

Selective nature of gold-black deposits

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Gold blacks made by evaporation from tungsten filaments in the presence of oxygen and in the absence of oxygen show different optical and electrical properties. The properties are found as a function of mass thickness for many different evaporation conditions. Electron microscopy was used to reveal the role of tungsten oxide in the deposit in breaking up the conducting paths and leading to selective optical behavior. Mie's theory may be used to calculate the optical properties of a gold sol and, at least for the blacks with the smallest conducting regions, agreement with experiment is good. The application of metal sols to the production of selective surfaces is discussed.

There has been a recent upsurge of interest in the production of selective absorbers that have high solar absorptance α and low emittance ϵ in the thermal infrared. The production of such surfaces using interference or bulk absorption effects of thin films is now well known.^{1,2} This paper is concerned with another selectivity mechanism, that of gold-black deposits. Under certain circumstances these deposits have high solar absorptance and high transparency in the thermal infrared. Placed on a reflecting substrate, such deposits form a selective absorber with the desired characteristics.

Gold-black deposits made by evaporation of gold from a hot tungsten source in a nitrogen atmosphere are often used as absorbing surfaces for radiation detection because of their wide-band absorption characteristics.^{3-13,20,21} Related deposits can be made by evaporation of other metals in other gases in the approximate pressure range from 0.1 to 20 torr. A variant of the gold-black deposit⁷ is made in nitrogen gas containing some oxygen, thereby causing reaction of oxygen with the filament, which produces volatile tungsten oxides. This type of deposit will be called type II gold black to distinguish it from the normal (or type I) gold black prepared in pure nitrogen. Type II gold black has selective absorption properties; it is transparent in the infrared region but has an absorption band in the visible region that does not extend much beyond 2 μm . The aim of this paper is to study the optical, electrical, and structural properties of gold blacks made in atmospheres that contain different amounts of oxygen, and to explain these properties in terms of simple theoretical models.

I. PREPARATION OF THE DEPOSITS

The coatings were prepared in a bell jar of 17 l volume, which is sealed after evacuation to 10^{-6} torr and admission of the gas mixture. The evaporation filament consisted of 0.5 mm diam. tungsten wire formed into a shallow "V" and clamped between brass terminals 30 mm apart. Evaporation was accomplished from

a globule of gold at the apex of the "V". In the preparation of the type I deposits, care was taken to exclude oxygen by using very dry (<10 ppm H_2O) oxygen-free nitrogen. Traces of oxygen that remained after admission of the gas were removed by a getter filament that consisted of 50 cm of 0.5 mm diam. tungsten wire heated by a current of 20 A for 5 min. In the preparation of coatings in atmospheres that contained oxygen, the atmosphere was replaced after each 15 s of evaporation, to avoid oxygen depletion.

The substrates were mounted beneath the source; they consisted of polished copper and Mylar film for optical measurements, glass slides with gold electrodes for resistance measurement, nitrocellulose-covered electron-microscope grids, and aluminum foil for measurement of mass thickness. The mass thickness of the deposit was measured by weighing the coated foil, removing the deposit, and reweighing. The accuracy of this method was tested by comparing the masses of foils mounted on the copper substrates with those of foils mounted beside them. The agreement was always better than 10%; the main source of error was the non-uniformity of the deposit. Transmittance and specular reflectance were measured by use of commercial instruments.

II. EXPERIMENTAL RESULTS

Coatings made under ostensibly similar conditions may have infrared transmittances that differ by as much as 20%. This is because the properties are directly dependent on the amount of tungsten oxides in the sample. The pattern of convection currents in the bell jar during evaporation influences the availability of oxygen at the filament, thereby determining the amount of tungsten oxides in the sample.

