Insulating Films Formed Under Electron and Ion Bombardment

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In an evacuated tube in which the slightest traces of organic vapors may occur, even with liquid air cooling, insulating layers are formed on surfaces subject to electron or canal-ray bombardment. These layers may be attributed to carbon compounds, and their formation is related to the polymerization of organic vapors by electrical discharges, α-particles, and ultraviolet light. The simple ion-deposition theory is inadequate as the layers are formed only at the point of impact of the rays on the surface. Electrical resistances and break-down potentials were observed for several films. The importance of these deposits in general experimental practice, such as the photometry of mass-spectra, is pointed out, and, amongst others, cases are cited of their influence producing contact potentials, pseudo high vacua, erroneous photographic recording and differential condensation of vapors upon previously bombarded surfaces.

AS is well known, metallic electrodes subjected to electron bombardment eventually become discolored if vacuum conditions are not sufficiently good. The purpose of this paper is, first, to point out the nature of the films which cause the surface to change and to discuss the importance of considering them in general experimental practice, and, second, to describe certain new features in the processes which occur in organic vapors subjected to a bombardment leading to polymerization.

In the present experiments, an electron gun, furnished with an oxide coated filament, was fixed in a vacuum tube to give a circular beam of electrons of $1\text{–}18\times10^{-6}$ amp., at a potential kept at 190–210 volts. The tube was connected through a stopcock to a mercury diffusion pump which, with accompanying liquid air trap, produced a vacuum of about 10^{-5} mm Hg. The beam formed upon the target a circular film with insulating properties, characterized by a circular distribution of interference colors.

Since a black deposit was obtained upon magnesium and deposits were formed upon glass targets, the films are not produced by oxidation. Moreover they are not soluble in any of the common solvents, but when deposited on glass, sometimes loosen in the liquids used and break up into very fine slivers.

The following facts are evidence that the deposit is a carbon compound. (1) When a platinum strip on which a colored film had been formed was heated in a vacuum the deposit turned black (enlarging slightly in area) instead of disappearing as it would in air. (2) Heating the platinum bright red *in vacuo* did not rid it of this black deposit. (3) This black film when tested with a telephone receiver was found to have become conducting. (4) It disappeared in air at the same temperature as an artificial film formed by charring a trace of stopcock grease put on platinum. (5) The films disappeared readily in air at 450°C to 470°C and more slowly at lower temperatures. Some turned black before diminishing noticeably, others merely grew thinner until they vanished.

At higher pressures, without liquid air, and with organic vapors present in quantity, solid films are not surprising, since solid polymers or compounds are commonly observed as products of organic vapors after bombardment by α-particles,[1] in various forms of electrical discharges,[2, 3, 4, 5] and even after exposure to

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ultraviolet light.[6, 7, 8] Spectrographic studies have been made of the intermediate products,[9, 10] and experiments are still in process to determine more fully the kinetics of the reactions. Also workers in the x-ray field find it difficult to avoid the K lines of carbon from the "'film de carbone'[11, 12] which results from the destruction by the cathode rays of the carbonized residual gases."

To test the simple ion-deposition theory of polymerization, a glass target was coated with fluorescent material, and a magnetic field was used strong enough to deflect the electrons just at the end of their path towards the edge of the target. The film then formed at the new point of impact only. Since such a magnetic field could not deflect the heavier ions as much as the electrons, the formation of the solid films at the point of impact only indicates the necessary conjunction of three factors: (1) The wall or target surface; (2) the organic vapor or its derivative; (3) the energizing particle.

Another new feature was the discovery that similar films were formed at the point of impact of hydrogen canal rays and also at the point of impact of neutral particles which had been accelerated when traversing the discharge tube in a charged state.

A self-deflection of the electron beam was observed which was probably due to charges accumulating upon the insulating deposit (on target or in gun). These deposits also altered the target current. This was shown by an increase in the reading whenever the electron beam was momentarily deflected from the center towards the cleaner edges. The thickness of the deposit, however, is not proportional to the time of running, for, though the deposition continued throughout, the rate varied. Resistance measurements were secured by the following device: a small drop of mercury was placed on the film and pressed upon it with a loop of platinum wire. Minimum values of the order of 10^6 ohms were obtained for the film beneath the drop, whilst corresponding rupturing voltages varied from 4–14 volts.

These films are likely to be an undetected disturbing factor in many types of experiment. A colorless layer extends beyond the colored center. (Under some conditions the whole film appears to be colorless.)[13]

When they form on fluorescent screens they render the original bright spot diffuse and "permanently fatigue" the spot bombarded.

When they produce contact potential differences they may quite frustrate the attempts of experimenters who by special method[14] or design[15] intend to avoid these potential differences.

In secondary electron experiments, copper oxide has been recommended for large secondary emission when the "oxide" referred to[16] was very probably a carbon compound deposit due to an unrecognized source of organic vapor.

They explain the phenomenon of the pseudo high vacuum, which has been ascribed to a changed condition of the cathode[17] or of the anode[18] or to a changed condition of the walls of the tube allowing them to collect a screening electric charge[19, 20]—that is exactly what these films would lead one to expect under differing experimental conditions; and also the case in photoelectric emission of a surface which was made insensitive by electron bombardment and remained so until restored to its former condition by heat.[21]

It is, however, in the case of photographic recording that the deposits have produced their most extensive though not their most important effects: They have been studied as a pseudo

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photographic effect,[22] where the observer, using a magnetic spectrograph, reported that lines appeared upon the plate even before development, that lines could be obtained upon metals also and upon glass, and that they could be removed from the glass by heating above 450°C.

Also a number of experimenters have done work upon the differential condensation of vapors on parts of metal surfaces exposed to light,[23] to various discharges,[24, 25] and to cathode-ray bombardment,[26] where doubtless this effect was involved; and an attempt[27] was made to use the differential condensation due to the unrecognized occurrence of the organic deposits for the registration of cathode rays in daylight without developing process.

From the examples selected it can be seen how readily this effect may vitiate results wherever intensity measurements of refined accuracy are desired, as in the photometry of mass-spectra.[28] The deposit forms a layer between the plate and the impinging beam that is not necessarily proportional to the time of exposure and that has optical properties of its own, which need not be additive, superimposed upon those of the image. The effect is equally vicious in electrical and magnetic deflection measurements of such delicacy that insulating layers of this character cause uncompensated deflections. And wherever it is important that thin films subjected to bombardment should retain their original thickness this effect has to be contended with. Also in spectrographic work the films often cause a darkening of the window which limits the effective length of exposure.

In summation, these deposits may be considered a very insidious and prevalent source of error.

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