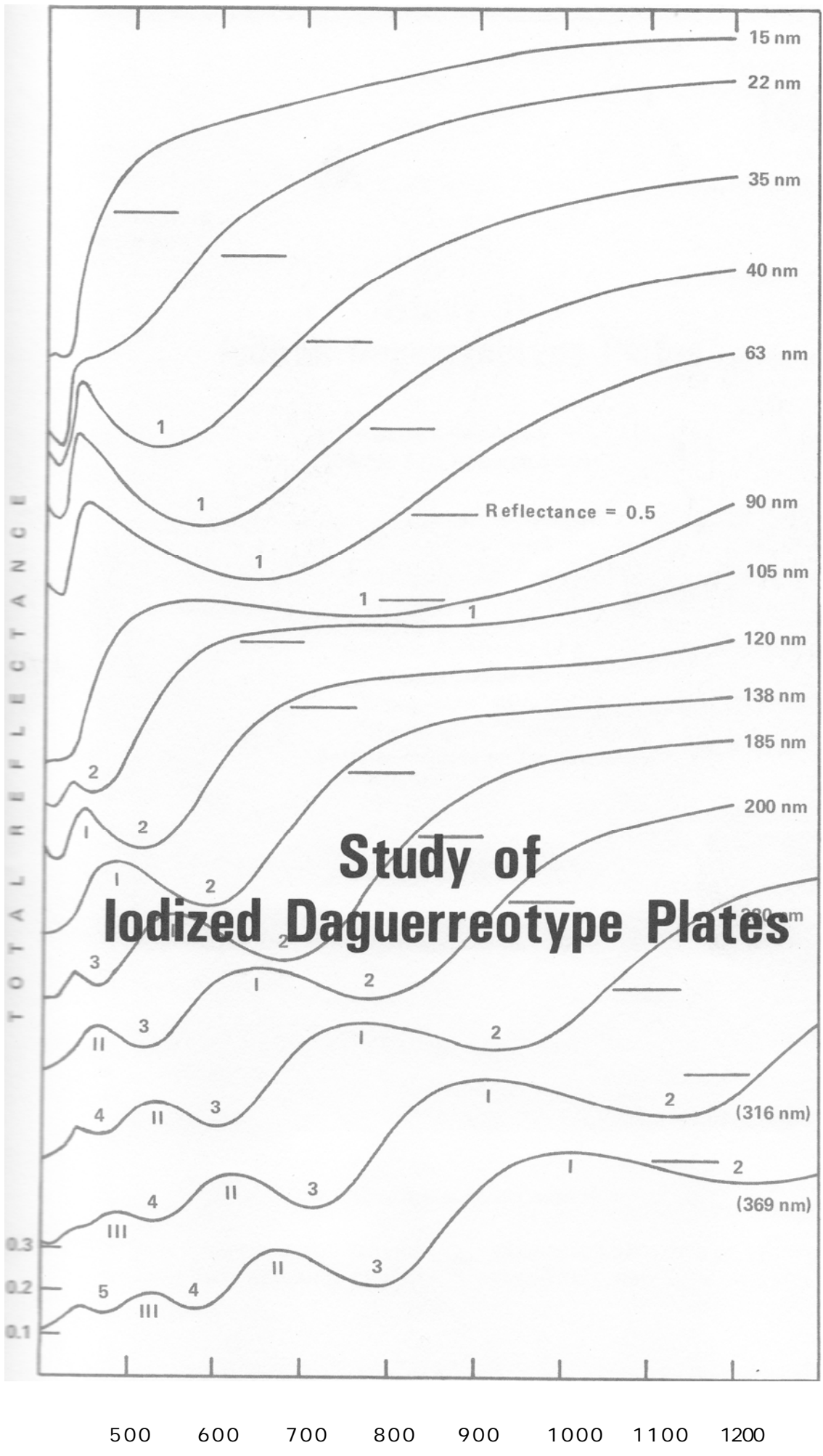


# Report

NUMBER .. 142



SILVER IODIDE THICKNESS (NM)

## Study of Iodized Daguerreotype Plates

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REPORT NO.

**142**

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# Study of Iodized Daguerreotype Plates

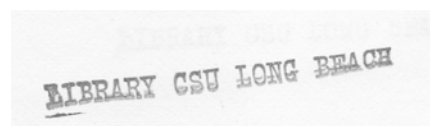
Irving Pobboravsky  
Graphic Arts Research Center

*In Partial Fulfillment of a  
Masters Degree in  
Photographic Science  
School of Photographic Arts and Science  
Rochester Institute of Technology*

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## STUDY OF IODIZED DAGUERREOTYPE PLATES

Irving Pobboravsky

### ABSTRACT

This paper deals with a study of a curious phenomenon observed while a daguerreotype plate is sensitized by fuming with iodine. As this sensitizing process continues, the surface of the plate is seen to go through a series of colors quite unrelated to the color of silver iodide. The objectives of this study are threefold: (1) to measure the thickness of the silver iodide layer for a series of plates that have been exposed to iodine fumes for various lengths of time and therefore have different colors, (2) to determine if interference or scattering is the cause of the observed colors, and (3) to measure the photographic speeds of a series of plates, each of which is differently colored.

In Part I, a series of differently colored iodide layers was prepared, each layer stripped from its silver support and its thickness measured by two different techniques, X-ray fluorescence analysis and spectral absorptance (Bouguer's law). The results of the methods were in good agreement; thicknesses were found to range between 15 and 230 nm.

In Part II evidence is presented indicating that both interference and scattering are taking place. The scattering is due to the optically rough surface which is seen (on scanning electron micrographs) to become rougher with increasing iodide thickness. The evidence for interference is qualitative since quantitative agreement between observed and calculated reflectance curves was not found. This disagreement was probably due to choosing a theoretical physical model having a plane parallel-sided layer which is not representative of the rough iodide layer found in daguerreotype plates.

Experimental evidence suggests that silver iodide layers less than 90 nm are discontinuous and therefore even such thin "layers" can scatter light. It was found that diffuse reflectance, and therefore scattering, increased with iodide thickness, levelling off at a thickness of about 75 nm.

This study has shown that the colors seen on iodized daguerreotype plates are not due to a single clear-cut cause but instead represent a very complex optical problem involving interference, scattering, and possibly absorption.

In Part III, the photographic speed of the iodide layer was found to depend on both its thickness and the method of development, that is, whether it was developed with mercury or by making use of the Becquerel phenomenon. The maximum speed of a plate was found when an iodide layer 30 nm thick was developed by the Becquerel phenomenon; this maximum speed is roughly equivalent to an exposure index of 0.0008 or 60 seconds at  $f/4.5$  on a bright, sunny day. Thick iodide layers (110 nm) result in characteristic curves of much lower contrast than obtained with thin layers (30 nm).

## STUDY OF IODIZED DAGUERREOTYPE PLATES

### INTRODUCTION

The earliest photographic process that achieved widespread use was the daguerreotype process, the details of which were announced in August of 1839. Daguerreotype plates consist of a thin silver layer on a thicker copper support. The silver layer is given a mirror-like polish, and by exposing it to iodine fumes, a light-sensitive layer of silver iodide is formed. The plate is then exposed in a camera and developed by placing it over a pool of heated mercury; the rising vapors of mercury selectively condense onto the latent-image silver, forming a silver-mercury amalgam. The unexposed areas are relatively free of mercury. Fixing is accomplished by dissolving the unexposed silver iodide in a solution of sodium thiosulfate. By the end of 1840, two substantial improvements had been made in the process. The first of these was gold toning which was introduced by Fizeau. This not only made the image far less fragile but it also increased the image contrast. In the second of these improvements, the speed of the plate was substantially increased by fuming the plate first with iodine and then with bromine.

Although the daguerreotype process after about 15 or 20 years was replaced by other processes, it is still unique among silver halide processes for a number of reasons. In most processes the photosensitive silver halide is suspended in a protective colloid such as gelatin; in the daguerreotype, the silver halide is unprotected and on the surface of the support. Because of this, the daguerreotype surface may be effectively more sensitive to short wave ultra-violet radiation than conventional gelatin emulsions which filter out these wavelengths. In addition, conventional emulsion layers are at least 100 times thicker than the photosensitive daguerreotype layer. This means that daguerreotype plates potentially offer better image resolution capabilities than conventional emulsions. Another unusual characteristic of the daguerreotype process is that dry rather than wet development is used. Conventional silver halide processes usually are wet-developed. Still another unusual characteristic is that while the image, in most processes, is the result of variations in light absorption, the daguerreotype image depends upon different degrees of back-scatter of light to produce the various tones.

Despite these unique characteristics and despite the passage of over 130 years since the process was first announced, very little of a fundamental nature is known about this process compared with what is known about conventional silver halide photography.



This paper will deal with a rather interesting phenomenon observed by early daguerreotypists while sensitizing their plates with iodine fumes. They found that as the iodizing proceeded, the color of the silver iodide layer changed gradually with the length of iodizing time (1). For example, after 20 seconds of iodizing, the plate appeared a light, low saturation yellow; after 35 seconds, the yellow had increased in saturation and taken on a reddish tinge; at 50 seconds, the silver iodide surface appeared magenta; at 60 seconds, blue with a slight magenta tinge, and so on. At some point, the plate would again become yellow, followed by another series of colors. In addition daguerreotypists soon recognized that the sensitivity of the plate changed as it changed color and would stop iodizing once a given color was achieved. This curious phenomenon led John Draper (2) in 1841 to hypothesize that these were interference colors caused by changes in thickness of the silver iodide layer. He further theorized that these interference colors accounted for the changes in sensitivity of the plate. Whenever the plate absorbed blue light the most, that is, when the plate was yellow, it would be most sensitive, and whenever the blue reflectance of the plate reached a maximum, it was least sensitive. He tested this by iodizing a series of plates, each to a different color, and exposing them for a standard length of time to the image of a gas flame. And as postulated, the sensitivity of the plate was at a maximum when yellow, decreased to a minimum when blue, and reached a second maximum upon turning yellow again.

This present study is an outgrowth of Draper's work. Although he thought that the various colors of the iodized plate were due to interference, no reference to a test of this hypothesis was found in the literature. Another possible hypothesis is that these colors are caused by selective scattering. The objectives of this thesis are: (1) to test the two hypotheses, interference and scattering, as the cause of the observed colors, and (2) to determine the relative sensitivity of the plate as a function of thickness of the silver iodide layer.

## **P A R T I**

### **THICKNESS MEASUREMENT OF SILVER IODIDE**

Since the thickness of a layer is fundamental to the interference phenomenon, layers of various thicknesses of silver iodide were measured by two independent methods. The first method involved making spectral absorption measurements of the silver iodide and computing the thickness using these data, the published absorption coefficients of silver iodide and Bouguer's law. These same silver iodide films were then measured by the second method, X-ray fluorescence analysis, which will be described later.

## EXPERIMENTAL PROCEDURE

### Preparation of Plates

The silvered surface of eight daguerreotype plates was given a mirror-like polish and half of each plate was iodized for one of eight different iodizing times from 20 to 660 seconds. The reason why only half of each plate was iodized was that the silver iodide layer would later be stripped from its silver support by coating the entire plate with gelatin; once dry and stripped from its support the gelatin half containing the silver iodide would be measured on a spectrophotometer relative to the "blank" gelatin half. This "zeroes out" the absorption of the gelatin so that only the spectral transmittance of the silver iodide is obtained. The iodizing time for each of the plates was chosen so that successive plates differed in color.

Since an iodized daguerreotype plate is relatively insensitive, it can safely be viewed by the light reflected from a white wall illuminated by a small tungsten lamp. The observer holds the plate between himself and the illuminated wall and views the plate obliquely, adjusting the angle of the plate until he sees the specular reflection.

### Stripping of Silver Iodide Layers

As mentioned before, each plate with its silver iodide layer was coated with a thick layer of a ten percent solution of high strength gelatin (Bloom value of 260) using a separate adjustable hopper and a laboratory emulsion coating block (3). It was then chilled to set and placed in a vacuum dessicator to dry. If the gelatin layer was thick enough, it separated from the support in one piece upon drying, taking the silver iodide layer with it. The thickness of the dried gelatin films used in this experiment ranged between 0.003 and 0.006 thousandths of an inch. Films much thinner than this either did no

separate from the support or would break up into small pieces if they did separate. When this happened, the silver iodide would usually not be uniformly removed from the support, some of it remaining behind as variously colored sections on the silver support. Another interesting observation is that while the silver iodide films were on the silver support they differed in color from one another, but once stripped off by the gelatin they had the same general yellow hue which increased in saturation with increasing iodide thickness. The color characteristics of silver iodide films viewed by transmittance and by reflectance will be dealt with later.

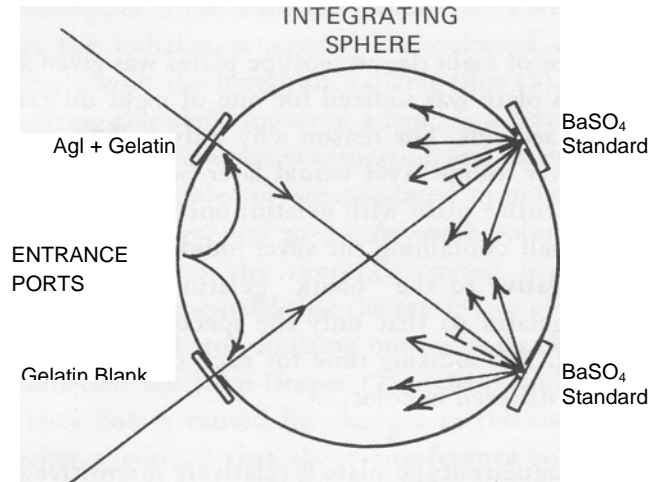


Figure 1. Top view of integrating sphere of spectrophotometer showing position of sample and blank when measuring uncorrected transmittance.

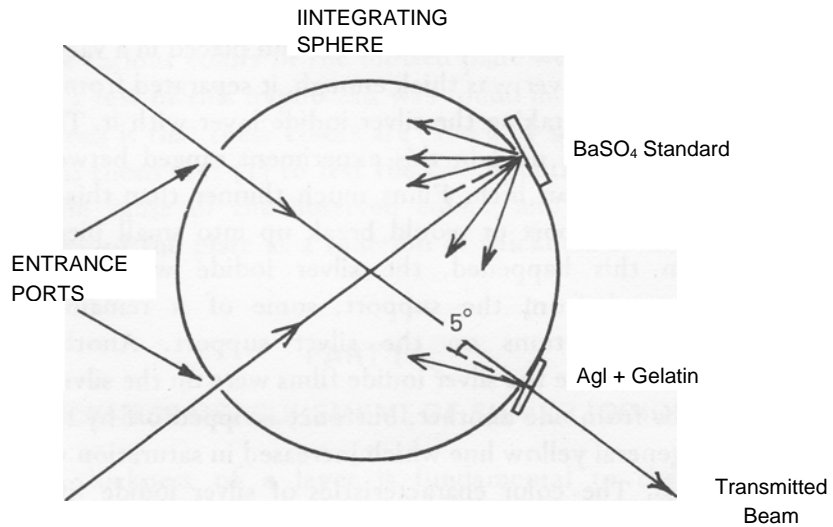


Figure 2. Top view of integrating sphere of spectrophotometer with sample positioned to measure first-surface and backward-scattered energy.

## SPECTROPHOTOMETRY OF STRIPPED SILVER IODIDE FILMS

The spectral transmittance of the samples was measured relative to the blank gelatin with a Beckman DK-2a recording spectrophotometer. The sample and blank were placed at the entrance ports of the integrating sphere and both exit ports were backed with barium sulfate standards, Figure 1. This arrangement measures all the light that gets through the sample but it does not take into account the light scattered backwards nor the first-surface reflection. Depending upon the thickness of the iodide, the back-scattered light can amount to as much as one third of the incident energy. This causes a significant error in the measured transmittance. However, the back-scattered energy can be measured by the arrangement shown in Figure 2 and this information used to correct the measured transmittance. Both sample and blank are removed from the entrance ports and the sample is placed at the sample exit port but not backed with barium sulfate, the silver iodide side of the gelatin film facing toward the sphere. Everything else remains unchanged. With this arrangement the front-surface reflection and the backward-scattered light are thrown into the sphere and measured while the transmitted beam is lost in the black chamber beyond the sphere. The corrected transmittance,  $t$  is given in equation 1.

$$t = \frac{t_u}{1 - r} \quad (1)$$

$t_u$  is the uncorrected transmittance and  $r$  is the first-surface reflectance and back-scattered light. Equation 1 is really the ratio of the transmitted over the incident energy; however, the incident energy is no longer taken as unity but as  $1-r$  because the reflected energy never had a chance to traverse the silver iodide.

