

NRL REPORT 3712

**THE PROPERTIES OF EVAPORATED GOLD
AND TUNGSTEN OXIDES**

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ABSTRACT

Gold blacks prepared by evaporating gold from a tungsten filament in tank nitrogen at several millimeters pressure were found to contain tungsten oxides which greatly affected the optical and electrical properties. Deposits containing more than 0.5 mol percent of tungsten oxides were black and showed resistivities 10^3 to 10^8 times that of bulk gold. The resistivities of gold blacks increased on exposure to oxygen. On the other hand, oxide-free deposits were yellow and possessed a low, stable resistivity, unaffected by exposure to oxygen. Exposure to air or oxygen caused an increase in the electrical resistance and optical transmission of films of tungsten dioxide and tungsten trioxide evaporated in high vacuum. It was concluded that evaporated films of pure gold are unaffected by exposure to air, and that the changes in optical and electrical characteristics often observed in evaporated gold films exposed to air may be attributed to contamination by oxides of tungsten. It was also concluded that so-called gold blacks are black because of the presence of tungsten oxides, since gold evaporated in pressures of several millimeters of oxygen-free nitrogen formed bright reflecting films rather than black absorbing deposits.

PROBLEM STATUS

This is an interim report on the problem; work is continuing.

AUTHORIZATION

NRL Problem P08-04R
NR 488-050

THE PROPERTIES OF EVAPORATED GOLD AND TUNGSTEN OXIDES

INTRODUCTION

High-vacuum-evaporated gold films are metallic in appearance and, immediately after preparation, show a fall in electrical resistance due to a decay of lattice defects introduced in the condensation process (1,2). On the other hand, gold deposits formed by evaporation in a poor vacuum, or in a gas such as unpurified tank nitrogen, are no longer metallic but are black in appearance and are good absorbers of radiation. These are therefore known as "blacks." Gold blacks are now almost universally used as absorbing coatings on thermocouples and bolometers.¹ The term "smokes," as used in this paper, includes both blacks and brownish-yellow deposits, both types being formed in a gas atmosphere. The blacks and some of the brown deposits prepared in this way showed no resistance decrease when exposed to air but, instead, showed an increasing resistance of the order of megohms. This effect has also been noted for evaporated deposits of silver (3), of lead (4), and of palladium, platinum, rhodium, and iridium (5).

Harris, McGinnes, and Siegel(6) have found considerable differences in the optical transmission of gold blacks prepared by heating a tungsten filament, coated with gold, in nitrogen containing oxygen in amounts varying from 0.3 to 5 percent. The deposits formed in the 0.3-percent oxygen and nitrogen mixtures showed low optical transmission from 0.4μ to 15μ , while those prepared in higher percentages of oxygen showed increased transmission beyond 2μ .

According to Langmuir (8), tungsten heated above 700° C reacts heterogeneously with low-pressure oxygen to form the volatile tungsten trioxide, while tungsten heated in oxygen-nitrogen mixtures forms an oxide of the stoichiometric formula W_2O_5 . Nitrogen, however, reacts only with tungsten vapor, which is present at a negligible pressure below 2300° C (8). Tungsten oxides formed by heating a tungsten filament to 1500° C in 2 microns of flowing oxygen have been used to shadow electron microscope specimens (9). Various oxides of tungsten with a stoichiometric formula corresponding approximately to W_4O_{11} have been investigated by X-ray diffraction (10), (11), (12), but the existence of a true molecule with this formula is not fully established. The crystallographic structures have been said to bear a resemblance to those of both WO_2 and WO_3 (13).

It is thought that all of the gold blacks measured by Harris (6) probably contained oxides of tungsten formed by simultaneous oxidation of the tungsten filament during the gold evaporation. Evidence is here presented to show that the optical and electrical properties of gold smokes are modified largely by impurities such as tungsten oxides and that, if no tungsten oxides are present in the deposit, it is a yellow, high-reflecting film, whether evaporated at high or low pressure.

¹Formerly, absorbing coatings frequently used were bismuth and zinc blacks whose properties have been described by A. H. Pfund(7).

