Activation of Electrical Contacts by Organic Vapors

By L. H. GERMER and J. L. SMITH

Unreproducibility of earlier work on the erosion of relay contacts has been traced to the effects of organic vapors in the atmosphere. Carbon from decomposition of these vapors greatly alters the conditions under which an electric arc can be initiated and can be sustained. The importance from the standpoint of erosion comes from the fact that for many circuit conditions contacts activated by this carbon cannot be protected against severe arcing by any conventional capacitance-resistance network. This paper reports investigations which have enabled us to understand the activation of contacts by organic vapors.

TABLE OF CONTENTS

INTRODUCTION

Contamination of surfaces by organic vapors is a subtle factor that influences the electrical erosion of relay contacts. Because of this contamination, contacts in the telephone plant sometimes erode very much more than one would expect from simple laboratory life tests. This caused considerable confusion until about 1945 when the influence of organic vapors was recognized. The term "activation" is used here to describe changes in the surfaces of electrical contacts which give rise to greater arcing when an electrical circuit is completed or broken than would occur if the metal surfaces were clean.* Although its cause is generally carbon from organic vapors, there are occasionally other causes. This paper is an account of recent research[1] on activation produced by organic vapors.†

It has been found that the carbon that causes activation is formed on the electrode surfaces by decomposition of adsorbed organic molecules. Microscopic examination of contacts gives a very sensitive way of detecting incipient activation, since the carbon can easily be seen before any electrical effects are observed. The minimum amount of carbon necessary for activation is of the order of 0.05 microgram.

Activation has been produced on noble metals only, and only by unsaturated ring compounds. When experiments are carried out on clean noble metal surfaces under controlled conditions which do not permit burning of carbon, it is found that the amount of carbon formed by an arc corresponds to approximately a monolayer of organic molecules on the area heated by the arc. After a surface has become active, the amount of carbon formed by each arc is considerably increased and corresponds to the decomposition of several monolayers of molecules. In air, the situ-

---

* The term "activation" has sometimes been used heretofore to signify enhanced erosion resulting from organic vapors. This is a different definition from that used in this paper, due to the fact that in some cases, long sustained arcs produce less erosion than arcs of shorter duration. This is often true for silver surfaces, as described below. In a case of this sort, a surface may have a great deal of carbon on it and be very "active" by our definition, when it would be considered not active at all by the definition that relates activation to rate of erosion.

† Other causes of activation will not be considered here. See Reference 2, page 961.

ation is much complicated by burning of carbon and by the impedance offered by air to diffusion of molecules to the electrode surfaces. Because of these complicating factors, activation will not occur in air if the vapor pressure is too low or if the time between arcs is too short.

Arcs at the making and breaking of clean contacts — clean in the sense that they are free from carbon — produce transfer of metal from one contact to the other with a resulting pit and mound of about equal volumes. The situation is greatly changed by carbon. The presence of carbon causes increased arcing, alters the characteristics of the arcs, and greatly changes the resulting erosion both in character and amount. With carbon present, some or even all of the eroded metal does not stick to the electrodes, and there is often loss of metal from both of them, the missing metal turning up mixed with carbon in a loose black powder. With carbon on the surfaces, successive arcs occur at different places, and the resulting erosion tends to be smooth with the electrodes worn down uniformly all over their surfaces. This is because each arc burns off carbon at its center, while it produces more around its periphery where the metal is cooler, and each new arc strikes on a newly carbonized surface.

Every arc, of either the active sort or of the "inactive" sort which occurs at clean surfaces, is predominantly an arc *in metal vapor*. The active arcs, as well as the arcs at clean surfaces, are of one or the other of two quite distinct types which have been called, respectively, "anode arcs" and "cathode arcs" (Reference 3 and 4 which are concerned with palladium electrodes only). In an anode arc, most of the metal of the arc is vaporized from the anode by electron bombardment, but in a cathode arc the metal is supplied from the cathode by the explosion of small areas due to Joule heating by field emission currents of enormous densities flowing through them. In an anode arc, the erosion is predominantly from the anode, and in a cathode arc from the cathode.

Whether a particular arc is of the anode or of the cathode type is determined by the electrode separation and the contact metal. For palladium electrodes, an arc is an anode arc if the separation is less than about 0.5×10^{-4} cm, but a cathode arc if the separation is greater than this value. The corresponding critical distance for silver is 3 or 4×10^{-4} cm. The carbon particles producing activation permit breakdown at separations for which it would not occur in the absence of carbon, and thus favor cathode arcs. The critical distance of palladium is so small that all active palladium arcs are cathode arcs, with the greater loss of metal from the cathode. For silver, on the other hand, the critical distance is so large that active arcs at silver surfaces are in many cases anode arcs, with the greater loss of metal from the anode as in the case of inactive silver arcs.

neath the electrodes. It is clear that the increased arcing of activation is caused by solid carbonaceous material made by decomposition of organic vapor and not by the vapor itself. Clean metal contacts can, in fact, be made to show all of the symptoms of activation by allowing soot from a flame to settle on their surfaces.*† Activation produced in this way is, of course, temporary, lasting only until the deposited soot is burned away.

When one looks for characteristics of arcs between active surfaces to which numerical values can be attached, four features come at once to mind — the electric field at which an arc strikes, the voltage across the arc after it is established, the minimum arc current (which is just the current at which the arc goes out), and finally, after the arc is over, the amount of metal that was gained or lost by each of the electrodes during the arc. All of these quantities have been measured for active arcs as well as for arcs at clean surfaces, and a brief summary of the results of the measurements is given here.

1.1 *Striking Field*

To measure the electrode separation at which an arc strikes between closing electrodes, relay contacts were operated repeatedly, discharging on each closure a capacitor charged to a measured voltage. An arc at each closure was assured by using short leads between the capacitor and the contacts to keep the circuit inductance very low. The time from the initiation of the arc to the touching of the contacts was measured on an oscilloscope.‡

Fig. 2 illustrates the results of measurements made by F. E. Haworth[7] upon palladium electrodes closing at 30 cm/sec to discharge a very small capacitor charged to 50 volts. Before the start of the experiment the electrodes had been cleaned by repeated arcing in air, and the first experimental point represents the closure of these clean electrodes. All of the other measurements were made in air containing a fairly high partial pressure of limonene vapor. Each point plotted on the curve rep-

---

* Unpublished work of P. P. Kisliuk.
† It is interesting to point out that a surface is not made active by rubbing petrolatum upon it, although activation will occur very quickly if an electric current is made or broken at such a greasy surface, so that some of the grease is decomposed.
‡ For inactive arcs, it is necessary to make a correction for the height of the mound of metal thrown up by the arc (Reference 6, page 1136). After the contacts become active, there is no appreciable mound thrown up (at palladium surfaces), and the electrode separation at the initiation of the arc is calculated at once from the closure time and the previously measured electrode velocity. The height of the mound produced before the contacts are active was minimized by using a capacitance of only 40×10^{-12} farad.
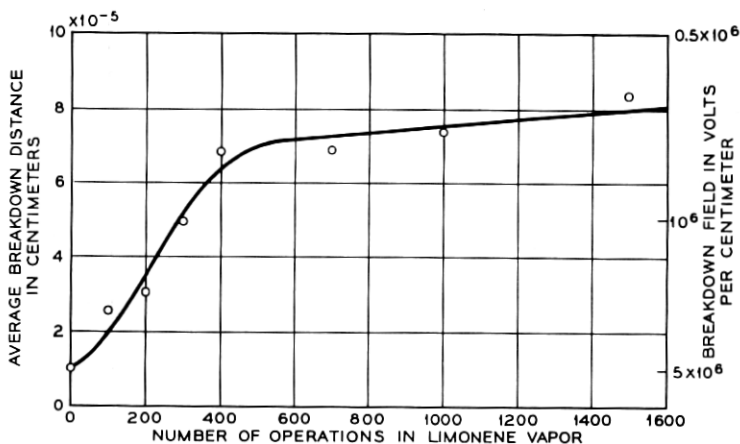
Fig. 2 — Breakdown distance, and apparent striking field, for arcing at relay contacts on closure in the presence of limonene vapor, plotted against number of operations. Each closure discharges a very small capacitor charged to 50 volts. Contacts are clean and inactive at the beginning of the test.

resents the average of 100 separate measurements. During tests of this sort, it was discovered that, with frequent microscopic examination of the electrodes, black sooty material could easily be seen after the first 30 closures, before certain evidence of activation could be obtained in any other known way. In Section 4.1, it is shown that this material is carbon.

The average electrode separation at which an arc struck between clean electrodes at the beginning of the curve of Fig. 2 was about 1×10^{-5} cm and after the electrodes became covered by sooty material, about 8×10^{-5} cm. The apparent striking field was decreased by activation from 5×10^6 to 0.6×10^6 volts/cm. When measurements were made at 250 volts, rather than 50 volts, the striking field in the active condition was only slightly higher, 0.8×10^6 volts/cm. Activation produces a lowering of the apparent striking field, regardless of the value of the applied voltage.*

1.2 *Arc Voltage*

The observed voltage across an arc at active palladium contacts agrees in general with that of palladium cathode arcs, which is about 16 (Reference 4, Fig. 7 and Reference 2, Table II), whereas the arc voltage of

---

* This apparent contradiction of the conclusion of F. E. Haworth[7] is clarified in Section 2.1.
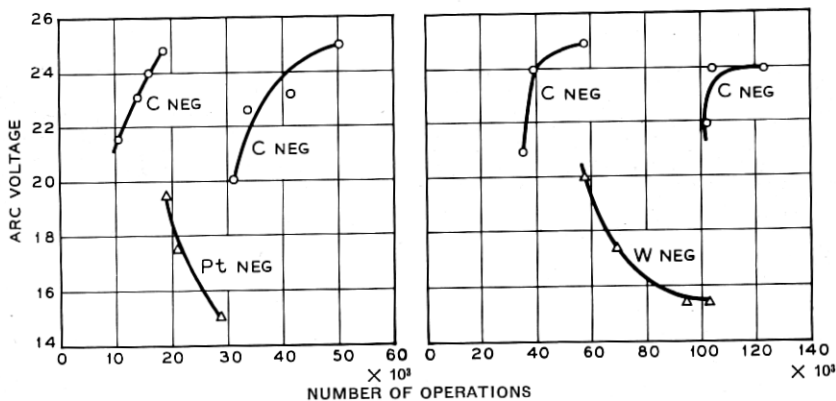
Fig. 3 — Measurements of arc voltage at cathode arcs between a carbon-platinum pair of electrodes, and between a carbon tungsten pair — at successive reversals of striking potential.

carbon is much higher and quite variable in the range from 20 to 30. One is tempted to conclude from this that the vapor in an arc between active palladium contacts is predominantly the metal of the electrodes, not carbon vapor. A more sound conclusion, however, as will be pointed out later, is that the source of electrons on the cathode of an active arc is palladium metal rather than carbon.*

When contact surfaces are very heavily carbonized, an arc voltage substantially higher than that characteristic of the metal of the electrodes is sometimes observed for a short time at the beginning and at the end of an active arc occurring at the discharge of a capacitor into an inductive circuit. An example of this is shown in the oscilloscope trace of Fig. 4. The higher arc voltage at the beginning of this arc, when the current was extremely small, is interpreted as the initiation of the arc between carbon surfaces, and the enhanced voltage at the end is evidence

---

* A very simple experiment has been carried out which proves conclusively that the character of an arc of the type which we call a cathode arc (see below, and Ref. 3 and 4) is determined by the properties of the cathode, and not by those of the anode. This is perhaps self evident, but a direct test is reassuring. The test is simply the observation that, for an arc of the cathode type between electrodes of different materials, the arc voltage is substantially the same as it would be if both electrodes were of the cathode material. The test is made by reversing the potential between the electrodes repeatedly, and after each reversal observing that the arc voltage changes gradually from that characteristic of the anode to that characteristic of the cathode. After each reversal the arc begins to clean from the cathode the anode material that was deposited there before the reversal, when what is now the cathode was the anode. Accompanying this cleaning, the arc voltage goes up or down until it reaches the value characteristic of the cathode itself. Measurements obtained in this way are reproduced in Fig. 3 for a carbon-platinum pair of electrodes and for a carbon-tungsten pair.

that when the current was again small the arc was localized at a new position on a fresh carbon surface so that it was again a carbon arc; during most of the arc time, when the current was larger, the cathode surface was maintained so free from carbon that the source of electrons at the cathode was palladium metal rather than carbon. For lightly carbonized surfaces, which may be just as active as judged by arc duration or any other test that we know of, no such enhanced arc voltage at the beginning or at the end of an arc has been observed. It may well be that for lightly carbonized surfaces the arc voltage is characteristic of carbon for a time too short to be detected by this crude means.