## CALCULATION OF SILVER IODIDE THICKNESS USING BOUGUER'S LAW

The thickness of a material can be calculated from Bouguer's law if its transmittance and absorption coefficient are known.

$$t = \exp(-kh) \quad (2)$$

where  $k$  is the absorption coefficient and  $h$  is the thickness of the material in centimeters. (All calculations are based on a single wavelength; the peak wavelength of silver iodide, which is roughly 424 nm.)

Solving for thickness, **h**

$$h = \frac{\ln t}{-k} \quad (2a)$$

The absorption coefficients for silver iodide obtained by treating silver with iodine vapor are published in the International Critical Tables (4). Figure 3 is a graph of these absorption coefficients as a function of wavelength. Note that the coefficient at the absorption peak is  $138 \times 10^3 \text{ cm}^{-1}$  which is of the order of the absorption coefficient of a dye at its maximum! And Note that the absorption past 450 nm is essentially zero.

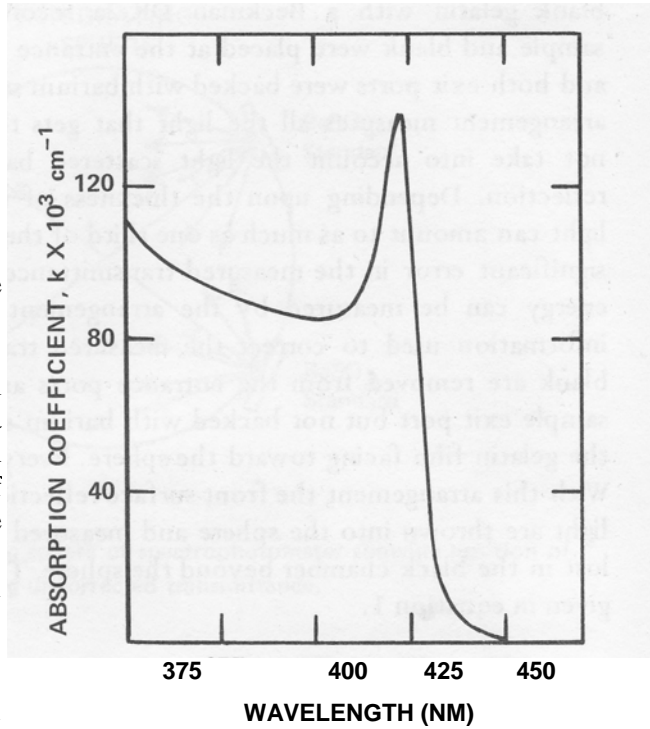


Figure 3. Absorption coefficients of silver iodide as a function of wavelength.

#### Calculation of Silver Iodide Thickness from X-ray Fluorescence Data

As mentioned before, these same silver iodide samples were also measured by X-ray fluorescence analysis (5). Very briefly, this method involves irradiating the sample with a strong burst of short-wavelength x-rays causing the silver in the sample to fluoresce longer wavelength x-rays. This fluorescent radiation is sorted out by a crystal spectrometer and a Geiger counter counts the number of quanta of a specific energy level. Once the system has been calibrated, an analysis can be made in a few seconds and the results are very repeatable.

These samples were measured through the courtesy of the Eastman Kodak Research Laboratories where this method is routinely used to determine the silver per unit area of a film or paper coating. The data were reported as milligrams of silver per square foot.

Silver iodide thickness can be computed as follows:

- a. Convert mg of Ag/ft<sup>2</sup> to mg of AgI /ft<sup>2</sup>:

$$\text{mg of AgI/ft}^2 = \frac{\text{molecular weight of AgI}}{\text{molecular weight of Ag}} \cdot \frac{\text{mg of Ag}}{\text{ft}^2} = 2.17(\text{mg of Ag/ft}^2)$$

- c. Convert mg of AgI /ft<sup>2</sup> to mg of AgI /cm<sup>2</sup>:

$$\frac{\text{mg of AgI}}{\text{cm}^2} = \frac{\text{mg of AgI}}{\text{ft}^2} \cdot \frac{\text{ft}^2}{929 \text{ cm}^2}$$

- e. Using the density of AgI, 5.675 x 10<sup>3</sup> mg of AgI/cm<sup>3</sup>, find thickness, h, in centimeters:

$$h = \frac{\text{mg of AgI}}{\text{cm}^2} \cdot \frac{\text{cm}^3}{5.675 \times 10^3 \text{ mg of AgI}}$$

and if thickness in nanometers is wanted, multiply h by 10<sup>7</sup>.

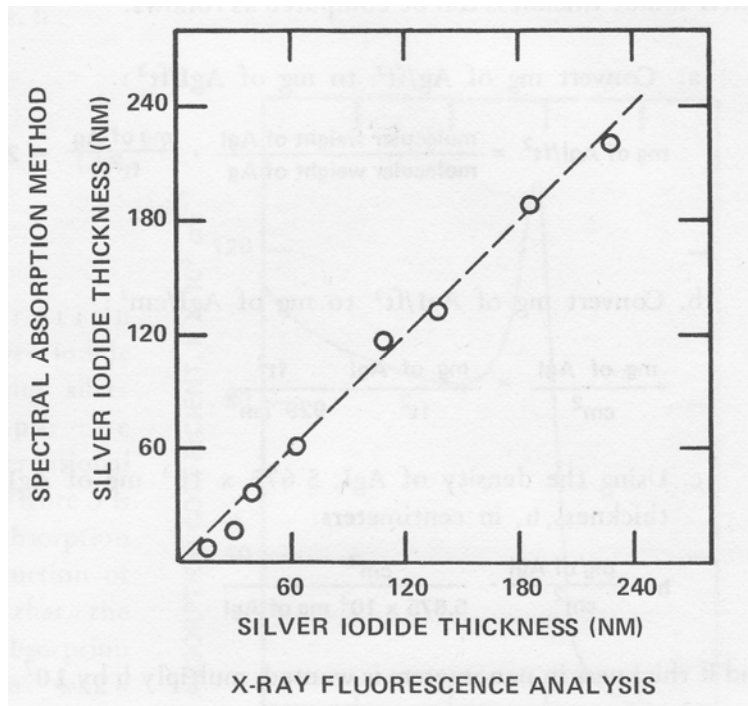
## RESULTS OF THICKNESS MEASUREMENT

TABLE I. Data and calculated thicknesses of silver iodide for eight samples by two measurement methods. Thickness is given in nm.

No.	Iodizing Time (sec)	Color	r	t <sub>u</sub>	t	AgI THICKNESS	
						Absorption	X-ray Fluor.
1	18	Light yellow	.207	.722	.910	7	15.5
2	40	Light, low saturation magenta	.342	.525	.798	16	29.6
3	60	Magenta-blue	.245	.462	.610	36	40.3
4	80	Light steel blue	.163	.370	.442	60	63.6
5	225	Deep yellow	.117	.178	.201	117	105.4
6	360	Deep magenta	.103	.145	.162	132	138.4
	420	Deep green with yellow tinge	.107	.067	.075	187	185.9
8	660	Medium magenta	.100	.043	.048	220	229.3

\*Average of two determinations made from two different areas, each approximately one square centimeter.

Figure 4 compares the silver iodide thicknesses obtained by the two different methods of measurement. Agreement is quite good except for thicknesses below 30 nanometers where the spectral absorption method gives lower values than the x-ray fluorescence analysis.



**Figure 4. Comparison of the thickness of silver iodide as determined by two different measuring methods; spectral absorption method and x-ray fluorescence analysis.**

Daguerreotypists would iodize their plates to a 'golden yellow with a reddish tinge'. Based on

this description and the above data, the thickness of the silver iodide layer must have been about 30 nanometers: about 1/15th of the wavelength of blue light! The only other estimate of the thickness of this golden yellow layer was made by Dumas (6) in 1839. He arrived at this estimate by weighing a plate before and after iodizing and taking into account the density of silver iodide. Using his data, one arrives at a thickness of 15 nanometers.

#### **COLORIMETRY OF SILVER IODIDE FILMS BY REFLECTANCE AND TRANSMITTANCE**

Although there are numerous references to the various colors seen on daguerreotype plates (1), no colorimetric description of such colors has been given. The following is the result of an experiment to specify the colors of iodide layers of various thicknesses as seen by both reflection and by transmitted light. The systems of color notation used are the C.I.E. and Munsell.

## The Experiment

A series of plates was prepared with silver iodide thicknesses ranging from 15 to 230 nanometers. These thickness estimates are based on the relationship between color and thickness of the iodide layer determined in the previous experiment. The spectral reflectance of each of the plates was measured on a Beckman DK-2a integrating-sphere spectrophotometer relative to a barium sulfate standard. The angle of illumination was five degrees to the normal, and the combined specular and diffuse reflectances were measured (total reflectance). Two spots on each plate were measured to obtain a better estimate of the color of the layer. From these spectral reflectance data, C.I.E. specifications were obtained for Illuminant C using the weighted ordinate method of tristimulus integration (7). These C.I.E. data were then converted to the Munsell system, which provides equal-visual spacing while expressing the color in terms which agree more closely with the psychological attributes of hue, saturation, and lightness. This conversion was accomplished using published charts (8).

The spectral *transmittance* data obtained in the previous section (Spectrophotometry of Stripped Silver Iodide Films) were also converted to the C.I.E. and Munsell\* systems to facilitate comparison of colors between silver iodide films viewed by reflection and by transmission.

Although the same samples were not used for both reflectance and transmittance spectrophotometry, each set covered roughly the same range of silver iodide thickness: reflectance samples, 15 to 180 nm; transmittance samples, 15 to 230 nm.

Table II lists the C.I.E. and Munsell data for various thicknesses of silver iodide viewed by reflection and by transmission. Figure 5 shows both sets of data plotted on the C.I.E. chromaticity diagram (enlarged section) while Figure 6 is a plot of the same data transformed into the Munsell system.

\**Conversion of C.I.E. data for transparent samples to Munsell Renotation is not strictly valid because the Munsell system was set up on reflectance samples only. Its use here is justified only if it is kept in mind that the visual spacing is likely different for transparent and reflection samples but that its use does provide an approximate hue name and a rough measure of saturation.*



**TABLE 11. C.I.E. and Munsell data for various thicknesses of AgI measured by transmittance and reflectance.**

**TRANSMITTANCE**

No.	AgI Thickness*	x	y	Y	Hue	Value	Chroma
1	15.5	.317	.328	.96	0.5GY	9.8	0.6
2	29.6	.326	.338	.87	7.5Y	9.4	1.2
3	40.3	.325	.337	.82	7.2Y	9.2	1.1
4	63.6	.320	.342	.82	6.7GY	9.2	1.5
5	105.4	.334	.354	.91	2.0GY	9.6	1.5
6	138.4	.331	.346	.87	8.5Y	9.4	1.6
7	185.9	.323	.352	.86	7.0GY	9.4	2.1
8	229.3	.334	.359	.87	2.5GY	9.4	2.3

\*X-ray fluorescence analysis

**REFLECTANCE**

No.	AgI Thickness**	x	y	Y	Hue	Value	Chroma
1	15	.349	.371	.81	8.3Y	9.1	3.2
2	25	.372	.374	.64	1.2Y	8.3	4.2
3	34	.344	.328	.50	10.0R	7.4	2.5
4	51	.299	.299	.49	8.9PB	7.4	2.2
5	73	.315	.338	.63	8.1GY	8.2	1.4
6	85	.391	.413	.58	5.3Y	7.9	6.0
7	110	.391	.337	.43	8.5 R	7.0	5.9
8	122	.340	.306	.32	7.3RP	6.2	3.6
9	147	.328	.378	.38	7.2GY	6.7	3.5
10	170	.370	.372	.41	1.9Y	6.9	3.6
11	180	.372	.342	.33	1.9YR	6.3	3.8

\*\*Estimate based on color of silver iodide layer

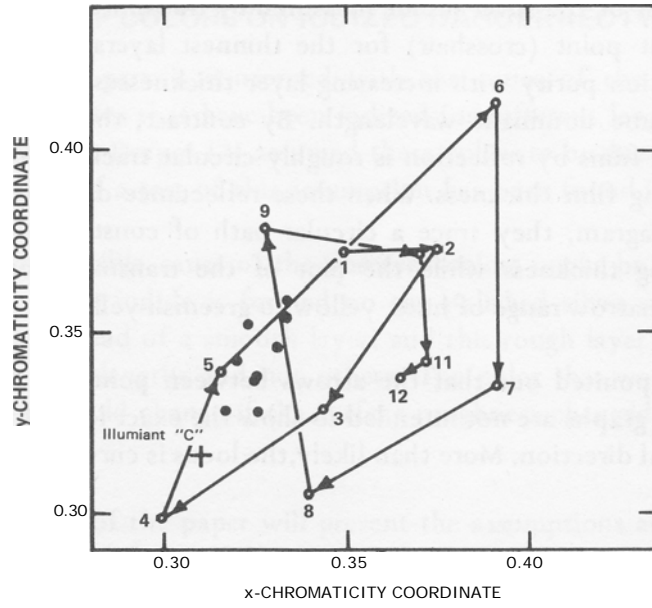


Figure 5. Enlarged section of C.I.E. diagram showing chromaticities of various silver iodide thicknesses measured by transmittance (closed circles) and by reflectance on a silver support (open circles).

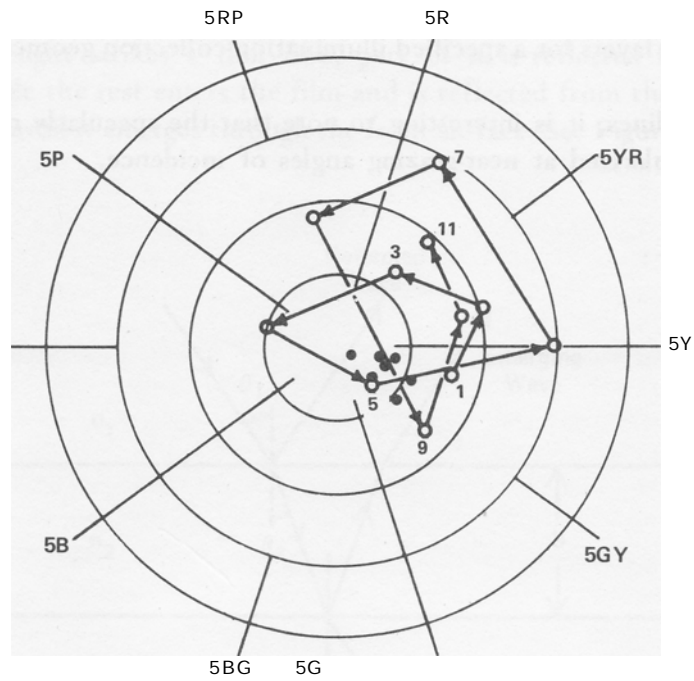


Figure 6. Munsell diagram. Points shown in previous diagram transformed into Munsell system.

The C.I.E. plot of the silver iodide measured by transmittance starts out near the illuminant point (crosshair) for the thinnest layers and generally increases in excitation purity with increasing layer thicknesses while roughly maintaining the same dominant wavelength. By contrast, the chromaticity locus of the iodide films by reflection is roughly circular tracing a clockwise path with increasing film thickness. When these reflectance data are plotted on the Munsell diagram, they trace a circular path of constantly changing hue with increasing thickness while the plot of the transmittance data is limited to a rather narrow range of hues, yellow to greenish-yellow.

It should be pointed out that the arrows between points in both the C.I.E. and Munsell graphs are not intended to show the exact locus but rather to indicate a general direction. More than likely, the locus is curved rather than straight.

It is regretted that the spectrophotometer could not imitate the illumination-collection geometry used by observers when viewing the iodide surface. The plate is usually viewed by specular reflectance at an angle of roughly 60 degrees to the normal. Viewing geometry is quite critical, especially for thicker layers, because the color seen depends upon the angle of view. However, the above data do provide a quantitative description of the color of the iodide layers for a specified illumination-collection geometry.

Along these lines, it is interesting to note that the specularly reflected light is linearly polarized at near-grazing angles of incidence.

