JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 38, NUMBER 7 JULY, 1948

The Preparation and Optical Properties of Gold Blacks* †

LOUIS HARRIS AND ROSEMARY T. MCGINNIES**
Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

BENJAMIN M. SIEGEL***
Weizmann Institute of Science, Rehovoth, Palestine

The optical properties of gold smokes deposited on cellulose nitrate films under different experimental conditions have been studied. The conditions of pressure of the inert atmosphere, purity of the gas, rate of evaporation, and the distance between source and deposition surface giving the highest infra-red absorption per unit mass have been found. The thermal mass required for high infra-red absorption is small compared to the thermal masses of other receivers used for infra-red measurements. The gold "blacks" turn yellow and have lower infra-red absorption when heated above 110°C.

Gold "blacks" with very high infra-red transmission (3–15μ) and low transmission at shorter wave-lengths are prepared when oxygen is present in the "inert" atmosphere.

The particle size and particle distribution of the gold smokes deposited under different experimental conditions have been investigated with the electron microscope at high resolution.

INTRODUCTION

THE use of deposits of metallic smokes for thermal receivers was suggested by Pfund[1,2] and by Burger and Van Cittert.[3] Gold "blacks" for absorbing thermal radiation have been reported by several investigators.[4,5] Measurements in this laboratory with a number of metallic smokes indicated that gold "blacks" might have a high ratio of (infra-red absorption/thermal mass). This is an important property for infra-red detectors designed to respond to rapid variations of incident radiation. The quality of the black obtained by evaporating gold in an inert atmosphere depends among other things on the gas pressure, the purity of the gas, the distance between the source and the surface of deposition, the mass of the receiver, the rate of gold evaporation, and the rate of heat conduction from the receiver. We have studied the influence of each of the parameters mentioned upon the quality of the gold "black" and correlated them with measurements of the mass/unit area of the gold deposit.

Absorption properties of the evaporated gold "blacks" were obtained from transmission and reflectance measurements of the smoke deposited on cellulose nitrate films. The transmission to the radiation of a 50°C blackbody, the specular reflection of the 50°C blackbody radiation incident at an angle of 45°, the spectral transmission from 0.4 to 15μ and the diffuse reflection in the visible spectrum, were all measured on deposits made under different conditions.

The fraction of incident radiation absorbed by a blackened film is given by

$$A = 1 - T - S, \tag{1}$$

where T is the fraction transmitted and S is the fraction scattered. By measuring the transmission of the blackened film, only an upper limit to the amount of radiation absorbed is obtained. However, it has been found here that gold "blacks" prepared under certain conditions have a small back scattering and therefore the absorption of such "blacks" can be calculated for comparative measurement from the transmission data alone. The absorption by the cellulose nitrate films used here has been found to be negligible.

* This work has been supported by the Navy Department under Contract NObs 25391.
† Contribution from Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.
** Present address: University of Alabama, Tuscaloosa, Alabama.
*** At the Polytechnic Institute of Brooklyn, New York, by special arrangement.
[1] A. H. Pfund, Rev. Sci. Inst. **1**, 397 (1930).
[2] A. H. Pfund, J. Opt. Soc. Am. **23**, 375 (1933).
[3] Burger and Van Cittert, Zeits. f. Physik **66**, 210 (1930).
[4] L. C. Roess and E. N. Dacus, Rev. Sci. Inst. **16**, 170 (1945).
[5] C. B. Aiken, W. H. Carter, Jr., and F. S. Phillips, Rev. Sci. Inst. **17**, 380 (1946).

Electron microscope studies were made on the gold smoke deposits in order to correlate the observed optical properties with the particle size and distribution of the deposits. They will be reported in detail elsewhere.

EXPERIMENTAL PROCEDURE

The technique employed in producing the gold "blacks" and measuring their properties will be described in detail.

Preparation of Specimens

1. Cellulose nitrate films. The films were made by spreading a solution of thirty-second-viscosity cellulose nitrate, containing plasticizer, on a water surface.

The films weighed $\sim 8\times 10^{-6}$ gram/cm^2, corresponding to a thickness of $\sim 5\times 10^{-6}$ cm.

