

REGISTRATION OF CATHODE RAYS BY THIN FILMS OF METALS AND METAL COMPOUNDS

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ABSTRACT

A search was made for a method of registering cathode rays analogous to the photographic method which could be carried out entirely in daylight and in which no development process would be required. For this purpose, thin metal films (Pb, Ag, Bi, Sn, Cd, As, Cu, Sb, Zn, Mg, Se) were deposited on glass by evaporation from a coiled tungsten filament in vacuum. These were then exposed, in vacuum, to a beam of 10 kv cathode rays. Films of Pb and Sn so thin as to be quite transparent before exposure, were darkened to a density of the order of 0.5 by exposure to 0.01 coulomb/cm². Also opaque films of the above metals were exposed to the vapors of various acids (HCl, HNO₃, HBr, HI, H₂S, H₂SO₄); this generally produced a lowered opacity, in many cases the films becoming quite transparent. Exposure to cathode rays tended to restore the original opacity. In general, the best effects were obtained with nitrates and bromides; Bi(NO₃)₃ seemed to show the most promise as to sensitivity and permanence of the record. The cathode ray bombardment caused practically all the films to fluoresce, the color and intensity of the fluorescence depending on the material.

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I. INTRODUCTION

In a previous investigation¹, in which very thin beaten gold foils were suspended in a vacuum and bombarded with cathode rays, it was noticed that the region of the foil struck by the cathode rays gradually became less transparent to visible light, and under continued bombardment became quite opaque. The gold foils used were about 0.09 μ thick, and the voltages, current densities, and times were of the order of 30 kv, 0.1 ma cm⁻², and 10 hours, respectively. The color of the transmitted light appeared to acquire a slight bluish tinge in the bombarded films, and spectral transmission measurements² between 440 m μ and 680 m μ showed that the transmission was lowered by the greatest factor in the red and by the least in the vicinity of the original transmission maximum at 500 m μ . The colors of the reflected light from the two portions of the films seemed identical, but spectral photometric comparison was not resorted to here. The me-

¹ W. W. Nicholas, B. S. Jour. Research, vol. 2 (RP60), p. 837: May, 1929.

² These measurements were kindly performed by Dr. Deane B. Judd of the colorimetry section.

chanical structure of the foils was somewhat changed as was evidenced by a fine wrinkling of the thin foils in the region bombarded.

Several workers have observed effects on metals which may well be related to the above phenomena. Webster and others³ have observed a discoloration of beryllium, and of thin silver films deposited on beryllium, when used as anticathodes in an X-ray tube. Coblenz and Hughes⁴ observed a differential condensation of moisture for the parts of metal surfaces exposed to ultra-violet light over long periods and the parts not so exposed. Eder⁵ has reviewed similar effects for sunlight. It was to have been expected that bombardment by cathode rays would produce similar surface effects; this has been verified for a large number of metals by both Carr⁶ and the writers. Carr investigated the condensation of a variety of vapors on surfaces of metals which had been exposed to cathode rays in air, or to low-speed electrons in vacuum, and discovered that in many cases mercury vapor causes a very clear development of the exposed region.

A consideration of the above observations suggested the possibility that many substances not appreciably sensitive to visible light may be capable of registering cathode rays in a way analogous to the ordinary photographic method. Further, the work on gold foils indicated that some of these materials might give a permanent record without the necessity of any development process to bring out a latent image. Since, for an investigation now in progress, such a process of registration of cathode rays was urgently required, a search was made of a considerable number of substances which it was thought might prove suitable for the purpose. Some of the results of this search are presented here.

II. EXPERIMENTAL METHOD

It is very advantageous in studying such effects as are described above to use thin films of material deposited on a transparent backing, such as glass. Since even moderately high-speed cathode rays can penetrate only a few microns of most solids, there should be no advantage in using greater thicknesses of the sensitive material. Metal deposits may readily be made by evaporation from a coiled tungsten filament in vacuum.^{7 8 9 10} Such films are very uniform, clean, smooth, and their thickness can be accurately controlled, thus allowing any changes in optical transmission properties to be readily studied. Films of various compounds of these metals can be made by exposing the metal films to various acid vapors for a period of several hours. Many of these compounds are practically completely transparent; such compounds are, of course, especially favorable for the purpose at hand.