## PART II

### THE CAUSE OF COLORS ON IODIZED DAGUERRETYPE PLATES

This second part is concerned with the cause of the colors seen on daguerreotype plates that have been iodized for different lengths of time. As mentioned before, Draper (2) assumed these colors to be due to interference, no mention of a test of this assumption has been found in the literature.

Another possible cause of the observed colors might be scattering; that is, when the silver iodide is formed on the polished silver substrate it may form a rough instead of a smooth layer, and this rough layer may selectively scatter some wavelengths and not others. The color that would result from this scattering would change if the surface roughness changed with increased iodizing.

This section of the paper will present the assumptions and evidence for both the interference and the scattering hypotheses as the cause of the observed colors on iodized daguerreotype plates. Interference will be dealt with first, then scattering, followed by a summary and conclusions.

### INTERFERENCE

#### Theory

When light strikes a thin film, part of it is reflected from the front surface while the rest enters the film and is reflected from the back surface, and then it emerges through the front surface. See Figure 7.

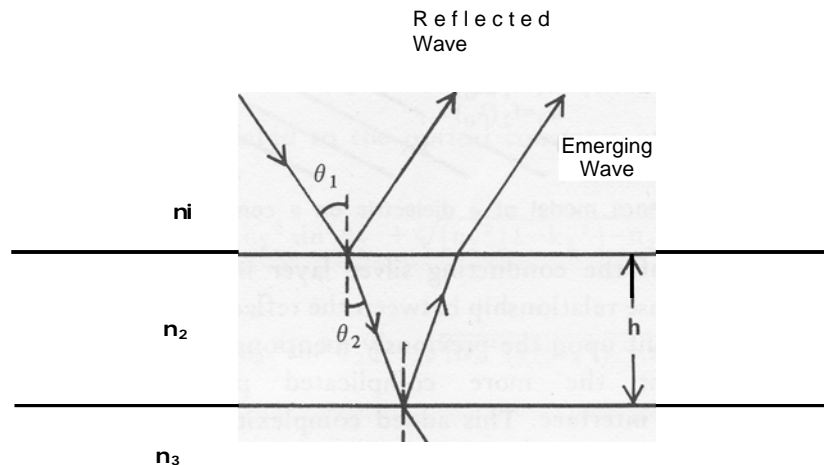
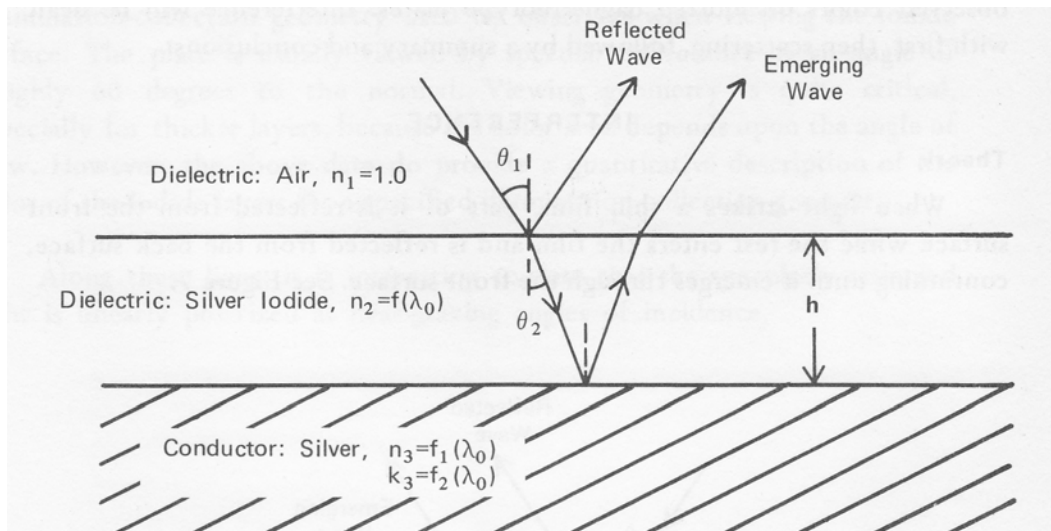


Figure 7. Simple interference model.

If this emerging wave is out of phase with the wave reflected from the front surface, destructive interference results; if the two are in phase, constructive interference occurs. The phase relationship between these waves is determined by such factors as the wavelength of the incident light, the angle at which the wave strikes the film, the thickness of the film, and its refractive index at that wavelength. If the light striking the film is composed of many wavelengths, destructive interference may occur at some wavelengths while, at the same time, other wavelengths may be undergoing constructive interference. This will show up as minima and maxima in the spectral reflectance curves of the film *even though the film is non-absorbing over that range of wavelengths*.

This is the simplest case of interference (Figure 7). The case of the iodized daguerreotype plate is more complicated in that the thin film (silver iodide) is on a conducting substrate (polished silver). Figure 8 shows a diagram of the physical model for the daguerreotype plate. It is important to note that both interference models assume a plane parallel film.



**Figure 8. Interference model of a dielectric on a conducting substrate.**

The addition of the conducting silver layer increases the complexity because now the phase relationship between the reflected and emerging waves is not only dependent upon the previously mentioned factors but must also take into account the more complicated phase change at the dielectric /conductor interface. This added complexity results from the fact that silver is a conductor and, therefore, strongly absorbing. As a consequence of its strong absorption, the optical properties of silver must be described by two constants instead of the usual one: an absorption index,  $k$ , and the refractive index,  $n$ .

To find out if interference can take place for the physical model given in Figure 8, it is necessary to calculate the reflectivity, R, as a function of wavelength. If minima and maxima appear in these reflectivity curves, it is of interference. The next step would be to compare these theoretically derived reflectivities with measured spectral reflectance curves made from daguerreotype plates having silver iodide films of comparable thicknesses. If the wavelength positions of the minima and maxima at which we arrive theoretically agree with those observed experimentally, it would be evidence that the interference hypothesis not only applies to the physical model but also to the daguerreotype plate.

The reflectivity, R, for the physical model shown in Figure 8 can be computed from the relationships given in Born and Wolf (9). Since the angle illumination used in the experimental measurements is near normal, it is -- necessary to make separate calculations for the components perpendicular J parallel to the plane of incidence. A single set of equations is sufficient and is given as follows:

$$R = \frac{r_{12} + \rho_{23} + 2r_{12}\rho_{23}\cos(\phi_{23} + 2\beta)}{1 + (r_{12})^2(\rho_{23})^2 + 2r_{12}\rho_{23}\cos(\phi_{23} + 2\beta)} \quad (3)$$

where the reflection coefficient,  $r_{12}$  for the air/silver iodide interface is:

$$r_{12} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad (4)$$

and the amplitude ratio,  $\rho_{23}$  at the silver iodide/silver interface is:

$$\rho_{23} = \frac{(n_2 \cos \theta_2 - u_3)^2 + v_3^2}{(n_2 \cos \theta_2 + u_3)^2 + v_3^2} \quad (5)$$

where  $u_3$  and  $v_3$  are related to the optical constants of silver,  $n_3$  and  $k_3$ , as follows:

$$2u_3^2 = n_3^2(1-k_3^2) - n_2^2 \sin^2 \theta_2 + \sqrt{[n_3^2(1-k_3^2) - n_2^2 \sin^2 \theta_2]^2 + 4n_3^4 k_3^2} \quad (6)$$

$$2v_3^2 = -[n_3^2(1-k_3^2) - n_2^2 \sin^2 \theta_2] + \sqrt{[n_3^2(1-k_3^2) - n_2^2 \sin^2 \theta_2]^2 + 4n_3^4 k_3^2} \quad (7)$$

The phase change at the 2-3 interface,  $\phi_{23}$  is given by:

$$\tan \phi_{23} = \frac{2v_3 n_2 \cos \theta_2}{u_3^2 + v_3^2 - n_2 \cos^2 \theta_2} \quad (8)$$

$$\beta = \frac{2\pi n_2 h \cos \theta_2}{\lambda_0} \quad (9)$$

$\theta_1$  and  $\theta_2$  are the angles of incidence and refraction respectively

$n_1$  refractive index of air, taken as 1

$n_2$  refractive index of silver iodide which varies as function of  $\lambda_0$  (see Figure 9)

$n_3, k_3$  - optical constants of silver, see Figure 10

$h$  - thickness of silver iodide layer

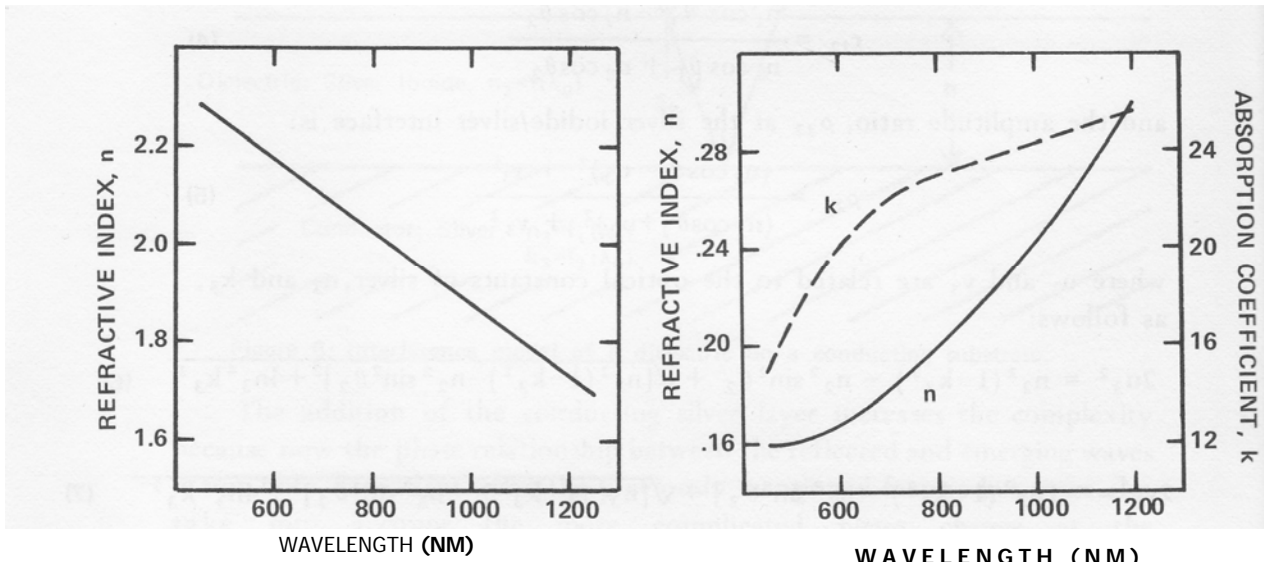


Figure 9. Refractive index of silver iodide versus wavelength.

Figure 10. Optical constants of silver.

The experiment consists of preparing a series of silver iodide layers of different, but known, thicknesses and measuring the spectral reflectance of each of these layers. Of course, just like any other daguerreotype plate, the iodide layer is on a silver substrate. The wavelength positions of the minima and maxima of the measured spectral reflectance curves are compared with the wavelength positions obtained from the computed reflectivities for comparable thicknesses of silver iodide. Agreement between the measured and calculated reflectivities could be taken as evidence for the interference hypothesis.

### Experimental Details

A single plate was iodized for 20 seconds, its spectral reflectance measured from 400 to 1200 nm, iodized again for 15 seconds (cumulative iodizing time of 35 seconds), remeasured, iodized some more, etc.; this procedure was repeated until a cumulative iodizing time of thirteen minutes had been given. A span of at least 15 minutes elapsed between iodizing periods. After each iodizing, the plate was examined visually and its color noted. This was done to provide an estimate of the silver iodide thickness since a previous experiment had established a relationship between thickness and color. These estimated thicknesses ranged from 15 to 230 nanometers and above. Also, between iodizing, the sample was measured on a Beckman DK-2a integrating-sphere spectrophotometer to obtain total spectral reflectance which is the combined effect of diffuse and specular reflectance. The sample is irradiated at five degrees to the normal ( $\theta_1 =$  five degrees) and the measurements were made relative to a barium sulfate standard.

Computed reflectivity implies an illumination-collection geometry that corresponds to what is known as specular reflectance. For this reason, the computed reflectivities should be compared with measured specular reflectance rather than with total reflectance. The spectrophotometer that was used does not provide specular reflectance directly. However, one should be able to compute specular reflectance from the data obtained by measuring the sample twice; once with the spectrophotometer set for total collection, the second time set for diffuse collection. Specular reflectance is the difference: "total" minus diffuse reflectance. Although it is theoretically possible to obtain specular reflectance by doing this, the design of the instrument forces the user to remove the sample in changing from one mode of measurement to the other. Since this makes it impossible to remeasure the same spot twice, it is uncertain whether both measurements were made on the same film thickness. Subtracting a diffuse measurement made at one thickness from a total reflectance measurement made at another would cause an error in the computed position of the minima and maxima on the wavelength axis.



To see the effect of total, diffuse and computed-specular reflectance on the position of minima and maxima, the sample with the thickest iodide layer was measured with both collection geometries and specular reflectance was computed from these -two measurements.

**TABLE III. Wavelength positions (in nm) of minima and maximum of Total, Diffuse and Computed-specular reflectance for an iodized daguerreotype plate.**

	<b>Total</b>	<b>Diffuse</b>	<b>Computed Specular</b>
<b>Minimum</b>	1250	930	1250
<b>Maximum</b>	785	635	775
Minimum	580	505	575

Roughly speaking, the wavelength positions for minima and maxima for total reflectance fall halfway between those found for diffuse reflectance while agreeing within 10 nm with those for computed-specular reflectance (see Table III). Some sections of the "computed-specular" curve (Figure 11) go below zero. This is due to measuring two different spots on the sample and illustrates the problem of obtaining computed-specular data. Because of this, "computed-specular" was not used. Instead, total reflectance was chosen since the wavelength positions of minima and maxima for total and computed-specular show fairly good agreement.

## RESULTS

Figure 12a shows the spectral reflectance curves for the series of silver iodide layers of increasing thickness. To better see the shift of minima and maxima to longer wavelengths as layer thickness increases, all the curves have been plotted on the same graph paper with a vertical displacement between curves to avoid overlap. They are arranged in order of increasing film thickness with the top curve representing the thinnest layer. To preserve the reflectance information, each curve has a short horizontal line to mark its 50-percent reflectance value. Also, part of the vertical axis for the lowest curve is calibrated to give the scale of the reflectance axis.

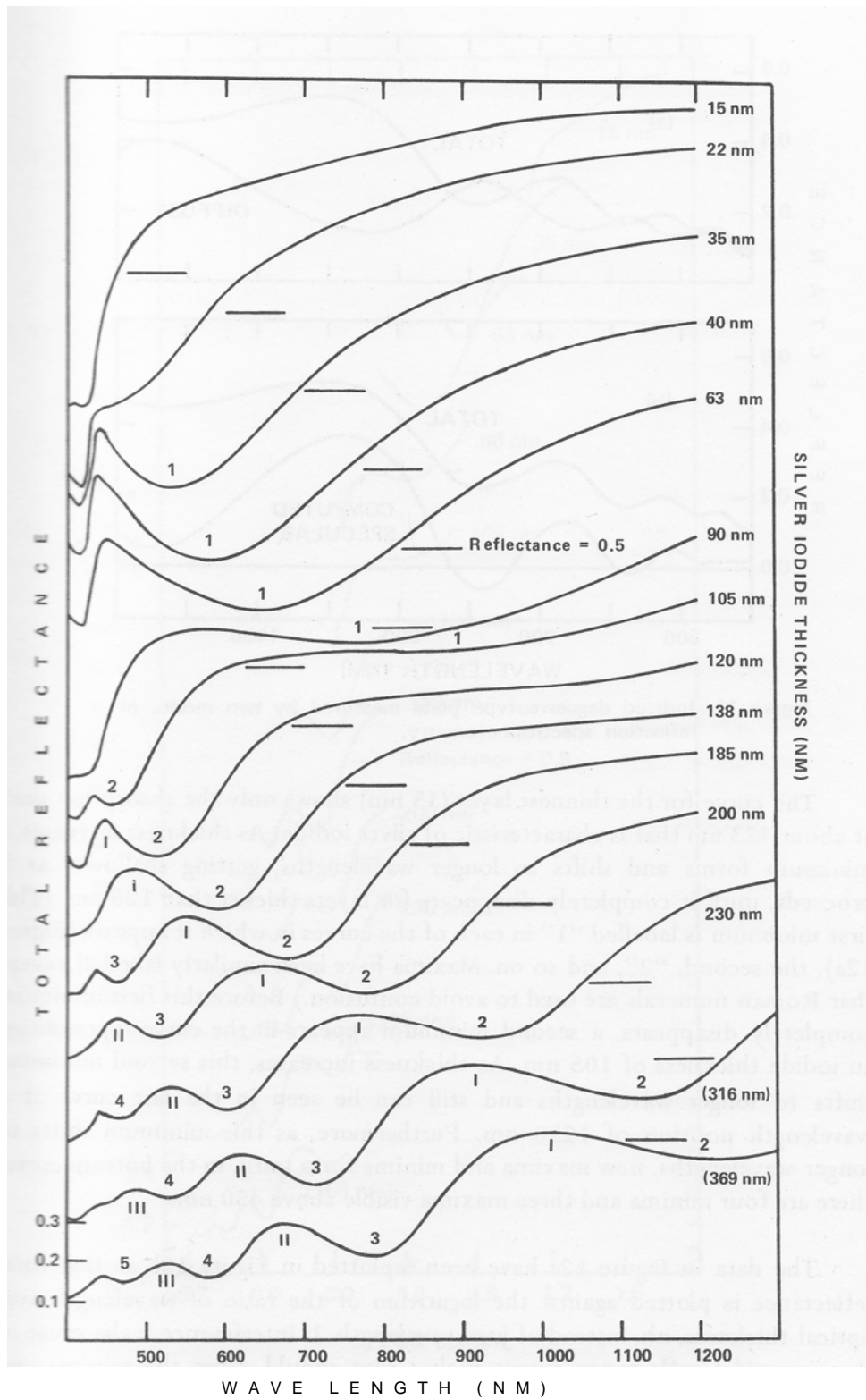


Figure 12a. Total spectral reflectance curves for various silver iodide thicknesses on daguerreotype plates.