The nitrocellulose films were mounted on brass frames 5 cm$\times$5 cm$\times$0.105 cm thick, having a hole 3 cm in diameter, in the center of the frame. A 5-cm square of 0.8-mm thick copper sheet was fastened to the back side of the frame. This copper backing served to dissipate the heat from the cellulose nitrate film during the gold evaporation. The front (film) side of the frame faced the filament from which the gold was evaporated.

2. Evaporation of gold. The "blacks" were prepared in an atmosphere of nitrogen to permit continued use of a tungsten filament. A 5-cm length of 0.5-mm diameter gold wire was wound around the "V" of a 30-mil tungsten filament, 8.7 cm long. The filament was heated in a high vacuum until the gold melted to form a drop at the bottom of the "V," and then the temperature was quickly raised well above that to be used in the preparation of the gold "blacks." The current through the filament was reduced as soon as the "spitting" of impurities ceased. The gold was kept just molten until after the nitrogen was introduced and the pressure adjusted; then the current through the filament was increased to the desired value. A filament can be used twelve to twenty times, if it is not broken while applying the gold wire. It is advisable to examine the filaments carefully under a microscope before inserting them in the electrodes. A crack $\sim 2\times 10^{-4}$ cm wide in the "V" of the filament produces a streaked gold "black" deposit.

A shield 1.3 cm from the filament screened the film from most of the tungsten filament.

A solenoid-operated-shutter, between the shield and film, permitted the film to be exposed to the gold-"black" smoke for a desired length of time, and only when the current through the filament was constant.

The apparatus for preparing gold "blacks" is shown in Fig. 1.

In all the experiments, the drop of gold was centered opposite the center of the film; the position of the filament was held fixed at 7 cm from the nearer side of the bell jar, and the position of the film was varied to give the required distance for the given experiment.

Description of Measurements

1. Weighings. The central area of the cellulose nitrate film has a uniform "black" deposit on a circle of diameter of 2.4 cm. A circle of 2-cm diameter was cut from this central area by means of a cork borer.

The circles of cellulose nitrate plus the gold "black" weighed from $\sim 0.05\times 10^{-3}$ gram to 0.9×10^{-3} gram. Since a cellulose nitrate film of this area weighed only 0.025×10^{-3} gram, variations of 20 percent in the thickness of the cellulose nitrate films could be tolerated without affecting the required accuracy of the gold weighings. The variations in thickness of cellulose nitrate film were, however, less than 20 percent. The weighings, made with an Ainsworth

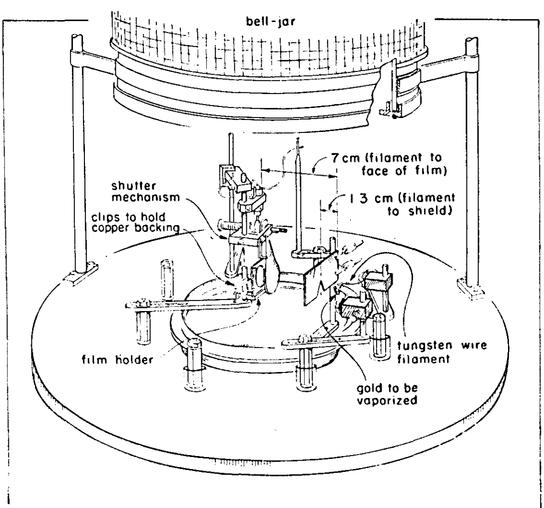

FIG. 1. Apparatus for the preparation of Gold Black.

micro-balance, were reproducable to $\pm 0.002 \times 10^{-3}$ gram. To achieve this accuracy it was necessary to maintain the films in desiccators between operations and measurements. In humid weather, the films were also dried at 60°C for thirty minutes before weighing.

2. *Infra-red transmission.* A blackbody as described by J. D. Hardy[6] was used as a source of infra-red radiation in the 10μ region. It consisted of a negative cone painted black and immersed in a constant temperature water bath maintained at 50.00 ± 0.05°C. An aluminum mirror was located at 45° to the optical axis and 23.4 cm from a limiting aperture in front of the radiating cone. This mirror was mounted on a rotatable holder so that the mirror could be replaced exactly by one of our experimental films and its function will be described under the reflection measurements. A thermopile connected to a General Motors d.c. Breaker Amplifier was located 2.9 cm from the mirror and adjusted to intercept the radiation reflected at 45°. The amplified response of the thermopile was indicated on a microammeter.