A. Optical properties

Curves of the specular reflectance of gold-black-coated polished-copper substrates are shown in Fig. 1

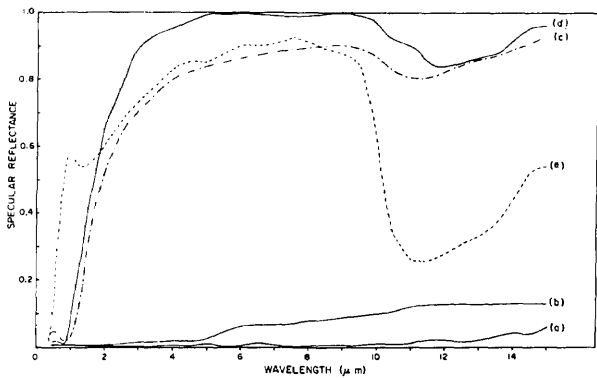


FIG. 1. (a) Gold-black deposit prepared in oxygen-free nitrogen at 3 torr, mass thickness 0.81 g/m^2 ; (b) Gold-black deposit prepared in nitrogen plus 5% oxygen at 3 torr, mass thickness 1.05 g/m^2 ; (c) Gold-black deposit prepared in nitrogen plus 20% oxygen at 3 torr, mass thickness 0.90 g/m^2 ; (d) Gold-black deposit prepared in nitrogen plus 20% oxygen at 3 torr, mass thickness 0.98 g/m^2 ; (e) Tungsten oxide deposit prepared in 100% O_2 at 3 torr, mass thickness 0.97 g/m^2 .

as a function of wavelength between 0.4 and $15 \mu\text{m}$ for gold blacks made in

- (a) oxygen-free nitrogen at 3 torr,
- (b) nitrogen plus 5% oxygen at 3 torr,
- (c) nitrogen plus 20% oxygen at 3 torr,
- (d) nitrogen plus 20% oxygen at 10 torr.

Also shown is the curve (e) for a deposit of tungsten oxide made by heating the tungsten filament in oxygen at 3 torr, without gold. In view of the negligible specular reflectance of gold black,¹¹ the measurement of specular reflectance is equivalent to the measurement of transmittance through twice the thickness of the coat-

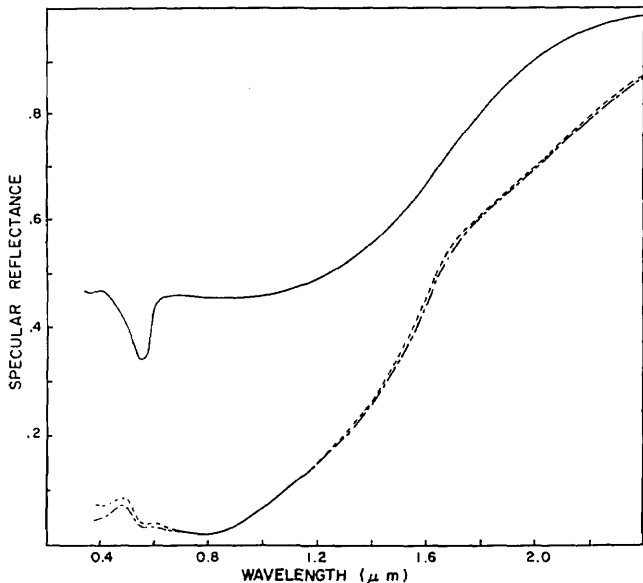


FIG. 2. Specular reflectance of a copper substrate coated with gold black prepared in 3 torr of a mixture of nitrogen with 10% oxygen, normalized to copper; ---, experimental; ----, corrected experimental; —, theoretical.