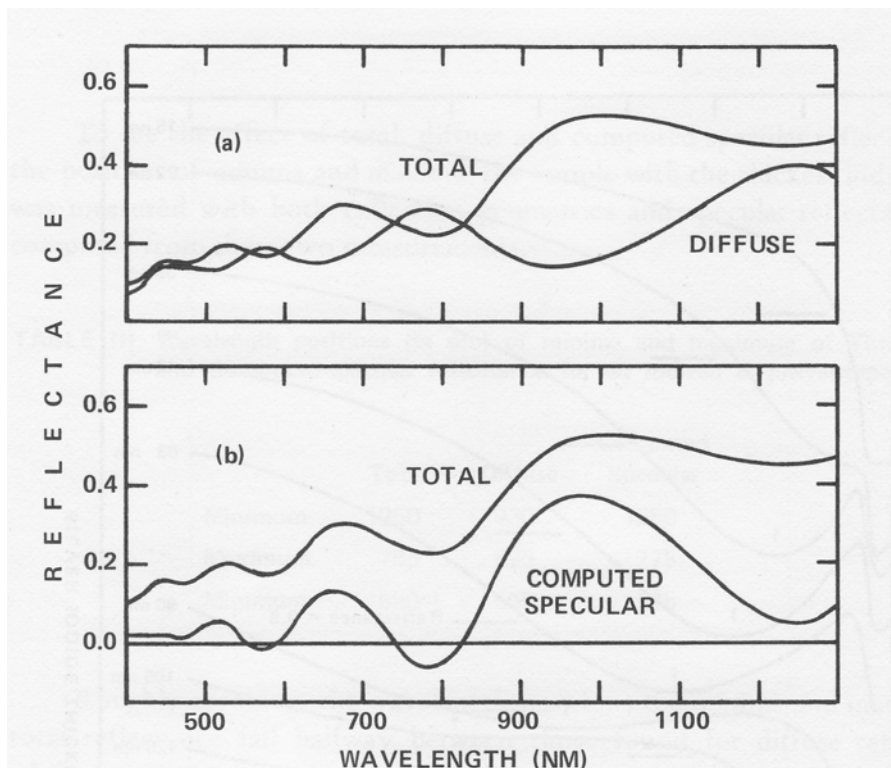


Figure 11. Iodized daguerreotype plate measured by two modes of reflection spectrophotometry.

The curve for the thinnest layer (15 nm) shows only the absorption peak at about 423 nm that is characteristic of silver iodide. As thickness increases, a minimum forms and shifts to longer wavelengths, getting shallower as it proceeds, until it completely disappears for layers thicker than 120 nm. (This first minimum is labelled "1" in each of the curves in which it appears (Figure 12a), the second, "2", and so on. Maxima have been similarly labelled except that Roman numerals are used to avoid confusion.) Before this first minimum completely disappears, a second minimum appears in the curve representing an iodide thickness of 105 nm. As thickness increases, this second minimum shifts to longer wavelengths and still can be seen in the last curve at a wavelength position of 1250 nm. Furthermore, as this minimum shifts to longer wavelengths, new maxima and minima form until, in the bottom curve, there are four minima and three maxima visible above 450 nm.

The data in Figure 12a have been replotted in Figure 12b so that total reflectance is plotted against the logarithm of the ratio of wavelength over optical thickness,  $A$ , instead of just wavelength. If interference is the cause of the sinusoidal reflectance curves, such a plot should cause the minima and maxima to line up. The use of the logarithm makes it possible to accommodate all the curves on a compact graph. Figure 12b shows that reflectance curves of iodide layers 90 nm and thicker do align themselves more or less. However, the curves for thinner layers do not.

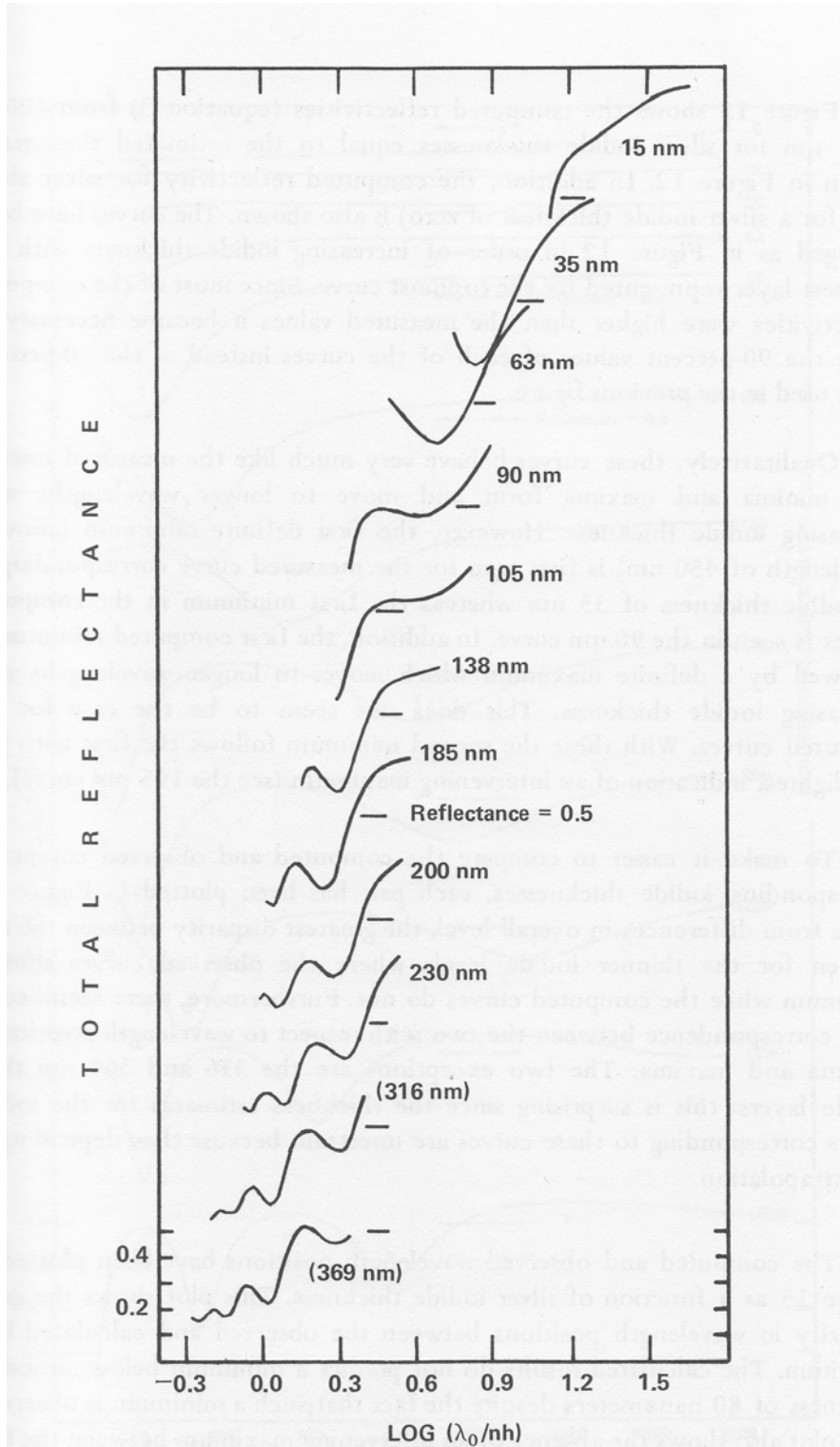


Figure 12b. Reflectances given in Figure 12a have been re-plotted versus the logarithm of wavelength divided by the optical thickness.

Figure 13 shows the computed reflectivities (equation 3) from 400 to 1200 nm for silver iodide thicknesses equal to the estimated thicknesses shown in Figure 12. In addition, the computed reflectivity for silver alone (i.e., for a silver iodide thickness of zero) is also shown. The curves have been arranged as in Figure 12 in order of increasing iodide thickness with the thinnest layer represented by the topmost curve. Since most of the computed reflectivities were higher than the measured values it became necessary to mark the 90-percent values of each of the curves instead of the 50-percent value used in the previous figure.

Qualitatively, these curves behave very much like the measured ones in that minima and maxima form and move to longer wavelengths with increasing iodide thickness. However, the first definite minimum (above a wavelength of 450 nm) is first seen for the measured curve corresponding to an iodide thickness of 35 nm whereas the first minimum in the computed curves is seen in the 90 nm curve. In addition, the first computed minimum is followed by a definite maximum which moves to longer wavelengths with increasing iodide thickness. This does not seem to be the case for the measured curves. With these the second minimum follows the first with just the slightest indication of an intervening maximum (see the 105 nm curve).

To make it easier to compare the computed and observed curves for corresponding iodide thicknesses, each pair has been plotted in Figure 14. Aside from differences in overall level, the greatest disparity between the two is seen for the thinner iodide levels where the observed curves show a minimum while the computed curves do not. Furthermore, there seems to be little correspondence between the two with respect to wavelength position of minima and maxima. The two exceptions are the 316 and 369 nm thick iodide layers; this is surprising since the thickness estimates for the iodide layers corresponding to these curves are uncertain because they depend upon an extrapolation.

The computed and observed wavelength positions have been plotted in Figure 15 as a function of silver iodide thickness. This plot shows the great disparity in wavelength positions between the observed and calculated first minimum. The calculated results do not predict a minimum below an iodide thickness of 80 nanometers despite the fact that such a minimum is observed. This plot also shows the absence of an intervening maximum between the first and second observed minima.

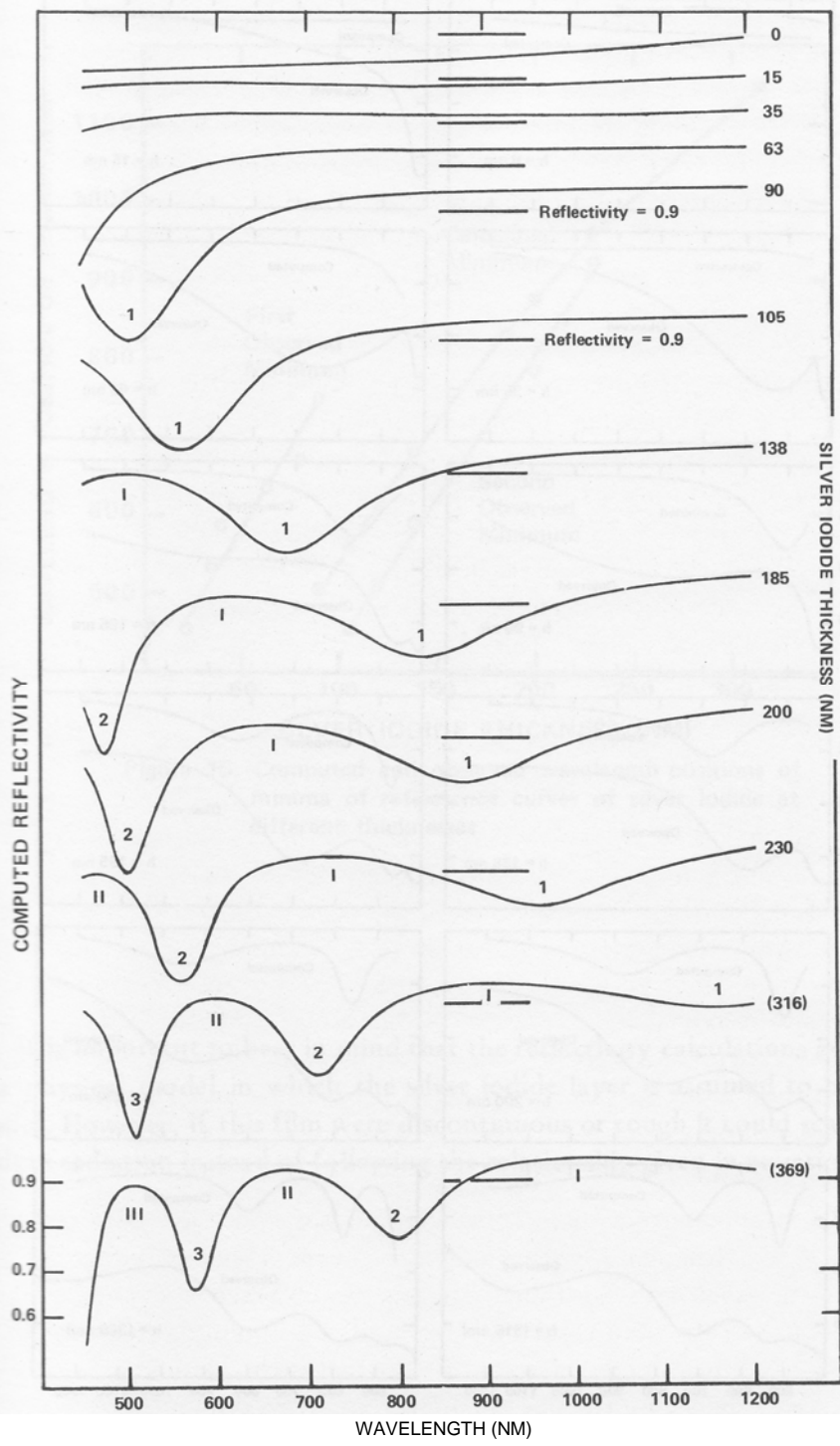


Figure 13. Computed reflectivities for eleven of the fourteen silver iodide thicknesses shown in Figure 12a.

