, about 5 ppm are needed.\* At the relatively infrequent rate of relay operation in telephone switching, the critical concentration might be expected to be still lower, perhaps a fractional part per million.

#### VII. PROPERTIES OF THE BENZENE PRODUCT

By extended operation of the 120-cycle device in benzene-saturated air, enough of the brown product was obtained to permit a closer examination of its properties. The material is a dark brown amorphous powder which transmits a reddish amber light under the microscope. It readily takes on a strong electrostatic charge. The powder is somewhat plastic and can be formed into pellets at high pressures. When such a pellet is heated in a closed tube, it does not melt but carbonizes with little change of form to produce a coke-like residue. An oily distillate collects at the cool end of the tube, suggesting the presence of considerable hydrogen in the original material.

A wide variety of solvents has been tried on the benzene product, the results of which are summarized in Table III. No solubility has been observed except with strong organic bases such as ethanolamine and pyridine. Even with these, solution is never complete. When the soluble portion in pyridine or morpholine is run into a silica-impregnated paper from a capillary tube a radial chromatogram is obtained with several colored bands, indicating a mixture of several substances.

\* P. Kisliuk,<sup>5</sup> using gas (hydrogen) pressure increase as an indicator of polymer production in an evacuated system, obtains polymer at a benzene concentration of about 4 ppm at 2.6 cycles per second, which is in general agreement with these conclusions.

TABLE III — EFFECT OF VARIOUS SOLVENTS ON THE BENZENE PRODUCT

| Solvent  | Action  |
|--|---|
| Aliphatic hydrocarbons (petroleum fractions)<br>Cyclic hydrocarbons (toluene, xylene, cymene, tetralin, etc.)<br>Chlorinated hydrocarbons — aliphatic and aromatic<br>Alcohols — methyl to amyl<br>Ethers — dimethyl, diethyl, dipropyl<br>Ketones — dimethyl, diethyl, methyl butyl<br>Esters — ethyl acetate, methyl salicylate, amyl acetate, dibutylphthalate<br>Acids — glacial acetic<br>Aniline, dimethyl aniline, dodecylamine, alpha-methylbenzylamine<br>Acetonitrile, dioxane, nitropropane, dihydropyran<br>Furfuryl alcohol, dimethylformamide, dichloroisopropyl ether | No Action   |
| Sulphuric acid 75%, zinc chloride (conc. aqueous)<br>Sodium thiocyanate (conc. aqueous), sodium hydroxide, 20%   | No Action   |
| Nitrobenzene, diethylene glycol monoethyl ether, ortho-cresol  | Slight swelling of particles under microscope   |
| Ethanolamine, isopropanolamine<br>Pyridine, quinoline, butylamine<br>Ethylene diamine, propylene diamine<br>Morpholine<br>Conc. sulphuric acid + chromic acid  | Largely soluble<br>Largely soluble<br>Partly soluble<br>Partly soluble<br>Slowly disperses and disappears with formation of CO <sub>2</sub> bubbles |
| 50% aqueous potassium hydroxide, triglycol, octoic acid, cresols; all in sealed tubes, heated to 200°C.  | Product swells slightly but no evidence of solution   |

The carbon-hydrogen atomic ratio was determined on two 500-microgram samples and found to be 1.36 and 1.18, giving an average of 1.27. The spread between these results probably reflects some non-uniformity in the sample material as well as the general difficulty of working with such small quantities. In any event, it is evident that, in the conversion from the benzene vapor to the brown deposit, much of the hydrogen is retained.

P. Kisiuk,<sup>5</sup> by measuring the pressure increase in a closed system containing benzene vapor and sliding palladium wires, has determined the hydrogen released during polymer formation. He concludes that the polymer retains approximately 65 per cent of the benzene hydrogen.

An attempt was made to obtain an infrared spectrum of the benzene product. The small quantity available together with its insolubility

created difficulties, but there was evidence of aromatic rings, alkene and carbonyl groups linked together to form long chain molecules. Electron diffraction studies also indicate an amorphous material of high molecular weight.

In reviewing these properties, one is inclined to regard the organic deposit as a complex mixture of high molecular weight, cross-linked materials. The infrared indication of carbonyl groups, the strong color of the deposit, and the fact that only basic solvents have any action on it, strongly suggest that, in the conversion from benzene vapor, oxygen has entered into combination. Perhaps cross-linkage is through oxygen-containing groups such as aldehyde or carboxyl, and, by attacking these, the basic solvents achieve splitting and solution. Since the deposits resemble mixed polymers in their properties, it is proposed to term them "frictional polymers".

#### VIII. BENZENE FRICTIONAL POLYMER FORMED WITH SLIDING SURFACES OTHER THAN PALLADIUM

Various sliding surfaces in benzene vapor were substituted for palladium in the 120-cycle device. Table IV presents the results. It is apparent that generation of the organic deposit is a phenomenon in which the platinum and palladium metals are especially active, although it is not exclusively confined to these. Molybdenum, tantalum and chromium, for example, give weighable quantities of deposit. On the other hand, alloys with only small percentages of platinum or palladium still produce the deposit, in reduced quantities. Silver on silver produces no detectable organic film, nor, curiously, is wear observed. Even when it 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. Gold produces a very small quantity of product, the nature of which appears to be identical with the deposit formed with palladium.

If the catalytic properties of the platinum and palladium metals are important in production of the polymer, one might also expect nickel to be active. In air, the only frictional product is nickel oxide. To prevent oxidation, benzene-saturated hydrogen (which gives polymer with palladium) was used, but only wear was observed.