SPECIMEN PREPARATION AND TESTING

The evaporations of gold were carried out in a bell jar modified to allow purified tank nitrogen² to flow through it at a constant rate. The gold was evaporated from a conical tungsten wire cup electrically heated and maintained at constant temperature by observation with a Leeds and Northrup optical pyrometer. In some evaporations, tungsten dioxide and tungsten trioxide were vaporized from a quartz cup fitted into a tungsten heater coil.

The films and smokes were deposited on electron microscope specimen screens coated with formvar and on microscope slides silver-tipped to permit measurements of electrical resistance. These were located at a distance of 7 cm from the tungsten cup. The clear area on the microscope slides measured 1.8 by 2.5 cm. The surface density of the deposit was determined by weighing a measured area with a microbalance.

Some later evaporations were made in an all-pyrex evaporator constructed from a five-liter flask which could be readily evacuated to 10^{-6} mm pressure and to which was attached a gas purification train, storage vessels, manometers, liquid-air traps, and a gas analysis system. The electrical resistance slides were located below and in thermal contact with a glass finger, sealed into the flask, which permitted cooling of the specimen with refrigerant if desired. The clear area of these electrical resistance slides measured 1 by 1-1/2 cm and were located 7 cm above the filament. This apparatus allowed evaporations to be carried out in highly purified flowing nitrogen with no danger of contamination. The pressures of nitrogen employed were 10^{-6} , 10^{-3} , 1, 5, 10, and 13 mm of mercury.

Tungsten trioxide was prepared from sodium tungstate by the method of Schumb and Hartford (14).

Tungsten dioxide was prepared by heating the trioxide in vacuo for 15 hours with tungsten powder at 1000° C.

The gold, in the form of 30-mil wire, was obtained from J. Bishop and Co. Platinum Works. It analyzed about 0.03 percent silver as the major impurity.

GOLD DEPOSITS CONTAINING TUNGSTEN OXIDES

By controlling the evaporation conditions, gold smokes may be prepared containing various percentages of tungsten oxides. The pyrex evaporator constructed in this Laboratory permitted the preparation of gold smokes in nitrogen containing as low as 0.001 percent oxygen. Gold smokes prepared in the presence of more than about 0.1μ pressure of oxygen always showed contamination with tungsten on spectrochemical analysis. With the greatest care being taken to insure purity of gas and gold, gold smokes were prepared in 1 mm of flowing nitrogen which were no longer black but possessed high reflectivity and a stable resistivity approaching that of bulk gold and unaffected by exposure to oxygen. No tungsten was detected in these deposits. Other samples of gold smokes containing a few percent copper and silver and no tungsten were also black in visual appearance. Blacks were also made by evaporating mixtures of tungsten trioxide and gold as well as molybdenum trioxide and gold in highly purified nitrogen.

²The tank nitrogen was purified by passing successively over copper gauze (heated to 500° C) and phosphorus pentoxide. The resulting gas was analyzed by bubbling through freshly precipitated manganous hydroxide. The $MnO(OH)_2$ released was then caused to displace an equivalent quantity of iodine, which was then titrated with 0.01 N sodium thio-sulfate.

The Chemical Composition of Gold Blacks

The percentage of tungsten found in a gold smoke prepared by evaporation in impure nitrogen depends entirely on the evaporation conditions. As has been shown previously (8,9), tungsten heated in even small partial pressures of oxygen forms oxides which readily evaporate. The rate of formation of tungsten oxides at a constant filament temperature depends on the rate at which molecules of oxygen strike the filament, which, in turn, is determined by the partial pressure of oxygen and the rate at which oxygen is passed through the evaporation chamber. Increasing pressures of nitrogen would be expected to decrease the rate of tungsten oxide formation by competing with oxygen for active centers on the filament. Also, the relative number of tungsten oxide molecules and gold atoms which reach the collecting surface would be expected to depend on the total pressure (mostly nitrogen) since these substances are carried along by convection currents of gas. Increasing the tungsten filament temperature raises the evaporation rate of gold in proportion to $T^{-\frac{1}{2}} \exp(-B/T)$ and the rate of oxide formation in proportion to $\exp(-A/T)$, where A and B are constants and T is the absolute temperature. Finally, the ratio of quantities of tungsten oxide to gold which are evaporated depends on the free surface area of the evaporating gold and on the exposed surface area of the tungsten filament.