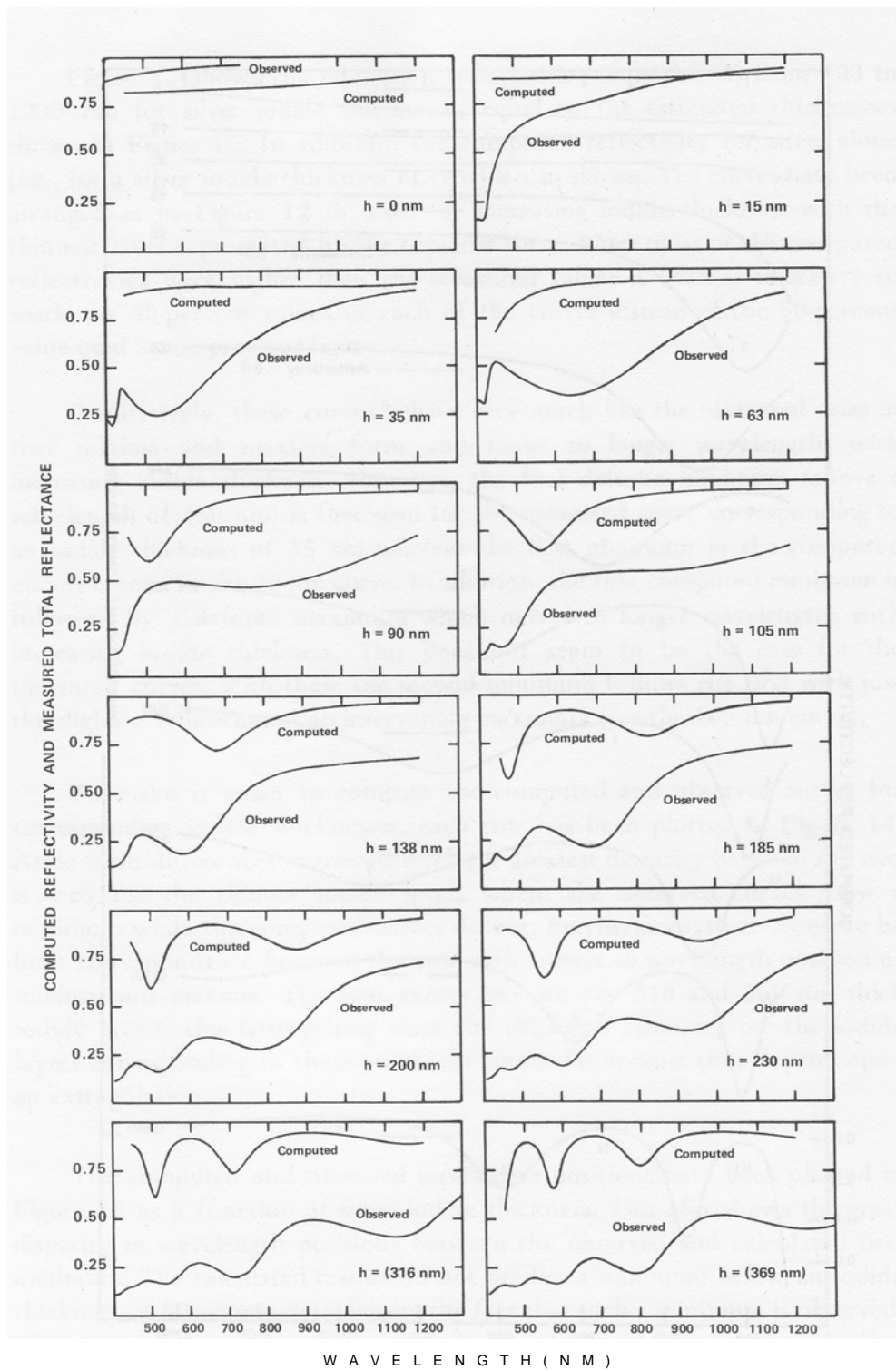


Figure 14. Comparison of computed reflectivity and observed total reflectance for different iodide thicknesses.

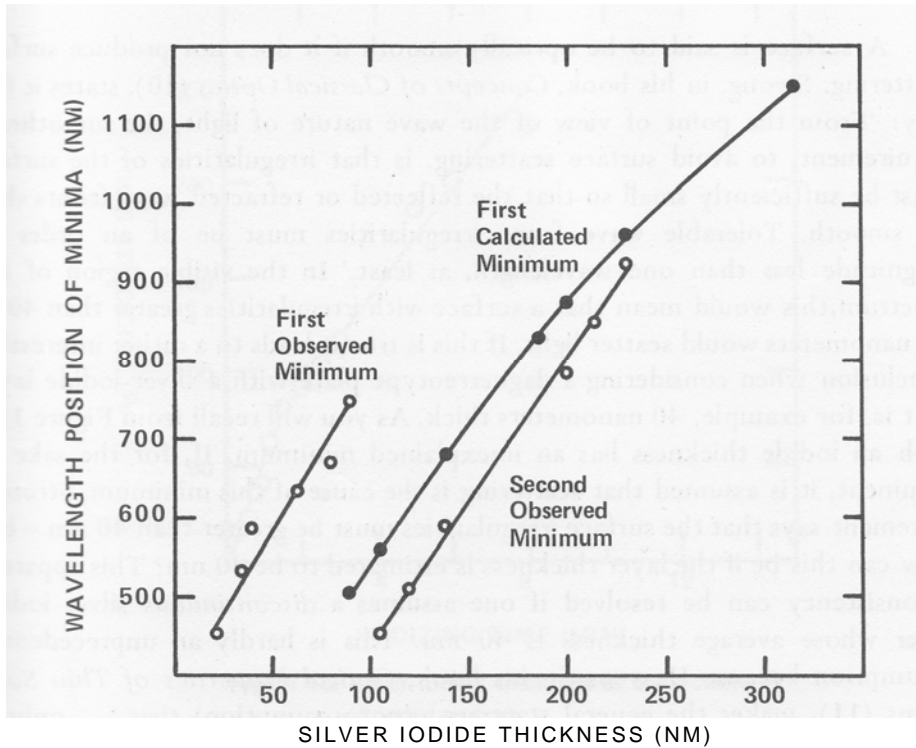


Figure 15. Computed and observed wavelength positions of minima of reflectance curves of silver iodide at different thicknesses

It is important to bear in mind that the reflectivity calculations are based on a physical model in which the silver iodide layer is assumed to be plane parallel. However, if this film were discontinuous or rough it could scatter the incident radiation instead of following the relationship given in equation 3.



## SCATTERING

A surface is said to be optically smooth if it does not produce surface scattering. Strong, in his book, *Concepts of Classical Optics (10)*, states it this way: 'From the point of view of the wave nature of light, the smoothness requirement, to avoid surface scattering, is that irregularities of the surface must be sufficiently small so that the reflected or refracted wave fronts shall be smooth. Tolerable wave front irregularities must be of an order of magnitude less than one wavelength, at least.' In the visible region of the spectrum, this would mean that a surface with irregularities greater than 40 to 70 nanometers would scatter light. If this is true, it leads to a rather interesting conclusion when considering a daguerreotype plate with a silver iodide layer that is, for example, 40 nanometers thick. As you will recall from Figure 12a, such an iodide thickness has an unexplained minimum. If, for the sake of argument, it is assumed that scattering is the cause of this minimum, Strong's statement says that the surface irregularities must be greater than 40 nm -- but how can this be if the layer thickness is estimated to be 40 nm? This apparent inconsistency can be resolved if one assumes a *discontinuous* silver iodide layer whose average thickness is 40 nm. This is hardly an unprecedented assumption because Heavens, in his book, *Optical Properties of Thin Solid Films (11)*, makes the general statement (not assumption) that '... only in rare cases does a [evaporated] film consist of a homogeneous parallel-sided layer. Films are found to exhibit a wide variety of structures, from irregular, amorphous aggregates to monocrystalline layers.' Among the reasons Heavens cites as causes of discontinuous films are the large surface tension forces known to exist in solids and evidence of mobility of atoms over the substrate surface.

## EXPERIMENTAL EVIDENCE OF DISCONTINUOUS LAYER

### Iodizing Rates

In addition to the above, there is experimental evidence to suggest that iodide films of daguerreotype plates below an average thickness of about 80 or 90 nm are discontinuous. One such piece of evidence is the plot of iodide thickness versus iodizing time (Figure 16). The data for this plot came from the previously described experiment in which a single daguerreotype plate was intermittently iodized to produce a series of silver iodide thicknesses which were measured on the spectrophotometer between iodizing cycles. As mentioned before, iodide thicknesses were estimated by noting the color of

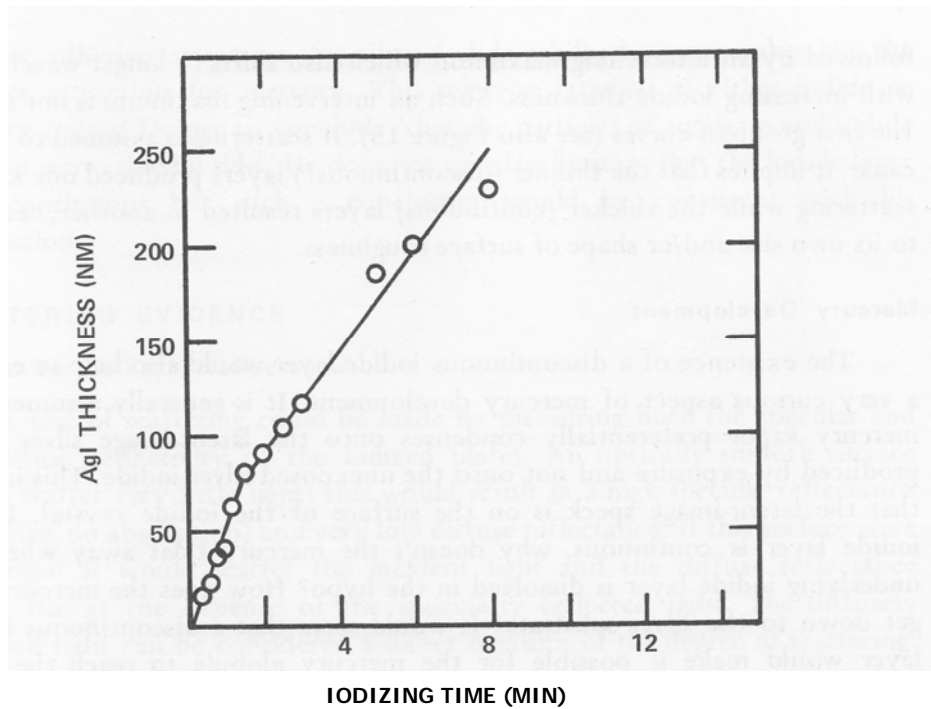


Figure 16. Silver iodide thickness as a function of iodizing time.

the layer between iodizing periods and using the relationship between iodide thickness and color determined in Part I of this paper. Figure 16 shows that the rate of iodide thickness growth is about 45 nanometers per minute over the thickness range from 0 to about 80 nm while thicknesses above this grow at a rate of only 25 nm per minute. It seems reasonable to expect a faster growth rate for a discontinuous film than for a continuous one in which growth rate is slowed because of diffusion through the iodide layer. This implies that iodide thicknesses below about 80 nm are discontinuous and therefore the thickness estimate refers to average thickness.

#### Spectral Reflectance Curves

In addition to the different growth rate, there is still another manifestation that seems to correspond only to these thinner layers and not layers above about 90 nm. This manifestation can be seen in the spectral reflectance curves of various iodide thicknesses (Figure 12). These curves show that the first minimum is restricted roughly to these thinner, supposedly discontinuous layers. Furthermore, these layers produce spectral reflectance curves that form a consistent group different from the group formed by the curves of the thicker layers. In this second group the minima are always

followed by an intervening maximum which also shifts to longer wavelengths with increasing iodide thickness. Such an intervening maximum is not seen in the first group of curves (see also Figure 15). If scattering is assumed to be the cause, it implies that the thinner (discontinuous?) layers produced one kind of scattering while the thicker (continuous) layers resulted in another, each due to its own size and/or shape of surface roughness.

### **Mercury Development**

The existence of a discontinuous iodide layer would also help to explain a very curious aspect of mercury development. It is generally assumed that mercury vapor preferentially condenses onto the latent-image silver speck produced by exposure and not onto the unexposed silver iodide. This implies that the latent-image speck is on the surface of the iodide crystal. If the iodide layer is continuous, why doesn't the mercury float away when the underlying iodide layer is dissolved in the hypo? How does the mercury ever get down to the silver substrate? It would seem that a discontinuous iodide layer would make it possible for the mercury globule to reach the silver substrate. The mercury globule is many times larger than the silver speck (hence providing the amplification necessary to make the latent image visible) and it seems probable that it would end up at the edge of the crystal aggregate where it meets the silver substrate.

### **Draper's Experiment**

This side-by-side arrangement of mercury and silver iodide is in agreement with the conclusion arrived at by Draper (12) from experiments he made in 1841. He concluded, 'that in an iodized daguerreotype, as taken from the mercury bath, there is no order of superposition of parts, that is to say, the iodide is neither upon nor beneath the mercury, but both are, as it were, in the same plane.' His experiments consisted of coating daguerreotype plates with a solution of *either* gum arabic or Russian isinglass. Before coating, the iodized plate had received an image-wise exposure in the camera and had been developed with mercury but the iodide layer was not removed by hypoing. When coated with the gum arabic solution and allowed to dry, the gum chipped up taking the mercury image with it but leaving a uniform coat of yellow iodide of silver still on the plate. However, when a similar plate was coated with isinglass solution and allowed to dry, just the opposite happened; i.e., the isinglass 'chipped off in the act of drying, tearing up the yellow film from end to end of the plate, and leaving the amalgam constituting the lights undisturbed. It is here to be understood that this action takes place without the *smallest disturbance* of the lights and demi-tints, the plate remaining in all the beauty and brilliancy and perfection that it would have had if it had been carefully washed in hyposulfite of soda'. Apparently the isinglass has a

stronger adhesive attraction for silver iodide while the gum arabic has the stronger attraction for mercury. This selective removal of either iodide or mercury caused Draper to conclude 'that the particles of amalgam and iodide lie as it were, side by side.' He does not specifically state that the iodide layer is discontinuous, but such a conclusion would be consistent with his observations.

## **SCATTERING EVIDENCE**

### **Diffuse Versus Total Reflectance**

A test of scattering could be made by measuring both the specular and the diffuse reflectivity of the iodized plates. An optically smooth surface would scatter very little light; this would result in a high specular reflectance (assuming no absorption) and very low diffuse reflectance. If this surface were roughened it would scatter the incident light and the diffuse reflectance would rise at the expense of the specularly reflected light. The diffusely reflected light can be considered a direct measure of the degree of scattering.

The above experiment was carried out on a series of daguerreotype plates that had been iodized for 0, 0.25, 0.5, 1.0, 2.0 and 13 minutes. The only exception was that total rather than specular reflectance was measured because the instrument that was used (Beckman DK-2a spectrophotometer) could not directly measure specular reflectance. Since total reflectance contains both specular and diffuse components, a decrease in total reflectance coupled with a rise in diffuse reflectance would imply a decrease in specular reflectance.

The spectral reflectance curves (relative to barium sulfate) for both modes of measurement (total and diffuse) are shown in Figure 17. As expected, a polished silver plate without silver iodide has a high total and a very low diffuse component. Most of the light is specularly reflected with very little scattering (Figure 17a). As soon as the iodide layer is added the surface begins to scatter and the total reflectance goes down. This trend continues until, at an estimated iodide thickness of 75 nm, there is practically no specular component (Figure 17e), just a scattered component.