When the slide is between quartz or glass and palladium, polymer is still produced (Fig. 13). Apparently metal-on-metal slide is not necessary. Although it may be argued that traces of palladium transfer to the quartz, no indication of this was obtained by microscopic or microchemical means. Attempts were made to use other non-metallic sliders

TABLE IV — BEHAVIOR OF VARIOUS SLIDING SURFACES  
IN BENZENE VAPOR(4 × 10<sup>6</sup> Wipes, 170-Micron Stroke, 120 Cycles/Sec, 30-gm Force)  
(Except Where Otherwise Indicated, in Benzene-Saturated Air)

| Sliding System*                       | Weight of Frictional Product (Micrograms) | Description of Frictional Product    |
|---------------------------------------|---|--------------------------------------|
| Pt/Pt                                 | 40  | Dark brown polymer, powder           |
| Pd/Pd                                 | 38  | Dark brown polymer, powder           |
| Pd/Pd (Benzene-sat. H <sub>2</sub> )  | 35  | Dark brown polymer, powder           |
| Ru/Ru                                 | 22  | Dark brown polymer, powder           |
| Pt 6%, Au 69%, Ag 25%/Pd              | 20  | Brown polymer, powder                |
| Pd 25%, Au 75%/same                   | 15  | Dark brown polymer, powder           |
| Ta/Ta                                 | 14  | Gray polymer, powder                 |
| Pd 60%, Cu 40% ("unordered")/<br>same | 13  | Dark brown polymer, powder           |
| Quartz/Pd                             | 12†                                       | Brown polymer, powder                |
| Au 91.7%, Ag 8.3%/Pd                  | 12  | Brown polymer, powder                |
| Rh/Rh                                 | 10  | Light brown polymer, powder          |
| Pd 60%, Cu 40% ("ordered")/same       | 9   | Dark brown polymer, powder           |
| Au 70%, Ag 30%/Pd                     | 8   | Dark brown polymer, smeary<br>powder |
| Mo/Mo                                 | 8   | Light brown polymer, powder          |
| Cr/Cr                                 | 8   | Mixed tan and light brown<br>polymer |
| Au/Pd                                 | 5-8                                       | Dark brown polymer, smear            |
| Pd 5%, Au 95%/same                    | 5†  | Brown polymer, powder                |
| Pt 6%, Au 69%, Ag 25%/same            | 5†  | Brown polymer, powder                |
| Pd/Quartz                             | 3-5†                                      | Brown polymer, powder                |
| Au/Au                                 | 1-3†                                      | Dark brown, smeary polymer           |
| Ag/Pd                                 | 1-3†                                      | Dark brown, smeary polymer           |
| Ni/Ni                                 | None                                      | Yellow brown oxide                   |
| Ni/Ni (Benzene-sat. H <sub>2</sub> )  | None                                      | Metallic wear products               |
| Ag/Ag                                 | None                                      | Little wear                          |
| Cu/Cu (Benzene-sat. H <sub>2</sub> )  | None                                      | Some metallic wear                   |
| Quartz/Quartz                         | None                                      | Fine quartz wear powder              |
| Fe/Fe (Benzene-sat. H <sub>2</sub> )  | None                                      | Wear products                        |
| V/V                                   | None                                      | Brown oxide                          |
| W/W                                   | None                                      | Oxide formed                         |
| Zn/Zn (Benzene-sat. H <sub>2</sub> )  | None                                      | Wear products                        |

\* The first member of the pair is the slider.

† Estimated microscopically.

such as nylon, Vinylite, and cellulose on palladium, but no polymer was obtained.

## IX. ATTEMPTS TO INHIBIT FRICTIONAL POLYMER FORMATION

Again assuming catalysis is involved, it would be reasonable to expect that the alloying of small amounts of certain metals with the palladium might produce a poisoning effect and inhibit the generation of the poly-

mer. Alloys containing arsenic, lead, antimony, phosphorus, bismuth and mercury were tested, but none showed any useful reduction in the quantity of polymer produced (Table V). These tests were carried out in the 120-cycle machine, both in benzene-saturated air and in air saturated with ethylene glycol dibutyl ether vapor. The latter was used on the assumption that agents which fail to inhibit in benzene-saturated air might work at low vapor concentrations. Ethylene glycol dibutyl ether gives a vapor concentration of about 120 ppm at room temperature and yields about 14 micrograms of a dark brown powdery polymer with  $4 \times 10^6$  wipes (palladium on palladium).

Polymer formation was completely prevented when an atmosphere of 50 ppm of mercury was maintained in the chamber. However, under these conditions, the sliding surfaces contained a high concentration of mercury, which practically eliminated palladium in the frictional process.

Pre-treatment of the palladium surfaces with various films was unsuccessful (Table V). This is not surprising, since most surface coatings such as sulphide or oxide would be worn through quickly by the sliding action. Benzoquinone and sulphur coatings were applied with the idea of saturating the air immediately around the wiped area with their vapors. Unsuccessful attempts were also made to prevent polymer formation by contaminating the palladium surfaces with lubricants such as silicone greases, petrolatum and graphite.

A number of gases and vapors were also examined for possible inhibiting effects. Such agents were chosen either for possible poisoning action on the palladium surfaces or blocking effect on the growth of the organic molecules to the polymer stage.



Fig. 13 — Polymer formed on 120-cycle machine by palladium slider on fused quartz, with reflected light. (Magnified 50 times.)

TABLE V — ATTEMPTS TO INHIBIT FRICTIONAL  
 POLYMER PRODUCTION
(4 × 10<sup>6</sup> Wipes, 30-gm Force, 120 Cycles/Sec)

A. By Alloying of Certain Metals With Palladium

| Palladium Alloyed with:<br>(Both Sliding Members) | Polymer Yield, Air Saturated with:      |  |
|---|---|--|
|   | Ethylene glycol dibutyl ether           | Benzene                                |
| Unalloyed Palladium                               | 14 micrograms                           | 38 micrograms                          |
| Lead 1%   | All yields were above<br>10 micrograms* | All yields were above<br>20 micrograms |
| Lead 15%  |   |  |
| Antimony 1%                                       |   |  |
| Antimony 15%                                      |   |  |
| Arsenic 1%  |   |  |
| Phosphorus 0.8%                                   |   |  |
| Bismuth 4%  |   |  |
| Mercury 0.1%                                      |   |  |

B. By Pre-treatment of Sliding Palladium Surfaces

| Pre-treatment   | Polymer Yield in Air Saturated with:    |  |
|---|---|--|
|   | Ethylene glycol dibutyl ether           | Benzene                                |
| Untreated Palladium   | 14 micrograms                           | 38 micrograms                          |
| Electrolytic sulphiding +<br>sulphur coating                        | All yields were above<br>10 micrograms* | All yields were above<br>20 micrograms |
| Benzoquinone deposited<br>from 5% acetone solution                  |   |  |
| Oxidation of surfaces   |   |  |
| Lubricant coating — graph-<br>ite, silicone grease, petro-<br>latum |   |  |

\* If the yield was substantially that of the pure palladium run, judged visually, it was not weighed, since then there was no significant inhibition.