A shutter in which the blackened films were mounted was placed 7 cm from the aluminum mirror so that the film could be placed in the path of the radiation or raised out of the way. A limiting stop was placed in front of the film so that only the central portion of the deposit was irradiated in these measurements. The transmission ratio was the quotient of the meter deflection with the blackened film in the radiation path and the deflection with the film removed.

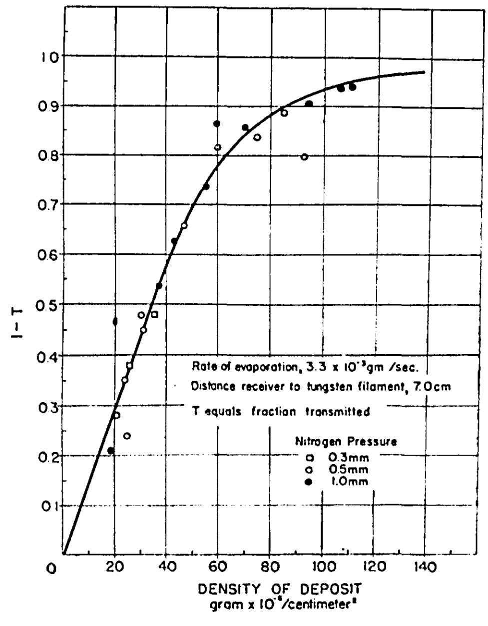

FIG. 2. Absorption of infra-red radiation by gold "blacks" as a function of density of deposit.

[6] J. D. Hardy, J. Clin. Investigation **13**, 593, 615 (1934).

3. *Infra-red reflection.* Relative reflections were obtained by mounting blackened films on the opposite side of the rotatable aluminum mirror described above and measuring the deflection of the microammeter when the radiation was reflected from the film and from the aluminum mirror. Thus the angle of incidence for all the infra-red reflectance measurements was 45°. The absolute reflection ratio was somewhat lower than the measured value because the aluminum mirror was not a perfect reflector. Its reflection ratio with respect to a new gold mirror was measured and found to be 0.9. The reflection ratios reported below are corrected to be relative to the reflection from the gold mirror. Black paint and black cardboard had reflection ratios of ~ 0.025.

A cellulose nitrate film had an infra-red transmission of 99 percent while the infra-red reflection for an angle of incidence of 45° varied between 4 percent and 7 percent. Reflection measured as described here gives a value in excess of the diffuse reflection.

4. *Infra-red spectral transmission.* The infra-red spectral transmissions were made at the M.I.T. Spectroscopy Laboratory with a Beckman infra-red spectrometer. The measurements extended from 1.0 to 15μ. A Beckman ultraviolet spectrometer was used for the measurements from 0.6μ to 1.0μ.

5. *Visible spectral transmission and visible spectral diffuse reflectivity.* Spectral diffuse transmissions and reflections in the visible spectrum were made at the M.I.T. Color Measurement Laboratory, using a Hardy colorimeter.

OBSERVATIONS AND MEASUREMENTS

1. *Infra-red transmission for different thicknesses of gold "black."* Figure 2 shows the infra-red transmission of gold "blacks" prepared at the optimum distance, 7 cm, between tungsten

filament and cellulose nitrate film, and at an intermediate rate of gold evaporation, for this distance, and at different pressures of nitrogen.

2. The effect of distance between filament and film on the nature of the deposit. Gold "blacks" were prepared at different rates of evaporation and at different pressures at distances between tungsten filament and cellulose nitrate film of 3.8 cm, 7.0 cm, and 14 cm.

2a. Deposits prepared at a distance of 3.8 cm. The deposits prepared at a rate of evaporation of 3.3×10^{-3} gram of gold per second and at nitrogen pressures of from 0.5 to 3.0 mm reflected 15 percent of infra-red radiation. The infra-red reflection increased for the deposits prepared at increased rates of evaporation; at the evaporation rate of 16×10^{-3} gram of gold per second, the reflection was 77 percent for a deposit having a transmission of 22 percent. The gold "blacks" prepared at a lower evaporation rate ($\sim1\times10^{-3}$ gram of gold per second) and at a pressure of 2.0 mm gave the best absorption coefficient at this distance (reflection $\sim$8 percent). The absorption "coefficient" was less, however, than that obtained for the 7.0 cm distance.