By maintaining the total pressure at a value between 1 and 13 mm, and the ratio of oxygen to nitrogen at $5 \cdot 10^{-3}$, a number of large samples of blacks were prepared and analyzed by spectrochemical methods. The following equation was found to hold (within 20 percent):

$$\text{Percentage tungsten oxides} = 10/G, \quad [1]$$

where G is the rate of deposit in $\mu\text{gm}/\text{cm}^2\text{-min}$, a quantity varied by changing the filament temperature (from 1190°C to 1430°C). Using this equation, the composition of small black samples prepared under like conditions could be estimated.

Resistance-Time Studies

The preliminary resistance-time studies were made on bright deposits prepared in the bell jar at one micron air pressure and on black deposits prepared in 13 mm of nitrogen. These deposits contained up to 14 mol percent tungsten oxides and showed increasing electrical resistivities when exposed to oxygen or air. The effect of various atmospheric gases on the electrical resistance of a bright deposit condensed at one micron pressure is shown in Figure 1. The resistance increased on initial exposure, then tapered off, and after several days became nearly constant. As seen in Figure 1, the initial rate of increase of resistance was much higher for oxygen than for air and was very small for carbon dioxide and nitrogen, the slopes of the curves in these latter cases probably being due to oxygen impurities and gas adsorption.

Similar results are shown in Figure 2 for a gold smoke prepared in nitrogen. The initial rate of increase of resistance was high upon exposure to oxygen and air and small upon exposure to nitrogen and carbon dioxide, as in the case of the bright deposits, and tapered off in a manner similar to the behavior of the bright deposits. The resistance of a black usually is of the order of megohms, and it frequently rises to several thousand megohms on standing in air for several days.

The Effect of Oxygen Pressure on the Resistance

If a gold smoke containing tungsten oxides is exposed successively to higher oxygen pressures, the initial rates of increase in resistance can be shown to be a function of pressure. This is illustrated in Figure 3 where $\log_{10} dR/dt$ is plotted against $\log_{10} P_{O_2}$. The initial exposure of this deposit to oxygen resulted in an abnormally high resistance increase which fell off rapidly as the pressure was increased. At about 30 mm pressure $\log_{10} dR/dt$ goes through a minimum, and above this pressure it is a linear function of $\log_{10} P_{O_2}$. This suggests that above 30 mm the change in resistance of the gold smoke with respect to time may be represented by an equation of the form:

$$dR/dt = KP_{O_2}^m, \quad [2]$$

in which the constants K and m may be determined empirically. The low-pressure anomaly shown in an extreme case in Figure 3 is more pronounced for blacks containing a smaller quantity of tungsten and having a relatively low resistance.

The Electrical Cross-section of a Gold Black

The computation of electrical resistivity requires a measurement of the thickness in addition to the width and length of the sample. Blacks are usually flocculent, loosely packed deposits, and the calculation of specimen thickness from a measurement of the weight of deposit per square centimeter depends on the density. However, what is needed is only an effective electrical thickness, i. e., the effective thickness of the material to be traversed by the electrons. Neglecting the comparatively small effects arising from varying contact resistances between the small particles for different samples, the assumption of bulk density (18.88 gm/cm^3) should be satisfactory for a calculation of resistivity although this will not, of course, give the apparent physical thickness.

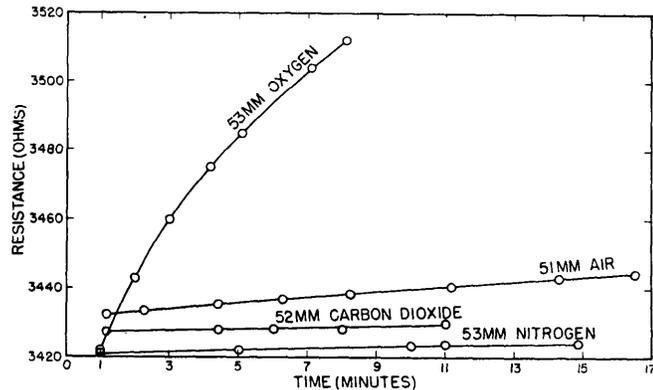


Figure 1 - The effect of atmospheric gases on the electrical resistance of a gold deposit condensed in one micron of air. Rate of deposition: one $\mu\text{gm/cm}^2\text{-min}$. Thickness: $34 \mu\text{gm/cm}^2$