Table VI summarizes the results. The tests were run with four polymer forming vapors — benzene, tetrahydronaphthalene, triethylbenzene and ethylene glycol dibutyl ether — to provide a range of vapor concentrations. Aqueous ammonia, methyl alcohol and carbon tetrachloride, all in high concentrations, displayed an inhibiting action when combined with the lower concentrations of polymer producing vapors; they also reduced the yield with benzene saturated air. These materials, which form no polymer by themselves, probably occupy portions of the palladium surface by virtue of their high concentration and therefore cannot be regarded as true catalyst poisons.

Hydrogen, used as the carrier gas, showed some inhibiting action, but only on the low concentrations of polymer formers. This was somewhat surprising in view of the known affinity of hydrogen for palladium.

TABLE VI — INHIBITION BY INTRODUCTION OF CERTAIN VAPORS

| Inhibiting Agent          | Polymer Yield (Micrograms) from Air Saturated with: |                            |                                  |                                  |
|---------------------------|---|----------------------------|----------------------------------|----------------------------------|
|                           | Ethylene glycol dibutyl ether<br>120 ppm            | Triethylbenzene<br>260 ppm | Tetrahydronaphthalene<br>450 ppm | Benzene<br>$1.2 \times 10^4$ ppm |
| None                      | 14  | 31                         | 32                               | 38                               |
| Water                     | >10†  |                            |                                  | >20                              |
| 1% Carbon monoxide        | >10   |                            |                                  | >20                              |
| 1% Nitric oxide           | >10   | >20                        | >20                              | >20                              |
| 100 ppm Hydrogen sulphide | >10   |                            |                                  | >20                              |
| * Carbon disulphide       | >10   |                            |                                  | >20                              |
| * Thiophene               | >10   |                            |                                  | >20                              |
| * Triethylamine           | >10   |                            |                                  | >20                              |
| * Carbon tetrachloride    | Trace   | Trace                      | Trace                            | 11, 15                           |
| * Methyl alcohol          | None  |                            | Trace                            | 11                               |
| * Aqueous ammonia (conc.) | None  | None                       | Trace                            | 7, 5                             |
| Hydrogen, replacing air   | 7, 7  | 10                         | >20                              | >20                              |

\* Capsules of inhibitor and polymer producing agent were exposed together in the closed chamber of the machine.

† If the yield was substantially that of the run without inhibiting agents, judged visually, it was not weighed, since then there was no significant inhibition. All of the values were judged visually.

#### X. FRICTIONAL POLYMER FROM VARIOUS ORGANIC MATERIALS

Thus far, benzene has been used almost exclusively as the vapor source in the laboratory while the various physical factors were being studied. The investigation would be grossly incomplete, however, without attempts to establish the range of organic materials which produce the organic deposit and to observe how vapor composition affects its yield and properties. To this end, a variety of vapors were tested in the 120-cycle machine. In most cases, air was saturated with the vapor by the passing of fine bubbles through the liquid. Fixed gases were metered to give a concentration in air of several hundred parts per million. Occasionally it was more convenient, particularly when the material was a solid, to place it in a capsule inside the glass envelope. At the end of each run the friction product was weighed and examined chemically and microscopically.

The wide range of organic compounds, many highly stable chemically, which produce a deposit is surprising. Except for a few simple materials such as methane and ethane and some of their derivatives, the only requirement seems to be that the substance have high enough vapor pressure to produce a concentration of 50 ppm or more. All of the products are colored, ranging from light brown to almost black. They are usually powdery, amorphous materials, although exceptions do occur



TABLE VII — FRICTIONAL POLYMER FROM VARIOUS ORGANIC COMPOUNDS\*

(Pd/Pd, 120 Cycles, 30-gm Load, 170-Micron Stroke,  $4 \times 10^6$  Wipes)






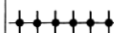





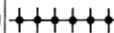





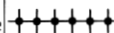







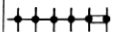



| Group A — No Polymer Formed           |                               |                              |
|---------------------------------------|-------------------------------|------------------------------|
| Methane                               | } down to $-60^\circ\text{C}$ | Formaldehyde                 |
| Ethane                                |                               | Carbon tetrachloride         |
| Propane                               |                               | Methylamine                  |
| Methyl alcohol                        |                               | Ethylene diamine             |
| Group B — Trace to 5 Micrograms       |                               |                              |
| Propane ( $-60^\circ\text{C}$ )       |                               | Ethyl alcohol                |
| Butane (down to $-60^\circ\text{C}$ ) |                               | Ethyl chloride               |
| Ethylene                              |                               | Ethyl ether                  |
| Group C — 5 to 19 Micrograms          |                               |                              |
| Pentane                               |                               | Propylamine                  |
| Hexane                                |                               | Butylamine                   |
| Propene                               |                               | Amylamine                    |
| Butene                                |                               | Hexylamine                   |
| Butadiene                             |                               | Triethylamine                |
| Propanol                              |                               | Pentadecafluorotriethylamine |
| Butanol                               |                               | Butylchloride                |
| Pentanol                              |                               | Hexachlorbutadiene           |
| n-Hexanol                             |                               | n-Nitrobutane                |
| 2-Hexanol                             |                               | Cyclohexanol                 |
| Acetaldehyde                          |                               | Benzyl alcohol               |
| Propionaldehyde                       |                               | Aniline                      |
| Acetone                               |                               | Hydroxybenzyl alcohol        |
| Methylethylketone                     |                               | Monochlorobenzene            |
| 2-Butanone                            |                               | Thiophene                    |
| 2,5-Hexanedione                       |                               | Pyridine                     |
| Acetonitrile                          |                               | Dioxane                      |
| Butyronitrile                         |                               | Phenol                       |
| Hexanenitrile                         |                               | Morpholine                   |
| Hexachlorbenzene                      |                               | o-Cresol                     |
| Group E — 20 to 40 Micrograms         |                               |                              |
| Acetylene                             |                               | Cyclohexane                  |
| Benzene                               |                               | Crotonaldehyde               |
| Toluene                               |                               | Butyraldehyde                |
| Xylene                                |                               | Cyclohexanone                |
| Naphthalene                           |                               | 5-Hexen-2-one                |
| Cyclohexene                           |                               | Limonene                     |
| Group F — Over 40 Micrograms          |                               |                              |
| Acrolein                              |                               | Styrene                      |
| Acrylonitrile                         |                               | Benzaldehyde                 |

\* The highest grade chemicals commercially available were used without further purification.