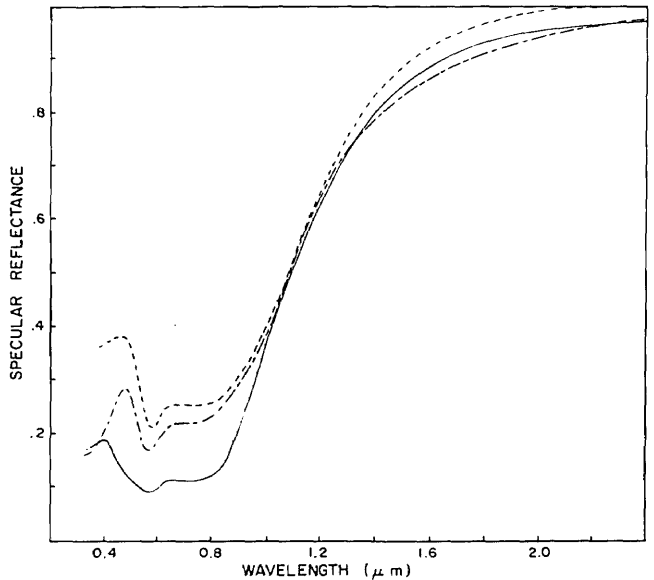


FIG. 3. Specular reflectance of a copper substrate coated with gold black prepared in 3 torr of a mixture of nitrogen with 50% oxygen normalized to copper; —, experimental; ----, corrected experimental; —, theoretical.

ing, and this was confirmed by the measurements on coated Mylar film. The coatings of Fig. 1 are of comparable mass thicknesses and the infrared transmittances of the deposits increase as the pressure of oxygen in which they were made increases. The dip in the curve at $12 \mu\text{m}$ also becomes more prominent. This absorption is present in the curve (e) of Fig. 2 and is therefore due to tungsten oxides, as suggested by Harris.¹¹

Figures 2–4 show the behavior between 350 nm and $2.5 \mu\text{m}$ for gold blacks produced in nitrogen–oxygen mixtures at 3 torr with 10%, 50%, and 100% oxygen,

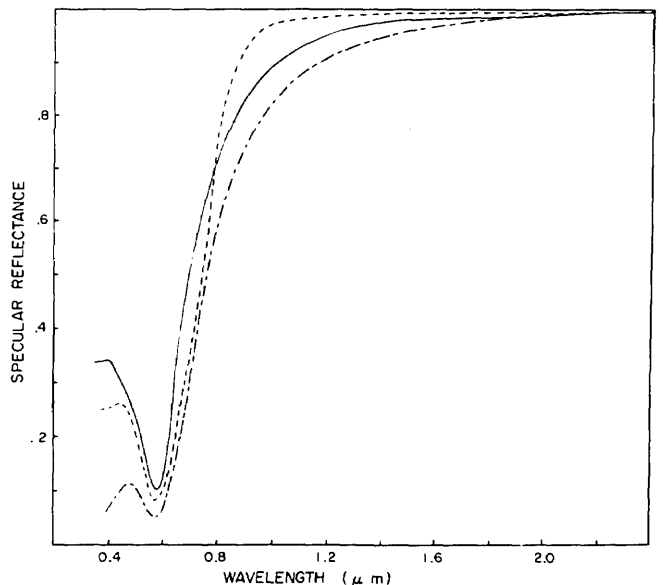


FIG. 4. Specular reflectance of a copper substrate coated with gold black prepared in 3 torr of oxygen, normalized to copper; ---, experimental; ----, corrected experimental; —, theoretical.

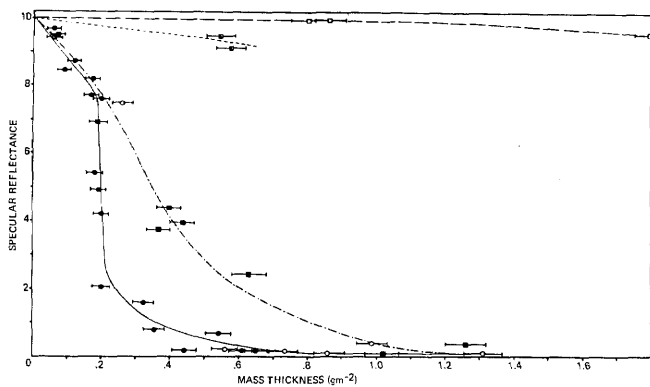


FIG. 5. Specular reflectance at $9.5 \mu\text{m}$ of copper substrates coated with gold blacks, plotted as a function of mass thickness; \square , 20% O_2 at 10 torr; \square , 20% O_2 at 3 torr; \blacksquare , 20% O_2 at 1 torr; \bullet , 10% O_2 at 0.5 torr; \circ , oxygen-free nitrogen.

respectively. These curves show a pronounced local minimum of reflectance near 550 nm and a local maximum near 475 nm . These features, together with the position of the steeply rising part of the curve in the red region, determine the color of thin deposits. The sample that corresponds to Fig. 2 was deep blue, that corresponding to Fig. 3 was purple, and that corresponding to Fig. 4 was reddish purple.