The apparatus used in the present investigation is outlined in Figure 1. Electrons, supplied by a tungsten filament *F* behind a narrow slit in a copper shell *C*, were accelerated in the space between *C* and *A*, and passed through a slit in *A* into the brass box *B*. There

³ Webster, Clark, Yeatman, and Hansen, Proc. Nat. Acad. Sci., vol. 14, p. 679; 1928.

⁴ W. W. Coblenz and C. W. Hughes, Science, vol. 60, p. 64; 1924; B. S. Sci. Paper No. 493, vol. 19, p. 577; 1924.

⁵ J. M. Eder, Handbuch der Photographie. Heft 2, Band 1, 2 Teil, 3 Aufl., (Photochemie) pp. 118, 396 1906.

⁶ P. H. Carr, Rev. Sci. Inst., vol. 1, p. 711; 1930.

⁷ See footnote 3, p. —

⁸ A. H. Pfund, Phys. Rev., vol. 35, p. 1434; 1930.

⁹ B. S. Circular, No. 389; 1931.

¹⁰ Cartwright and Strong, Rev. Sci. Inst., vol. 2, p. 189; 1931.

they were deflected by a magnetic field to cause them to strike the various prepared plates *P* mounted on *N*; this permitted making a number of exposures with a single pumping of the apparatus. *N* was a cylindrical brass tube with numerous springs similar to *S* mounted along the upper edge; these springs performed a double duty as clamps and electrical contacts to the sensitive surfaces of *P*. A slot cut in the side of *N* permitted the entrance of the electron beam. This

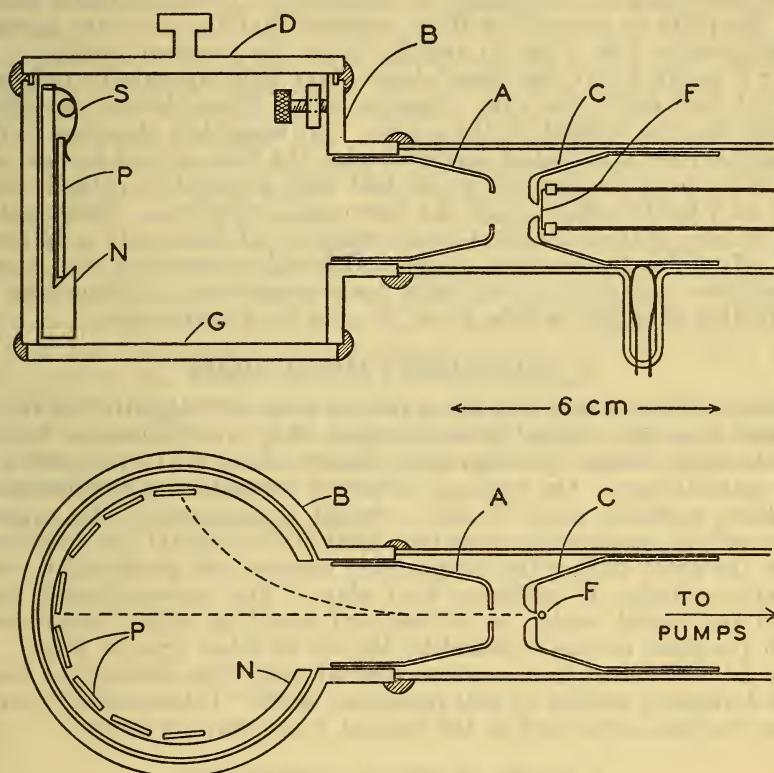


FIGURE 1.—Apparatus for testing the registration of cathode rays by various substances

beam had a cross section of about 1 cm by 2 mm when it struck the plates. *B* was closed at one end with a glass plate *G*, for visual observation, and at the other end by a brass cover which could be removed for replacements of plates *P*. Sealing wax was used for the vacuum joints. The tube was evacuated with a mercury vapor pump and Hyvac. Only constant d. c. potentials were used on the tube. Breakdown usually occurred at about 40 kv. Only 10 kv cathode rays were used in the present experiments, and the exposure used with all the films was about 0.15 coulombs/cm².