1.3 *Minimum Arc Current*

The current at which an arc goes out is readily found by observing on an oscilloscope the potential across closing contacts discharging a capacitor through a non-inductive resistor R. At extinction, the potential rises from the arc voltage v to that across the capacitor V_1. The minimum arc current is then $(V_1 - v)/R$. An oscilloscope trace showing such a determination of minimum arc current at the arc initiation potential of 400 volts is reproduced as Fig. 5. (See also Reference 2, Fig. 5 and

Fig. 4 — Oscilloscope trace representing the voltage across an arc at the closure of very heavily carbonized electrodes. Discharge through an inductance of 10^{-4}h of a capacitor of 10^{-8}f charged to 50 volts. Near the beginning and near the end of the arc the source of electrons at the cathode was a carbon surface.
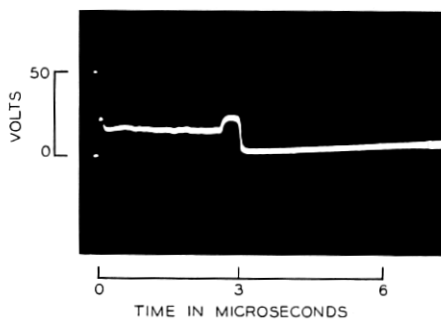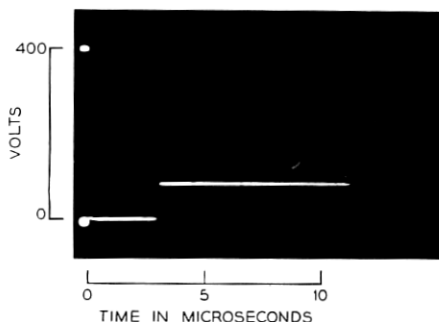

Fig. 5 — Voltage across clean palladium contacts when a capacitor charged to 400 volts is discharged through a resistor of 200 ohms. The closure arc went out at the minimum arc current 0.42 amp.

Reference 8, Fig. 1). The minimum arc current is much lower for active contacts than for inactive or clean contacts, and one can perhaps think of the decrease of the minimum arc current for noble metal contacts from a value of the order of 1 ampere for clean surfaces to 0.1 ampere or less for active surfaces as the chief characteristic of activation.

1.4 *Erosion*

Active contacts of palladium and of silver transfer metal in quite different ways. The transfer at active silver contacts is the more complex, and for this reason the transfer that occurs at active palladium contacts
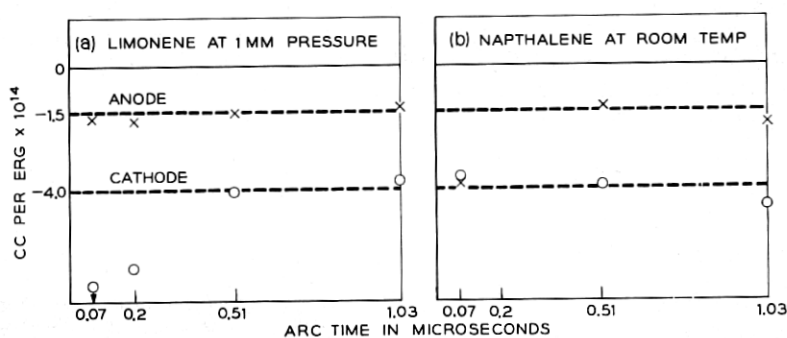
Fig. 6 — Results of measurement by weighing of the erosion of palladium electrodes produced by active arcs in limonene vapor (a) and in napthalene vapor (b).

will be taken up first. The behavior of platinum is in general like that of palladium, and gold is like silver.

1.4 (a) Palladium and Platinum. It is found that arcing on closure at active contacts of palladium or platinum causes loss of metal at the cathode of the order of 4×10^{-14} cc/erg. The anode often loses metal also, but the loss at the anode is considerably less and may be zero in some cases. The results of two sets of measurements upon active palladium contacts are plotted in Fig. 6. These data represent changes in volume (calculated from weighings) per unit of arc energy after repeated arcs in limonene vapor at a vapor pressure of 1 mm Hg, Fig. 6(a), and in the vapor of napthalene saturated at room temperature, Fig. 6(b). Tests were made by closing electrodes to discharge on each closure a properly terminated fixed length of cable charged always to 200 volts, to give in each case a constant arc current of 4 amperes, with the arc lasting for the time determined by the cable length. For the shortest arc time, the energy of

each of the individual arcs was 40 ergs, and for the longest arc time 600 ergs. The results indicate no significant variation of the erosion per unit of energy over this range.

There is some evidence that arcs at the break of active palladium surfaces give significantly lower cathode erosion per unit of energy (1 or 2 $\times$ 10^{-14} cc/erg) than do arcs at closure. The reason for the difference is not clearly understood, but widely different currents and electrode separations may be significant factors.

By examining contacts of palladium or platinum after many active arcs (on either break or closure), it is found that the erosion tends to be uniform over the surface, wearing each electrode down smoothly, with much less loss from the anode than from the cathode. This type of wear is quite different from that produced by arcs at clean surfaces. Erosion by arcs at clean surfaces always gives a mound of metal on one electrode, with a corresponding pit in the other; the loss of metal from one electrode is not appreciably greater than the gain by the other, the entire erosion consisting simply of transfer of metal between the contacts.

Now the inactive arcs at clean surfaces are known to be of two types which have been called "anode arcs" and "cathode arcs."[3, 4] In anode arcs, the transfer of metal is about 4 $\times$ 10^{-14} cc/erg and is from anode to cathode, with a resulting pit in the anode and a matching mound on the cathode (Reference 9, page 1085–1086). In inactive cathode arcs, measurements made in the same way and not yet published have shown that the transfer is smaller — about 1 $\times$ 10^{-14} cc/erg — and is in the opposite direction, from cathode to anode, with a resulting pit in the cathode and a matching mound on the anode.[10] It will be shown later, Section 2.4(a), that arcs at active palladium surfaces are of the cathode type, each individual arc being not readily distinguishable from an inactive cathode arc in the effect it produces on the cathode surface. The reason for the net cathode loss being greater in an active cathode arc than in a cathode arc at clean surfaces is due, at least in part, to some reverse transfer in an arc at clean surfaces.

1.4 (b) Silver and Gold. The erosion of silver surfaces is quite complex, and an adequate description of all of the phenomena encountered is reserved for later publication.[10] A simplified description of the main features of the erosion of silver contacts is given here. Tests upon active gold contacts have been less extensive than upon active silver contacts, but as far as the observations go, gold has been found to behave just like silver.

At active silver surfaces the erosion is, in most cases, from the anode, as it is at inactive surfaces. The arcs are active anode arcs, see Section

2.4(b), which have never been observed at palladium contacts. The metal lost from the anode after a great many active anode arcs tends to be eroded smoothly over the entire surface, like the cathode loss in arcs of the cathode type at palladium contacts. At a moderate pressure of activating vapor, almost all of the metal eroded from a silver anode is transferred to the cathode, but at a high pressure much of it is lost. Whether the metal from the anode is transferred or lost is correlated with the amount of carbon formed by the active arcs; if the production of carbon is small, metal is transferred, but in the presence of much carbon, the metal does not stick to the cathode and is lost. The amount of carbon formed (in air) by active anode type arcs at silver surfaces is very much less than the amount formed by active cathode type arcs at palladium surfaces, and this difference accounts for the fact that a great deal of the eroded metal is transferred at active silver surfaces, although there is always very little transfer at active palladium surfaces.* The erosion of a silver anode by active anode arcs may be as great as 10^{-13} cc/erg, but is lower than this whenever the carbon formation is sufficiently slight to permit much transfer of metal.

Long, sustained break arcs at active silver surfaces become cathode arcs when the electrode separation becomes sufficiently great. Such arcs give cathode erosion resembling that at active palladium surfaces. For a long sustained break arc, the cathode erosion suffered when the electrode separation becomes very large may be greater than the anode erosion occurring when the electrodes are closer together, so that the net loss from the cathode may be the greater. There may even be a small net anode gain.

Measurements of transfer at electrical contacts have sometimes been very confusing in the past, both because of their complexity and because of their apparently erratic character. Now, with well developed insight into the mechanism of short arcs, this complexity of transfer and its varied character have been most useful in improving our understanding of short arcs and of the transfer of metal to which they give rise.

The over-all picture of activation will be given in the following pages.

2. INTERPRETATION OF ACTIVATION

After one has concluded that activation is due to solid carbonaceous material, it is natural that tests should be made upon contacts of solid

---

* At extremely low pressures of activating vapor, active anode arcs at silver surfaces may not only transfer to the cathode practically all of the metal lost from the anode, but the type of erosion may even be changed to the mound and pit type characteristic of inactive arcs.[1]

carbon, and upon metal surfaces on which carbon particles have been dusted. The results of these tests have supplemented measurements upon active noble metal contacts and have led to a great increase in our knowledge of activation. In fact they open the way to a fairly thorough understanding of the subject.

2.1 *Striking Field*

Five different experiments have been carried out, which were designed to discover the reason for the low striking field at active contacts. Although the results of these experiments do not establish the reason for the low striking field in any definitive fashion, they do lead to an explanation which seems entirely satisfying.

The simplest of these experiments has already been reported at the end of Section 1.1. It is the observation that the striking field at active contacts is much the same at different striking voltages, of course below air breakdown only.

In another experiment, not heretofore published, W. S. Boyle and P. Kisliuk produced active spots at various points along a palladium wire. The wire, which lay on the axis of a glass cylinder, was made active at these selected points by repeated short arcs in an atmosphere containing limonene vapor. The other electrode was operated by an electromagnet outside the cylinder, with the magnet arranged so that the electrode could be placed at any location along the wire or withdrawn completely at any time. After activating a number of points, as determined by continuous oscilloscopic observation, the cylinder was exhausted and field emission currents were drawn from the wire to the cylinder. From observation of a fluorescent coating on the inside of the cylinder, it was found that the positions along the wire, which gave the largest currents, were quite unrelated to the active spots. From this experiment, one can conclude that the work function of active spots along the wire was not lower than the work function of other parts of the wire, and also that there was no significant enhancement of field emission at these spots because of roughness. Thus, the activation of contacts by organic vapors is *not* due to enhanced field emission currents because of lowering of the work function or because of greater surface roughness.