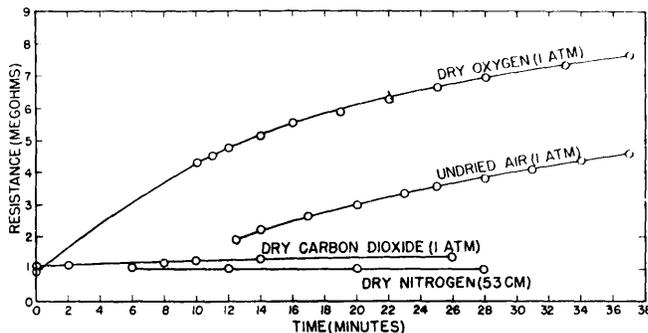


Figure 2 - The effect of atmospheric gases on the electrical resistance of a gold black condensed in 13 mm of nitrogen. Rate of deposition: $9.6 \mu\text{gm/cm}^2\text{-min}$. Thickness: $105 \mu\text{gm/cm}^2$. Sample contained 1 mol percent tungsten oxides

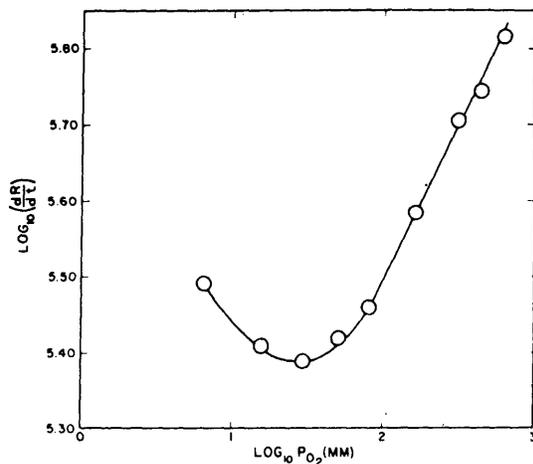


Figure 3 - The rate of change of electrical resistance as a function of oxygen pressure for a gold black condensed in 13 mm of nitrogen. Rate of deposition: $4.4 \mu\text{gm}/\text{cm}^2\text{-min}$. Thickness: $160 \mu\text{gm}/\text{cm}^2$. Sample contained 2 mol percent tungsten oxides.

slowly above 3 mol percent until it reached 0.6 at 14 mol percent. The exponent m is also seen to rise (Figure 5) from 0.18 at 0.5 mol percent and gradually flatten out with a value of 0.55 at 14 mol percent oxides.

Heating Gold Smokes

Heating gold smokes to $100\text{-}350^\circ\text{C}$ causes a change in appearance from a black to a yellowish color accompanied by an increase in reflectivity (6), which is, of course, undesirable when these materials are used as absorbing coatings in bolometers and thermocouples. On heating for 70 minutes at 350°C , one of our smokes showed a 4-percent loss in weight accompanied by a decrease in tungsten content and a change from a black to a yellow color. This effect is probably connected with evaporation of the volatile tungsten trioxide and possibly a chemical change in other impurities.

Conclusions

In order to produce a gold black it is thus necessary to employ a gas atmosphere and to evaporate simultaneously a foreign substance such as tungsten trioxide with the gold. The best absorbers of radiation probably contain greater than 2 mol percent tungsten oxides. These blacks have resistances of the order of megohms. It is suggested that gold blacks containing silver or copper might be good radiation absorbers in the infrared and would possess a much lower stable resistance.

The Electrical Properties and Composition of Gold Smokes

For a number of small samples of blacks prepared under standardized evaporation conditions, the percentage of tungsten oxides was calculated from Equation [1] and the initial electrical resistivity, ρ_i , before oxygen was admitted, and the constant K (in resistivity units) was calculated. Thus, in Figure 4, $\log_{10} \rho_i$ is seen to rise rapidly from -3.23 ($\rho_i = 6.10 \times 10^{-4}$) at 0.1 mol percent to 1.1 ($\rho_i = 13$) at 2 mol percent tungsten oxides. Above 2 mol percent, $\log_{10} \rho_i$ rises much more slowly to a value of 1.97 ($\rho_i = 93$) at 14 mol percent. The visual color of these samples varied from yellow at 0.1 mol percent to dark brown at 1 mol percent and became black at higher values. In like manner, the constants K and m in Equation [2] are functions of the total tungsten oxide content, as shown in Figure 5. At the top is given $\log_{10} K$, which increased from -3.6 at 0.7 mol percent to -0.2 at 3 mol percent oxides and changed

