CHARGED SURFACE LAYERS FORMED ON THE ELECTRODES OF VACUUM TUBES.

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Introduction.

SEVERAL years ago one of the writers observed that metals which had been used as cathodes in an X-ray discharge, in the attempt to obtain fresh clean surfaces, exhibited abnormal and very erratic photoelectric properties. In some cases the emitted electrons appeared to possess extremely high velocities while in other cases a strong field in addition to the action of the light was required to free the electrons from the surface. A later investigation[1] showed that such apparently abnormal photoelectric velocities, which had been observed by several investigators, were due to some sort of surface phenomenon which had the effect of greatly changing the contact difference of potential between the emitting and receiving electrodes and thus exposing the electrons to a strong accelerating or retarding field. Recently Seeliger[2] has found evidences of an electrical double layer, formed on the cathode of an X-ray bulb, which has the effect of changing the normal potential of the cathode by about 3 volts.

Because of the frequent use in research of metallic films sputtered from cathodes and of metals which have been exposed to X-ray discharges it is of practical importance as well as theoretical interest to understand the nature of this surface phenomenon, the cause of its erratic behavior and the methods by which it may be controlled.

For the experimental investigation we employed the following apparatus. Enclosed in the brass cylindrical vessel MN were the disk-shaped plates P and B, of platinum and brass respectively, which served as the electrodes for the vacuum discharge. The vessel could be opened at FF, where the upper part fitted into an accurately ground groove cut in the base and around which wax was melted to render the joint airtight. The vacuum was maintained by a Gaede pump connected to the vessel by the brass tube A.

The effect of X-ray discharges on the nature of the surfaces of the

[1] Otto Stuhlmann and Karl T. Compton, Phys. Rev., Vol. 2, p. 199 (1913).

[2] Phys. Zeit., XIV., p. 1273 (1913).

plates P and B was determined by measurements of the contact difference of potential between the opposing surfaces of these plates. These measurements were made by Kelvin's method.[3] The plate P could be moved up or down by turning the ground-glass joint J_1 and this formed, with B, a parallel plate condenser of variable capacity. The plate B was connected with a quadrant electrometer E. When the potential of the plate P was adjusted by the potentiometer S so that no deflection of the electrometer was observed when the plate P was raised or lowered, then the voltmeter V indicated the contact difference of potential between P and B.

The plate B was so large (6 cm. diameter) as to leave only one milli-

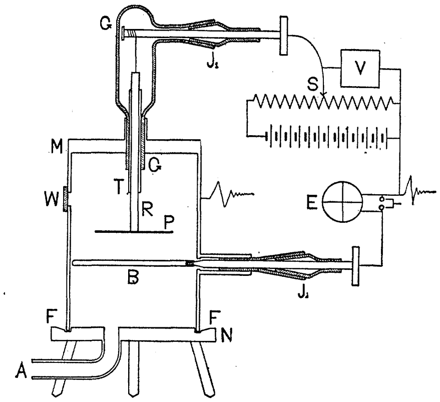

Fig. 1.

meter clearance between it and the vessel MN. During each X-ray discharge the plate B and the vessel MN were earthed and the plate used as anode or cathode as desired. In this way the lower side of the plate B was shielded from the effects of the discharge. By rotating the ground-glass joint J_2 the plate could be reversed and its shielded face tested for contact potential.

The sensitiveness of the system was such that one volt difference of potential between B and P caused a deflection of about 40 millimeters when the plate P was raised or lowered. In most of the work quickness rather than high accuracy was desirable.

Experiments with Clean Surfaces.

For the first tests the inside of the vessel was rendered as free as possible from wax and insulating materials. The inside of the vessel and all metal parts were vigorously polished with emery and tripoli

[3] Lord Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

powders and wiped clean. All insulation on the inside of the vessel was shielded from the direct discharge and so disposed as to reduce to a minimum effects due to charges accumulated on the insulation.

Under these conditions we passed discharges of various durations

Table I.

Duration of Discharge.	Contact Potential.	Duration of Discharge.	Contact Potential.
0 sec.	0.30 volt	80 sec.	−0.25 volt
2	0.21	140	0.00
12	−0.04	440	0.15
20	−0.23	1,040	0.12
40	−0.25	1,940	0.06

between the plates P and B, using P as the cathode, and measured the contact difference of potential after each discharge. Some typical results are indicated in Table I. The contact difference of potential is called positive when of the normal sign, *i. e.*, brass positive with respect to platinum. Evidently the discharge produces a very slight disturbance in the contact difference of potential. A comparison of these results with others in which less care was taken to eliminate wax from the vessel indicates that these are due to slight traces of wax (possibly due to the vapor pressure of the wax in the joints) remaining in the vessel in spite of the efforts made to avoid them.

Experiments with Insulating Films.

The effect is on the wax film. When films of various kinds of wax were placed on the plate P and this plate was used as anode or cathode, the apparent values of the contact difference of potential after the discharges varied between $\pm$ 500 volts and the value in every case was unchanged by reversing the plate B and testing with its shielded side opposed to P. But when the plate P was cleaned and wax was placed on the upper side of the plate B it was found, after each discharge, that the high contact difference of potential between B and P entirely vanished when the clean side of B was placed opposite P. These tests show conclusively that the abnormal contact potentials are due to and exist in the insulating films.