The effect of oxygen on the infrared transmittance of gold blacks can be seen clearly in the set of curves in Fig. 5, which display the reflectance of coated copper samples at $9.5 \mu\text{m}$ as a function of mass thickness. The wavelength $9.5 \mu\text{m}$ was chosen to avoid the absorption band at $12 \mu\text{m}$, which is due to oxides of tungsten. Coatings prepared with oxygen pressures of greater than about 1 torr are infrared transparent (type II) and do not appreciably reduce the reflectance of the copper substrate (apart from the band at $12 \mu\text{m}$) even in very thick coatings of 2 g/m^2 . Coatings made with oxygen pressures of less than 0.1 torr are infrared absorbing (type I). Coatings made at intermediate oxygen pressures are intermediate in properties. An interesting feature of the type I deposits is the sudden increase of transmittance at mass thicknesses less than 0.2 g/m^2 . The transmittance in the visible region of the spectrum does not show a similar dramatic increase.

B. Electrical properties

The electrical resistances in ohms per square are plotted in Fig. 6 on a logarithmic scale as a function of mass thickness. High electrical resistance correlates well with high infrared transmittance. Coatings made with oxygen pressures greater than 1 torr (type II) show exceedingly high resistances, whereas those made with low oxygen pressures (type I) show low resistances. Deposits made at intermediate oxygen levels show intermediate resistances. There is a sudden increase of resistance for type I deposits for mass thicknesses less than 0.2 g/m^2 ; this sudden increase corresponds exactly to the sudden increase of infrared reflectance shown in Fig. 5 for these samples. This behavior is understandable in terms of the model to be presented in Sec. III.

C. Electron-microscope observations

The deposits prepared at pressures greater than about 0.1 torr consist of crystallites that are linked together to form long chains. The crystallite size is dependent upon the pressure, the rate of evaporation, and the source/substrate distance. For coatings prepared with a deposition rate of $10^{-2} \text{ gm}^{-2} \text{ s}^{-1}$ and 70 mm source/substrate distance, the crystallite diameters were found to be essentially as given by Harris *et al.*⁵ at pressures of 0.5, 1, and 3 torr. A diameter of 28 nm was found at 10 torr, for which Harris *et al.* made no measurement.

Coatings prepared in pure nitrogen have quite a uniform distribution of crystallite chains. The presence of oxygen in the nitrogen, however, has an effect on the chain structure that causes it to become more irregular, with some clustering of the chains and open spaces between. Harris *et al.*⁵ reported this effect and suggested that it was the cause of the selective behavior in the type II blacks. This is not correct, however, because deposits prepared in 0.5 torr of a mixture of nitrogen with 10% oxygen show the more open structure but do not have selective optical properties.

Electron-diffraction patterns of the deposits were photographed. Deposits prepared in an oxygen partial pressure of less than about 0.05 torr showed only the diffraction rings of gold (face-centered-cubic). Deposits prepared in atmospheres that had greater partial pressures of oxygen showed additional diffraction rings, the intensities of which increased with oxygen partial pressure. These rings correspond to oxides of tungsten, as was shown by diffraction patterns of the oxide deposit formed when the filament alone was heated in oxygen. These oxides are strongly implicated in causing selectivity because the appearance of their diffraction rings coincided with the onset of type II behavior. To establish conclusively the role of the tung-