In a third experiment by F. E. Haworth,[7] measurements were made of the electrode separations at which an arc strikes between a palladium electrode and a smooth palladium surface upon which carbon particles had been deposited. For this experiment, solid carbon particles of fairly uniform size were obtained by blowing air at a low controlled rate

TABLE I — EFFECT OF CARBON PARTICLES UPON
STRIKING DISTANCE

Range of Particle Size (by microscopic measurement)	Average Striking Distance at 50 Volts	Apparent Striking Field
No Particles	0.10×10^{-4} cm	5×10^6 volts/cm
0 to 1 $\times$ 10^{-4} cm	1.4	0.36
0 to 2.5	2.5	0.20
4 to 5	4.3	0.12

through agitated carbon dust and collecting the particles that had been carried upward for a considerable distance in the air stream. The time of deposition of these particles upon the smooth surface was adjusted to give an average distance between particles of about 10 times their diameters. The smooth palladium surface with a fairly uniform, but sparse covering of carbon particles was made the cathode in measurements of striking distance by the oscilloscope method, Section 1.1. For a particular size of particle, 100 measurements were made of striking distance, each measurement at a different point on the surface, so as not to include any measurement of striking distance at a place on the surface where the original particles had already been burned off.* Table I gives the ranges of particle size as found microscopically and the corresponding average measured values of striking distance. The increase of striking distance was just equal to the particle size. At each arc, a particle was destroyed so that the time to closure measured on the oscilloscope corresponded, not to the true striking distance, but to the distance from the anode to the cathode surface upon which the particle rested. The electric field at which the arc struck was very much higher than the calculated values of the third column of Table I, and was not significantly different from the striking field for inactive surfaces.

In the fourth experiment, the striking field was measured between electrodes of solid carbon. One of these was mounted upon a cantilever bar in such a way that it could be moved through extremely small measured distances by pushing on the end of the cantilever bar using a micrometer screw (Reference 4, page 33). The zero point was found by touching the contacts through a high resistance galvanometer circuit; then the contacts were separated and the striking distance found after applying the voltage. Measurements made in this way by M. M. Atalla (Reference 11, Table I) have given, for the striking field for carbon elec-

---

* A correct measure of striking distance is obtained only when the arc energy is sufficient to burn up the carbon particles completely. No appreciable mound of metal is thrown up to falsify the distance measurement, because the arcs are of the cathode type, see Section 2.4(a).

trodes, 2.4×10^6 volts/cm, and our unpublished measurements agree with this. The striking field for carbon surfaces is thus only a little less than that found for cathode arcs at clean metal surfaces (Reference 4, Fig. 8), and very different from the field at which arcs strike between active surfaces.*

In another experiment, tests were carried out upon carbon particles in the 4 to 5×10^{-4} cm range of diameters, deposited sparsely upon a palladium surface as before. A careful comparison was made of the electrode separations at which an arc struck at 50 volts and at 250 volts. At the higher voltage, the distance was greater than at the lower voltage by the factor of only 1.3, offering confirmation that the isolated carbon particles act chiefly as chunks of material, partially closing the electrode gap.

The one way in which the carbon that produces activation differs from other carbon, and in particular from small carbon particles dusted sparsely upon a smooth metal surface, is in the very large number of its particles and in its state of subdivision. This gives an eminently plausible clue to the great electrode separation at which breakdown occurs between active surfaces. According to this model, breakdown occurs at a great separation between active surfaces because, at the electric field corresponding to this separation, electrostatic forces become sufficient to cause motion of small particles which decreases the separa-

---

* In measuring the striking field at carbon surfaces for low voltages by the oscilloscopic method, a value of the order of 0.6×10^6 volts/cm was found earlier (Reference 6, Table I). This result was certainly in error, because of burning of carbon in the arc, so that the separation of the electrodes when the arc ended was greater than it was at the arc initiation.

To check this explanation of the earlier incorrect result, an experiment was carried out in which the time to closure for carbon electrodes was measured as a function of the energy in the arc. In successive tests, a number of different capacitors, each charged to 50 volts, were discharged on the closure of carbon electrodes. The time to closure was found to increase progressively with capacitance for the values 10^2, 10^3, 10^4 and 10^5 $\mu\mu f$. Carrying out the measurements many times and taking average values, it was found that the time to closure increased linearly with the cube root of the capacitance. This suggests strongly that a hole was being burned in one of the electrodes and the increased time to closure was just the time for one electrode to move the depth of the hole. A quantitative value for the volume of the hole can be obtained from the data, on the basis of an assumed hole shape. In earlier work (Reference 9, page 1088), a pit on a metal electrode was assumed to be a spherical segment with the depth equal to one-half of the pit radius. Making the same assumption for the hypothetical hole in the present tests, and assuming an electrode velocity on closure of 30 cm/sec, it turns out that the relationship between volume of the hole and energy of the arc is $V = 4.5 \times 10^{-12}$ cm³/erg. The agreement of this result with that for the erosion of the metal anode in an anode arc (Reference 9, page 1088), is remarkable and must be largely fortuitous. The agreement does, nevertheless, make almost certain that burning of one of the electrodes (the cathode, as we know from other work) is the reason for the oscilloscopic method giving incorrect values for the electrode separation at which an arc strikes between carbon electrodes (Reference 6, Table I).

tion. The experimentally observed field of 0.6×10^6 volts/cm is the field at which this motion becomes appreciable for the very small sooty particles. With the start of motion of this sort the field is increased, and further motion is assured making the situation unstable. The gap is greatly decreased in length before *electrical* breakdown takes place, and the field at electrical breakdown is probably as high as it is at any carbon surface.

2.2 *Arc Voltage*

At the beginning of an active arc, at least one carbon particle is always exploded by the arc current, but only when the surface is very heavily carbonized is an enhanced arc voltage observed, Fig. 4. It must not be thought that the higher arc voltage occasionally found at the beginning of an arc is to be attributed directly to the presence of carbon vapor in the arc during its early stages, because carbon does not have an exceptionally high ionization potential. P. Kisliuk has shown[12] that, in a field emission short arc, the arc voltage should be just slightly larger than the sum of the ionization potential of the metal of the electrodes and of its thermionic work function. Now this result holds quite well for a number of different metal arcs, but does not hold at all for carbon. The short carbon arc is apparently of a different type, and has no well defined arc voltage. On the other hand, although carbon, unlike the noble metals, gives out thermionic electrons copiously long before it is hot enough to vaporize, a true thermionic arc cannot have the enormous current densities that occur in short arcs. (It does not seem impossible that thermionic emission may help to maintain an arc when the current is lower near its end.) The high arc voltage at the beginning and end of an active arc between heavily carbonized surfaces may be due to a dearth of positive ions, requiring a higher applied field to maintain the field emission. In any case, it is like the higher arc voltage of carbon which we do not understand. When the higher arc voltage is not detected, the vaporization of metal must be profuse, and only when vaporization is reduced, as it is when the current is very small near the beginning and end of an arc at the discharge of a capacitor into an inductive circuit, is the higher arc voltage observed. On rare occasions heavily carbonized surfaces show a suddenly enhanced arc voltage for a short interval near the middle of an arc. That this should occur very much less often than at the beginning or end of an arc is understandable.

The observation that the arc voltage sometimes becomes high near the end of an arc suggests strongly that an active arc is moving continually during its life. Only when the current is insufficient to vaporize carbon and underlying metal freely, and thus to maintain the large ion

density necessary for the low voltage field emission arc, does one observe the high and erratic arc voltage characteristic of carbon.

2.3 *Minimum Arc Current*

Values of minimum arc current for carbon electrodes have already been published. They are of the order of 0.02 to 0.06 ampere and agree fairly well with measurements of minimum arc current for very active metal contacts (Reference 2, Table V). The very low value of the minimum arc current for carbon, either in solid form or dispensed upon the surfaces of active contacts, is related to the low electrical and thermal conductivities of carbon. These low conductivities permit explosion of carbon particles on the cathode by currents too small to vaporize any metal. It has already been pointed out that it is this very low value of minimum arc current which accounts for the greatly enhanced energy that is dissipated at active relay contacts.

From the low value of minimum arc current for active surfaces, one concludes that near its end an active arc is always located at a fresh point on the electrode surfaces, one from which carbon was not burned off earlier in the life of the arc. It had already been concluded from occasional high values of arc voltage near the end of an active arc that this is sometimes true, but the minimum arc current values extend this earlier conclusion to indicate that it is *always* so. An active arc cannot remain in a fixed position as does an inactive anode arc (For example, Reference 4, Fig. 1). The implication is thus suggested that any arc between active palladium contacts is a cathode arc. Further presumptive evidence for this is, of course, furnished by the very much greater electrode separation in the case of active arcs; it is well known[13] that large distances favor cathode arcs, because at great distances the anode cannot be efficiently heated by electron bombardment.

The interpretation of minimum arc current of active cathode arcs to which we have been led can be written down in words, but we have not succeeded in any quantitative formulation. It is well known that every cathode arc is made up of a great number of small arcs moving continually over the electrode surfaces and exploding one point, or one particle after another on the cathode.[3, 4] In the case of an *active* arc, the end comes when the current gets so low that it will no longer explode a carbon particle, or when no suitable particles are available.* The much

---

* This is a necessary criterion for the end of an active arc only in the case of very short arcs. For electrodes that are being pulled apart to break a current larger than the minimum arc current, an arc will, of course, finally fail because of the great electrode separation, even though the current is above the minimum arc current, as in the final failure of the arc in the oscilloscope trace of Fig. 1(b). For inactive anode arcs the minimum arc current arises in a quite different way and has been interpreted in fairly satisfactory quantitative fashion.[14]

higher minimum arc currents for cathode arcs at clean surfaces is attributed to the higher thermal and electrical conductivities of metals and to the absence of loose material making poor contact with the surface. This picture is supported by the observation that metal contacts are made temporarily active by almost any kind of loose surface particles of very small size (Reference 2, Page 961).

2.4 *Erosion*

2.4(a) Palladium and Platinum. Further evidence that an active arc at palladium or platinum surfaces is always a cathode arc is furnished by the fact that the cathode loses much more metal in an active palladium arc than does the anode. (See also Reference 4, Table I).

The direct way of proving that an active arc at palladium or platinum surfaces is a cathode arc would, of course, be microscopic examination of the contact surfaces after a single arc. This is not practicable because surfaces become active only after repeated arcs, but one can do what is apparently quite equivalent by looking at the damage done by a single arc to surfaces on which small carbon particles have been dusted. Experiments by Haworth do indeed prove that arcs at such surfaces are cathode arcs, even at the low striking potential of 50 volts, and when the maximum diameter of the carbon particle is only 1×10^{-4} cm. Fig. 7(b) is typical of many examinations by Haworth of palladium cathodes after a single arc at surfaces upon which carbon particles had been deposited. The striking potential was 50 volts and the capacitance that was discharged was $C = 10^{-8} f$, so that the energy $C(V_0 - v)v$ was 50 ergs. For comparison, photographs are reproduced in Figs. 7(a) and
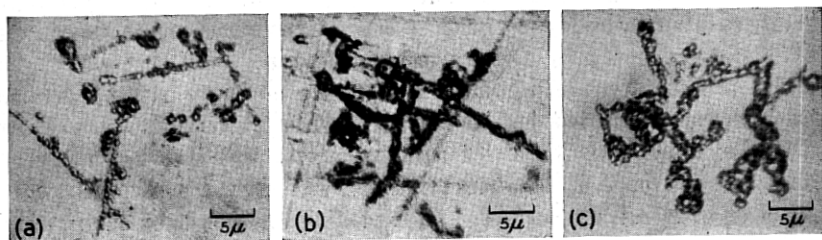
Fig. 7 — Photomicrographs of palladium cathode surfaces after single cathode arcs. The photograph of (b) was obtained after a 50 erg arc with 50 volt striking potential at a surface upon which carbon particles has been deposited. This sort of cathode damage was observed for all of the different sizes of carbon particles which were tested, even for the smallest having diameters of only 10^{-4} cm. The comparison photographs (a) and (c) represent the damage done respectively by 40 erg and 80 erg arcs to palladium surfaces without carbon particles, each arc at the striking potential of 400 volts.

7(c) which show clean palladium cathodes after constant current cathode arcs of 4 amperes lasting, respectively, for 0.072 microsecond and for 0.14 microsecond. The striking potential in each of these arcs was 400 volts, the total arc energy being 40 ergs and 80 ergs. The three photographs of Figs. 7(a), 7(b) and 7(c) represent then the markings made on the cathode by arcs of 40, 50 and 80 ergs respectively. The voltage of 400 was chosen for the two comparison photographs of Figs. 7(a) and 7(c) because this is above the minimum air breakdown potential, and arcs on closure at striking potentials above this value are known to be always cathode arcs (Reference 4, Fig. 4).