TABLE VIII — FRICTIONAL POLYMER FROM STRAIGHT  
 CHAIN COMPOUNDS

 ( $4 \times 10^6$  Slides, Pd/Pd, in Air Containing High Concentrations of  
 Vapor; Yield in Moles  $\times 10^{-5}$  in Lower Right-hand Corner)

 (Yields for Propane and Butane Given at  $-60^\circ\text{C}$  and  $+20^\circ\text{C}$ )

| CLASS                          | C <sub>1</sub>  | C <sub>2</sub>  | C <sub>3</sub>  | C <sub>4</sub>   | C <sub>5</sub>  | C <sub>6</sub>   |
|--------------------------------|---|---|---|--|---|--|
| SATURATED<br>HYDRO-<br>CARBONS | <br>METHANE<br>0       | <br>ETHANE<br>0        | <br>PROPANE<br>(+20)0<br>(-60)tr | <br>BUTANE<br>(+20)tr<br>(-60)0.7 | <br>PENTANE<br>1.4       | <br>HEXANE<br>1.9     |
| SATURATED<br>ALCOHOLS          | <br>METHANOL<br>0      | <br>ETHANOL<br>0.6     | <br>PROPANOL<br>1.3              | <br>BUTANOL<br>1.6                | <br>PENTANOL<br>1.9      | <br>HEXANOL<br>2.1    |
| SATURATED<br>AMINES            | <br>METHYL-<br>AMINE 0 | <br>ETHYL-<br>AMINE tr | <br>PROPYL-<br>AMINE 1.1         | <br>BUTYL-<br>AMINE 1.0           | <br>PENTYL-<br>AMINE 1.1 | <br>HEXYLAMINE<br>0.7 |
| SATURATED<br>ALDEHYDES         | <br>METHANAL<br>0      | <br>ETHANAL<br>1.8     | <br>PROPANAL<br>2.0              | <br>BUTANAL<br>2.7                |   |  |
| OLEFINS                        |   | <br>ETHYLENE<br>0.2    | <br>PROPYLENE<br>1.4             | <br>BUTYLENE<br>0.9               |   | <br>HEXENE<br>2.1     |
| OLEFIN<br>ALDEHYDES            |   |   | <br>ACROLEIN<br>10.0             | <br>CROTONALDE-<br>HYDE 3.8       |   |  |
| ACETYLENE                      |   | <br>ACETYLENE<br>13.8 |   |  |   |  |

in which smeary products or peculiar fibrous structures are produced. In the latter case, needle-like outgrowths are sometimes encountered which suggest the existence of some sort of molecular ordering. Examination in polarized light, however, has never revealed any optical activity in these structures. Table VII lists all of the compounds studied, grouped on the basis of polymer yield in micrograms.

Table VIII compares the polymer yield for a number of straight chain compounds ranging from C<sub>1</sub> to C<sub>6</sub>. The yield is reported in moles  $\times 10^{-5}$  for better comparison of molecules transformed. The saturated hydrocarbons form an interesting series. Methane and ethane, boiling at  $-161^\circ$  and  $-88^\circ\text{C}$ , respectively, produce no deposit at temperatures

as low as  $-60^{\circ}\text{C}$ . Propane (boiling point  $-42^{\circ}\text{C}$ ) gives a trace of deposit at  $-60^{\circ}$  but none at room temperature, while butane (b.p.  $+1^{\circ}\text{C}$ ) yields a weighable deposit at  $-60^{\circ}$  and a trace at room temperature. Pentane and hexane, both boiling above room temperature, give, respectively,  $1.4$  and  $1.9 \times 10^{-5}$  moles at room temperature. From this series it would appear that the deposit yield is influenced both by the length of the hydrocarbon chain and the difference between its boiling point and the machine's operating temperature. The importance of this temperature differential would be understandable if it is assumed that the saturated hydrocarbons are held to the palladium only by relatively weak adsorptive forces.

The dependence of the deposit on chain length is better demonstrated by the alcohol series, all of which boil above room temperature. There is a regularly increasing yield from ethanol to hexanol. Methanol, the single carbon member, gives no deposit.

The introduction of carbonyl oxygen, especially in a terminal position on the molecule (aldehyde), gives a darker product and markedly increases the yield as well as its solubility. Ethanal, for example, gives three times as much product as ethanol, and the product is dispersible in aqueous ammonia, methanol, dimethylformamide and other solvents which have little effect on the deposits yielded by hydrocarbons or alcohols. The butanal product is fairly typical of the aldehydes. Under the microscope it disperses readily in a drop of 10 per cent aqueous ammonia, yielding a dark amber suspension which appears clear in direct transmitted light but scatters light in a Tyndall beam. When introduced into filter paper from a capillary, the suspensoid does not travel with the liquid front but separates as a ring between the point of entry of the solution and the wet boundary. The suspensoid may be precipitated from the ammonia by adding a crystal of sodium chloride or other salt. Thus, the butanal polymer suspension in ammonia behaves much as a typical colloid. This increased dispersability of the aldehyde and ketone products, particularly in aqueous ammonia, suggests that acidic oxygen groups may account for a considerable portion of the linkages. By attacking these polar links, basic solvents bring the material into colloidal dispersion. An infrared examination of the butanal product gave indication of both carbonyl and carboxyl groups.