2b. Deposits prepared at a distance of 7.0 cm. The deposits prepared at a rate of evaporation of 3.3×10^{-3} gram of gold per second showed an infra-red reflection of 15 percent for a pressure of 0.3 mm. The deposits formed at a pressure of 0.3 mm had a yellowish appearance. Of the deposits formed at a pressure of 0.5 mm, the deposits of lower mass reflected 5 percent of the incident radiation; the reflection increased to as much as 15 percent for the heavier deposits. The deposits prepared at a pressure of 1 mm had the lowest reflections. The infra-red reflection increased from less than 1 percent to 4 percent as the evaporation rate increased from 0.5×10^{-3} gram of gold/second to 3.3×10^{-3} gram/second.

Deposits formed at an evaporation rate of $\sim12\times10^{-3}$ gram of gold per second, and at pressures below 1.0 mm, were yellowish. The deposits formed at pressures of 1.0 to 3.0 mm, at this rate, reflected $\sim$11 percent of the incident radiation.

2c. Deposits prepared at a distance of 14 cm. The optimum pressure for the deposition of good infra-red absorbers, at this distance, was also 1 mm. The infra-red absorption per unit mass for the deposits formed at this distance was uniformly lower than for the 7.0-cm distance, except for light deposits.

TABLE I. Infra-red absorption for different rates of gold evaporation.

Filament current (amperes)	Approx. rate of evaporation of gold (gram/sec.)	Time (seconds)	Infra-red (*BB*) transmission, *T* fraction	Infra-red 45° reflection fraction	Weight of gold (gram/cm²)	k^*
21.2	0.5×10^{-3}	300	0.08	<0.01	83×10^{-6}	13,000
23	0.9×10^{-3}	160	0.19	<0.01	58×10^{-6}	12,000
25	1.5×10^{-3}	120	0.21	0.03	56×10^{-6}	12,000
27	2.3×10^{-3}	60	0.21	0.03	57×10^{-6}	12,000
30	3.3×10^{-3}	50	0.225	0.04	55×10^{-6}	12,000

$k^*=(1/\text{gram/cm}^2)\log_{10}1/T$

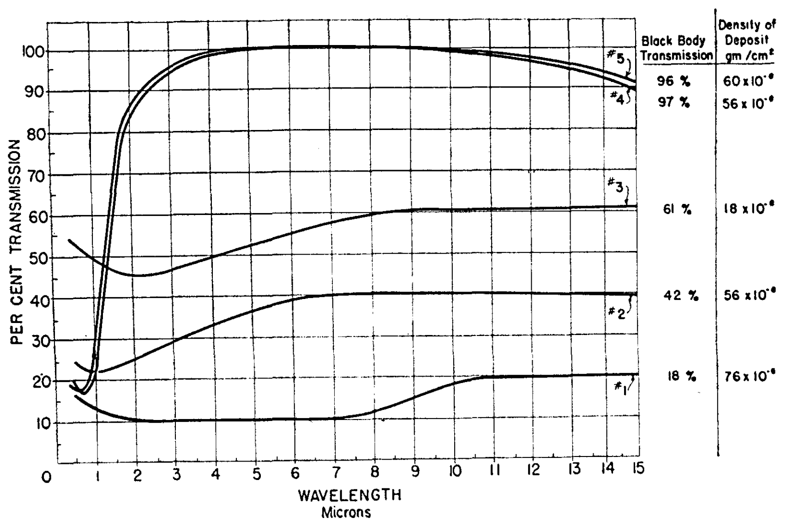

FIG. 3. Infra-red transmission of gold "blacks."

TABLE II. Change in transmission of gold "black" deposits on being heated.

Pressure	Rate of evaporation (g/sec.)	Density of gold "black" (g/cm^2)	Before heating T	Before heating R^*	Before heating $A=1-(T+R^*)$	After heating T	After heating R^*	After heating $A=1-(T+R^*)$[a]
0.5 mm	3.3×10^{-3}	41×10^{-6}	0.52	0.13	0.35	0.31	0.35	0.34
0.5	10.0×10^{-3}	66×10^{-6}	0.37	0.15	0.48	0.14	0.45	0.41
1.0	3.3×10^{-3}	106×10^{-6}	0.06	0.03	0.91	0.03	0.09	0.88

[a] R^* = infra-red reflectance at 45 degrees.