III. OBSERVATIONS

1. OPAQUE METALLIC FILMS

Opaque films of Pb, Ag, Bi, Sn, Cd, As, Cu, Sb, Zn, Mg, and Se showed, without exception, after bombardment, the differential condensation of moisture referred to above. The best way to observe this phenomenon is to gradually cool the plate until an opalescent film of moisture is seen to condense on its surface. Then, gradually allowing the plate to warm, it will be observed that the moisture appears to evaporate not quite so rapidly from the exposed portion. As Carr¹¹ pointed out, for best observation light specularly reflected should not enter the eye. Opaque silver films showed an effect which may be related to the above. On being left standing in the laboratory for a period of several weeks, the films turned brown, but the color over the portion which had been exposed to cathode rays was of a lighter shade than the surrounding portions. Presumably the surface of the metal had been turned to sulphide, with a differential effect for the exposed areas. Although interesting, the above effects are apparently of no value for a comparison of intensities, so no further attention will be given them in the present note.

2. TRANSPARENT METAL FILMS

Several films of lead and tin so thin as to be only slightly less transparent than the original glass on which they were deposited turned considerably darker (photographic density about 0.5) on exposure to the cathode rays. On exposure to air for several days, the darkened portions regained most of their original transparency. To explain these effects, one may suppose that most of the original film combined with the glass during the evaporation process and produced a combination similar to ordinary lead glass. The bombardment then freed the metal, which on subsequent standing either recombined with the glass or was oxidized by the air to a less opaque form. It may be mentioned that semitransparent gold films showed no trace of a darkening similar to that described in the "Introduction"; however, the exposures used in the present work were far lower.

3. FILMS OF METAL COMPOUNDS

These films showed the greatest promise for the permanent registration of cathode rays. Each of the metals listed above was exposed to the vapor of each of the following acids: HCl, HNO₃, HBr, HI, H₂S, and H₂SO₄. Other metal films were heated in air in order to form the oxides. The nitrates and bromides were generally the most sensitive to cathode ray bombardment in that they formed the strongest images. Bismuth nitrate, which was originally transparent, gave especially dark images (photographic density of the order of 1) but no exact significance can be assigned to the comparison with other metals without a better knowledge of their comparative thicknesses. Generally, the color of the bombarded portion was brown, with a metallic appearance, but this was not always the case. The most striking exception was with ZnI, which was originally fairly

¹¹ See footnote 6, p. 62.

transparent but which was changed by the bombardment to a brilliant orange color.

Permanence of the images was not tested over very considerable periods. Many of them faded in a few hours on being left standing in the laboratory. However, many of the records, especially with Bi, Sn, and Cd persisted over a period of weeks; this is more than adequate to obtain permanent photographic or photometric records.

It is important, before using any substance for actual work, to investigate the conditions under which the best films are obtained. This was indicated by some special experiments with films of bismuth nitrate of various thicknesses. The best results were obtained when the films were made from metal deposits which were fairly transparent (say, having a density of 0.5). The nitrate films from these deposits gave sharper, stronger, and more permanent images than did the films from opaque metal deposits. The images on the thick films sometimes faded very appreciably in a few hours, whereas those on the thin films persisted unchanged for months. The density of the images with the thin films was of the order of 1 for current densities of 0.01 coulombs/cm², when 10 kv cathode rays were used. The thin films were smooth and uniform and somewhat opalescent, especially if they had been nitrated in a desiccator, whereas the thick films were less uniform due to the formation of large crystals.

With only one or two possible exceptions, all the films, both metallic and otherwise, fluoresced on exposure to the cathode rays. The fluorescence was in various colors and with various intensities, the colors ranging from a deep green to violet.

WASHINGTON, October 7, 1931.