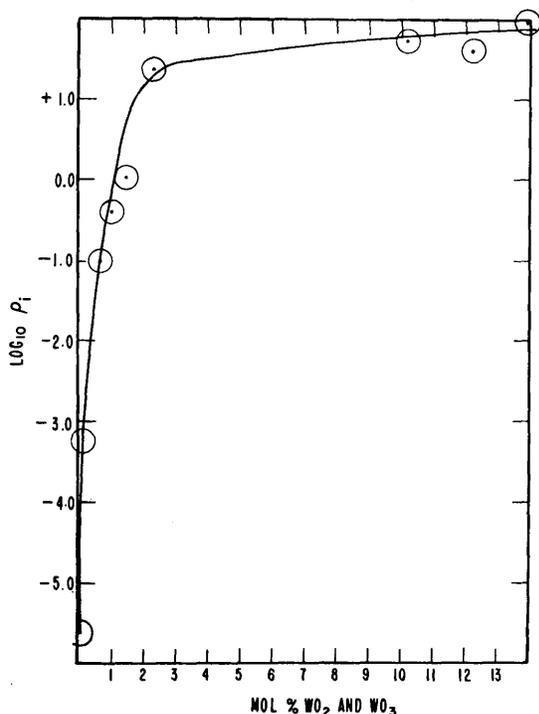
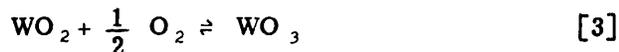


Figure 4 - The initial resistivity of various gold blacks as a function of the total mol percent tungsten dioxide and trioxide

value of m for both of these last two samples is nearly the same as the values obtained on tungsten dioxide and tungsten oxide containing gold smokes. In the calculation of the sample thickness for computation of resistivity, the density of tungsten dioxide was assumed equal to the bulk density (12.11 gm/cm^3). For tungsten trioxide and tungsten oxides formed by filament oxidation, the density was assumed to be that of tungsten trioxide (7.16 gm/cm^3).

Thermodynamic Properties of Tungsten Oxides

It is probable that the above observations can be explained by an oxidation of the conductive tungsten dioxide to the less conductive tungsten trioxide (15) according to the equation:



for which the equilibrium constant is 4.10^{41} at 300°K (16, 17, 18). When tungsten trioxide is evaporated in vacuum from a quartz cup, considerable dissociation occurs by the reversal of Equation [3] in the gas phase above about 1400°K . The equilibrium constant of this reverse reaction is $1.9 \cdot 10^{-5}$ at 1500°K and $2.6 \cdot 10^{-3}$ at 2000°K . When the trioxide is evaporated in vacuum in contact with metallic tungsten, the thermodynamic conditions are even more favorable, and reduction proceeds according to the reaction:



for which the equilibrium constant is $3.2 \cdot 10^6$ at 2000°K (16, 17, 18).

EVAPORATED TUNGSTEN OXIDES

Electrical Properties of Tungsten Oxides

Chemically prepared tungsten trioxide and dioxide, when evaporated in contact with a bare tungsten filament or from a quartz cup, and oxides produced by tungsten filament oxidation show, on exposure to oxygen, the phenomenon of increasing electrical resistivities, which is very similar to that previously noted for gold smokes and films. In Table 1 are given some values of ρ_i , m , and K for a number of samples. The first four examples show that increasing the surface density of tungsten dioxide evaporated at one micron from a quartz cup causes ρ_i , m , and K to decrease. The values of these constants are of the same order of magnitude as those for gold smokes containing tungsten oxides. Tungsten trioxide evaporated at one micron from a quartz cup gave values for the initial resistivity and for K of 2.7 ohm-cm and 2.3 ohm-cm/min respectively, both somewhat higher than those obtained for the dioxide. Tungsten oxides formed by filament oxidation in a mixture of 4.7 mm of nitrogen and 0.5 mm of oxygen gave high values of the initial resistivity and of K as shown. The

TABLE 1 †
Electrical Properties of Evaporated Tungsten Trioxide
and Tungsten Dioxide