Cathode markings such as those of Fig. 7(b) are occasionally produced by arcs at 50 volts on relatively clean palladium surfaces. In general, however, an arc at this low striking potential between clean surfaces is an anode arc, leaving a single well defined pit on the anode, and on the cathode, a single roughened area with considerable metal spattered over from the anode (Reference 9, Fig. 6). While a cathode arc, making on the cathode the type of markings shown in Fig. 7, is rather rare between clean palladium surfaces at a striking voltage as low as 50 (Reference 4, Fig. 4) it is the usual kind of arc between surfaces upon which carbon particles have been dusted, and by implication, it is the sort of arc that occurs between active surfaces. That this arc should cause loss of metal from the cathode is clear from the photographs of Fig. 7, and from the fact that the damage done to the anode sometimes cannot be detected and is always rather slight.*[10] Between clean surfaces, this sort of arc occurs more frequently at higher striking voltages, and invariably on closure when the potential is above the minimum breakdown potential for air. It is the greater striking distance that favors the cathode type of arc, and for active arcs also it is just this enhanced electrode separation, resulting from carbon particles, which can be thought of as the reason for the arc being of this type. There is obviously a critical distance above which arcs are of the cathode type, and for palladium electrodes this critical distance is less than 1×10^{-4} cm. Earlier experiments can be used to define this critical distance better. From the data of Fig. 8 of Reference 4 it appears that this distance for palladium is about 0.5×10^{-4} cm.

Markings made on the cathode by a single arc between active palladium surfaces are doubtless not easily distinguishable from those resulting from a single arc that has been constrained to be of the cathode type only by a high striking potential and the resulting great electrode separation. Nevertheless, when many times repeated, the over-all results

* See the footnote relating to Fig. 3, see page 776.

of cathode arcs between active surfaces, and of cathode arcs between inactive surfaces, are markedly different, as has been pointed out earlier.

The fact that erosion by inactive, or clean-surface, arcs takes the form of a mound on one electrode and a crater in the other means simply that successive arcs tend to occur at the same place on the electrode surfaces. This is because each arc must occur where the electric field between approaching electrodes is highest, and the roughening from one arc will be the site of the highest field before the next discharge occurs.

With carbon particles on the surface, the situation is different. In the case of active cathode arcs, the electric field between approaching electrodes is highest at a point where a group of carbon particles, perhaps pulled up by electrostatic forces, closes a large part of the electrode gap, and an arc must necessarily strike at such carbon particles. In the activating process, carbon is always being formed by an arc, but only at its periphery; at the hottest parts of the arc, carbon which was formed earlier, is completely removed. Not only does each arc move during its lifetime, continually searching out new carbon which was formed earlier, but a later arc will not strike at a point from which carbon was just cleaned by an earlier arc. This restless movement from point to point results finally in erosion that spreads over the surface in a way which is likely to be statistically uniform.

2.4(b) Silver and Gold. Although the character of the erosion at silver (and gold) surfaces, and also its magnitude, are drastically altered by activation, Section 1.4(b), the "direction" of the erosion is still in most cases that characteristic of anode arcs. The predominant loss of metal on closure is usually from the anode for active silver electrodes at voltages too low for air breakdown, just as it is for inactive silver electrodes at low striking voltages. This is in marked contrast to the behavior of palladium surfaces when they become active; for active palladium surfaces, loss of metal is always chiefly from the cathode. The behavior of silver leads naturally to the hypothesis that even when the surfaces are active arcs at low striking voltages are anode arcs, as they are when the surfaces are inactive.

This hypothesis has been subjected to test by F. E. Haworth by the same method used in the case of palladium surfaces. Small carbon particles were dusted on a polished silver surface, and the surface was examined microscopically after it had been subjected to a single arc under the circuit conditions used in similar tests at palladium surfaces. When the maximum particle diameter was 5×10^{-4} cm, it was found from the microscopic examination that all arcs were of the cathode type (see, for example, Fig. 7), but when the maximum diameter was 2.5×10^{-4}

cm all arcs were of the anode type with the characteristic pit on the anode and a roughened spatter of metal on the cathode. It is clear from these tests that active arcs at silver surfaces are of the anode type if the layer of carbonaceous material responsible for activation is not heavy enough to permit an arc to strike at a separation greater than 2.5×10^{-4} cm, but that they are of the cathode type when the layer is sufficiently thick to permit arcs at 5×10^{-4} cm. The electrode separation at which an arc takes place determines the character of the arc.* The critical distance for silver surfaces lies between 2.5 and 5×10^{-4} cm. Erosion at active silver surfaces on closure must be predominantly from the anode unless the layer of activating carbonaceous material is so heavy that arcs strike when the electrode separation is greater than 2.5×10^{-4} cm.

After long continued operation at very high pressures of activating vapor it is sometimes, but not always, found that arcs on closure result in erosion that is chiefly from the cathode. The conclusion drawn from these measurements is that the striking distance at active surfaces on closure at low voltages can sometimes, with considerable difficulty, be made greater than 2.5×10^{-4} cm. Unless great pains are taken to keep surfaces very heavily carbonized, the striking distance on closure at active surfaces at low voltages is of the order of 2.5×10^{-4} cm or less. On closure at voltages that give air breakdown, the erosion of silver is predominantly from the cathode whether the surfaces are active or inactive, because the minimum distance for air breakdown (15×10^{-4} cm) is much above the critical distance for silver.

On breaking active silver contacts in an inductive circuit, erosion is chiefly from the anode unless the arc lasts long enough for the electrode separation to exceed the critical distance of 3 or 4×10^{-4} cm. During the time an arc persists at distances greater than this, the loss is predominantly from the cathode. For velocities typical of a U-type relay, the critical distance may be reached in 10 or 20 microseconds, and equal erosion may be attained in a time of the order of 40 microseconds. If the partial pressure of activating vapor is very high and the surfaces unusually heavily carbonized, much of the eroded metal will be lost. Under more usual conditions of lower vapor pressures, most of the eroded metal is transferred to the opposite electrode. Thus there may be a critical arc duration for which the erosion of each silver electrode is nearly

* Similar tests were carried out upon polished gold surfaces upon which sparse layers of carbon particles had been dusted. For particles of maximum diameter 2.5×10^{-4} cm all arcs were found by microscopic examination of the electrodes to be anode arcs, and for particles in the range of diameters from 4 to 5×10^{-4} cm all arcs were found to be of the cathode type. These results are identical with those found for silver.

zero, and for an arc lasting longer than this time, there may be cathode loss and actual net gain by the anode. No such balancing effect is possible for palladium.

2.4(c) Anode Arcs and Cathode Arcs. The model of an active cathode arc to which we have been led seems fairly clear and rather well established, but the model of an active anode arc is more poorly defined. From electron micrographs of the damage done to the cathode by an arc of the cathode type (Reference 4, Fig. 3), it is known that an arc of this type is intermittent, striking over and over again. In an *active* arc of the cathode type, a carbon particle on the cathode is blown up each time the arc strikes, but always there is metal vaporized from the cathode at the site of the particle and the amount of vaporized cathode metal is greater than the amount of vaporized carbon, so that the arc is an arc in metal vapor.

We know less of an active anode arc, and it may well be that some experiments described above seem to imply a model which is not consistent with other observations. The facts that we know are, that at a lightly carbonized silver surface an arc strikes at an electrode separation much greater than the separation at which it would strike if there were no surface carbon, that the resulting arc produces loss of metal predominantly from the anode, and finally that the minimum arc current is very low. The arc is a true anode arc by our implied definition of such an arc, yet it is certainly an active arc. When the arc current is high, a crater is being produced on the anode as in the case of an inactive anode arc, and also in the case of an active anode arc at a surface on which a few carbon particles of diameters not greater than 2.5×10^{-4} cm have been dusted. When the current becomes too low, or is too long sustained, one presumes that the arc is extinguished as in the case of inactive anode arcs.[14] It may then restrike at another carbon particle. One speculates that an anode arc is intermittent when the arc current is very low, being initiated over and over again as are cathode arcs throughout their lives. A carbon particle is exploded repeatedly on the cathode. Yet, because the separation is less than the critical distance, at each re-ignition of the arc, metal vapor is derived from the anode rather than from the cathode, and possibly the over-all anode erosion results in a single anode pit produced when the current was sufficiently high, plus an array of very small anode pits formed while the current was small and intermittent. This model must be regarded as a plausible speculation without support in direct observation. The existence of the active anode arc is well established although the course of such an arc is speculative.

Some insight into the reason for the existence of a critical electrode

separation, determining whether an arc is of the anode type or of the cathode type, can be obtained from a simplified picture of the evaporation of metal in an arc. One assumes a field emission arc just being established between a cathode point and the anode surface, the initial ions being supplied by oxygen and nitrogen of the air with as yet no metal vaporization. The electrons from the point are assumed to travel in straight lines to the anode and cover uniformly an area $\pi(L \tan \theta)^2$ where L is the electrode separation. If i is the total electron current and v the arc voltage, the power density on the anode is $iv/\pi(L \tan \theta)^2$, decreasing with increasing separation. A lower limit for the power put into the cathode point is $(\rho/d)i^2$ where d is the diameter of the point and ρ the resistivity of the cathode metal. Whether the anode begins to vaporize before the cathode, or vice versa, is determined in some way by the ratio of these quantities $BL^2\rho/d$, where parameters unimportant for the present discussion are grouped together in B. For $L^2\rho/d$ greater than some critical value, we shall have cathode evaporation and an ensuing cathode arc, but for $L^2\rho/d$ less than this value, the anode will begin to evaporate first with a resulting anode arc.

The resistivity that probably counts is the resistivity at the melting point. At the temperature of melting, the resistivity of palladium is nine times greater than that of silver. Thus one can expect from this simple model that the critical distance which determines whether an arc is of the cathode or anode type will be three times greater for silver than for palladium. If a silver point is less sharp than a palladium point, d greater for silver than for palladium, as it may be because of the well known property of silver atoms to migrate at room temperature, the factor will be greater than this value of three. Now we have the experimental estimate of 0.5×10^{-4} cm for the critical distance for palladium. This simple theory predicts that the critical distance for silver shall be greater than this by a factor of three, or perhaps more. The experimental critical distance for silver is between 2.5 and 5×10^{-4} cm.

Quantitative measures of the erosion of contacts of palladium and of silver, which were given in Section 1.4, are collected in Table II for ready reference.

From additional experiments, not reported in Section 1.4, it is known that these values of transfer apply approximately for potentials both above and below the minimum breakdown potential for air. Not all types of arcs occur, however, for both palladium and silver at potentials above and below the minimum breakdown potential. At potentials that give air breakdown, all arcs on closure are of the cathode type for both metals whether active or inactive. At potentials that do not give air

TABLE II— LOSS OR GAIN OF METAL FROM ARCING FOR
PALLADIUM OR SILVER

(in units of 10^{-14} cc per erg)

	Cathode	Anode	
Inactive Arcs			
Anode Type............	4 gain	4 loss	mound and pit
Cathode Type.........	1 loss	1 gain	mound and pit
Active Arcs			
Anode Type............	(loss)	10 loss*	smooth erosion
Cathode Type.........	4 loss†	(loss)	smooth erosion

* This high figure refers to arcs on closure at very heavily carbonized surfaces; for lightly carbonized silver surfaces the anode loss is less and most of the metal is transferred to the cathode.

† This figure refers to arcs at closure of palladium surfaces. The rate of cathode loss at break of palladium surfaces is significantly less, as pointed out in Section 1.4(a); and in cathode arcs at active silver surfaces the rate of loss is still less.