By way of contrast, deposits formed from unsaturated hydrocarbons are usually light colored and highly insoluble, even in powerful basic solvents such as ethanalamine. Here the cross-linkage is probably mostly through the double bond, with relatively little oxygen in the molecule.

The olefin hydrocarbons (containing the double carbon-carbon bond) show an increase in yield over the corresponding saturated members. With ethene, this increase is not spectacular, a barely weighable amount being obtained at  $-60^{\circ}\text{C}$  and only a trace at room temperature. Although this gas is known to chemisorb on palladium,<sup>5</sup> its low boiling point ( $-104^{\circ}\text{C}$ ) may operate against this sorption to reduce the yield. The increase is most marked for the  $\text{C}_3$  member, propene. Propane (b.p.  $-42^{\circ}\text{C}$ ) and propene (b.p.  $-47^{\circ}\text{C}$ ) have almost the same boiling points, so that this factor practically cancels out. However, propene yields  $1.4 \times 10^{-5}$  moles at room temperature while propane gives only a trace of polymer even at  $-60^{\circ}\text{C}$ , clearly indicating the influence of the double bond. The difference becomes less pronounced when butane and butene, also having similar boiling points, are compared, and the difference is still less between hexane and hexene. Apparently, with the higher members, the effect of the longer chain is more important.

When the molecule contains both the double carbon-carbon bond and the terminal carbonyl oxygen, especially when these are conjugated as in acrolein, the yields are among the highest observed. It is interesting that yield is reduced with crotonaldehyde, in which the carbonyl double bond and the olefin double bond are no longer conjugated. The products are dark and have solubilities similar to those of the saturated aldehydes. In addition, there is often a tendency toward a needle-like structure in the deposit around the slider.

The nitrile group acts similarly to carbonyl oxygen to enhance the yield. Thus, methyl nitrile (acetonitrile) is one of the few methane derivatives which yield polymer, giving  $2.4 \times 10^{-5}$  moles. Acrylonitrile gives  $13.2 \times 10^{-5}$  moles — even more than acrolein.

Acetylene, containing the triple carbon-carbon bond, despite its low boiling point ( $-82^{\circ}\text{C}$ ) and simple structure gives the highest molar yield so far observed, even at room temperature. In this case it is probable that sorption on the palladium is so strong that the acetylene is held readily at a temperature  $100^{\circ}$  above its boiling point. The high chemical reactivity of this substance is well known. The deposits obtained are dark brown and highly insoluble. A C/H atomic ratio of 2.7 was obtained for the acetylene product. Evidently more hydrogen is lost in this conversion than in the case of benzene.

The amine group ( $\text{NH}_2$ ) appears to have a slight but definite depressing action on the polymer yield, especially on the longer chain members.

Apparently hydrogen is not necessary to the production of the polymer. A completely chlorinated unsaturated compound, hexachlorbutadiene, was run with a yield of  $0.9 \times 10^{-5}$  moles, against  $1.3 \times 10^{-5}$  for

butadiene. Triethylamine and its completely fluorinated derivative (pentafluoroethylamine) were run, and about the same volume of deposit was obtained in each case. Hexachlorobenzene also produces polymer.

The yields of polymer obtained from compounds having a cyclic structure are generally higher than those from straight chain compounds having the same number of carbon atoms. Furthermore, the yields are little affected by the degree of saturation or by the presence of hydrocarbon side groups. Thus benzene, toluene, xylene, cyclohexane, cyclohexene, and styrene give practically the same molar yields. The introduction of aldehyde in the side group (benzaldehyde) does little here to raise the yield. Apparently the cyclic structure is the controlling factor. Table IX gives the yields for these compounds.

In reviewing the behavior of the various vapors, it seems clear that factors in the molecular structure which promote polymerization reactions in the bulk material also tend to enhance the yield of frictional polymer. However, it is equally clear that many stable compounds which would not undergo polymerization, except possibly with extreme heat and pressure, readily undergo conversion to frictional polymer. In all cases where polymer was formed, the pronounced lubricating effect already described for benzene was observed. With vapors such as methyl alcohol, carbon tetrachloride and ethylamine which formed no polymer, metallic wear was high, resulting in a deep pit in the plate.

There has been some speculation as to whether polymer formation and activation of contacts may be related. Germer<sup>5</sup> obtained activation on all noble metals including gold and silver, but only with unsaturated cyclic vapors. Polymer is not formed on silver and only in traces on gold, but it is formed with all manner of vapors including saturated and unsaturated cyclic and straight chain compounds. It seems probable that initial adsorption of the vapor is common to both phenomena. From this point on, however, the events take different courses.

TABLE IX — CYCLIC COMPOUNDS — YIELD OF DEPOSIT  
(Pd/Pd,  $4 \times 10^6$  Wipes, 30-gm Force, 120 Cycles/Sec)

| Compound       | Yield in Moles $\times 10^{-5}$ |
|----------------|---------------------------------|
| Benzene        | 4.9                             |
| Toluene †      | 4.9                             |
| p-Xylene       | 5.2                             |
| Styrene        | 4.9                             |
| Cyclohexane    | 5.1                             |
| Cyclohexene    | 4.9                             |
| Benzyl Alcohol | 4.6                             |
| Benzaldehyde   | 5.5                             |

## XI. FRICTIONAL POLYMERIZATION IN THE LIQUID PHASE

In view of the conversion of organic vapors to complex solids on palladium friction surfaces, one naturally wonders what would happen if the sliding were to occur under an organic liquid. The friction devices described for vapor phase studies are not well suited to use under liquids, so another arrangement was devised, in which a palladium wire attached to a vibrating steel reed slides on a stationary wire at right angles to it. The stationary wire is mounted on a phosphor bronze spring which maintains the desired load between the sliding surfaces. The whole device fits into a small glass cylinder, with the wires immersed in about 1 cc of the liquid under study. An electromagnet, positioned outside the tube, drives the steel reed at 120 cycles per second (Fig. 14).