Sample	Surface Density $\mu\text{gm/cm}^2$	ρ_1^*	m	K
WO ₂ evaporated at one micron from a quartz cup	27	0.60	0.51	0.20
	30	0.21	0.47	0.18
	116	0.072	0.14	0.086
	162	0.0161	0.04	0.0078
WO ₃ evaporated at one micron from a quartz cup	573	2.7	0.39	2.3
Tungsten oxides formed by filament oxidation PN ₂ = 4.7 mm PO ₂ = 0.5 mm	520	510	0.39	4.2

† The quantity ρ_1 is the initial resistivity, and m and K are constants in the equation $d\rho/dt = KP_{O_2}^m$.

* For the calculation of electrical thickness, the density of WO₂ was taken as 12.11 gm/cm³, and that of WO₃ was taken as 7.16 gm/cm³. For the oxides produced by filament oxidation, the density was taken as 7.16 gm/cm³.

Optical Transmission of Tungsten Oxides

Optical transmission measurements on evaporated films of tungsten dioxide support the electrical evidence for room-temperature oxidation to the trioxide. Vacuum evaporated films of tungsten trioxide and dioxide both appear blue by transmitted and reflected light, adhere well to the glass collecting surface, and become more transparent on aging in air. The transmission measurements were made by means of the Beckman Spectrophotometer in the range from $320m\mu$ to $1000m\mu$. The spectral transmission of a dioxide film evaporated in vacuo is shown in Figure 6 for various times after preparation. The peak transmission occurs in the blue at $400m\mu$, which is in agreement with its blue color. A broad absorption region occurs at about $800m\mu$ with an apparent narrower band developing at about $470m\mu$. Again as shown in Figure 6, the transmission increased considerably over the 16-day period because of oxidation to the trioxide. During the same time, the electrical resistance increased from 1800 ohms to 2000 megohms.

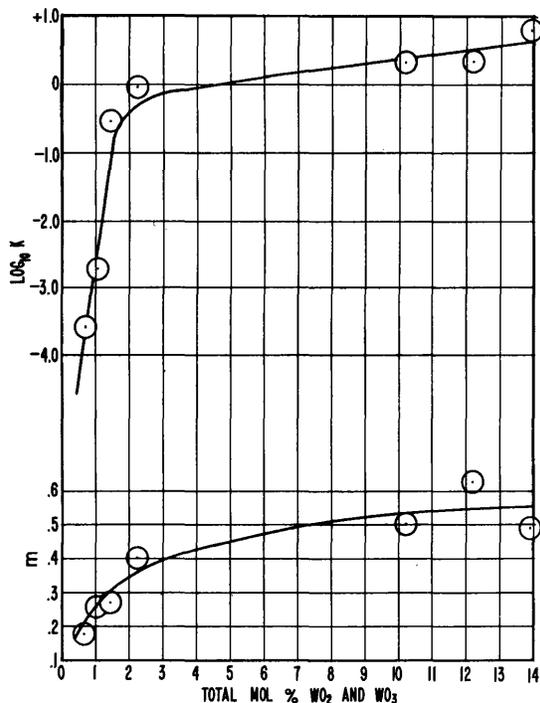


Figure 5 - The constants K and m (in equation $d\rho/dt = KP_{O_2}^m$) for various total concentrations of tungsten dioxide and trioxide in gold blacks

brane which developed holes in the process. The large agglomerates shown consist of many small particles with an average size of $60A$.

Figure 9 is an electron micrograph of tungsten trioxide evaporated in 10mm of nitrogen and also condensed on a formvar membrane. The similarity with Figure 8 is striking.

Figure 7 shows the spectral transmission over the same wavelength region of a tungsten trioxide film vacuum-evaporated from a quartz cup. A broad absorption region occurs at about $900m\mu$, and a transmission maximum is observed at $420m\mu$. As can be seen qualitatively from Figures 6 and 7, the trioxide is much more transparent than the dioxide. The trioxide showed small increases in transmission and resistance on aging in air, a circumstance which can readily be explained by assuming a partial thermal conversion to the dioxide during the evaporation process and subsequent oxidation.