TABLE III— OCCURRENCE OF DIFFERENT TYPES OF ARCS

	Below Air Breakdown	Air Breakdown
Inactive Arcs		
Anode Type...............	Palladium, Silver	No*
Cathode Type.............	Palladium Only	Palladium, Silver
Active Arcs		
Anode Type...............	Silver Only	No*
Cathode Type.............	Palladium, Silver	Palladium, Silver

* This applies to arcs at closure. Between separating electrodes, air breakdown often occurs when the electrodes are too close together for air breakdown over the shortest path. Under such conditions, arcs between silver surfaces, which are *initiated* by air breakdown, can become anode arcs, and the transfer resulting from such arcs gives dominant anode erosion.

breakdown, all inactive arcs at silver surfaces are of the anode type, and active arcs of the anode type occur for silver only. These facts are tabulated for reference in Table III. All of them are at once predictable from the values of the critical distances for palladium and silver, and from knowledge of the way in which breakdown distance is changed by activation.*

* The difference between the transfer behavior of palladium and silver electrodes in the active condition suggested to R. H. Gumley that the damaging effects of activation can be greatly reduced by constructing a relay with negative contacts of silver and positive contacts of palladium. He tried out this idea and found it to be effective. In the absence of activating vapor, a relay in which the negative contacts are silver and the positive contacts palladium has no merit over a relay in which all contacts are palladium, but when vapor is present, the erosion can, under some circumstances, be much reduced by replacing the negative palladium contacts by silver contacts.

The sort of erosion produced by the different types of arcs is shown in the somewhat conventionalized sketches of Fig. 8. These sketches represent cross-sections of the square mating areas (about 1.3 mm on a side) of heavy type U relay palladium contacts. The contact contours are drawn to scale after the metal transfer resulting from repeated arcs with a total energy of 10^8 ergs, using the values of Table II to convert this energy into volumes of metal. The mounds and pits produced by inactive anode arcs and by inactive cathode arcs are assumed to be spherical segments, each having a height equal to half its radius. The smooth erosion resulting from active arcs would have depths which do not show up at all on the scale of this figure. For each electrode in each of the four cases, the erosion is less than 2 per cent of the total volume of the metal of the contact, and represents a fairly early stage in the expected contact life. The electrode separations at which arcs occur correspond respectively to fields of 8×10^6, 4×10^6 and 0.5×10^6 volts/cm. The striking voltage is assumed to be 50 and the separations are drawn
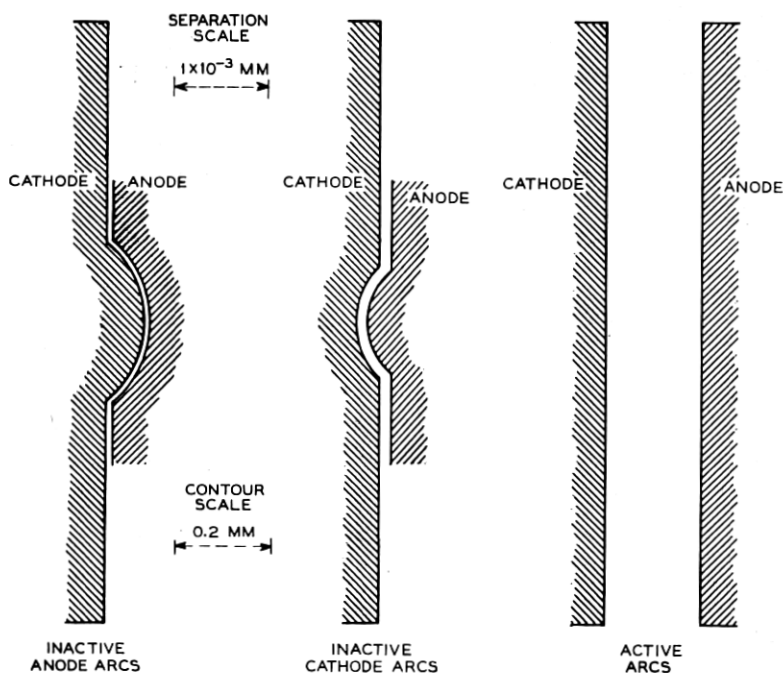

Fig. 8 — Erosion produced by anode arcs at clean surfaces, by inactive cathode arcs and by active arcs of either type, the total energy in each case being 10^8 ergs. The electrode separations at which these arcs strike correspond to 50 volts and are represented here on a greatly expanded scale.

to a scale 200 times greater than the scale of the electrodes. For potentials that give air breakdown, the scale of separation would be changed by large factors.

The sketches of Fig. 8 are of assistance in understanding some of the qualitative erosion differences observed in the four types of arcs (Table II). All of the metal lost from one of the electrodes in an inactive arc of either type comes from the surface of a pit, and from the figure it seems clear that all of it must obviously be intercepted by the other electrode because there is no way for it to escape. This is true even for the case of air breakdown where the electrode separation is much greater ($\sim$15 $\times$ 10^{-4} cm). But for active arcs some of the metal coming from each electrode is permanently lost and not transferred to the other side, even though the separation is much less than it is for the case of air breakdown. The permanent loss of metal in the case of active arcs is due to the presence of carbon. When there is carbon on the surfaces, the metal simply does not stick. Chemical analyses have been made of the black powder produced by active cathode arcs at palladium surfaces, and these analyses show palladium metal as well as carbon. The palladium metal lost from the electrodes turns up in this black powder rather than at new locations on the electrodes.

At palladium surfaces, the net loss amounts to most of the eroded metal, but at silver surfaces, most of the metal is transferred. This difference is related to the amount of carbon left on the surfaces. Carbon is found much more abundantly on palladium than on silver, which accounts for the failure of eroded metal to stick to palladium. The greater net carbon production on palladium is due to the low efficiency of cathode arcs (at active palladium surfaces) in burning carbon; the anode arcs, which occur in general at active silver surfaces, are more effective in burning off carbon. It is to be presumed that the amount of organic vapor decomposed per unit of energy at a silver surface is not so very much less than that decomposed at a palladium surface, even though the net carbon left on the surface is tremendously less in the case of silver.

3. RECAPITULATION

We are ready now to state briefly some of the conclusions about active arcs which have been developed above. All of the observations refer to contacts of palladium or of silver. Less extensive tests upon platinum and upon gold have indicated that platinum behaves the same as palladium, and gold the same as silver.

An active arc is an arc that strikes between one electrode and car-

bonaceous material lying upon the other. If one calculates striking field by dividing the potential by the separation between the metal electrodes, a very low value is obtained, but this is the field at which electrostatic forces cause movement of carbon particles to decrease the separation; the true field at which the arc finally strikes between carbonaceous material and the opposing electrode is not significantly lower than the striking field for arcs at clean surfaces. Some or all of the local carbonaceous material is burned up by the arc, and metal vaporized from one of the electrodes is soon fed into the arc so that for most of its life the ions of the arc are metal ions supplied by atoms from one or the other of the electrodes. This is true for even the most heavily carbonized electrodes.

There is a critical electrode separation, characteristic of the metal of the electrodes, which determines whether the arc is an anode type of arc with metal supplied by the anode or an arc of the cathode type with metal supplied by the cathode. If the separation is greater than this critical value the arc is a cathode arc, and less than this value an anode arc. This critical distance is about 0.5×10^{-4} cm for palladium electrodes and of the order of 3 or 4×10^{-4} cm for electrodes of silver. The ratio of these distances is somewhat greater than the ratio of the square roots of the electrical conductivities of the metals at their melting points. The critical distance for palladium is so small that all arcs at active palladium surfaces are cathode arcs. For silver, on the other hand, the critical distance is so large that most arcs at low voltages at silver surfaces are anode arcs. In any practical application of silver electrodes, the carbonaceous material formed is rarely or never in a sufficiently thick layer to result in cathode arcs for closure at low voltages. In the case of separating silver electrodes, an active arc may last until the electrode separation is beyond the critical distance for silver; the erosion occurring after this distance is reached is predominantly from the cathode, and the larger net loss may, on occasion, be from the cathode.

The erosion resulting from repeated arcing at active surfaces is different in character from that produced by inactive arcs. Inactive arcs give rise to a crater on one electrode and a matching mound on the other, with most of the metal from the crater transferred to the mound. Active arcs, on the other hand, produce smooth erosion without craters and mounds, often with considerable net loss of metal which appears mixed with carbon as a black powder. This smooth erosion is accounted for by the striking of each new arc on carbon formed by preceding arcs, together with the burning off of carbon at the center of each arc and the formation of new carbon around its periphery.

PART II — ACTIVATING CARBON

4. COMPOSITION OF ACTIVATING POWDER AND RATE OF PRODUCTION

Experiments have been carried out designed to discover the chemical composition of the carbonaceous material responsible for activation, how much is made per unit of energy in an arc, and where it is made. Now it has been pointed out above that the reason for the uniform erosion in an active arc is the burning off of this black powder by arcs and the consequent continual wandering of successive arcs always to neighboring spots from which the powder has not been burned. This burning off of black powder makes quantitative measurements in air of its rate of formation quite impractical. Activation in vacuum avoids the destruction by burning, and makes possible direct measures of rate of formation; in these tests, the chemical composition of the powder can be found also. All of the quantitative studies of activation in vacuum were made by P. Kisliuk, but the results have not been previously published.

In Kisliuk's experiments two electrodes, which were of platinum, were mounted in a glass chamber so they could be operated by the magnetic field of a coil placed outside the chamber, in the manner of a dry reed switch. The electric circuit was arranged to discharge on each closure a capacitor charged to a fixed voltage, with no current flowing in the circuit as the platinum contacts are separated. Air was pumped out and the contacts operated in benzene vapor at a constant rate, discharging the capacitor a convenient number of times per minute. Every experiment consisted of measuring the pressure in the system, from which was deduced the rate of disappearance of benzene and the rate of evolution of hydrogen resulting from its decomposition, hydrogen being distinguished from benzene by freezing out the latter in liquid nitrogen. The pressures were measured by an RCA thermocouple gauge (1946) which was shown in control tests not to produce benzene decomposition. The benzene, which had been distilled repeatedly to remove water vapor, was used at initial pressures not to exceed 10^{-2} mm Hg determined by a dry ice-acetone bath. The experimental arrangement is shown in Fig. 9.

4.1 *Composition*

In the first experiments with this system it was found, as had been expected, that with continued operation of the contacts in benzene vapor, the pressure rose steadily, although benzene continued to disappear. The pressure changes corresponded to the evolution of 3.2 ± 0.6 molecules of H_2 for each vanishing molecule of benzene, agreeing well with

the theoretical value of 3 for complete decomposition of benzene into carbon and hydrogen. The conclusion from this experiment is that the organic material in the black activating powder is just carbon. The precision allows one to say that, if there is any hydrogen at all left in the black powder, it does not exceed 2 hydrogen atoms for every 15 carbon atoms.

4.2 Rate of Production

In experiments in which the energy in individual arcs was varied, by using different capacitors in the range from 610 $\mu\mu f$ to 40,000 $\mu\mu f$ and by using the two potentials 58 volts and 232 volts, it was found that a particular arc energy gives the same carbon formation per erg whether the striking voltage is 232 or 58, from which one deduces that formation of carbon depends upon energy rather than upon capacitance or voltage separately. The amount of carbon formed per individual arc increases with the energy of the arc but not so fast as linearly. The experimental values M of amount of carbon formed can be related to arc energy E by the empirical formula $M = KE^{2/3}$, over the range studied from 5 ergs to 1,250 ergs. A tentative explanation of this $\frac{2}{3}$ power relation is given in the next section.