3. *The variation of infra-red absorption with rate of gold evaporation.* The data obtained for a pressure of 1 mm and for a distance of 7 cm are given in Table I. There is, thus, very little change in absorption with rate of gold evaporation up to rates as high as 3.3×10^{-3} gram/second; at still higher rates the absorption becomes less. The deposits prepared at the lowest rate have the lowest reflection.

4. *Effect of purity of the gas.* Gold blacks with the largest k^* (such as those represented in Table I) were made with the purest gas used, nitrogen containing less than 0.3 percent of oxygen, or a partial pressure of 0.003 mm of oxygen. When the nitrogen was enriched in oxygen, the k^* decreased, so that for a gas mixture containing 5.5 percent oxygen the k^* decreased to a value of approximately 1 percent of that for the deposits prepared with the purer nitrogen. For gas mixtures containing between 0.3 percent and 5 percent the k^*'s had values intermediate between that for the purest gas and the low value given.

In order to be certain of obtaining a "black" having a high absorption in the visible and low absorption in the infra-red, the inert gas should contain at least 2 percent oxygen and the rate of gold evaporation should be approximately 0.5 $\times10^{-3}$ gram/second. (We have obtained deposits having such characteristics with gas mixtures containing even less than 1 percent oxygen, at rates less than 0.5×10^{-3} gram/second.)

5. *Spectral transmission in the infra-red.* The transmission of radiation of a number of deposits of gold smoke prepared under different conditions is given as a function of wave-length from 0.5μ to 15μ in Fig. 3. The percent transmission of each of these deposits to radiation from the 50°C blackbody is given in the first column on the right and their respective masses in the second column on that side. All the deposits were prepared at a distance of 7.0 cm.

Curves 1 and 3 are given by deposits of different mass produced at 1 mm nitrogen, minimum amount of oxygen, and intermediate rate. The transmission can be seen in both cases to decrease slightly to a minimum just beyond 2μ and then to rise gradually a few percent, remaining constant beyond 8μ to 10μ. Curve 2, obtained from a deposit made in 1.0 mm of nitrogen but at a fast rate of evaporation (approximately 12×10^{-3} g/sec. of gold) has similar characteristics but is a poorer absorber per unit mass.

Curves 4 and 5 show the very interesting characteristics of deposits produced when oxygen present. These curves have a pronounced minimum at 0.8μ and then a sharp rise to 2μ so that

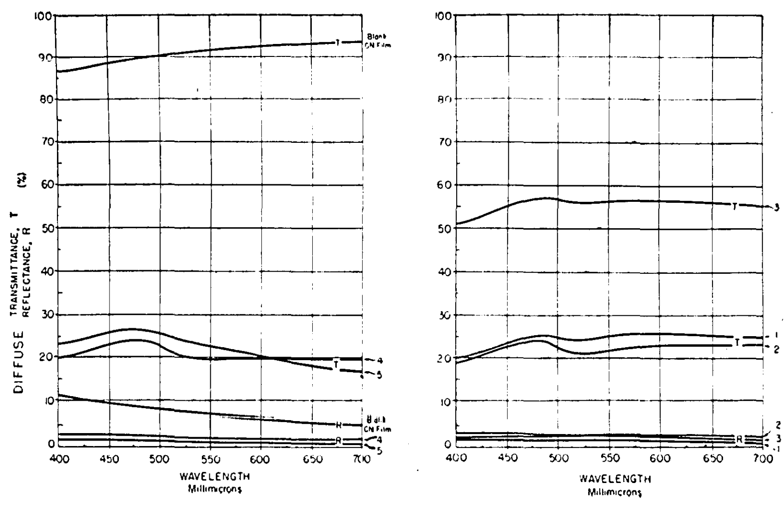

FIG. 4. Visible diffuse transmission and reflection of gold "blacks."

TABLE III. Summary of electron microscope studies of gold smoke deposits.