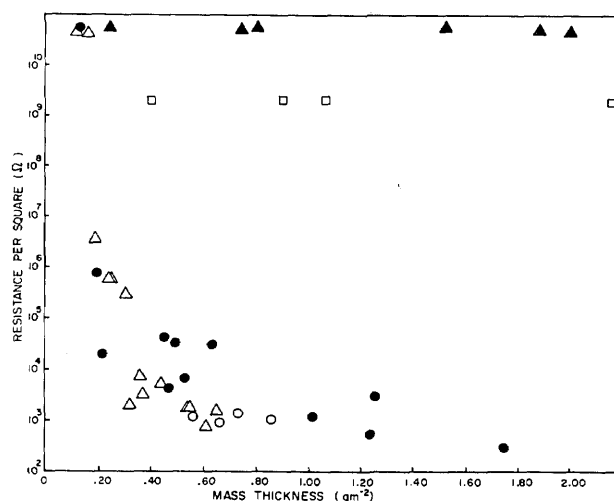


FIG. 6. The electrical resistances of gold black in ohms per square, plotted as a function of mass thickness. The deposits were prepared in nitrogen with added oxygen; \blacktriangle , 20% O_2 at 10 torr; \square , 20% O_2 at 3 torr; \bullet , 20% O_2 at 1 torr; \triangle , 10% O_2 at 0.5 torr; \circ , oxygen-free nitrogen 3 torr. Resistances of $5 \times 10^{10} \Omega$ were the maximum reading of the instrument.

sten oxides, a series of bright-field and dark-field electron micrographs was taken. Figure 7(a) shows a bright-field micrograph of part of a chain of crystallites. Figure 7(b) shows a dark-field electron micrograph made with electrons diffracted into a portion of the two innermost tungsten oxide diffraction rings. Therefore, of the crystallites in the chain of Fig. 7(a), some are gold and some are tungsten oxide, deposited side by side with the gold in the same chain; the tungsten oxide crystallites insulate the gold crystals from each other.

It is known¹¹ that, when heated to temperatures above 100 °C, the type II gold blacks lose their high resistivities and selective properties and become similar to the type I deposits. Type I deposits, with prolonged heat treatment, develop metallic properties. These processes can be observed directly in the electron microscope by heating the deposit gently with the electron beam. The gold crystals in a type II deposit, when heated, coalesce to form larger particles by ejection of the tungsten oxide crystallites. The larger crystals of gold are then in direct contact with each other and produce an electrically conducting chain.

III. THEORETICAL MODELS

A. Type II black

The structure of the type II black has been shown by electron microscopy to consist of gold crystals arranged in chains. The sequence of gold crystals is interrupted periodically by insulating crystals of tungsten oxide. The gold black thus resembles a gold sol whose effective particle size is determined by the concentration of tungsten oxide. The gold particles are suspended in a dielectric medium that is a dilute mixture of tungsten oxide in air. As a first step, the theory of such sols can be applied to the case of the type II gold blacks. If the particles of a sol are spherical and sufficiently insulated from each other, the attenuation of a light beam passing through it may be calculated by use of Mie's theory¹⁴ for the scattering and absorption of electromagnetic radiation by a sphere of complex refractive index. The Mie theory allows the exact calculation of the extinction efficiency Q for a single sphere, Q being the ratio of the energy scattered and absorbed by the sphere to the energy incident on the cross-sectional area of the sphere. The intensity of a beam after traversing a coating that contains mass M per unit area of spheres of radius r and density ρ is

$$I = I_0 \exp\left[-\frac{3}{4} \frac{M}{\rho r} Q\right]; \quad (1)$$

Q is given by the standard formula.¹⁵ Equation (1) is derived by assuming that the same extinction efficiency Q applies for a sphere in the deposit as for an isolated sphere. This will be the case if the fields around neighboring spheres do not interact strongly; the formula is exact in the limit of small M . A computer program that used the method of logarithmic-derivative functions¹⁶ was used for calculation of the values of Q ; average values of the dielectric constants of gold from