Starting with clean electrodes and measuring the total amount of carbon formed as a function of number of arcs, it was found that the rate of production of carbon is initially low but increases with time, soon
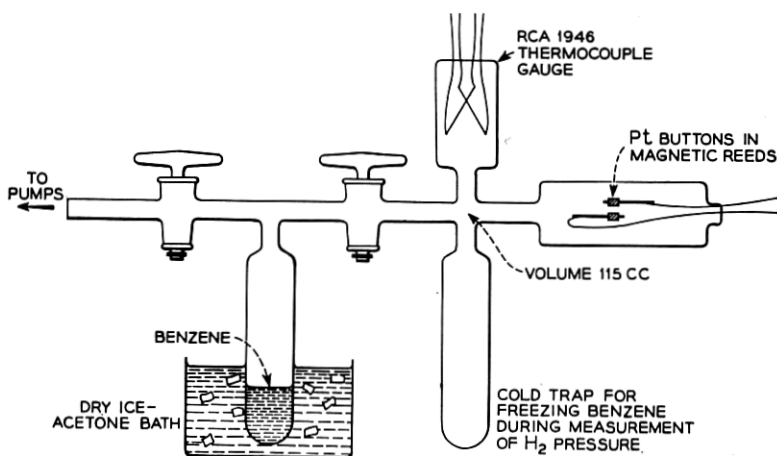

Fig. 9 — Diagram of apparatus used by P. Kisliuk in quantitative measurements of the decomposition of benzene vapor at arcing contacts.

becoming constant. One such set of measurements is plotted as Fig. 10. In this experiment the striking voltage was 232 and the energy in each arc 1,250 ergs. The final slope of the curve of Fig. 10 corresponds to the production of 4.5×10^{-11} gm of carbon per arc — 3.5×10^{-14} gm/erg, 1.8×10^9 atoms/erg — which is 0.04 carbon atom for every electron flowing in the arc, or the decomposition of 3.7×10^{11} benzene molecules per arc, 3×10^8 molecules per erg, or 70×10^{-4} molecule per electron. The lower slope, before the break in the curve, represents the decomposition of 1.1×10^{11} molecules of benzene per arc, or the production of 5×10^8 carbon atoms per erg.

From continuous oscilloscopic observations it was found that the contacts were inactive up to the point where the slope of the curve increased. Here they were slightly active, and beyond this point they were fully active, exhibiting the usual apparent low striking field and low minimum arc current. The amount of carbon required to make the contacts fully active was about 5×10^{-8} gm (2.5×10^{15} atoms) which, if it were in a single spherical speck, would have a diameter of 3.5×10^{-3} cm. Such a speck can be seen quite easily with the naked eye, although an actual deposit of this volume probably could not be seen without a microscope because of its dispersed state.

5. SURFACE ADSORPTION

5.1 Benzene Molecules on Contact Surfaces

In an early experiment, the rate of formation of carbon (from measured rate of evolution of H_2) had been found to be independent of benzene pressure down to the lowest pressure tested, which was of the order of 10^{-3} mm Hg. For this reason it was unnecessary to mention absolute pressures in describing the above tests. This lack of dependence on pressure suggests strongly that benzene had been adsorbed on the electrode surfaces and decomposed there, rather than in the space between the electrodes, and that the lowest pressure tested was sufficiently high to keep the surfaces completely covered. This tentative conclusion is confirmed by other considerations given below.

At the pressure of 10^{-2} mm Hg and an electrode separation of 10^{-4} cm, one calculates that only one electron in 3×10^4 can collide with a benzene molecule in the space between the electrodes in the experiment of Fig. 10. The discrepancy between the measured decomposition (70×10^{-4} benzene molecule per electron) and the possible frequency of collision (0.3×10^{-4}) is proof that most of the carbon responsible for activation comes from benzene adsorbed on electrode surfaces rather than from molecules in the space between them.

One gets some insight into the adsorbed films responsible for activation from estimates of the cross-section of an arc and of the amount of benzene adsorbed in a monolayer over an area of this size. A reasonable estimate of the number of molecules in a monolayer of benzene is 7 $\times$ 10^{14} cm^{-2} (Ref. 16), or 14 $\times$ 10^{14} cm^{-2} taking into account the two electrodes. Estimates of cross-sectional size have been published for anode arcs, but for cathode arcs the areas are quite different. Since all of the arcs after a surface has become active are certainly cathode arcs, our first concern is with the cross-sectional areas of cathode arcs. It has been observed that the over-all area of the cathode markings made by inactive cathode arcs increases somewhat less rapidly than linearly with total arc energy, and seems to be independent of arc current and arc duration except as they influence the total energy. In one series of experiments, the areas observed (Ref. 10) for low energy arcs corresponded to somewhat less than 10^7 ergs/cm^2, and to somewhat more than this value for high energy arcs. Assuming for an average value 10^7 ergs/cm^2, we obtain 1.2 $\times$ 10^{-4} cm^2 for the area of the arcs of the curve of Fig. 10.* This area should have adsorbed on it 1.7 $\times$ 10^{11} benzene molecules. The observed rate of decomposition is 3.0 $\times$ 10^8 benzene molecules per erg or 3.7 $\times$ 10^{11} molecules per arc. Looking at photographs such as those of Fig. 7, one does not feel at all confident that all of the surface in the over-all area of the arc ever became hot enough to decompose benzene. If all of it did become hot enough, the surface must, on the average, have been covered by 2 layers of molecules, and if all of the surface did not become sufficiently hot, by more than two layers. For lower energy arcs, when the number of benzene molecules decomposed per erg is appreciably greater, it is natural to assume that the surface must, on the average, be covered by a still deeper layer of benzene. At least part of the difference between the estimated thicknesses of the layers of benzene molecules for high energy arcs and for low energy arcs can, however, be attributed to the fact that the energy per square centimeter increases with increasing energy, 10^7 ergs/cm^2 being only an average value. The data indicate only that the adsorbed benzene layer is several (greater than 2) molecules thick.

The observed expression $M = KE^{2/3}$ of the above section, relating amount of carbon formed M to total arc energy E, can be accounted for if, in the particular experiment in which this relation was found, the over-all arc area increased with the $\frac{2}{3}$ power of the energy. In various tests

---

* One should note that the energy density measurements were made upon clean surface or *inactive* cathode arcs, but are being applied here to *active* cathode arcs. Some justification for this is afforded by the fact that the active 50 erg cathode arc of Fig. 7(b) had an over-all area of about 3 $\times$ 10^{-6} cm^2 giving for the energy density 1.5 $\times$ 10^7 ergs/cm^2.

it has been noted that area increases less rapidly than linearly with energy, but it is certain that no universal rule applies in all cases; for example, by restricting the total electrode area, the over-all arc area can be forced to be constant independent of energy.[10] One can conclude only that all of the facts are accounted for by a benzene layer several molecules thick on the electrode surfaces with decomposition by each arc of all of the benzene within its over-all area.

We are now in a position to consider the much lower rate of decomposition of benzene during the initial period before the electrodes became active. In Fig. 10, this lower initial rate is 1.1×10^{11} molecules per arc. This is somewhat less than the number of molecules calculated to lie in a monolayer on the surface covered by an arc. The area used in this calculation was that of a cathode arc, but it is well known that before contacts become active a large proportion of the arcs are anode arcs which have smaller areas (Reference 9, page 1088). The estimated area may, however, be about correct because in the case of an anode arc, carbon is decomposed by heat over an area larger than that of the arc itself.

Within the precision of the estimates we are able to make, it can be said that for inactive contacts operating in benzene vapor each arc decomposes a single layer of adsorbed molecules of benzene. After the contacts become active, the amount decomposed by each arc is greater and is the equivalent of several layers of molecules. It was surmised long ago that much of the vapor adsorbed on active contacts is held by carbon already on the surface rather than by the surface metal. The increased
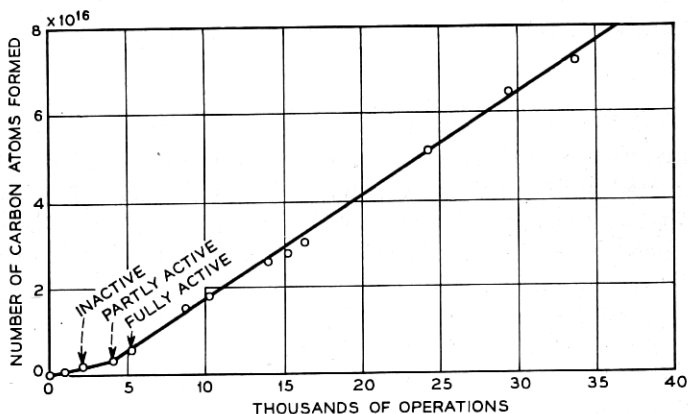

Fig. 10 — Measurements by P. Kisliuk of the amount of carbon formed at arcing platinum contacts, each arc 1,250 ergs. The final slope represents the production of 3.5×10^{-14} gm of carbon per erg of arc energy, or one benzene molecule decomposed for every 150 electrons flowing in the arc.

TABLE IV — BENZENE DECOMPOSITION IN ACTIVE AND INACTIVE ARCS

Measurements		1250 erg arcs (232 volts)	15 erg arcs (58 volts)
Carbon required for full activity	1	2.5×10^{15} atoms	No data
Carbon formed in active arcs	2	1.8×10^9 atoms/erg	7×10^9 atoms/erg
Carbon formed in inactive arcs	3	5×10^8 atoms/erg	No data
Benzene decomposed in active arcs	4	3.0×10^8 molecules/erg	13×10^8 molecules/erg
	5	70×10^{-4} molecule per electron	300×10^{-4} molecule per electron
Calculations			
Absorbed benzene in a monolayer (Ref. 16)	6	14×10^{14} molecules per cm²	14×10^{14} molecules per cm²
Benzene molecules struck in space (Compare lines 5 & 7)	7	0.3×10^{-4} molecule per electron at 10^{-2} mm Hg	0.03×10^{-4} molecule per electron at 10^{-3} mm Hg
Active Arcs			
Arc area at 10^7 ergs/cm²	8	1.2×10^{-4} cm²	0.015×10^{-4} cm²
Number of molecules in one monolayer on arc area	9	1.7×10^{11} molecules	0.02×10^{11} molecules
Decomposed per arc (from line 4)	10	3.7×10^{11} molecules of benzene	0.2×10^{11} molecules of benzene
Effective* thickness of adsorbed layer on basis of 10^7 ergs/cm²	11	2.2 molecules	10 molecules
Inactive Arcs			
Arc area	12	$<1.2 \times 10^{-4}$ cm²	
Number of molecules in one monolayer on arc area	13	$<1.7 \times 10^{11}$ molecules	
Decomposed per arc (from line 3)	14	1.1×10^{11} molecules	No data
Thickness of adsorbed layer	15	1 molecule	No data

* The benzene is probably adsorbed on spongy carbon of much greater true area.

adsorption for contacts already active is doubtless due to the greater surface area resulting from the presence of this carbon.

Many of the numerical values considered here are collected in Table IV for ready reference. These data refer to arcs at platinum surfaces. It is our present opinion that the amount of carbon formed at silver surfaces in similar experiments would be found to be only slightly smaller per unit of energy, although unfortunately no experiments were carried out upon silver.

5.2 *Inhibiting Surface Films*

One concludes from the above experiments that activation by benzene vapor is the result of firm adsorption of benzene molecules on the elec-

trode surfaces, with heat producing decomposition into carbon and hydrogen rather than evaporation of undamaged molecules. Surface films prevent such strong adsorption, and metals with surfaces that are normally covered by oxide films cannot be activated.

In some very recent experiments in extremely high vacuum, P. Kisliuk has found[17] that benzene molecules are strongly adsorbed upon a tungsten surface that is perfectly clean, but if there is on the surface just one single layer of oxygen molecules, benzene molecules are not adsorbed. M. M. Atalla has reported (Reference 5, page 1090), on the other hand, that tungsten (and nickel also) can be activated if the pressure of air is as low as 10^{-3} mm Hg. It seems probable that arcs at operating contacts remove adsorbed oxygen temporarily, and at sufficiently low air pressures this may be replaced in part by organic molecules rather than by oxygen.