The effect of reversing the plate was as here described only provided the discharge had not been excessively heavy and long. It was found that very heavy discharges vaporized the wax, which condensed all over the inside of the apparatus and vitiated the above tests.

The nature of the effect depends on the conditions of the discharge. We found that the nature of the effect did not depend appreciably on the degree of vacuum, within wide limits, but that it was determined jointly by the time and the intensity of the discharge. Typical sets of measurements are shown in Table II. The effect on the wax film of a short discharge or of a weak one is to leave the outer surface of the film coated with an electrified layer of sign opposite to that of the waxed plate during the discharge. A long and heavy discharge reduces the intensity of electrification of the layer and may even reverse the sign.

TABLE II.

Discharge.		Contact Potential. Soft Wax on		
Time.	Nature.	Pt. Cathode, Volts.	Pt. Anode, Volts.	Brass Anode, Volts.
Before	Sputtering	0.40	0.40	0.40
0.5 sec.	Weak	−120	35	− 75
Several 0.5 sec.	Medium	−160	130	−130
30 sec.	Heavy	− 50	− 6.5	− 60
30 sec.	Heavy	− 30	....	− 40
1 min.	Heavy	− 10	−13	− 12
1 min.	Light	−100	2	
1 min.	Heavy	− 45	− 6.5	
Several 0.5 sec.	Heavy	−160	75	−100
15 min.	Heavy	2	−11	− 2

These contact potentials decay with time. A typical rate of decay curve is shown in Fig. 2, in which the waxed plate P was the anode. This

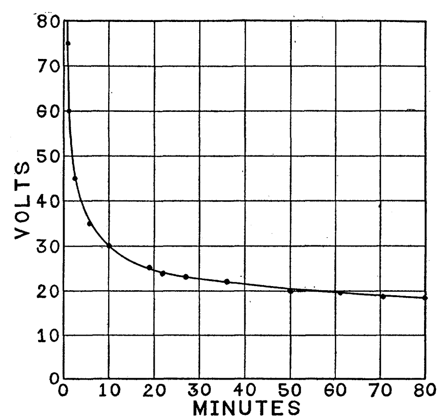

Fig. 2.

change is initially much too rapid to be represented by a logarithmic curve. The largest values in Table II. are evidently not the maximum values since the measurements could not be made instantaneously after shutting off the X-ray discharge. The rate of decay was distinctly more rapid in air than if a good vacuum was maintained.

Discussion of the Results.

These results are consistently and reasonably interpreted as due to two processes which are effective during the discharge. The first of these is the deposition of a layer of gaseous ions over the outer surface of the insulating film and the second is a convection current in the wax itself, whereby charged portions of the viscous wax are repelled from the metal to the outer surface. Obviously these two processes tend to give rise to contact potentials of opposite sign and the one which predominates depends on the nature of the discharge. We should expect the latter effect to be relatively important when the wax is heated and thus rendered less viscous. This was actually the case, for in Table II. we noticed that long and heavy discharges, which warmed the wax, produced effects of the latter sort. Short, light discharges on the contrary, produced strongly charged layers of sign opposite to that of the plate during the discharge.

In this connection it is significant that the largest effects due to convection currents in the wax occurred when the wax was on the anode, subject to the intense heat developed by the bombarding cathode rays. In this position only was the sign of the resultant potential easily reversed by long heavy discharges. It is also significant that long heavy discharges produced relatively larger effects when the wax was on the platinum plate than when it was on the brass plate, for the platinum plate was thin and of comparatively small heat capacity and its temperature was more easily raised by the discharge. In every case in which the reverse effect was marked evidences that the wax had been strongly agitated during the discharge were noticed when the apparatus was taken apart. This roughening of the surface was not noticed after short or light discharges.

This explanation of the phenomena is strongly supported by experiments in which sealing wax and stopcock grease were substituted for the soft wax on the electrodes. We should expect, in the case of sealing wax, that the effect due to the deposited ions would strongly predominate and that, because of the high viscosity, the maximum contact potential would be larger and the rate of decay smaller than in the case of soft wax. In the case of stopcock grease we should expect the contrary peculiarities.

We found, with sealing wax, contact potentials larger than 500 volts in the direction to be accounted for by deposited ions. The rate of decay was very slow. Only once, after a very heavy discharge, did we find a reversal of sign in the contact potential. In this case the wax had been melted by the discharge. With stopcock grease the highest measurement recorded was 21 volts and most values were about 5 volts. We also found that reverse effects, *i. e.*, contact potentials of the same sign as the applied potential, were observed even after applying potentials too small to produce a vacuum discharge, for instance 150 volts. In all cases the rate of decay was very rapid.

Conclusions.

1. The abnormal contact potentials produced on the electrodes by high potential discharges are due to and exist in insulating films such as wax or grease on the surfaces of the electrodes and are reduced or eliminated by shielding or avoiding all such substances.

2. On insulating films of small viscosity surface charges are produced by convection currents in the film set up by the applied field, even though this field may be too small to produce a vacuum discharge.

3. During a vacuum discharge a charged layer of gaseous ions is deposited on the surface of the insulating film. This charge is of a sign opposite to that of the potential of the electrode during the discharge and is therefore opposite to that produced by convection currents.

4. The apparent contact difference of potential is the resultant of these two effects, whose relative importance depends on the viscosity of the film and the nature of the discharge.

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