With a 300-micron amplitude under benzene, a copious quantity of brown, insoluble product was produced in four million wipes. This product was identical in all its observable properties to that formed in benzene vapor. Similar results were obtained under butyl alcohol, tetralin, limonene and a light petroleum fraction. The same high degree

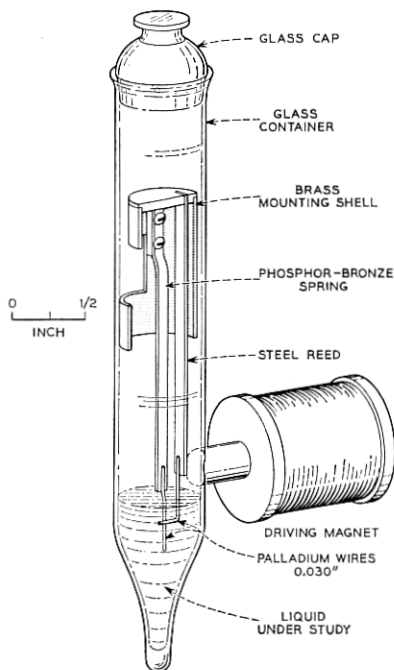


Fig. 14 — Device for generating frictional polymer in liquids.

of lubrication was observed as when the vapors were used — far more than would be expected from the parent liquids.

In all cases, the polymer was held tenaciously to the palladium wires, building up around the point of slide until the mass became great enough to jar off as a sizable flake. There was no indication of any soluble or colloiddally dispersed product in the parent liquid. After a 20-hour run in redistilled benzene ( $16 \times 10^6$  wipes), the polymer was filtered out and the liquid was evaporated to recover any soluble matter. None was found. Another portion of the filtered benzene was examined in the infrared spectrograph, with negative results. From these observations, it would appear that the polymer grows to its ultimate insoluble form directly from adsorbed layers on the metal surface rather than through an intermediate soluble or dispersible stage.

As in the case of their vapors, neither methyl alcohol nor carbon tetrachloride produced polymer. In both of these liquids, wear was marked. Since methyl alcohol showed some inhibiting tendencies in the vapor form, it was decided to test this action in the liquid phase, where the concentration ratios of polymer producer and inhibitor can be conveniently and precisely regulated. Mixtures of benzene and methyl alcohol were run, the benzene fraction being increased until polymer definitely formed. It was found that polymer was inhibited completely until a concentration of 95 per cent benzene was reached, confirming the indications obtained with the vapors.

The study of frictional polymerization under liquids is in a preliminary stage at the time of writing. This approach appears to hold considerable promise. The precise control of concentration ratios, the use of reactants not available as vapors and the retention of all reaction products in a small volume of liquid are attractive features. This device also permits studies requiring vacuum-tight, all-glass systems employing the friction mechanism.

## XII. FRICTIONAL POLYMER FROM ORGANIC STRUCTURAL MATERIALS

Table X lists a number of tests made on piece parts and materials used in relays or associated with them in wired equipment units. For these tests, the 6-cycle cam-driven device was used and, because of the low yields of polymer frequently encountered, the number of wipes was raised to  $14 \times 10^6$ .

The parts or quantities of the bulk material, equivalent to five relays, were placed in the glass chamber of the friction device with the outlet and inlet tubes left open to simulate roughly the enclosure of a relay in

TABLE X — FRICTIONAL POLYMER FROM VAPORS RELEASED  
BY ORGANIC STRUCTURAL MATERIALS  
(Pd/Pd, 6-Cycle Cam-Driven Device,  $14 \times 10^6$  Wipes,  
170-Micron Stroke)

| Piece Part or Material                              | Temp. °F | Polymer Yield<br>Micrograms |
|---|----------|-----------------------------|
| Relay coil with cellulose acetate interleaving      | 125      | 34                          |
| Relay coil with Mylar interleaving                  | 125      | 11                          |
| Relay coil, wire only (enameled)                    | 125      | 8                           |
| Phenol fiber spoolheads (2C)                        | 120      | 29                          |
| Phenol fiber cards (#4)                             | 120      | 22                          |
| Phenol fiber cards (#4) after baking 110°C, 48 hrs. | 120      | <5                          |
| Durez 265 molded relay structures                   | 120      | Trace                       |
| #2 Phenolic resin molding compound                  | 120      | 5                           |
| Selectron terminal strip                            | 80       | None                        |
| Lucite relay contact cover                          | 80       | 19                          |
| Cellulose acetate-butyrate contact cover            | 80       | <5                          |
| Neoprene grommets                                   | 80       | <5                          |
| "Scotch" electrical tape, white                     | 80       | <5                          |
| Wire, cotton, acetate rayon, lacquer (insulation)   | 80       | 12                          |
| Wire, polyvinyl chloride (insulation)               | 80       | 22                          |
| <i>Foils</i>  |          |                             |
| Laminated Mylar (polyethylene terephthalate)        | 120      | Trace                       |
| Koppers polystyrene                                 | 80       | 8                           |
| Tenite II, 217A                                     | 80       | Trace                       |
| Benzene saturated air (for comparison)              | 80       | 130                         |

an individual can cover. Where the material would normally be subject to heating by relay operation (coil materials, for example), the chamber was heated, with 120 to 125°F being chosen as an average operating temperature.

These results indicate that, when heated, the cellulose acetate interleaving sheet and the phenol fiber spoolheads and cards yield the most polymer. The acetate material is plasticized with diethyl phthalate which distills out in noticeable quantities at 125°C.\* When the acetate is replaced by Mylar the polymer yield is reduced to one third, most of which is accounted for by the wire enamel. Baking of the phenol fiber parts markedly reduces the subsequent release of polymer-forming vapors.

Complete control of the polymer by selection and improvement of materials, however, does not offer any great promise because of the large variety of these materials used, not only in the relay but also in associated equipment enclosed with it.

\* It is interesting that L. H. Germer also has found that the plasticizer in the coil is the chief source of contact activation (private communication).



Attempts were made to adsorb the organic vapors on activated carbon. In practice, the idea did not work out satisfactorily because of the difficulty of locating the adsorbent where it would take up the vapors before they reached the contact. This experience does not rule out the possibility, for special cases, of air being circulated through the adsorbent and blown against the contacts.