Even at palladium surfaces, some cleaning by arcs seems to be necessary before benzene molecules can be adsorbed. This conclusion is reached in unpublished adsorption experiments carried out by W. S. Boyle upon palladium surfaces in air containing benzene vapor. In this work, two optically flat palladium surfaces are separated by an exceedingly small distance to make an electrical capacitor. With a very sensitive capacitance bridge, one can detect the change in capacity that would be produced by the adsorption on the palladium surfaces of even a small fraction of a monolayer of benzene molecules. In experiments carried out with this equipment it was found that benzene molecules are not adsorbed upon a palladium surface in air at atmospheric pressure. To reconcile this conclusion with the well known facts of activation, it seems necessary to conclude that even a palladium surface can adsorb benzene molecules only after it has been partly cleaned by arcing.

5.3 Alloys

When a base metal is mixed with a noble metal, the result can be an alloy which is activated less readily by organic vapors than would be the noble metal constituent alone. In the curve of Fig. 11 is plotted the number of operations required under a particular set of standard conditions to activate a series of alloys of palladium and nickel. In air, nickel itself cannot be activated at all. The amount of carbon formed from benzene decomposition on the surface of a palladium-nickel alloy is always less than the amount which would be formed under the same conditions upon pure palladium. One does not know whether benzene is held less firmly on the alloy surface so that there is more likelihood
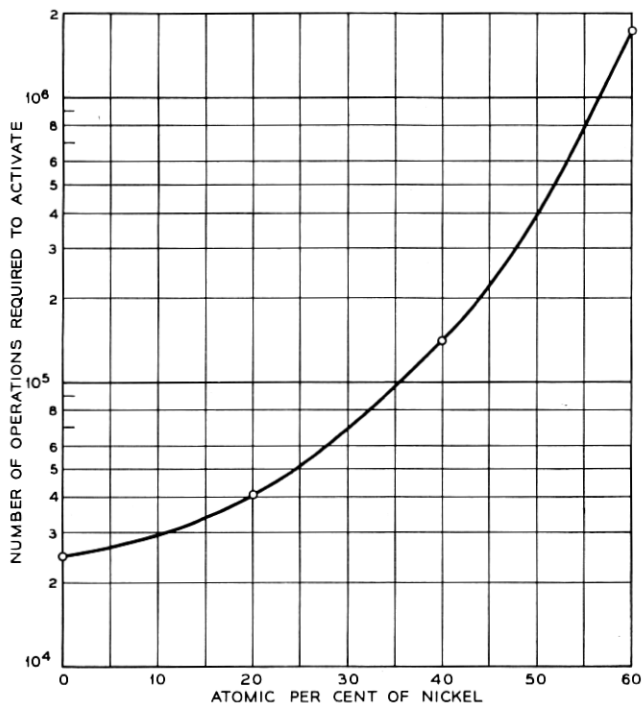
Fig. 11 — Resistance to activation of various alloys of nickel and palladium.

that a heated molecule will evaporate rather than decompose, or whether there are just fewer sites on the surface which can take molecules.

6. ACTIVATION IN AIR

Electrical contacts are not so readily activated by organic vapors in the presence of air as they are when air is absent. Air inhibits the activating process in at least three different ways, and sometimes in a fourth way. These are:

1. Covering up the metal surface so that activating molecules cannot be adsorbed upon it until some of it has been cleaned temporarily by arcing.

2. Offering obstruction in the path of organic molecules on their way to an adsorption site on the metal, so that the molecules diffuse slowly through air up to the surface, whereas in the absence of air, an adsorbed film is formed much more quickly at the same pressure of the organic vapor.

3. Burning off in each arc some of the carbon formed on the surface in preceding arcs.

4. Sputtering and burning off carbon from the cathode in a glow discharge, when such a discharge occurs.

The first of these effects of air has made itself evident in the experiments of Kisliuk, Atalla and Boyle described above. It will not be discussed further. Observations and experiments have been made upon the other three effects of air, and these will be described below. Burning off of carbon in an arc is mentioned first because it can be most nearly separated from other effects and studied individually.

6.1 *Burning of Carbon*

On a surface uniformly covered by organic molecules, carbon must be burned off on the area covered by an arc, but new carbon can be formed on an annular ring surrounding the arc where the metal temperature is lower. As a consequence of this, whereas in the absence of air contacts are activated very much more promptly by high energy arcs than by low energy arcs, in air the situation is less simple. The general result of many experiments is that in air high energy arcs are less efficient in producing activation than are low energy arcs. On the other hand, arcs of extremely low energy are also quite ineffective. There seems to be an optimum arc energy at which contacts can be activated most promptly, which may be of the order of 100 ergs. Activation can be expected to be most prompt when the difference between the area of the arc and the area of the annular ring around the arc is a maximum.

The outer edge of this annular ring is the position on the metal surface at which the maximum temperature just reaches the decomposition temperature of adsorbed organic molecules, about 600°C for the case of benzene. If the width of the ring is Δ and its inner radius R, each arc can be assumed to burn carbon from an area πR^2, and to form new carbon on an area $\pi[(R + \Delta)^2 - R^2]$. Now Δ certainly increases with increasing energy (being zero for zero energy), but on the simplifying assumption that it is independent of energy, the difference area, which is

$$A = \pi[(R + \Delta)^2 - 2R^2] \tag{1}$$

will be a maximum for that energy that makes R equal to Δ. It is interesting to find the value $R = R_1$ for a 100 erg arc, which is known to be very efficient in producing activation, and then to estimate the maximum temperature reached at the outer edge of the annular ring for $\Delta = R_1$. The simple model predicts that this maximum temperature should be 600°C. When the calculation is carried out in rough fashion, the

temperature is found to be of the order of 300°C, rather than 600°C. The correct order of magnitude gives support to the general ideas behind the theory.

According to this very simple model, activation takes place most promptly for arcs of 100 ergs energy, and for such arcs the *net* carbon formed per arc corresponds to the benzene molecules adsorbed on the area $2\pi R_1^2$, which is obtained from Eq. (1) by setting $R = \Delta = R_1$. In vacuum at the same energy, the carbon formed per arc would come from benzene on the area $4\pi R_1^2$. Thus for 100 erg arcs activation will occur almost as quickly in air as in vacuum, but for arcs of greater energy, much more slowly than in vacuum. Qualitative observation has confirmed this general conclusion.

That this picture is, however, over simplified in a fundamental manner is clear from the effect of electrode contours upon ease of activation. For flat electrodes, activation is very much more prompt when the surfaces make good contact over a large area than when misalignment results in contact on a rather small area. Furthermore, flat contacts can often be activated very promptly under conditions for which crossed wires cannot be activated at all. (Reference 8, page 335). In a qualitative way this is understood, but the inhibiting effect of restricted areas is not amenable to quantitative consideration. This effect makes quite clear that the model of an annular ring about an arc is too idealized to be of much quantitative value.

One might expect that the burning off of carbon would be greatly influenced by atmospheric conditions, and thus the ease of activation would depend upon such conditions. This is indeed found to be the case in experiments in which the air contains water as well as the activating vapor. In unpublished experiments F. E. Haworth determined the number of operations required to activate contacts under a particular set of standard conditions for a wide range of relative humidity. In the range from 10 to 88 per cent relative humidity, the number of operations to make contacts fully active increased exponentially from 1.4×10^3 to 1.0×10^6, and at relative humidities of 95, 98 and 100 per cent, activation was not attained at all. Furthermore the process of activation could be reversed by water vapor, and contacts that had been made fully active in dry air containing an organic vapor were made completely inactive by continued operation in the same vapor after the addition of water. The effect of water in these experiments may have been due to covering the surfaces so thoroughly with water molecules that the activating vapor could not be adsorbed, or to burning carbon by the water gas reaction, $C + H_2O \rightarrow CO + H_2$. The exponential relationship between num-

ber of operations required to make contacts active and relative humidity has no clear interpretation in our present state of knowledge.

6.2 *Diffusion of Activating Vapor*

In Kisliuk's vacuum experiments the amount of carbon formed and the degree of activation attained was independent of benzene vapor pressure. This is not at all the case when activation is produced by operating contacts in air. In fact, one of the earliest observations was a minimum vapor pressure below which contacts could not be activated (Reference 2, Table I). In more careful later tests it was found that the minimum vapor pressure is a function of rate of operation of the contacts, the minimum pressure being actually proportional to the rate of operation over a factor of 100 which was the range tested (Reference 8, Fig. 2). Obstruction offered by air supplies the explanation of this rate effect. Activation cannot occur if electrodes are separated between one arc and the next for a time which is short in comparison with the time required to cover the surface with one monolayer of organic molecules. A rough order of magnitude calculation confirms this conclusion.

As an approximation, one assumes one dimensional diffusion to an electrode surface from the space in front of it, with all molecules reaching the surface sticking to it. Boundary conditions for the solution of the diffusion equation, $\partial C/\partial t = D\partial^2 C/\partial x^2$, are then:

$$C = C_0 \text{ at } t = 0 \text{ for } x > 0$$

$$C = 0 \text{ at } x = 0 \text{ for all values of } t$$

The concentration of activating molecules in the space in front of the electrode is then $C = C_0 \operatorname{erf} [x/2 (Dt)^{1/2}]$. The total number of molecules to have reached the surface at any time t_1 is,

$$m = \int_0^{t_1} D \left. \frac{\partial C}{\partial x} \right\}_{x=0} dt = 2C_0(D/\pi)^{1/2} t_1^{1/2}$$

expressed in molecules/cm^2, when C_0 is given in molecules/cm^3. We are interested in the value of t_1 for which m is the number of molecules in a monolayer, and the maximum rate of operation of contacts for activation to occur can be expected to be comparable with

$$n = \tfrac{1}{2}t_1 = 2C_0^2 D/\pi m^2 = 8.1 \times 10^{22} D(p/m)^2, \tag{2}$$

where p is the partial pressure of activating vapor in mm Hg. The factor $\frac{1}{2}$ in $n = \frac{1}{2}t_1$ appears because diffusion to the surface can occur only when the electrodes are separated, and it is assumed that they are separated for half of the time.

The best data we have for testing this relation are represented by ex-

periments upon activation in vapor of the organic compound fluorene.[3] According to the observations, the critical rate of operation was found to be proportional to the partial pressure of fluorene rather than to its square as in (2). This is a discrepancy which must be overlooked in our present state of knowledge. To test (2) for fluorene at 20°C, we require values of D, the diffusion coefficient of fluorene in air, p, the partial pressure of fluorene at 20°C, and m, the number of adsorbed fluorene molecules per cm² of surface. The value of $D = 0.067$ cm²/sec. was obtained from a linear relation between $1/D$ and (molecular weight)$^{1/2}$, which holds quite well for a number of organic compounds. The value $p = 0.04$ mm Hg is the geometrical mean between 0.23 and 0.007 mm Hg, respectively the vapor pressures of napthalene and anthracene at 20°C. We have estimated $m = 3.3 \times 10^{14}$ molecules/cm², which is related to the corresponding number for benzene, 7×10^{14} in the inverse ratio of the molecular weights.[16] These numerical values give from (2)

$$n = 0.75 \text{ operation/second}$$

as the critical rate that will just permit one monolayer in the time the contacts are separated. The observed critical rate for activation at 20°C from Fig. 2 of Reference 8 is 3. The agreement is pretty good when the crudeness of the model is considered.

6.3 *Sputtering and Burning in a Glow Discharge*

If both arcs and glow discharges occur when electrical contacts are operated in an atmosphere containing an activating organic vapor, the activation of the contacts resulting from the arcs is inhibited by the occurrence of the glow discharges.* This effect is sometimes very beneficial in extending the life of telephone relay contacts. In fact a very simple protective network, consisting only of an inductance of the order of 10^{-4} henry placed very close to one of the contacts, has been devised which, under some conditions, will increase the contact life by a factor of about 10.