Rate of gold evaporation	Nitrogen pressure	Size of unit colloid particle limits	average	Number of particles in initial aggregates	Type of aggregation
0.5 to 3.3 $\times 10^{-3}$ gram/sec.	0.5 to 1.0 mm*	10–150A	50A	many	open network
	3.0 mm*		250A	many	open network
3.3×10^{-3} gram/sec.	0.3 mm	15 to 100A	50A	few	uniform
	0.5 mm	25 to 200A	100A	intermediate	sponge-like
	1.0 mm	75 to 250A	150A		sponge-like
10×10^{-3} gram/sec.	0.5 to 1.0 mm	10 to 200A	40A	few	uniform

* One percent oxygen present.

the deposits are almost completely transparent between 3μ and 10μ and falling to approximately 90 percent at 15μ. The deposit for curve 5 was made at a total pressure of 1 mm and at a low rate of gold evaporation. Such a curve is characteristic of deposits made at 1 mm pressure, slow rate, and oxygen partial pressure of 0.02 mm. Curve 4, which has the same optical characteristics as curve 5, was obtained for a deposit made at a total pressure of 3.0 mm and at an intermediate rate. It is characteristic of intermediate rates of deposit if the partial pressure of oxygen is greater than 0.06 mm.

If care is exercised that no oxygen is introduced with the introgen, that the bell jar system is tight, and that there is a minimum of adsorbed oxygen, good quality deposits such as illustrated by curves 1, 2, and 3 and in Table I can be obtained at 1-mm pressure with low rates of evaporation or at 3.0 mm and intermediate rates.

The transmissions indicated in Fig. 3 show that the transmissions obtained with the 50°C blackbody are satisfactory measures of the transmission between 2μ and 15μ.

6. *Spectral properties in the visible.* The diffuse reflection of visible radiation was measured as a function of wave-length on several deposits to determine whether there is a characteristic scattering in the visible region which might be used as a criterion for the character of the "black" as an absorber of infra-red radiation. These data are shown in Fig. 4.

All the gold "blacks" show low reflection, nearly all show slightly less reflection in the red than the blue.

All the deposits are characterized by a maximum transmission at 480 mμ. *Bright gold* deposits have the maximum transmission at 500 mμ.

The gold "black" deposits with the highest infra-red absorption per unit mass (No. 1 and No. 3) have greater transmission in the red than in the blue, while gold "black" deposits with low infra-red absorption coefficient (No. 5 and No. 4) have nearly the same or slightly lower transmission in the red than in the blue. In a number of cases, deposits prepared under the conditions used for No. 5 and No. 4 appeared blue to the eye by transmitted light (incandescent source).

7. *Effects of heating gold deposit.* There are several other factors which influence the character of the gold deposit and one of them is the temperature of the receiving surface, or the subsequent heat treatment to which the deposit is subjected. In our study the deposits whose transmission and reflection had been measured, were heated to 120°C for two to three hours and then the changes in transmission and reflection were observed. (The cellulose nitrate film upon which the gold was deposited limited the temperature for heating to a maximum of 120°C.) The "black" deposits took on a yellowish appearance after this heat treatment. Table II lists the observations which were made on such deposits.

It is immediately evident that there is a loss in transmission upon heating and that this loss is caused by increased reflection. There is a tendency for the amount absorbed to decrease and in some cases the reflectivity increased

TABLE IV. Comparison of gold "blacks" and carbon as infra-red absorbers.

	Percent absorption	Mass	Thermal mass
Gold "black"	80	56×10^{-6} g/cm²	1.7×10^{-6} cal./°C/cm²
Carbon†	72	180×10^{-6} g/cm²	36×10^{-6} cal./°C/cm²

† Clemens Schaefer and F. Matossi, Das Ultrarote Spektrum (Verlag Julius Springer, Berlin, 1930).

considerably above the loss in transmission, indicating that elevated temperatures introduce a definite limitation in gold "black" as an absorber.

At higher temperatures there is apparently a sintering of the metal deposit, and since gold diffuses readily at relatively low temperatures, this sintering effect already occurs to a considerable extent at 120°C. Beeck, Smith, and Wheeler[7] found in studying the sintering of nickel deposited in this manner that the same effects were observed if the original deposit was made on a massive surface heated to a given temperature during deposition or if the metal were deposited on the same surface at room temperature and then heated to the elevated temperature.