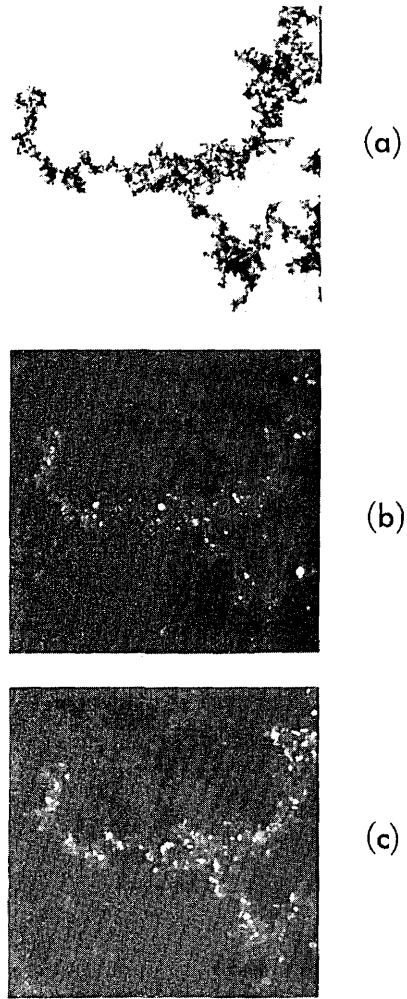


FIG. 7. Electron micrographs of gold black prepared from a tungsten filament in 10 torr of air. (a) Bright-field image; (b) Dark-field image, from (111) and (220) rings of gold; (c) Dark-field image, from diffraction ring due to WO_3 .

the published literature¹⁷ were used. Tests for round-off errors and convergence were made. Also, agreement was obtained with the simple Maxwell-Garnett^{18,19} result in the limit of small τ . The Maxwell-Garnett theory neglects scattering and assumes that the particles are negligibly small compared to the wavelength. The attenuation due to a coating of mass M per unit area is given, in this limit, by

$$I = I_0 \exp\left[\frac{-36\pi k}{(n^2 - k^2 + 2)^2 + 4n^2 k^2} \frac{M}{\rho\lambda}\right], \quad (2)$$

where the dielectric constant of the metal is written $n - ik$. In both theories, the matrix was assumed to be a vacuum.

To test agreement with experiment, the reflectance of films of gold black on copper have been calculated by use of the Mie theory for the particular cases shown in Figs. 2–4. The effect of absorption due to tungsten oxides, which becomes strong at short wavelengths, has been removed. The attenuation coefficient for a tungsten oxide deposit was determined experimentally as a function of wavelength. The values were obtained

TABLE I. Particulars of samples whose reflectance is shown in Figs. 2, 3, and 4.

Sample in figure	Total mass thickness (g/m ²)	Mass thickness of tungsten oxide (g/m ²)	Effective particle diameter deduced using Mie theory (nm)	Color
2	0.58	0.05	320	blue
3	1.03	0.14	240	purple
4	0.71	0.35	160	reddish purple

for tungsten oxide deposits produced in low oxygen partial pressures; a deposit of 0.5 g/m² gave values similar to those of a deposit of 0.9 g/m². Because the absorption band at 12 μm is due solely to tungsten oxide, its strength in a particular sample allows calculation of the mass of tungsten oxide present. If the tungsten oxide is assumed to attenuate the beam independently of the gold black, each curve may be corrected for the tungsten oxide absorption. The details of the samples are listed in Table I.

The particle diameter indicated in each case was the one that gave the best fit to the data. No other variable parameter was used. The curves are drawn with both the corrected and uncorrected data in Figs. 2-4. The agreement is best for the smallest particle size, Fig. 4. This is to be expected because that sample contains the most tungsten oxide and the gold crystals are more likely to act as isolated spheres as Mie's theory requires. Also, the approximation of a spherical shape for the gold crystals is then more likely. In the sample of Fig. 2, the spherical approximation is least valid. The scatterers form a chain that, on the average, contains about 11 individual crystallites in electrical contact.

B. Type I black

The broad-band absorption of this black cannot be explained by the Mie theory for any particle size. The interaction of the fields induced on neighboring particles is very strong in this case; an isolated-sphere treatment is not correct. An impedance theory, such as that of Zaeschmar and Nedoluha¹³ may be applicable.