Quantitative measurements have been made of this inhibiting action of a glow discharge, and from them it has been concluded that the effect is attributable to sputtering and burning of carbon in the discharge. In making these measurements, a pair of contacts was operated in an atmosphere containing limonene vapor in such a way that arcs and glow discharges occurred alternately in controlled fashion. A charged capacitor was discharged in an arc at each closure. By the use of an auxiliary synchronized relay in series with one of the contacts, the circuit was

---

* It should be pointed out incidentally that a glow discharge in air can also activate silver electrodes. It produces silver nitrite on their surfaces,[18] and silver electrodes with a layer of nitrite are fully active until the layer is burned off.

changed periodically so that a glow discharge could be made to occur at each contact break, or at every 6th, 60th, or 600th break. The glow current was always 0.04 ampere lasting for a time that could be accurately set by means of a synchronized shunt tube.

In all of the tests, the energy in each closure arc was 190 ergs. Measurements were made at partial pressures of limonene of 0.05 and 1 mm Hg. At the lower pressure it was found that the contacts remained inactive indefinitely whenever the time of glow discharge on break was on the average more than 0.25 microsecond for each closure arc, and activation would ultimately take place if the average glow time per closure arc was less than this value. (At the limonene pressure of 1 mm Hg there was a corresponding critical glow time of about 1 microsecond). The obvious interpretation of these tests is that a glow discharge of 0.04 ampere lasting for 0.25 microsecond sputters and burns off as much carbon as is made by an arc of 190 ergs under the conditions of the experiment. To test this conclusion, one needs to know how much carbon is produced by an arc of 190 ergs, and one needs to know the sputtering rate of carbon in a normal glow in air at atmospheric pressure.

Measurements of the sputtering of carbon in a normal glow discharge were undertaken by F. E. Haworth, since such data are not available in published literature. Carbon and graphite electrodes were weighed before and after a normal glow discharge of 0.006 ampere lasting for various lengths of time. The loss of the carbon or graphite negative electrode in nitrogen was found to amount to about 0.15 atom per ion of the discharge. In air the loss was much greater, four times larger for graphite and 15 times larger for carbon (2.3 carbon atoms/ion for carbon in air). The increase in air was attributed to burning, and the difference between carbon and graphite losses in air was believed to be due to smaller crystal size and looser bonding in the carbon case.*

If we use the highest loss figure of 2.3 carbon atoms/ion we find that a glow discharge of 0.04 ampere for 0.25 microsecond should remove 14×10^{10} carbon atoms. From Table IV, one finds that a 190 erg inactive arc in activating benzene vapor produces 9.5×10^{10} carbon atoms in the absence of air (line 3), and an active arc produces 34×10^{10} carbon atoms (line 2).† The net carbon which is left after each arc in air is, of course, considerably less than it would be in the absence of air (Section 6.1), but the order of magnitude agreement between these numerical

---

* The sputtering rate of 0.15 atom/ion for carbon in nitrogen in the normal glow is about what is reported by Güntherschulze[19] for silver in the *abnormal* glow but is greater by a factor of about 400 than that found for silver in the *normal* glow in experiments by Haworth.[18] Obviously sputtering rates for carbon are exceptionally high.

† It is believed that these figures are substantially the same for limonene and for benzene.

values leaves little doubt that we have correctly interpreted the inhibiting effect of glow discharges upon activation.

6.4 *"Hysteresis" Effects*

Sometimes a pair of completely inactive electrical contacts of a noble metal can be activated very quickly, and an apparently identical pair of contacts cannot be activated at all under exactly the same experimental conditions. In the first case a great amount of carbon may be formed, and in the second case no detectable carbon at all. In order to clear up this confusion, some controlled experiments were carried out upon the activation and deactivation of silver and palladium electrodes in air containing benzene vapor at various partial pressures. From these experiments, it has been possible to relate the variability of earlier results to previous history of the contacts, and the entire behavior is now quite well understood.

In these tests adjustable benzene vapor pressure was obtained by first bubbling air at a controlled rate through benzene maintained at constant temperature by a bath of acetone and dry ice, and then mixing the saturated air with clean air in the proper proportions. In certain tests silver contacts were operated in air flowing from this apparatus, discharging a capacitor on each closure. The number of operations required to produce complete activation was measured for many different values of the benzene vapor pressure. With contacts that had been cleaned in a standard way before each test, it was found that the number of closures required for activation rose extremely rapidly with decreasing vapor pressure over a narrow range of pressures. There was always a lower pressure limit below which it seemed impossible to activate the contacts at all. All of the tests were made at the high operating rate of 60 closures per second.

When the contacts had been cleaned by abrasion before each individual test, the minimum pressure below which activation could not be attained was of the order of 2 mm Hg. (This pressure was exceptionally high because of the high operating rate, see Section 6.2.) A different result was found for contacts that had been previously activated and then cleaned only by repeated arcing; for these contacts the minimum pressure for activation was about 0.7 mm Hg. The factor of 3 between these minimum pressures is doubtless related to the fact that, for those electrodes which had been cleaned by arcing only, there existed neighboring carbonized areas which were never cleaned. Each such area can be expected to hold about three times as much adsorbed benzene on the average as does the same area of clean metal, see Section 5.1, and especially lines 2 and 3 of Table IV. Thus for such surfaces more carbon can

be expected to be formed by each arc. The model is not sufficiently well defined to permit any more exact conclusions.

In another experiment, silver electrodes, which had first been completely activated, were operated for a long period at a greatly reduced benzene vapor pressure. It was found that they remained completely active unless the pressure was very much less than the minimum of 0.7 mm Hg at which activation could be produced. In repeated tests at a variety of low benzene vapor pressures, the number of operations required for the contacts to become inactive was recorded. This number was found to increase very abruptly with increasing vapor pressure, and above about 0.02 mm Hg the contacts remained active indefinitely. This result must again be related to the capacity of a mass of spongy carbon to hold a great amount of adsorbed benzene. Very probably the upper limit of pressure below which contacts cannot be deactivated, depends upon the thickness of the carbon layer produced before the benzene pressure is lowered.

Similar but less extensive experiments were carried out with palladium electrodes.

These hysteresis effects observed in the activation and deactivation of contacts seem capable of explaining the erratic observations that had been made previously. If the immediate history of contacts is sufficiently well known, behavior can perhaps be predicted fairly well for various experimental conditions.

7. BROWN DEPOSIT

Closely related to the activation of relay contacts is the formation of polymerized layers of organic material upon contact surfaces as a result of friction. This material, which is commonly known as "brown deposit", is produced at contacts which do not make or break current. Its mode of formation is thus entirely different from that of the carbon which is the cause of activation. Both have, however, a common origin in layers of organic molecules adsorbed upon surfaces. Discovery of brown deposit and most of the invest: ... 'on of it were carried out elsewhere (Ref. 20), but some discussion of brown deposit is appropriate here because of its relation to the carbon of activation and because of a study of its formation by P. Kisliuk.

7.1 *Composition*

The composition of brown deposit was determined by Kisliuk in an apparatus similar to that used to investigate the carbonaceous material responsible for activation, Fig. 9, and by the same analytical procedure. The apparatus was modified so that a palladium or platinum electrode

could be rubbed back and forth upon another electrode of the same material. The driving force was a magnet outside the glass apparatus.

In tests carried out in benzene vapor in the absence of air, it was found that the deposit formed on the electrodes contained 65 per cent as much hydrogen as was in the original benzene, about 2 atoms of hydrogen for every 3 carbon atoms, this figure having a possible experimental error of as much as 20 per cent. The brown deposit formed by friction thus differs significantly from the pure carbon produced by arcing which is responsible for activation.* The experimentally determined composition of the brown deposit does not, of course, distinguish between hydrogen or benzene simply adsorbed in the deposit and hydrogen existing in it in some combined form.

7.2 Rate of Production

In Kisliuk's experiments, which were carried out in the absence of air, the rate of production of brown deposit was found to be independent of benzene vapor pressure down to 3×10^{-3} mm Hg, which was the lowest pressure tested, just as was the case in the formation of carbon by arcs.

When air is present, the rate of formation of brown deposit may depend upon vapor pressure of the organic molecules. Unpublished experiments have indicated, furthermore, that there may be a limiting vapor pressure below which the deposit does not form, with this pressure dependent upon the idle period between operations.[20]

In some of Kisliuk's vacuum tests a palladium electrode was rubbed back and forth over an area determined microscopically to be about 4×10^{-3} cm^2, and produced the polymerization on each rub of 2.1×10^{10} molecules of benzene, or 5×10^{12} molecules per cm^2 of rub. This is smaller than the number of molecules in a monolayer (7×10^{14} per cm^2, Reference 16) by a factor of 140. Part of the discrepancy is certainly due to the fact that the true area of contact of the electrodes is less than the apparent area as seen under the microscope. From more careful estimates of area it has been found by other observers that the amount of benzene that is polymerized by friction is, in general, comparable with that adsorbed as a monolayer on the rubbing surfaces.

7.3 Brown Deposit and the Carbon of Activation

Although both brown deposit and the carbon of activation are produced from the decomposition of adsorbed organic molecules, there are

---

* In this connection, it is interesting to point out, however, that any metal surface, upon which brown deposit has been produced by friction in an appropriate atmosphere, is found to be fully active when tested in a suitable circuit. This activity naturally does not last after the brown deposit has been burned off. In this characteristic, the brown deposit behaves like any foreign more or less insulating layer upon a contact surface.

several differences in the conditions necessary for formation. The carbon is produced on a noble metal but not on a base metal (in air); brown deposit, on the other hand, has been formed on vanadium, molybdenum and tantalum, but it has never been produced on silver and only sparingly on gold.[20] The failure of electrodes of silver and of gold to form brown deposit has been associated with the high thermal conductivities of these metals, with the idea in mind that polymerization of organic molecules to brown deposit requires frictional heat. Whether this is true has not been established.

Both brown deposit and the carbon of activation can be formed from any of a great variety of unsaturated ring compounds. Various unsaturated aliphatic compounds which have been tested, and some saturated aliphatic compounds (for example, pentane), can be made to produce brown deposit to a limited extent, but activation has never been attained with any aliphatic compound. It seems probable that some activating carbon is produced from these compounds but the burning off in the arc makes activation impossible.

REFERENCES

1. R. H. Gumley, Bell Lab. Record, **32,** p. 226, 1954.
2. L. H. Germer, J. Appl. Phys., **22,** p. 955, 1951.
3. L. H. Germer and W. S. Boyle, Nature, **176,** p. 1019, 1955.
4. L. H. Germer and W. S. Boyle, J. Appl. Phys. **27,** p. 32, 1956.
5. M. M. Atalla, B.S.T.J., **34,** p. 1081, Sept., 1955.
6. L. H. Germer, J. Appl. Phys. **22,** p. 1133, 1951.
7. F. E. Haworth, J. Appl. Phys., **28,** p. 381, 1957.
8. L. H. Germer, J. Appl. Phys. **25,** p. 332, 1954.
9. L. H. Germer and F. E. Haworth, J. Appl. Phys., **20,** p. 1085, 1949.
10. L. H. Germer, to be published.
11. M. M. Atalla, B.S.T.J., **32,** p. 1493, Nov., 1953.
12. P. Kisliuk, J. Appl. Phys., **25,** p. 897, 1954.
13. L. H. Germer, Electrical Breakdown between Close Electrodes in Air, to be published.
14. W. S. Boyle and L. H. Germer, J. Appl. Phys., **26,** p. 571, 1955.
15. J. J. Lander and L. H. Germer, J. Appl. Phys., **19,** p. 910, 1948.
16. B. M. W. Trapnell, Advances in Catalysis, Vol. III, Academic Press, New York, 1951, pp. 1–24.
17. P. Kisliuk, to be published.
18. F. E. Haworth, J. Appl. Phys., **22,** p. 606, 1951.
19. A. Güntherschulze, Z. Physik, **36,** p. 563, 1926.
20. H. W. Hermance and T. F. Egan, 1956 Electronics Symposium, Electrical Engineering, to be published.