ELECTRON MICROSCOPY

ELECTRON MICROSCOPY

Figure 8 is an electron micrograph of a gold smoke which contained about one mol percent tungsten oxides. The specimen was made by condensing the smoke in 13 mm of nitrogen on a formvar mem-

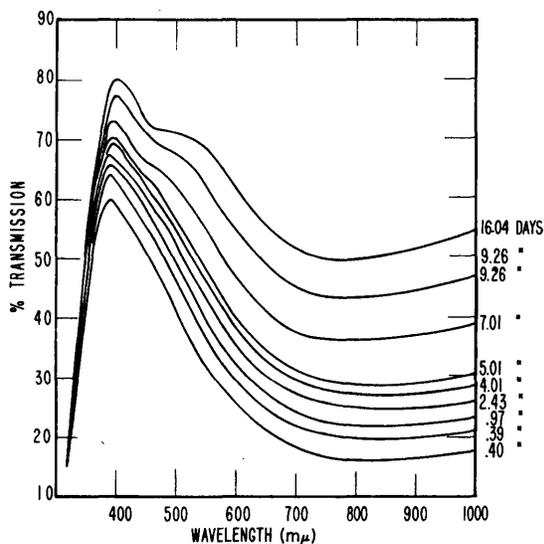


Figure 6 - The transmission of a vacuum-evaporated tungsten dioxide film over a 16-day period. Rate of deposition: $28 \mu\text{gm}/\text{cm}^2\text{-min}$. Thickness: $570 \mu\text{gm}/\text{cm}^2$

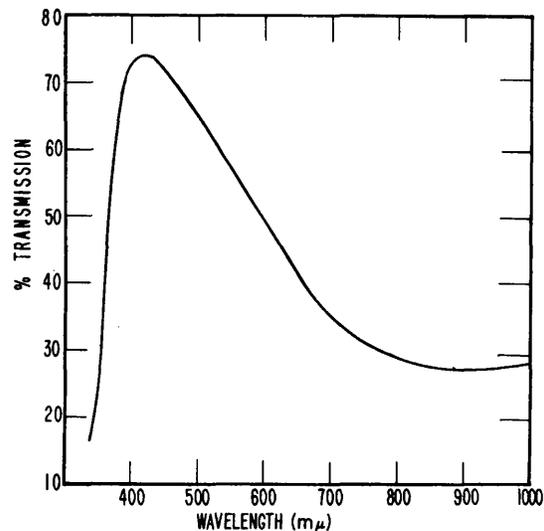


Figure 7 - The transmission of a tungsten trioxide film vacuum-evaporated from a quartz cup. Rate of deposition: $28 \mu\text{gm}/\text{cm}^2\text{-min}$. Thickness: $570 \mu\text{gm}/\text{cm}^2$

Figure 10 is an electron micrograph of a gold smoke which was condensed in 1 mm of purified nitrogen onto a formvar support and which contained less than 0.1 mol percent tungsten oxides. The particles formed irregular crystals, varied in size from less than 100A to 2000A, and were hardly distinguishable from high-vacuum-evaporated gold (2). They were always obtained when the smoke contained less than about 0.5 mol percent tungsten oxides.

Electron micrographs of chemically prepared tungsten trioxide and dioxide films deposited at one micron pressure appeared structureless and identical with those formed by filament oxidation (9). These materials can also be used for shadowing electron microscope specimens.

CONCLUSIONS

It is well known that presence of foreign metals causes a considerable increase in the resistivity of a metal, and it is not entirely surprising that traces of foreign oxides in gold should cause the tremendous increase shown in Figure 4. It is difficult to predict the magnitude of the effect, since the physical state of the tungsten oxides in gold smoke is unknown. No particles typical of pure gold are found on electron microscope examination of smokes containing greater than 0.5 mol percent tungsten oxides. When both types of particles are present, the smoke has a low resistivity, is little affected by exposure to air, and has a dark brown appearance.