8. Effect of backing. The metal backing behind the cellulose nitrate film has been described above and its function pointed out. Without a backing only a very small amount of gold deposits on the cellulose nitrate film and the same effect has been observed in the case of very thin metal foils. The distance between the film and the backing has a pronounced effect on the quality of the gold deposits obtained.

The rate of deposition and the optical properties of the black deposit are determined, in addition, by the nature of the receiving surface. A few observations have been made on surfaces of other materials. For example much lighter gold deposits are formed on thin strips of nickel, having masses of 86×10^{-6} g/cm^2, than on the cellulose nitrate films having masses of 8×10^{-6} g/cm^2, as used in our experiments, for the same time and rate of evaporation. It was necessary to bring the metal backing in contact with the nickel strips in order to obtain a good deposit of gold "black." On massive surfaces the gold smoke deposits readily.

9. Electron microscope studies. The gold smokes deposited under varying conditions show pronounced differences in particle size and distribution. We shall only summarize the results of these studies, since they will be treated in detail elsewhere.

The electron micrograph images of thin deposits indicate that the gold deposits in small spheroidal particles, and the broadening of the diffraction rings indicate crystal sizes of about 50A. The unit spheroids observed in the electron microscope could appear to be crystallites.

The electron micrographs clearly show an increase in size of the unit colloidal particle and increasing tendency to cluster with increasing pressure of nitrogen in which the evaporation takes place.

The results of the electron microscope studies are summarized in Table III.

Electron diffraction patterns of all gold deposits show randomly distributed crystallites. The effect of oxygen could not be detected in the electron diffraction patterns; only the lattice spacing of pure gold was apparent.

DISCUSSION OF RESULTS

Gold smoke deposits upon thin cellulose nitrate films have the best properties for the absorption of infra-red radiation when produced under conditions which are in an intermediate range of nitrogen pressure, rate of evaporation, and distance between source and surface of deposition. The partial pressure of oxygen in the gas should be less than 0.003 mm. The optimum range of experimental conditions for gold "blacks" having the highest infra-red absorption per unit mass is: (a), an atmosphere about 1.0-mm pressure of nitrogen; (b), evaporation rate of 0.5×10^{-3} to 3×10^{-3} gram of gold per second; (c), distance of about 7 cm between the source of evaporation and the surface on which the gold is depositing; (d), copper backing 0.1 cm or closer behind the film being deposited.

The "blacks" produced under these conditions have excellent characteristics for infra-red absorbers of low thermal mass. Deposits having a mass of only 45×10^{-6} gram/cm^2 can be prepared which will absorb 68.4 percent ($\sim$90 percent for a double traversal) of the incident radiation to 15μ.

It is of interest to compare the absorption of infra-red radiation (average for 9μ) of the best gold "blacks" with deposits of carbon, as is done in Table IV. Thus, these gold "blacks" have a thermal mass of approximately 1/20th that of carbon.

An important application of the gold "blacks" deposited in an atmosphere of oxygen-enriched nitrogen is as a filter for transmitting infra-red

[7] Otto Beeck, A. E. Smith, and Ahlborn Wheeler, Proc. Roy. Soc. **A177**, 62 (1941).

radiation beyond 2μ. Such deposits have a sharp cut-off at about 1μ and are good absorbers of the shorter wave-lengths. A triple filter of this type will transmit less than 1 percent of the radiation below 1μ and more than 90 percent of the radiation beyond 3μ.

SUMMARY

We have studied the optical properties of gold smokes deposited on cellulose nitrate films under different experimental conditions. The conditions of pressure of the inert atmosphere, the rate of evaporation, and the distance between source and deposition surface, and the backing for the film giving the highest infra-red absorption per unit mass have been found. The particle size and particle distribution of the gold smokes deposited under the different experimental conditions have been investigated with the electron microscope at high resolution.

ACKNOWLEDGMENTS

We are indebted to Miss Beatrice Alexander and to Miss Alice M. Pearson for their excellent technical assistance, to Dr. Charles W. Young for his many helpful discussions and suggestions, and to Mr. David Jeffries for his able assistance with many of the measurements.