### XIII. THE PRACTICAL CONTROL OF POLYMER BY SELECTION OF CONTACT METAL

By reference to Table IV it can be seen that, of all the metals that might be considered for use as relay contacts, gold and silver alone might be expected to be free of polymer difficulties. Silver is ruled out for speech transmission because of its tendency to form noise-producing sulphide films. Gold forms polymer, but in quantity so small that it does not interfere in ordinary telephone uses. Under heavy arcing, however, gold erodes badly; also, because of its softness, wear is a problem. In addition, gold is relatively expensive. In all of these respects, except for polymer formation, palladium is an excellent contact metal.

Fortunately, a way out of these difficulties was found by combining gold and palladium structurally so as to obtain the advantages of both metals.<sup>6</sup> The resulting general purpose contact consists of a 1-mil overlay of gold, containing 8 per cent silver, on a 9-mil palladium base. The silver imparts sufficient hardness to the gold to meet the wear requirements. The gold prevents troublesome quantities of polymer from forming when the contacts break little or no current (see Fig. 15). When heavy currents are broken the thin layer of gold will be lost, exposing the erosion-resistant palladium, but build-up of polymer is prevented by the arc. Cost is only slightly increased because only a thin cap of gold is used.

Laboratory and field trials of these gold overlay contacts have proved their superiority in all environments. These trials are discussed in detail in the associated paper by Keefer and Gumley.<sup>2</sup>

### XIV. GENERAL DISCUSSION

The cumulative conversion of traces of organic vapors to a visible complex solid when certain metals slide on one another is a startling effect. It seems unlikely that it would have been anticipated from our present knowledge of the physics and chemistry of surfaces, and it has been the primary purpose of this paper to report what is currently known of the phenomenon.

Experimental clarification of the mechanism of the frictional poly-

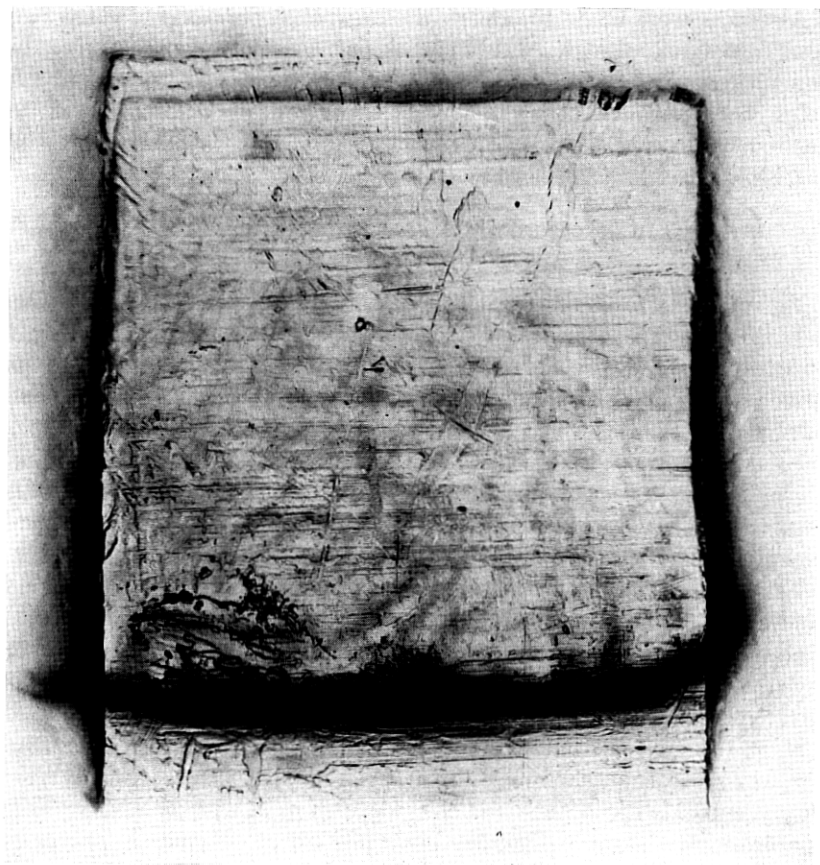


Fig. 15 — Replica of a gold contact operated  $10^6$  times in the vapors of the organic structural relay parts, showing the small quantity of organic deposit. (Magnified 75 times.)

merization has progressed slowly because of many practical difficulties, not the least of which is the necessity of working on a micro-scale with products not easily characterized chemically. In the absence of an established mechanism, one is left to speculate. Several views have been proposed, none of which is completely without objection. At this point, it might be well to review the observations which need to be explained by any proposed mechanism.

1. When certain metals, notably palladium, are subjected to sliding friction in organic vapors or liquids these are rearranged to form amorphous, colored solids of high molecular weight at the point of slide.

2. This effect is highly sensitive, requiring only trace concentrations of vapors to produce visible quantities of the product.

3. The process is highly efficient, calculations having shown that a monolayer of benzene is converted to the solid product on each palladium surface for each wipe.

4. The conversion occurs with almost every class of organic compound, including many highly stable materials. The presence of hydrogen is not essential; completely halogenated compounds also give a solid product.

5. While the platinum group metals are most active, the effect is not confined to these alone. Molybdenum, tantalum, chromium and gold, for example, also produce solid products. Furthermore, only one of the sliding surfaces need be an active metal. Thus, conversion is obtained when palladium slides on quartz or glass.

6. In all cases, formation of the solid product is accompanied by remarkably effective lubrication.

7. Efforts to inhibit the process by typical catalyst "poisoners" such as carbon monoxide or metallic additions have been unsuccessful. Agents such as benzoquinone and nitric oxide also were without effect. Ammonia, methyl alcohol and carbon tetrachloride in high concentrations prevent or reduce polymer formation by active vapors. However, this suppression of polymer production may simply be the result of monopolizing most of the palladium surface by these strongly adsorbed but non-polymer-producing vapors.

8. Lowering of the temperature has not reduced the yield of polymer in the limited number of cases so studied. On the contrary, in a few instances the yield was increased.