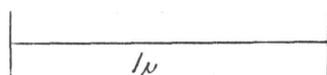
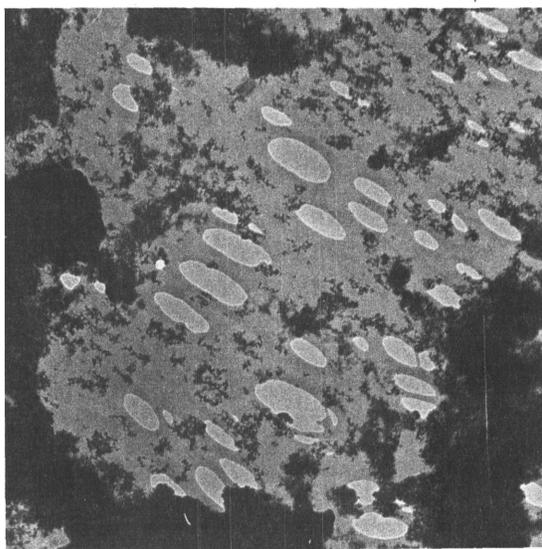


Figure 8 - Electron micrograph of a gold black evaporated in 13 mm of nitrogen on formvar. Particle size: 60A. Sample contains about 1 mol percent tungsten oxides

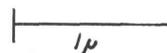
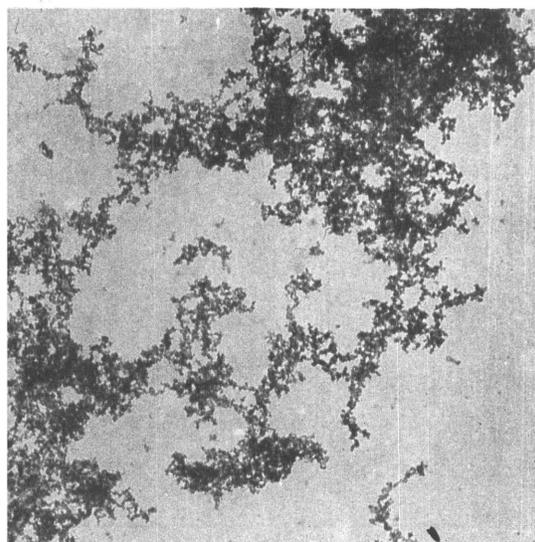


Figure 9 - Electron micrograph of tungsten trioxide evaporated in 10 mm of nitrogen

It is suggested that some of the aging effects observed in the transmission of evaporated gold films may be due to an oxidation of the tungsten dioxide probably present as an impurity.

To produce a gold black requires evaporation of the gold in a gas atmosphere and the simultaneous evaporation of a foreign substance such as tungsten trioxide. It is not necessary to produce the tungsten oxides by oxidizing the tungsten filament; blacks are readily formed by evaporating, in purified nitrogen, a mixture of a few percent tungsten trioxide and gold powder. Both the nitrogen and the tungsten oxides (or other impurities) must be present; otherwise a yellow deposit results.

The blacks prepared by Harris et al. (6) probably contained tungsten oxides in just the right concentrations to be good radiation absorbers. Harris, Jeffries, and Siegel (19) have also reported some gold blacks whose electrical resistance decreased as much as 70% after preparation and apparently did not increase on exposure to air. These deposits probably do not contain tungsten oxides but may contain small amounts of other metals such as silver and copper which could influence the optical and electrical properties.

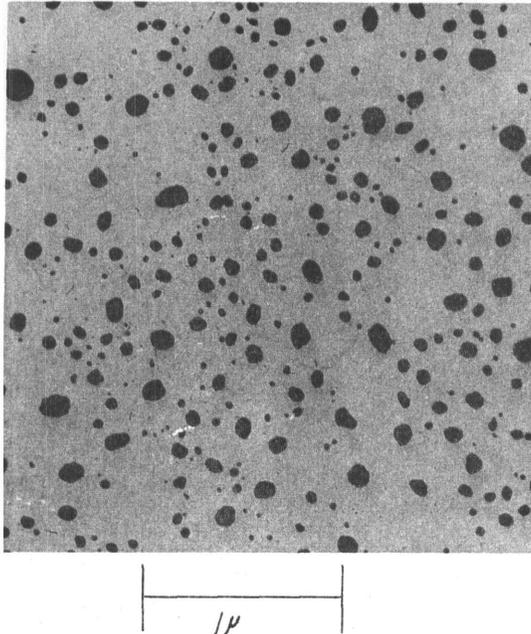


Figure 10 - Electron micrograph of a gold smoke formed in 1 mm of nitrogen and containing no tungsten oxides. Particles are typical of high-vacuum-evaporated gold

ACKNOWLEDGMENT

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