The behavior of the resistance versus mass-thickness curves of Fig. 6 are worthy of comment here. The sudden decrease of resistance, accompanied by a sudden increase of infrared absorption, is expected as the number of interconnections between chains of gold crystals increases. There is a similarity to the percolation problem for water flowing between interconnected reservoirs. As the number of interconnections is increased, a critical point is reached, whereupon water can flow through the entire network. The same situation occurs when the thickness of a type I gold black is increased; there is a point at which the network becomes conducting, namely at 0.2 g/m².

IV. DISCUSSION

Although the gold-black system does not lend itself to practical application for collection of sunlight at high

temperature because of the sintering property, it nevertheless demonstrates the possibility of using the phenomena of absorption and scattering to produce selective surfaces. The gold-black reflectance curve shown in Fig. 1 for a sample of thickness 0.81 g/m² deposited from 10 torr air onto copper gives a value of solar absorptance $\alpha = 0.88$ and an emittance of $\epsilon = 0.10$ at 400 °C, even allowing for the tungsten oxide absorption, which is not inherent to the mechanism of selectivity. The theoretical curve in Fig. 3 for 240 nm gold particles of mass thickness 0.89 g/m² on copper gives values of $\alpha = 0.75$ and $\epsilon = 0.07$ at 400 °C. These figures can be optimized by choosing the correct particle size and mass thickness.

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- ¹B. O. Seraphin and A. B. Meinel in *Optical Properties of Solids—New Developments*, edited by B. O. Seraphin (North-Holland, Amsterdam 1975).
- ²R. N. Schmidt, *J. Spacecr. Rockets* 2, 101 (1965).
- ³E. Ando, *Jpn. J. Appl. Phys.* 11, 986 (1972).
- ⁴L. Harris, E. T. McGinnies, and B. M. Siegel, *J. Opt. Soc. Am.* 38, 582 (1948).
- ⁵L. Harris, D. Jeffries, and B. M. Siegel, *J. Appl. Phys.* 19, 791 (1948).
- ⁶L. Harris, D. Jeffries, and B. M. Siegel, *J. Chem. Phys.* 18, 261 (1950).
- ⁷L. Harris and J. K. Beasley, *J. Opt. Soc. Am.* 42, 134 (1951).
- ⁸L. Harris and A. L. Loeb, *J. Opt. Soc. Am.* 43, 1114 (1953).
- ⁹L. Harris and K. F. Cuff, *J. Opt. Soc. Am.* 46, 160 (1956).
- ¹⁰L. Harris, *J. Opt. Soc. Am.* 51, 90 (1961).
- ¹¹L. Harris, *The Optical Properties of Metal Blacks and Carbon Blacks*, Monograph Series No. 1 (Eppley Foundation for Research, Newport, R.I., 1967).
- ¹²P. G. Wilkinson, *J. Appl. Phys.* 22, 226 (1951).
- ¹³G. Zaeschmar and A. Nedoluha, *J. Opt. Soc. Am.* 62, 348 (1972).
- ¹⁴G. Mie, *Ann. Phys.* 25, 377 (1908).
- ¹⁵M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, (Academic, New York, 1969).
- ¹⁶A. L. Aden, *Appl. Phys.* 22, 601 (1951).
- ¹⁷*American Institute of Physics Handbook, 3rd Edition*, edited by Dwight E. Gray (McGraw-Hill, New York, 1972).
- ¹⁸J. C. Maxwell-Garnett, *Philos. Trans. R. Soc. (London)* 203, 385 (1904).
- ¹⁹J. C. Maxwell-Garnett, *Philos. Trans. R. Soc. (London)* 205, 237 (1906).
- ²⁰W. R. Blevin and W. J. Brown, *Metrologia* 2, 139 (1966).
- ²¹R. L. Peterson, G. W. Day, P. M. Gruzensky, and R. J. Phelan, *J. Appl. Phys.* 45, 3296 (1974).