The Optical Properties of Metallic and Crystalline Powders

A. H. Pfund, *The Johns Hopkins University*
(Received June 21, 1933)

The method of preparing finely divided metallic "blacks" is described and measurements on the transparency of these blacks in the infrared are presented. The use of sodium and thallium chlorides, distilled as finely divided powders on radiometer vanes, yields a selective receiver the far infrared. A new type of transmission band, shown by coarse powders of quartz and calcite is described.

RECENTLY it was found that the procedure originally developed for the production of very finely divided bismuth (bismuth-black)[1] could be applied to a wide variety of metals and crystals. Metallic "blacks" of the following materials have thus far been produced: gold, silver, nickel, copper, zinc, cadmium, lead, bismuth, antimony, selenium and tellurium. In the following, the mode of preparation of these blacks will be described and their unique optical properties will be discussed.

The production of metallic blacks is brought about by the distillation of metals at relatively high pressures. The apparatus is shown in Fig. 1

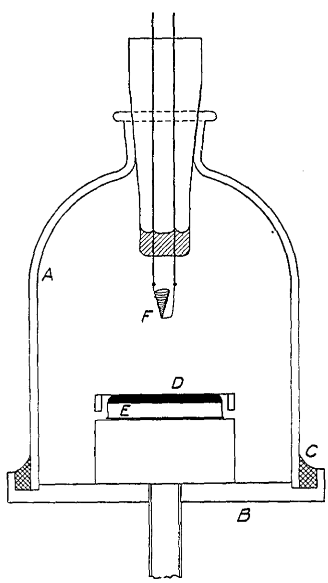

Fig. 1.

where A is a portion of a bottle whose lower edge is ground flat. This rests on a metal plate B so made as to present an annular trough C which is filled with a solid solution of paraffin and vaseline. A vacuum-tight seal is readily effected by melting the surface of the wax with a small, pointed gas-flame. The necessary time for cooling is less than a minute. Upon completion of a run, the bottle, when removed, is virtually free from wax. The surface to be coated, D, is placed 3–4 cm away from the tungsten spiral. While no difficulty is encountered in the coating of massive plates, it is found that a film of nitrocellulose (too thin to show interference colors) acquires only a light coating. To provide the necessary backing it has been found convenient to float the film, which is stretched tightly over a brass ring, on the clean surface of mercury E contained in a shallow pill-box. Since the metal coating comes down heavily only on those areas directly in contact with the mercury, care must be exercised in avoiding the inclusion of air-bubbles under the film. The actual distillation of the metal is brought about by a conical spiral of tungsten wire F (0.18 mm in diameter) within which a small piece of the metal is placed. To avoid the short-circuiting of several turns of the tungsten spiral by the contained metal, it is advisable to dip the spiral into a fluid mixture of water and alundum cement. Successive dippings and heatings bring about the formation of a thin but resistent coating of alundum. In most cases, however, a preliminary heating of the spiral to redness in a gas flame is quite sufficient to bring about the desired result. Because of the relatively high pressure of the gas (3–5 mm) used in the

[1] A. H. Pfund, Rev. Sci. Inst. 1, 379 (1930).

distillation chamber, it is most advantageous to use hydrogen, particularly for metals having high melting-points. In most cases, however, air is used. At pressures less than 0.5 mm it frequently happens, as in the case of Cd and Zn, that a white, reflecting film is deposited. This difficulty is overcome by increasing the gas pressure to about 3 mm and by increasing the rate of evaporation. In general, low pressures and slow distillation favor the formation of very fine particles; conversely, higher pressures and rapid distillation favor the formation of coarser particles.

These powder-films are particularly interesting from the standpoint of their transparency to infrared rays. For such measurements a single prism rocksalt spectrometer of the swinging-arm type[2] was employed in conjunction with a single-junction vacuum thermopile. In most cases the powder-film was distilled on a thin nitrocellulose membrane.

Selenium

Selenium when evaporated at a pressure of 3 mm yields a fluffy, brick-red powder-film. The character of the infrared transmission is shown in Fig. 2.

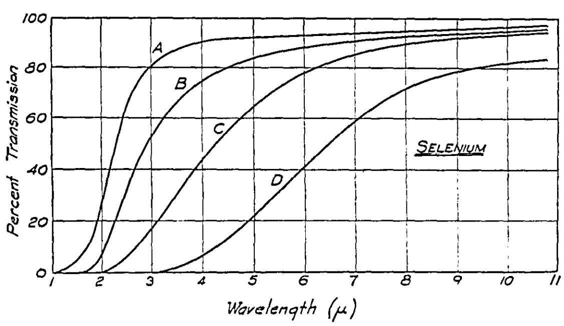

Fig. 2.