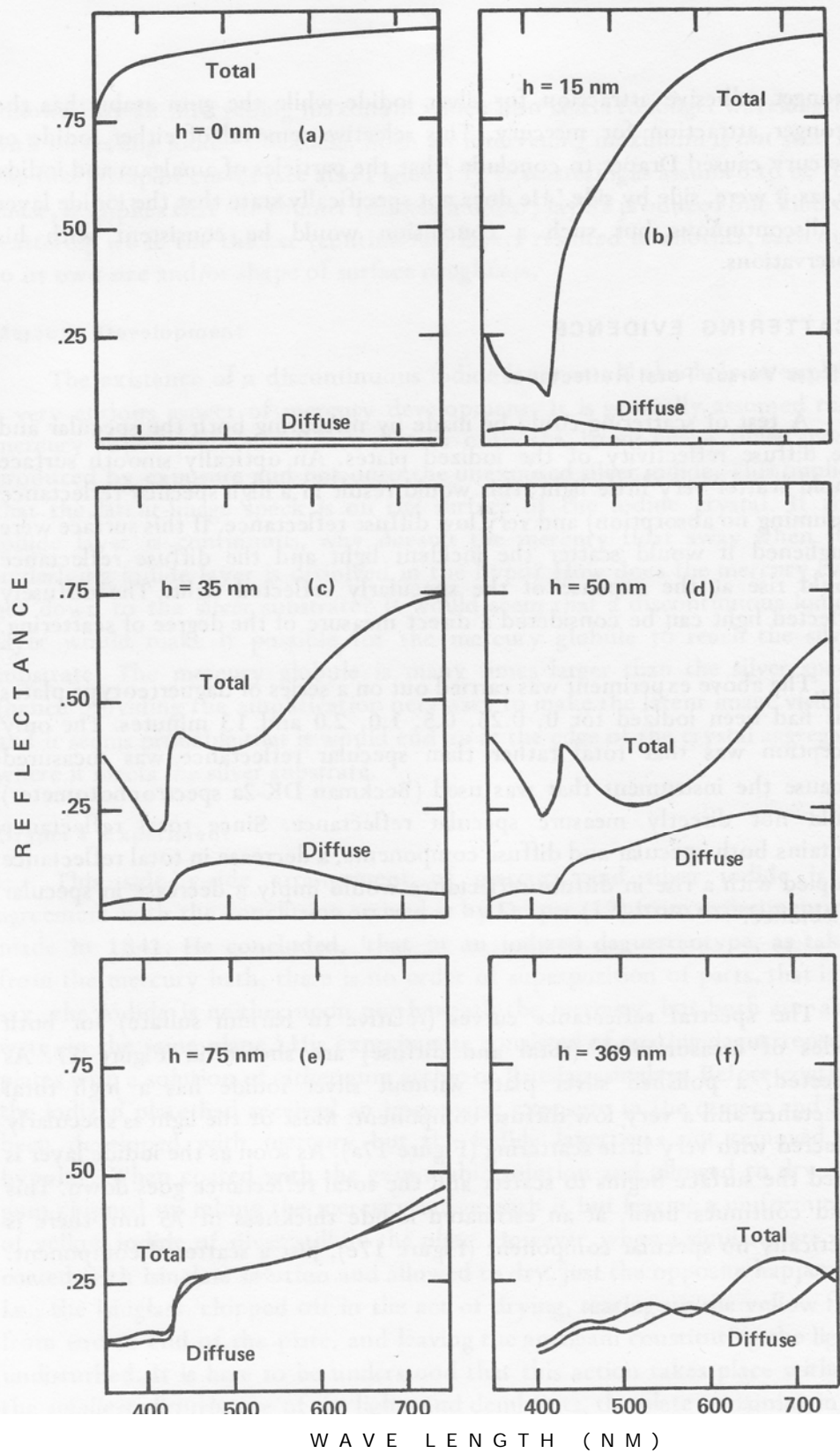
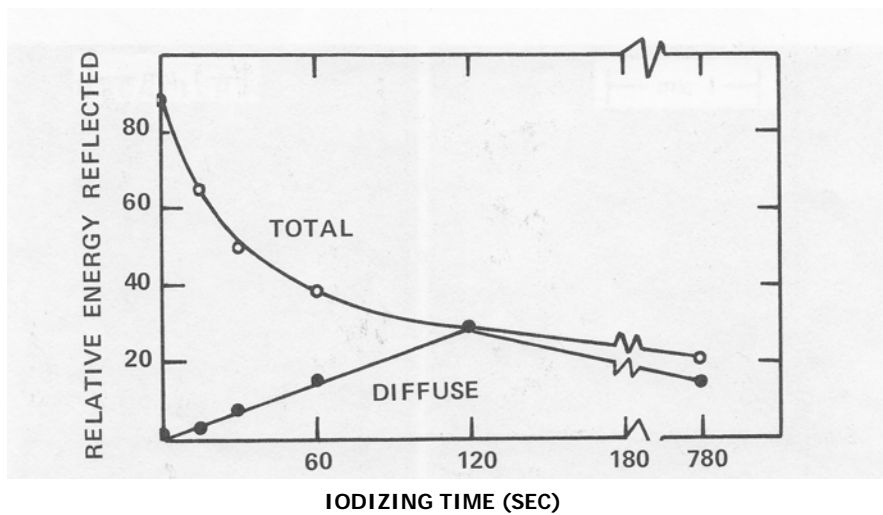


Figure 17. Diffuse and total reflectance measurements of daguerreotype plates iodized for various lengths of time. ( $h$ =AgI thickness).



**Figure 18. Relative energy reflected from silver iodide films varying in thickness as measured by two modes of reflectance, total and diffuse.**

Figure 18 is a graph of the percent of energy reflected from the iodized daguerreotype layer versus iodizing time. The percent of energy reflected is the area under each of the curves in Figure 17 relative to the area under the 100 percent line. This graph clearly shows how the scattered or diffusely reflected light increases with iodizing time until it meets the decreasing total reflectance at an iodizing time of two minutes.

This experiment clearly shows that scattering is taking place on iodized daguerreotype plates.

#### **Surface Structure of Iodide Layer**

Figure 19 shows scanning electron micrographs of the surface of daguerreotype plates at a magnification of 20,000 times. The iodide thicknesses of the four plates are 25, 75, 110, and 185 nm, respectively. These micrographs do indeed show that the surface roughness increases with increasing film thickness. However, it is not possible to tell if the layer is continuous or not.

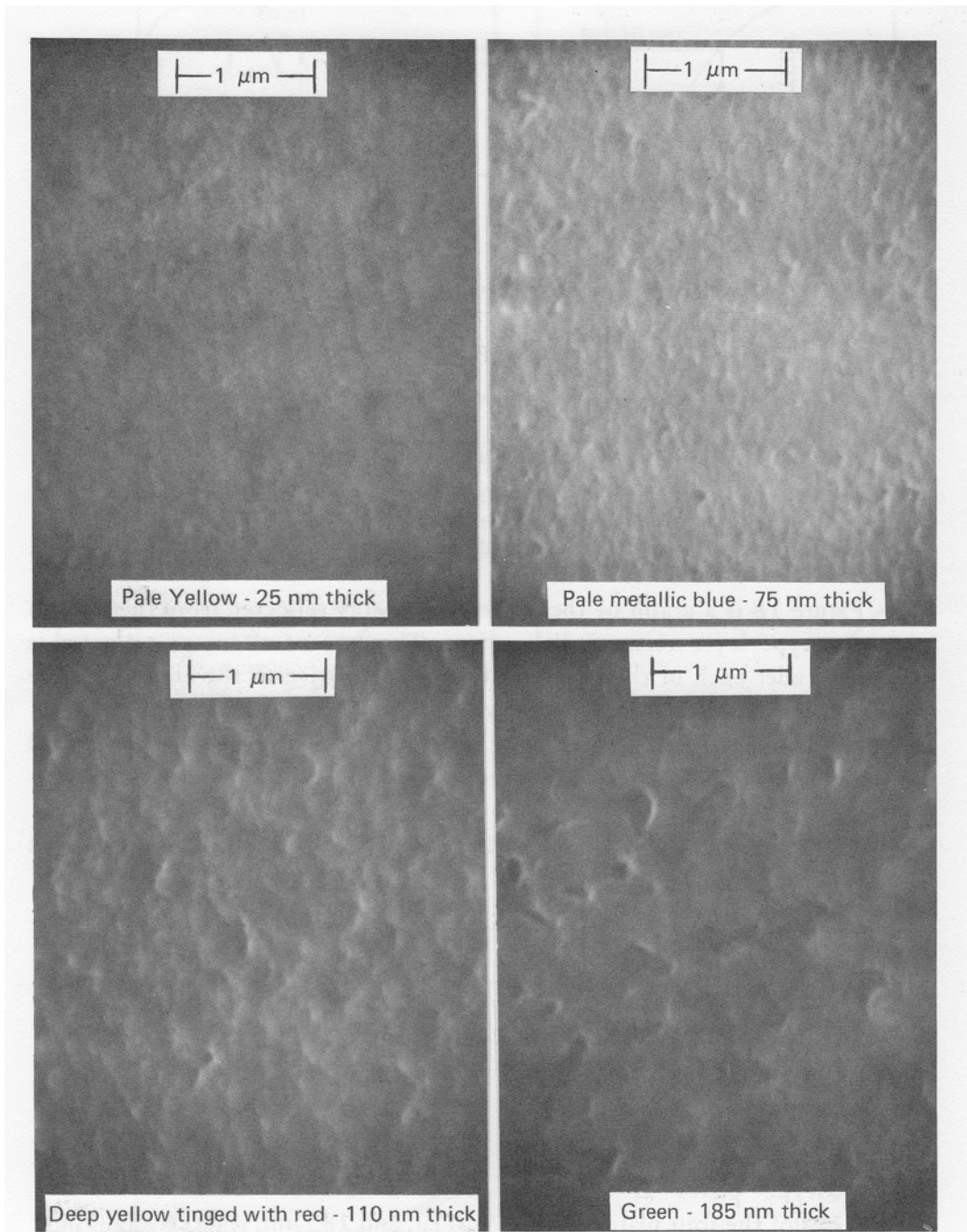


Figure 19. Scanning electron micrographs (X20,000) of iodide films showing surface roughness increasing with layer thickness.

## SELECTIVE SCATTERING

Up to now we have established that the daguerreotype plate scatters radiation, but it has not been shown that scattering can produce the spectral reflectance curves shown in Figure 12. Scattering is a very complicated phenomenon whose analytical treatment is beyond the scope of this paper

Instead of trying to show quantitative agreement with the observed curves, it will be enough to show that scattering can produce reflectance curves that qualitatively agree with the observed sinusoidal shape. Figure 20 is an illustration taken from King and Wu's book, *The Scattering and Diffraction of Waves*

13). It is a plot of back-scattering cross section versus alpha. Back-scattering cross section is a quantity characteristic of the power scattered backward toward the source and is roughly analogous to diffuse reflectance

factor that depends on the wavelength of the incident radiation and the radius of the sphere causing the scattering. This particular graph is for water spheres. Similar graphs were found in the literature (14) for other materials and shapes. These graphs show the same general sinusoidal shape and are similar to the spectral reflectance curves observed for iodized daguerreotype plates.

### SUMMARY AND CONCLUSIONS FOR THE TWO HYPOTHESES

In the attempt to account for the colors seen on iodized daguerreotype plates, two hypotheses were examined. These were the interference and scattering hypotheses.

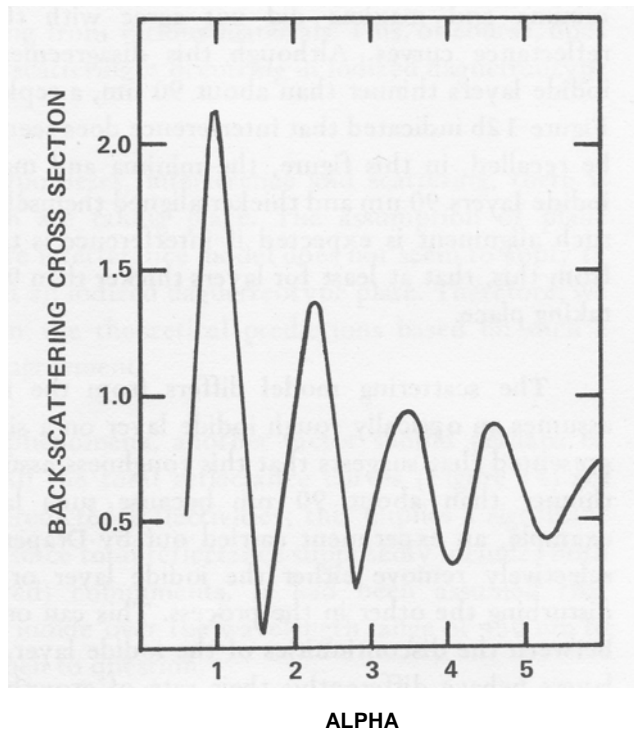


Figure 20. Back scattering from water spheres.



The physical model for interference assumes that the silver iodide is a plane parallel-sided layer on a silver support. Having made this assumption, spectral reflectivities were computed for such iodide films and compared with total spectral reflectances measured on actual iodide films. The computed reflectivities did show maxima and minima indicating that interference could take place with the assumed model. However, the wavelength positions of minima and maxima did not agree with those found on the observed reflectance curves. Although this disagreement was found, especially for iodide layers thinner than about 90 nm, a replotting of the observed data in Figure 12b indicated that interference does seem to be taking place. As it may be recalled, in this figure, the minima and maxima of reflectance curves of

iodide layers 90 nm and thicker aligned themselves when plotted against  $\lambda/nh$ ; such alignment is expected if interference is taking place. So it would seem from this, that at least for layers thicker than 90 nm, interference is probably taking place.

The scattering model differs from the interference model in that it assumes an optically rough iodide layer on a silver support. Evidence is then presented that suggests that this roughness assumption is true even for layers thinner than about 90 nm because such layers are discontinuous. For example, an experiment carried out by Draper showed that it is possible to selectively remove either the iodide layer or the mercury image without disturbing the other in the process. This can only be if the mercury image is between the discontinuities of the iodide layer. Moreover, the thinner iodide layers behave differently: their rate of growth with iodizing time is faster, which is consistent with what one would expect from a discontinuous layer.

Further evidence of surface roughness was presented in the form of scanning electron micrographs showing that this roughness increases with layer thickness. However, it was not possible to see from the micrographs if the thinner layers were discontinuous.

After establishing that thin iodide layers are probably rough and discontinuous, it was shown experimentally that such iodide layers do indeed scatter light. The surfaces are optically rough, so much so, that when an iodide layer reaches an average thickness of about 75nm, almost all the light is scattered or diffusely reflected. This is direct evidence of scattering.

The next step was to show that scattering could produce sinusoidal reflectance curves with minima and maxima like those observed in iodized daguerreotype plates. Since scattering is a very complex phenomenon for which it is very difficult to account quantitatively, we had to be content with resorting to the literature, where it was found that curves of this general shape could be produced by scattering from various materials. This, of course, does not establish whether *selective* scattering is occurring in iodized daguerreotype plates.

After examining both hypotheses, interference and scattering, there is evidence to suggest that both are taking place. The assumption of plane parallel-sided layers for the pure interference model does not seem to apply to the physical situation found in an iodized daguerreotype plate. Therefore, we should not be surprised when the theoretical predictions based on such a model fail to give quantitative agreement.

In addition to the two phenomena, another factor should perhaps be considered; i.e., absorption. All the total reflectance curves (Figure 14) are significantly lower than the predicted reflectivities; this implies a significant energy loss. This is surprising since total reflectance supposedly includes both specular and diffuse (scattered) components. It had been assumed that absorption was zero for silver iodide over the wavelength range of 450 nm to 1300 nm. This must now be open to question.

This study has shown that the colors seen on iodized daguerreotype plates are not due to a single, clear-cut cause but instead represent a very complex optical problem involving interference, scattering and possibly absorption.

## PART III

### COLOR OF SILVER IODIDE LAYER AND ITS RELATIVE SENSITIVITY

The fundamental law of photochemistry was discovered by Grotthus (15) in 1817. This same law was independently rediscovered by Draper in 1841 while studying the relative sensitivities of a series of daguerreotype plates that had been iodized for different lengths of time so that each successive plate in the series was of a different color. He exposed each of these plates to the image of a gas flame for a standard length of time and processed each plate in a standard way. Draper found that the sensitivity of the plate was at a maximum when yellow; decreased to a minimum when blue, and reached a second maximum upon turning yellow again. In other words, plate sensitivity was directly related to blue light absorption by the silver iodide. From this, Draper concluded 'that the chemical action produced by the rays of light depends upon the *absorption* of those rays by sensitive bodies'(1c). This is now known as the Grotthus-Draper law.

This experiment by Draper was qualitative and since the popularity of the daguerreotype process declined before the development of sensitometry, no quantitative measure was ever made of the photographic speeds of these differently colored iodide layers. This part of the thesis describes such a quantitative study.

### THE EXPERIMENT

The determination of the sensitometric characteristics of photosensitive materials is a fairly straightforward procedure for modern-day materials, but this is not the case for daguerreotype plates. To help appreciate the differences, a brief description is given of some of the unusual requirements and considerations that enter into a sensitometric study of the daguerreotype process. To begin with, flat copper plates must be obtained and these plated with silver. Immediately before iodizing, the silver surface of the plate must be polished to a mirror-like finish because, as explained later, the maximum density of the finished daguerreotype is directly related to its degree of polish. Iodizing of the polished plate is monitored by a visual assessment of the color of the silver iodide and, because of this, is subjective in nature. Available sensitometers cannot be used to expose the plate because the speed of the iodized plate is at best five orders of magnitude slower than modern films. Also, once iodized, the sensitivity is said to be variable: the literature states that the sensitivity of the plate depends upon the length of time between

iodizing and exposure (16). A plate exposed immediately after iodizing is not as fast as one exposed some hours after. The literature (17) also warns that latent image fading is significant within an hour after exposure, and the image is virtually nonexistent after 24 hours. This would mean that the length of time between exposure and development is an important factor affecting the measured speed. Still another factor is reciprocity failure. In the first years of the daguerreotype, Fizeau and Foucault (18) reported quite considerable departures from reciprocity for a range of intensities of 50:1. Development of the plate with mercury fumes is dangerous unless safety precautions are taken. And once developed, the image is so fragile that it can be wiped off by just brushing against it. This would rule out measuring the density of the developed image with a densitometer that touches the surface of the plate. Gold toning however, will reduce the fragility of the image so that densitometer measurements can be made, but at the same time, it strengthens and increases the contrast of the image and hence could conceivably affect the measured speed if not standardized. Not all of these difficulties were of concern to the daguerreotypist working in the 1840's. Still, there are enough difficulties to make one wonder how this process achieved the widespread popularity and superb quality that it did.