Perhaps the simplest explanation would assume the original molecules to be so strongly sorbed on the metal surface that their structures are put under strain and they are rendered highly reactive. These active molecules then combine among themselves, possibly with simultaneous splitting off of hydrogen or simple hydrocarbons, to produce complex molecular structures. A very thin layer of high molecular weight material thus would coat the surface of any active metal so exposed, the reaction coming to a standstill when the active metal surface was completely covered. The role of sliding friction in this process would be merely to wipe away the reacted product, thus promoting a continuous conversion to polymer at the area of slide. The product wiped away would accumulate at the periphery of the slide area.

This explanation receives some support from studies of the sorption of simple aliphatic and olefinic hydrocarbons on palladium and other metals, in which it has been shown that new compounds are formed.

Typical is the study of chemisorption of ethene on palladium (unpublished work, S. J. Stephens) in which ethane and butane are formed as reaction products. On the other hand, there is no direct evidence to date that such surface reactions have produced the complex, high molecular weight solids encountered as the frictional polymer. Also, where sufficient concentrations of vapor exists, lowering of the temperature has in no case reduced the yield of polymer. To the contrary, certain low-boiling hydrocarbons produce polymer at  $-60^{\circ}\text{C}$  but not at room temperature. This negative temperature effect would not be anticipated if chemisorption were a controlling factor.

If the postulated invisible layer of polymer formed directly on the metal surface could be removed without use of friction, the argument for this mechanism would be well established. One attempt was made by the authors, in which a palladium surface under benzene was exposed to supersonic radiation. It was hoped that any polymer film present would be continuously stripped off in this way. Although cavitation was evident at the palladium surface, no polymer appeared in the benzene, infrared examination of which showed no change.

The failure to prevent production of the deposits by recognized catalyst poisons would also seem to argue against the mechanism of direct polymerization.

Another objection to this explanation is the assumption that the wiping action re-exposes the catalytically active metal surface. If this is so, one should expect considerable wear to attend the production of the polymer. However, it should be recalled that a high degree of lubrication is one of the most striking and consistent effects associated with its production. It seems quite probable that a large part of the slide is not that of metal on metal, but that a film of some sort is interposed. Nevertheless, calculations have shown that about a monolayer of benzene is transformed to polymer per wipe on each surface. It would be difficult to reconcile this high efficiency of polymer production with the high efficiency of lubrication if metal-to-metal wipe were a necessary condition.

This objection might be met by assuming slide to take place principally between chemisorbed "primary" organic layers, through which the influence of the active metal is still exerted on superimposed layers. On wiping, shear might then take place at or near the primary layer, leaving it intact but highly reactive chemically. In such a mechanism, the role of friction becomes more important. This suggests the possibility that part of the work of sliding friction may go into raising the chemical activity of the adsorbed organic layers, with resulting formation of the

high molecular weight products. Such an explanation would admittedly lack the simplicity of the direct polymerization idea, since it would involve two or more steps. Certainly the sorption of the organic molecules on specific metal surfaces would be the first step. Work then performed on these layers by friction would convert the sorbed layers to polymer in one or more additional steps.

Just how frictional work would bring about polymerization is a highly speculative question. While friction is a well known phenomenon from an engineering standpoint, the changes taking place on a molecular scale when one surface slides over another are certainly not fully understood.

Where friction is involved, one immediately thinks of heat and, in the present case, of the possibility that temperatures might be reached at which organic molecules would be broken down into active fragments with ultimate recombination into more complex structures. However, the slide velocities at which polymer forms are such that the temperature rise for the clean metals would be less than 50°C on the basis of Bowden's measurements,<sup>7</sup> and, in this case, the temperature would be even lower because of the lubricating effect of the polymer. A run was made on the cam-driven machine using benzene-saturated air for  $4 \times 10^6$  wipes at 22 wipes per minute. This corresponds to a slide velocity of only 0.006 cm/sec. A full yield of polymer (> 40 micrograms) was obtained, giving further evidence that frictional heat is not necessary. Already mentioned are the polymer yields obtained at -60°C. Experiments were also performed in which the operating temperature of the machine was raised to 150°C with no effect on the yield of the benzene polymer. Unsuccessful attempts were also made to form similar polymers without friction on platinum and palladium surfaces subject to cycles of heating and cooling. Thus it does not appear that frictional heat, at least as we understand it, produces the polymer.

The action of sliding one metal surface over another is usually thought of in terms of gross mechanical effects, such as seizure and galling, which of course are very important in lubrication engineering. These effects are believed to be the cumulative result of shear motion and the strong molecular attractions which occur when the surface structures are forced into sufficiently intimate contact. When chemisorbed organic films cover the sliding metal surfaces it seems quite possible that the interplay of attractive forces with straining and deformation of the molecules may supply the activation energies necessary to bring about drastic chemical rearrangement. Such a mechanism would place emphasis on sliding friction as the primary source of the polymerization, although

strong bonding of the organic molecules to the metal surface would be a requisite. Associated with this "frictional working" of the adsorbed layer would probably be a profound disturbance of the valence electrons. The possibility of free radicals existing in the friction product was suggested by D. Tabor<sup>8</sup> and was experimentally explored by the writers. The deposit generated from benzene vapor on palladium surfaces was allowed to fall into a capsule containing acrylonitrile, through which a Tyndall beam was passed. It was assumed that any free radicals in the deposit would initiate mass polymerization in the acrylonitrile with the development of increasing turbidity. This failed to occur. Liquid acrylonitrile was also subjected to palladium-to-palladium slide in the "capsule" device already described. There was no evidence of any polymerization beyond the actual friction area. These experiments do not rule out the possibility that something akin to free radicals may exist in a "captive state" on the metal surfaces, held there by adsorptive forces.

#### XV. ACKNOWLEDGMENTS

The authors are happy to acknowledge their gratitude to G. T. Kohman for his interest and advice. They are deeply indebted to Miss Blanche Russiello for much of the laboratory work, to W. G. Guldner for the C/H ratio determinations, and to D. L. Wood and J. P. Luongo for infrared spectrographic examinations. The numerous suggestions made in discussions with R. L. Barns, W. L. Hawkins, L. S. Nelson and S. J. Stephens of the Laboratories and with C. E. Schildknecht of the Stevens Institute were also very helpful.

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