These films which were quite opaque to visible light became very transparent in the infrared. The conditions under which distillation took place are as follows:

Curve *A*—pressure 0.7 mm—unbacked nitrocellulose film
Curve *B*—pressure 2.0 mm—unbacked nitrocellulose film
Curve *C*—pressure 3.0 mm—unbacked nitrocellulose film
Curve *D*—pressure 4.2 mm—mercury backed nitrocellulose film.

In passing from *A* to *D* the conditions under which distillation took place became progressively favorable to an increase in particle size. Since the individual particles were found to be below the limit of resolution of the microscope no measurements of particle-size could be carried out. It was observed, however, that the color of film *A* was brick red while that of *C* was a dark maroon.

The usefulness of these films as powder-filters[3] was investigated and it was found that they are superior to MgO and other white filters in the sharpness of their cut-off. While it is true that any of the preceding curves may be shifted in the direction of greater wave-length by increasing the thickness of layer, it is nevertheless believed that the steepest rise from opacity to transparency may be achieved through the use of uniform particles having a "best" size.

Electrical Conductivity

For a series of metallic blacks having the same particle-size, those materials will be most opaque for which the extinction coefficient is the greatest. As shown by the work of Rubens and Hagen[4] the reflecting power and extinction coefficient increases with electrical conductivity. It might, therefore, be anticipated that, other things being equal, the transparency of metallic blacks in the infrared would lie in the inverse order of their electrical conductivities. While, unfortunately, identity of particle-size could not be established, it was found possible to find a series of metals having relatively low melting-points and yielding a series of powder-films having the same short wave-length limit of transparency. The specific resistances of these metals are[5]

$$\text{Se} - 10^{23} \text{ ohms-cm}^3 \times 10^{-6}$$
$$\text{Te} - 2 \times 10^5$$
$$\text{Bi} - 1.1 \times 10^2$$
$$\text{Zn} - 5.7$$

[2] A. H. Pfund, J.O.S.A. 22, 281 (1932).

[3] A. H. Pfund, Phys. Rev. 36, 71 (1930).

[4] Rubens and Hagen, Ann. d. Physik 11, 873 (1903).

[5] Smithsonian Tables, p. 323 (1929).

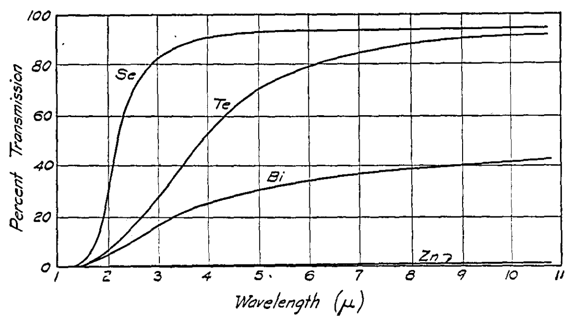

FIG. 3.

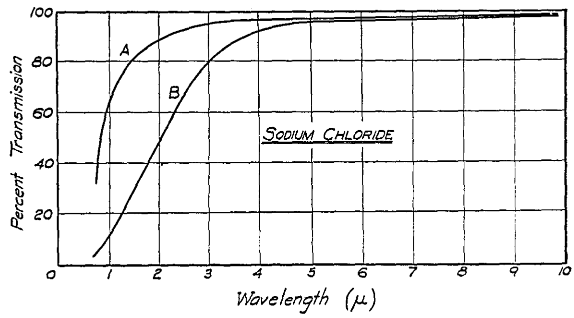

FIG. 4.

An inspection of the curves presented in Fig. 3 reveals a parallelism between infrared transmission and electrical resistance.

It was attempted to add sulphur to this list, but it was found that this material upon being distilled under the usual conditions appeared in the form of small transparent globules, which, after several hours, became opaque because of the development of a crystalline structure. Had the receiving surface been cooled with liquid-air, a powder-film would, presumably, have resulted.