#### **Experimental Details**

**Plates:** Sixteen gauge (1.65 mm thick) photoengraver's copper was cut into plates 82 mm by 108 mm.

**Plating:** One surface was commercially electroplated with a thickness of about twelve micrometers of silver.

**Polishing:** Three hand buffs were used in the following order:

(1) Chrome oxide abrasive on a damp, felt-covered buff to remove deep scratches. The buff was dampened with distilled water to increase the buffing rate; however, excess moisture caused pitting of the silver surface.

(2) Dry jeweller's rouge (iron oxide powder) on a chamois buff to produce a mirror-like polish.

(3) A clean chamois buff to remove any remaining abrasive particles from the plate.

A critical means of visually checking the degree of polish is to examine the plate in a darkened room with a small light source illuminating the plate at 45 degrees. A plate with a mirror-like polish will appear black to an observer viewing the plate perpendicularly. Rotation of the plate in its own plane will

cause scratches to stand out as white lines on a black background when orientation to the light source is correct. An objective measure of the degree of polish can be obtained with a reflection densitometer that illuminates at one angle and measures at another. Assuming no stray light in the optics of the instrument, a well polished daguerreotype plate will have a density between 2 and 3, while one that is poorly polished will be below 1. Of course, care must be taken not to scratch the surface while making the measurement.

**Iodizing:** An iodizing box of the kind originally used by daguerreotypists was borrowed from the George Eastman House for this thesis. In principle, it is like an air tight dessicator: a rectangular jar with a sliding glass cover. Both the daguerreotype plate and the glass cover are held on a sliding wooden frame. By sliding this frame horizontally, the glass cover is slid off the jar bringing the daguerreotype plate over the iodine fumes. A small amount of dry iodine crystals is put in the jar; the distance between the crystals and the plate is 80 mm. Iodizing times longer than one minute would result in uneven coatings unless the total iodizing time was broken into one minute iodizing periods with one minute "rest" periods in between to allow the iodine vapor to refill the glass jar before the next iodizing period. In addition, the plate is turned end-for-end between iodizing periods to promote a more even coating.

A series of eleven plates was iodized so that each successive plate was of a different hue. Iodide thicknesses ranged between 15 and 180 nm.

**Spectrophotometry:** Immediately after iodizing, the total spectral reflectance of each plate was obtained over a wavelength range of 380 to 700 nm with a Beckman DK-2a spectrophotometer.

**Exposing:** A thousand-watt, quartz-iodine lamp was used 90 cm from a print frame containing a 21-step, 0.1 increment, step tablet arranged in a 42 mm by 62 mm rectangle. A variable step-down transformer reduced the line voltage to 70 volts and a voltmeter was used to monitor voltage during exposures. Operating the lamp at this reduced voltage allowed the desired exposure time of ten seconds. With this arrangement, illuminance at the exposing plane was 8600 meter candles or about 800 foot candles. Measurement of an eighteen percent gray card at the exposure plane gave a reading of "50 minus" with a Weston Master III exposure meter. To minimize speed changes due to variation in the time between iodizing and exposure, all plates were exposed from two to three hours after iodizing.

**Developing:** Since neither a fume hood nor an adequate device for developing with mercury vapor was initially available, another developing method was used. This method makes use of a phenomenon first observed by Becquerel (19) in 1840. He observed that the latent image on a daguerreotype plate can be printed-out by exposing the plate for some minutes to a uniform red or yellow light. Unexposed silver iodide is normally insensitive to red or yellow light. However, exposure in the camera produces latent-image silver specks large enough to act as optical sensitizers so that yellow or red light can selectively photolyze the exposed crystals, leaving the unexposed crystals unchanged. The image consists of finely divided, powdery silver instead of the mercury-silver amalgam found in conventional daguerreotypes. This developing process is safe, dry, uniform and very predictable. A plate printed-out by this Becquerel phenomenon is brownish in tone compared with the neutral tones found in mercury developed images. After gilding, the printed-out brownish tones become bluish while the neutral tones of the mercurized image become somewhat brownish.

The light source used for "Becquerel development" was a 500-watt, 3200° K lamp in a reflector, and the distance between bulb and daguerreotype plate was 30 cm. At this distance, a reflected-light reading from an eighteen-percent gray card was "100 minus" on a Weston Master III exposure meter approx. 1600 foot candles). To minimize effects from latent image fading, the plate was developed immediately after exposure. This was done by putting the plate in a plate holder, covering the holder with a transparent yellow plexiglas, no. 2208 (see Figure 21 for spectral transmittance curve), and exposed for twenty minutes to the 3200° K lamp. A fan directed at both the lamp and the film holder kept them from heating up. Normally, the image appears within one minute and strengthens with time.

**Fixing:** A solution of sodium thiosulfate that has dissolved oxygen in it will dissolve the finely divided image silver as well as the

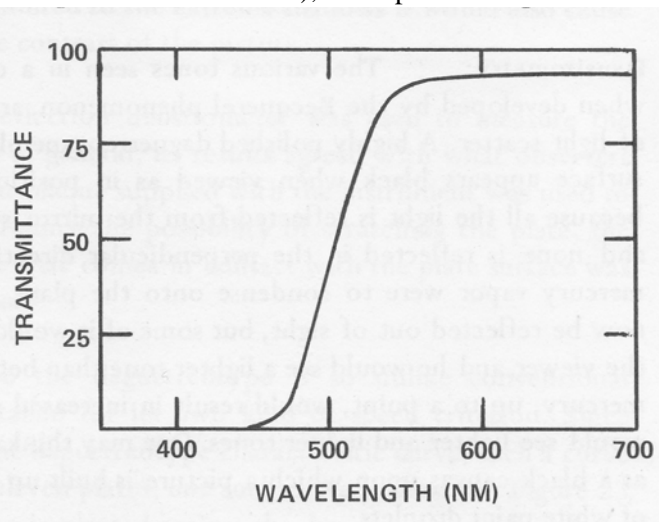


Figure 21. Spectral transmittance of transparent yellow plexiglas used in Becquerel development.

unexposed silver iodide. To remove only the unexposed iodide, the fixer must be free from dissolved oxygen. Such a solution was made with 15 gms of sodium thiosulfate and 15 gms of sodium sulfite in a liter of distilled water. After mixing, the solution was de-aerated by placing in a vacuum chamber until all bubbling stopped. Fixing was very rapid with the thin iodide layers: about ten seconds; the thickest layers required a minute or two.

**Rinsing:** The plate was rinsed in tap water, followed by a distilled water rinse, and was kept under distilled water until the gilding operation.

**Gilding:** The gilding solution consists of two parts, A and B.

A: Gold chloride (chlorauric acid,  $\text{AuCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ ), 1 gm in 500 ml of distilled water.

B: Sodium thiosulfate, 4 gms in 500 ml of distilled water.

Equal volumes of A and B were mixed just before use (A added to B) and just enough solution was mixed to cover the plate surface. The plate was placed in a teflon-coated skillet just large enough to hold the plate; premixed gilding solution was poured over the plate and the skillet was placed on a preheated Corning laboratory hotplate whose heater dial had been set at 5. With the skillet in constant contact with the hotplate, the hotplate was rocked to flow the gilding solution back and forth over the plate for 90 seconds. A heater setting of 5 was chosen so that the solution would not boil during the 90 second gilding. At the end of this time, the gilding solution was poured off and the plate rinsed with tap water for a few seconds. This was followed by a distilled water rinse, and the plate was dried with forced hot air from a hair dryer to prevent water spots. The plate was dry within a minute.

**Densitometry:** The various tones seen in a daguerreotype image, even when developed by the Becquerel phenomenon, are due to different amounts of light scatter. A highly polished daguerreotype plate without mercury on its surface appears black when viewed as in position 1 in Figure 22. This is because all the light is reflected from the mirror surface at an oblique angle, and none is reflected in the perpendicular direction. If a small amount of mercury vapor were to condense onto the plate, not all of the light would now be reflected out of sight, but some of it would be scattered to the eye of the viewer, and he would see a lighter tone than before. Increasing amounts of mercury, up to a point, would result in increased scattering, and the observer would see lighter and lighter tones. One may think of the daguerreotype plate as a black canvas upon which a picture is built up by adding various numbers of white paint droplets.

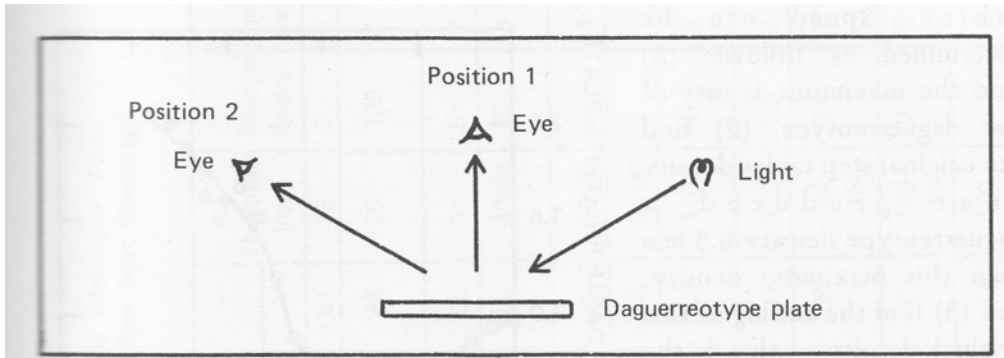


Figure 22. Angles of illumination and viewing of a daguerreotype plate.

The illumination and viewing geometry profoundly affects what a viewer

When he looks at a daguerreotype. It follows from this that the densitometer must imitate the illumination-viewing geometry of the observer if one hopes to have it respond like an observer. The effect of

illumination-viewing geometry is so profound that it can cause the daguerreotype image to appear either as a negative or a positive. In Figure 22, observer at position 1 would see a positive, but if he moved to position 2, the image would appear negative. A daguerreotype looks best when viewed at right angles and illuminated obliquely, while the rest of the room is kept dark.

viewed in a brightly lit room, light could come from all directions and reflect to the observer from areas in the pictures which should be the shadows (the mirror-like areas without mercury). This would make them appear lighter, and since this effect is not limited to the extreme shadows it would also cause overall degradation of the contrast of the picture.

A Macbeth RD-100 reflection densitometer was used to measure the densities of the plates, and in general, its results agreed with what observers saw. A two-point calibration plaque supplied with the instrument was used to "zero" the instrument. To reduce the possibility of scratching the plate, the part of the measuring probe that comes in contact with the plate surface was covered with thin tissue paper.

**Speed Criterion:** Since the daguerreotype is so unlike conventional photographic materials, it called for its own kind of speed criterion. Since speed is determined from the daguerreotype characteristic curve, such a curve was plotted for each of the eleven plates; one such curve is shown in Figure 23. Density of the daguerreotype is plotted against the density of the original step



tablet. Speed can be determined as follows: (1) find the maximum density of the daguerreotype, (2) find the original step tablet density that produced a daguerreotype density 0.5 less than this maximum density, and (3) find the antilog of this original density -- this is the speed. To make it easier to compare all the daguerreotype speeds to the fastest daguerreotype plate, each speed was divided by the speed of the fastest daguerreotype plate and then multiplied by 100. The result is called Relative Speed. The

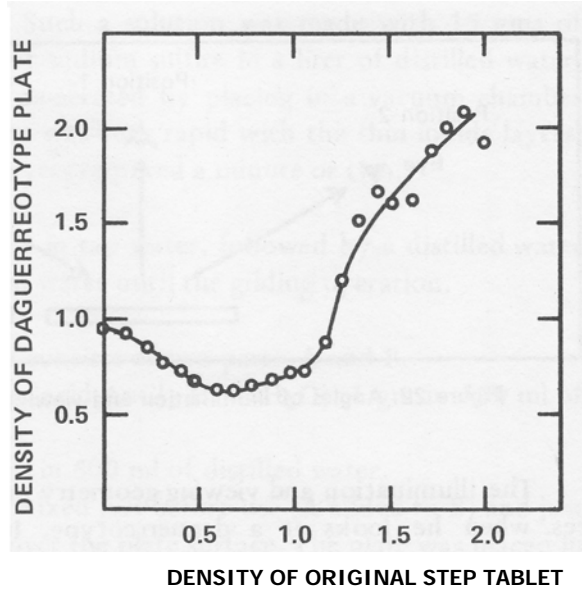


Figure 23. Typical characteristic curve of a daguerreotype plate.

fastest iodized plate can produce a good image when given an exposure of 60 seconds at f/4.5 on a bright sunny day and developed by the Becquerel phenomenon. This is roughly equivalent to an exposure index of 0.0008.

## RESULTS

Four of the eleven characteristic curves have been plotted in Figure 24. Two of the curves, representing iodizing times of 20 and 35 seconds (iodide thicknesses of 15 and 25 nm), show a region

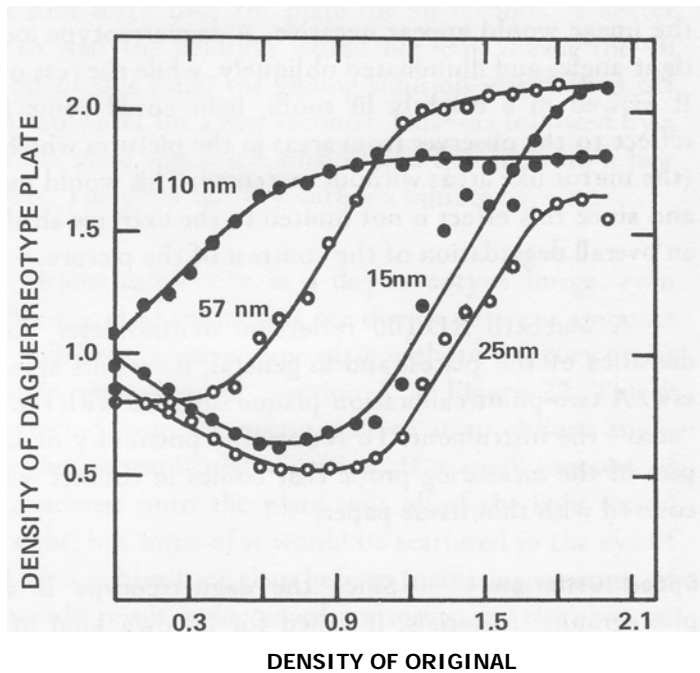


Figure 24. Characteristic curves of four daguerreotype plates that had silver iodide layers 15, 25, 57 and 110 nm thick and developed by the Becquerel phenomenon.

TABLE IV. Relative speed and color of a series of daguerreotype plates having different silver iodide thicknesses. Plates have been given a standard exposure to a step tablet and developed by exposure to yellow light (Becquerel phenomenon ▶).

No.	Time (sec)	SPECULAR VIEWING			MUNSELL RENOTATION			C.I.E.			Agl Thickness (nm)	Relative Speed	
		Hue	Lightness	Saturation	Hue	Value	Chroma	x	y	Y		Speed	Ranking
1	20	Yellow	High	Low	8.3Y	9.1	3.2	.349	.371	.81	15	?	3
2	35	Yellow with red tinge		Medium	1.2Y	8.3	4.2	.372	.374	.64	25	100	1
3	50	Red	High		10R	7.4	2.5	.344	.328	.50	34	54	2
4	65	Reddish magenta			8.9PB	7.4	2.2	.299	.299	.49	43-60	35	3
5	120	Blue		Low	8.1GY	8.2	1.4	.315	.338	.63	70-75	29	4
6	180	Yellow	Light	Low	5.3Y	7.9	6.0	.391	.413	.58	80-90	0	7
7	240	Yellow with reddish tinge		High	8.5R	7.0	5.9	.391	.337	.43	110	8	5
8	300	Magenta	Medium	Medium	7.3RP	6.2	3.6	.340	.306	.32	122	0.5	6
9	360	Green	Medium	Medium	7.2GY	6.7	3.5	.328	.378	.38	144-150	0.4	6
10	420	Yellowish Green '			1.9Y	6.9	3.6	.370	.372	.41	169-171	0	8
11	480	Yellow	Medium	Medium	1.9YR	6.3	3.8	.372	.342	.33	180-181	0	8

of solarization at the left, a toe, and a nominal straight line. (Solarization is said to be caused by heavy exposures that produce so much latent image silver and halogen that some of the silver and halogen recombine thereby reducing the exposure efficiency.) You will also note that, in general, the minimum density is fairly high (the lowest is 0.53); therefore, these highlights are not as bright as those found in conventional prints. Another observation is that the maximum density among the eleven curves varied unexpectedly from 1.4 to 2.1. The average slopes are about the same except for the curve representing the thickest iodide layer (110 nm), which is lower.