In the series of metals just discussed, zinc is much of the greatest importance. A film of zinc-black of such thickness as to transmit a barely recognizable image of a tungsten lamp filament will transmit less than one percent in the spectral range 1–14μ. Likewise no reflection as great as one percent is found in the same range. In the wave-length range 40–70μ zinc-black transmits less than five percent. While no reflection measurements were carried out in this spectral region, it is believed that zinc-black will be found an excellent material for coating the receiving areas of thermopiles and radiometers.

SODIUM CHLORIDE

If sodium chloride be distilled at a pressure of 3 mm a powder-film showing a pale yellow color in transmitted light will result. Upon admitting air, the film acquires a deeper color. By allowing the film to stand for some time in a humid atmosphere (or, simply, by breathing on it) the film will transmit only a deep red image of an incandescent lamp filament. These changes are interpreted as being due to a growth in particle-size occasioned by a solution and recrystallization of smaller particles on larger ones. Curve A, Fig. 4, was obtained immediately after the deposition of the salt film while curve B was obtained after the film had stood in a humid atmosphere for five hours. The latter curve indicates that a growth in particle-size had taken place.

SELECTIVE RADIOMETERS

The difficulties met with in far infrared are increased by the presence of contaminating radiations of short wave-length carrying much energy. An attempt was made to minimize the effect of these radiations by distilling thick NaCl powder-films on the gold foil overlying the vanes of a Nichols radiometer. As a result of former work[6] it was anticipated that the radiations of short wave-length, which are not absorbed, would be eliminated while the radiations of wave-length greater than 30μ would be absorbed. Since NaCl becomes increasingly transparent beyond 90μ, a thick coating of $TlCl_2$ was distilled on top of the NaCl—to form a fluffy powder-film at least 0.1 mm thick. The radiometer was tried out by Dr. R. B. Barnes in his grating spectrometer and was found to respond vigorously through the interval 30–135μ and to reduce greatly the effect of short wave-length radiations. A detailed account of his work will appear later.

COARSE POWDERS

While previous work has been confined to fine particles, it was recently found that coarse particles yielded an unexpected result. The transmission of a powder-film of crystalline quartz

[6] Pfund and Silverman, Phys. Rev. 39, 64 (1931).

having a particle diameter of 5μ was investigated and it was found (as shown in Fig. 5) that a relatively sharp band of transmission existed at 7.3μ. The reflection curve for a polished plate of

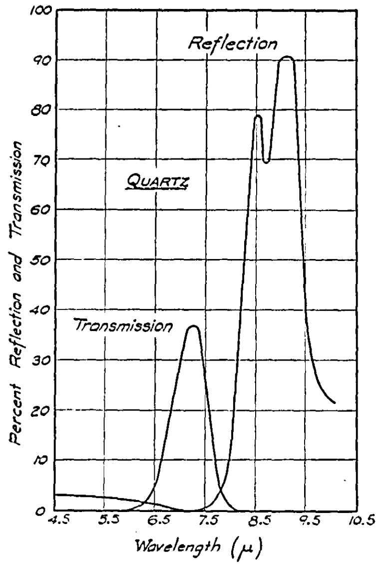

FIG. 5.

crystalline quartz, obtained with the same spectrometer, showed a minimum of less than one percent at the same wave-length 7.3μ. Since here, the refractive index approaches unity, little or no reflection will result. That coarse powders in general will yield a transmission maximum on the short wave-length side of their reflection maximum was further proved for the case of calcite. A calcite powder-film of 7μ particle diameter gave the results shown in Fig. 6 where, again, the reflection curve for a polished plate of the same material is given. The transmission band is limited on the short wave-length side by the copious reflection from coarse particles and on the long wave-length side by the true absorption band.

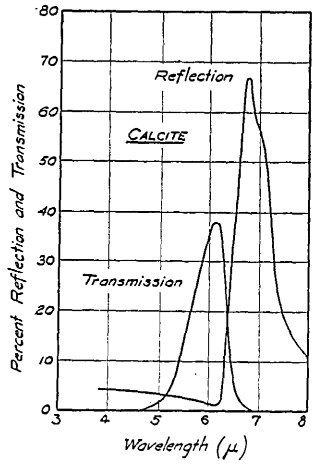

FIG. 6.

It became evident that the conditions for the realization of a filter having a high but narrow transmission band are somewhat critical. If the particles be too fine they will only scatter and hence, be inefficient in removing the shorter wave-lengths. If, on the other hand, the particles be too coarse, the number of reflecting surfaces necessary for the removal of the shorter wave-lengths will involve the use of so much material that the true absorption will greatly reduce the intensity of the transmitted radiation.