Table IV lists the relative speed as well as some of the other pertinent data for the eleven plates.

Figure 25a shows a plot of Relative Speed versus estimated thickness of silver iodide while Figure 25b shows total reflection density at 424 nm versus estimated thickness.

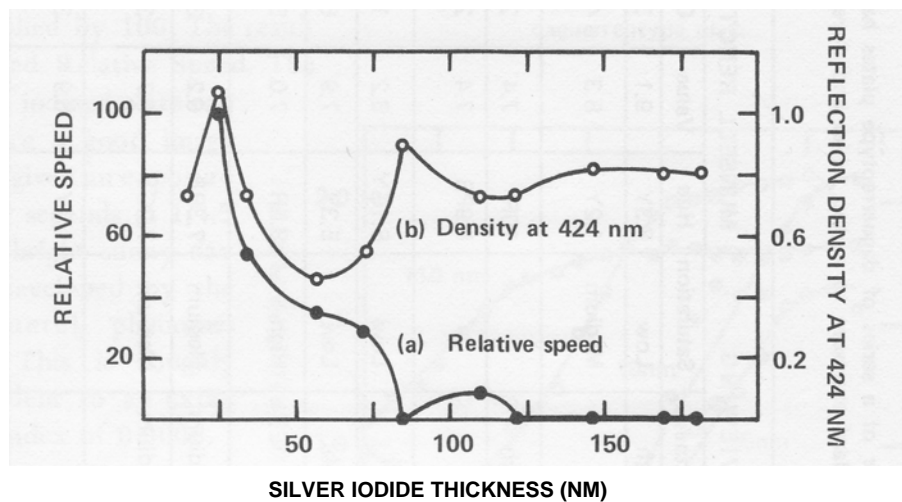


Figure 25. (a) Relative speed versus estimated silver iodide thickness.  
 (b) Reflection density versus estimated silver iodide thickness.

## DISCUSSION

### Comparison with Draper's Results

Relative speed correlates well with spectral reflection density at 424 nm for iodide thicknesses of 50 nm and below, but above this thickness there is an inverse correlation. Although the second relative-speed maximum at 110

nm was produced by a yellow iodide layer, this maximum would not be predicted from its blue light absorption at 424 nm. Draper reported that the plate had regained its full sensitivity whenever it appeared yellow. From this we would expect equal relative speeds for the two maxima; instead the data show the first maximum to be twelve times that of the second. Furthermore, the 180 nm plate, which also appears yellow, is almost completely insensitive. Draper's conclusion -- that whenever an iodized layer turned yellow it would regain its full sensitivity -- is not supported by the evidence from this experiment.

Of course, Draper's plates were developed with mercury while in this experiment, development was accomplished by using the Becquerel phenomenon. It could very well be that the sensitivity of the plate depends upon the method of development. To check this possibility it would be necessary to mercury-develop either another series of plates or a single plate containing Talbot rings (20).

Talbot rings are a series of colored rings made by placing an iodine crystal on the surface of a polished daguerreotype plate. As the iodine fumes diffuse radially, rings differing in color are formed. These rings can be thought of as topographical contour lines defining the loci of constant iodide thickness. In a set of Talbot rings, iodide thickness decreases radially from the center. If the plate with the iodine crystal is covered with an inverted watch glass to eliminate air currents, these rings will be quite circular and concentric. If the covered plate is placed on a warm laboratory hotplate, Talbot rings 70 mm in diameter can be produced in ten minutes; at room temperature it would take an hour. Interestingly enough, these rings were first described by Fox Talbot (20) in 1839, before the details of Daguerre's discovery were published.

### **Mercury Development**

Since a plate with Talbot rings contains all the iodide thicknesses used in the previous experiment, it can serve as a rough and rapid check on what effect different developing methods have on plate sensitivity. Two plates with Talbot rings were prepared. On each plate, the distances from a reference edge (along a line going through the center) were recorded for each of the observed hues. Half of each plate was covered with an opaque mask while the half containing the reference edge was given a uniform ten second exposure using the quartz-iodine source as described before. One of the plates was developed with mercury in a newly borrowed mercurizer for two and a half minutes with

the mercury at a temperature of 90 degrees centigrade. The other plate was "Becquerel-developed" as in previous experiments. The exposed half of each plate was fixed, leaving the unexposed half of the Talbot rings intact. Gilding was omitted. Developed semi-rings were found on both plates. The hue corresponding to these developed maxima can be identified by measuring the distances between the various maxima and the reference edge, and by referring to the original data relating hue and distance. Another means of finding the hue of the iodide ring that produced a given maximum is by centering over the Talbot rings a transparent acetate overlay with concentric circles drawn on it, observing the relative position of the maximum to one of the concentric circles, and finding a colored ring in the same relative position.

The "Becquerel-developed" Talbot rings show two maxima; the first and most prominent was produced by the outermost pale yellow and pale magenta rings; the second and very much weaker maximum resulted from the saturated magenta ring. The previous experiment showed that the second maximum was caused by the yellow-tinged-with-red iodide layer the thickness of which was estimated to be 110 nm. Judging by the color, the saturated magenta ring represents an iodide thickness of 122 nm, just 12 nm more. This is fairly good agreement considering that the Talbot rings were exposed at just one illuminance level rather than a range of levels as when a step tablet was used.

The mercury-developed Talbot rings show the following maxima and minima:

First maximum .....	outermost magenta ring
First minimum .....	light metallic blue ring
Second maximum .....	saturated yellow ring
Second minimum . . .	blue (between saturated magenta and saturated green)
Third maximum .....	yellow and magenta rings.

Also, surprising as it may seem, no mercury was precipitated on the bare silver even though it was unprotected by silver iodide. A similar observation was reported by Claudet (21).

The relationship between color and sensitivity for this mercury-developed plate is in good qualitative agreement with what Draper found. From this, it would seem that development method does have an influence on the sensitivity of the plate.

To get a quantitative comparison between mercury and Becquerel development, a number of iodized plates were exposed, using the quartz-iodine lamp and the step tablet as before. It was decided to examine the characteristic curves for the 30 and 110 nm layers because they correspond to the two maxima observed in z a c h o f t h e Talbot-ring plates and because both of these iodide layers appear yellow-tinged-with-red. Figure 26a shows Elie characteristic curves for the 30 nm layer, one plate developed with mercury, the other by the Becquerel phenomenon. A similar comparison is shown in Figure 26b for the 110 nm layer. The overall slopes of the characteristic curves seem to be a function of layer thickness rather than development method; thin layers have a significantly greater slope than the thick

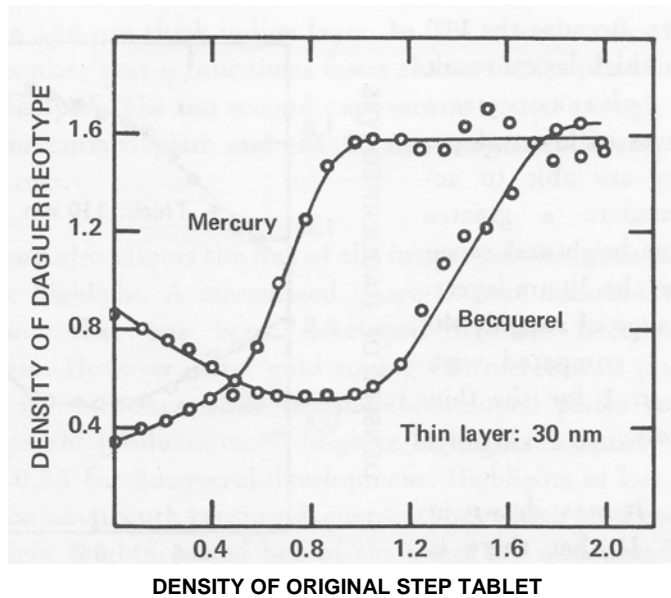


Figure 26a. Characteristic curves of thin (30 nm) iodide layers developed by mercury and by the

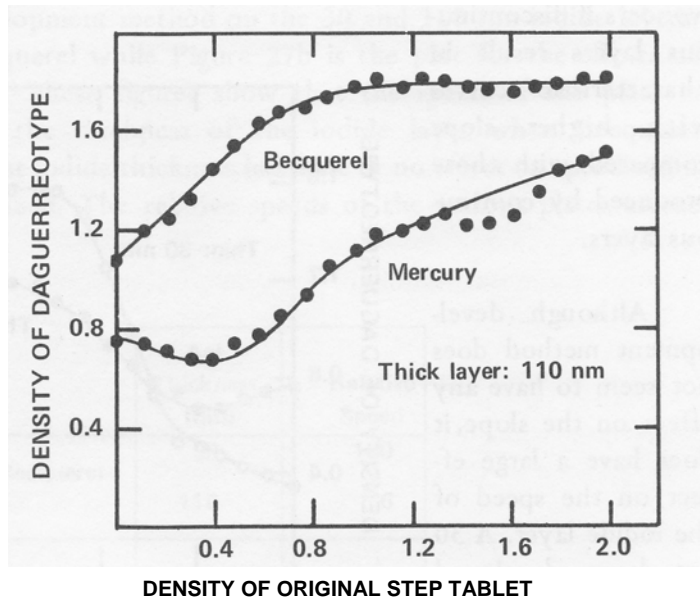
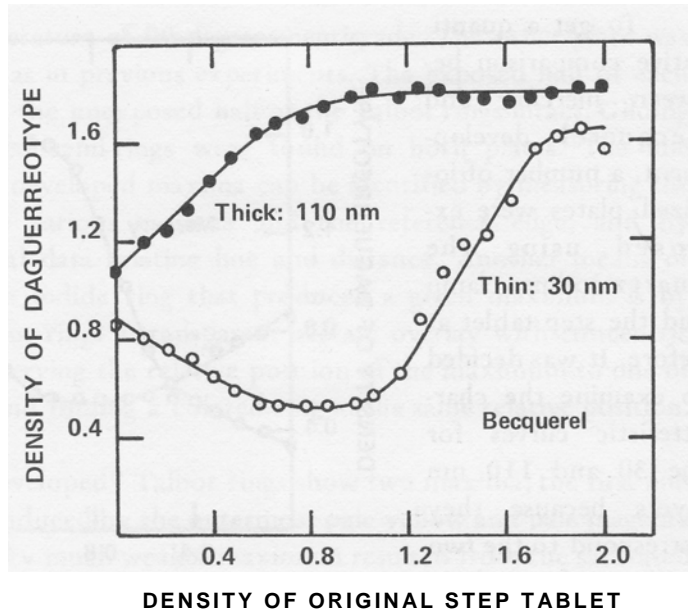


Figure 26b. Characteristic curves of thick (110 nm) iodide layers developed by mercury and by the Becquerel phenomenon.

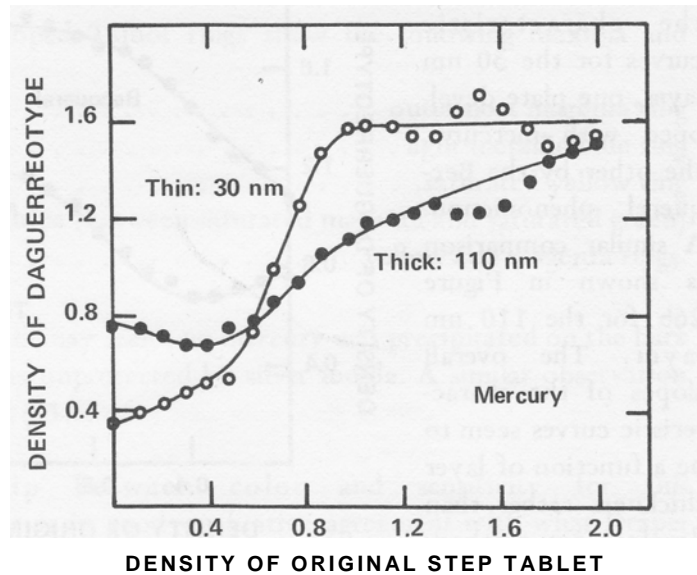
ones. Because the 110 nm thick layers result in characteristic curves of lower slope, they are able to accommodate a greater scene brightness range than the 30 nm layers: a range of roughly 40 to 1 compared with 10 to 1 for the thin layers.

It was shown in Part II that there is reason to believe that a 30 nm layer is discontinuous, while a 110 nm layer is probably continuous. One wonders if discontinuous layers result in characteristic curves with higher slope compared with those produced by continuous layers.

Although development method does not seem to have any effect on the slope, it does have a large effect on the speed of the iodide layer. A 30 nm layer developed by the Becquerel phenomenon is five times faster than one developed with mercury.



**Figure 27a.** Characteristic curves of thick and thin iodide layers developed by the Becquerel phenomenon.



**Figure 27b.** Characteristic curves of thick and thin iodide layers developed with mercury.

The reverse is true for a 110 nm thick iodide layer. In this case the mercury development results in a plate that is four times faster than a similar plate that has been Becquerel-developed. The ten second exposure has been enough to solarize the 110 nm mercurized plate and the 30 nm Becquerel-developed plate and not the other two.

Development method also effects the hue of the image and the maximum brightness of the white highlight. A mercurized image is quite neutral after development while one that has been developed by the Becquerel phenomenon is brownish. However, after gold toning the mercurized plate becomes brownish in its midtones while Becquerel-developed plates turn bluish. Mercury development produces much brighter highlights: a density of 0.34 for mercury and 0.52 for Becquerel development. Highlights as low as 0.26 have been found on nineteenth century daguerreotypes which have been mercurized. Both highlight brightness and hue of the image are undoubtedly due to differences in scattering- of the image caused by differences in size of the image elements. A mercurized image is generally more pleasing than one developed by the Becquerel phenomenon.

The curves in Figure 26 have been replotted in Figure 27 to compare the effect of a given development method on the 30 and 110 nm iodide layers. Figure 27a is for Becquerel while Figure 27b is the plot for the effects of mercury development. These figures show that the speed of the plate is strongly affected by the thickness of the iodide layer when Becquerel development is used, but iodide thickness has little or no effect on speed when the plates are mercurized. The relative speeds of the various plates are as follows:

	Agl Thickness (nm)	Relative Speed
	<b>Becquerel</b>	30
	110	6
<b>Mercury</b>	30	18
	110	25



It should be pointed out that these comparisons are based on a small sample size; this is especially true for the mercurized plates. Furthermore, mercury development, in general, was found to be much less predictable than Becquerel development. The cause or causes for its unpredictability were not identified in these short experiments. Some general observations on mercury development are as follows: (1) mercurizing times longer than about two and a half minutes tend to produce overall mercury fog; that is, mercury droplets deposit less selectively in exposed and unexposed areas, (2) even unexposed areas will have a small number of mercury droplets, and their number and size increase with mercurizing temperature, and (3) developing at higher mercury temperatures results in stronger images and brighter highlights.

At one point, it was thought mercury development could be explained if one assumes a discontinuous iodide layer which would allow mercury to get to the silver substrate. Figure 27b shows little or no difference in relative speed or development efficiency between iodide layers which are 30 or 110 **nm** thick. Since these thicknesses are believed to represent a discontinuous and a continuous layer, respectively, we are left with the mystery of how a mercury image on a continuous iodide layer is able to attach itself to the silver substrate. Why doesn't the image float away when the intervening iodide layer is removed by hypoing?

A number of hypotheses were proposed to explain why Becquerel development is less efficient for thick layers than for thin. Each hypothesis was tested and all were rejected. The first assumed that Herschel latent-image destruction was taking place for thick layers and not for thin (22). However, no improvement was obtained when a normally exposed 110-nm thick iodide layer was Becquerel developed using green light only (red and infrared were excluded). The second hypothesis assumed that the prolonged iodizing necessary to produce a thick layer resulted in adsorbed iodine which combined with the latent image silver, thereby decreasing the efficiency of the exposure. Treatments to remove the alleged adsorbed iodine (heating the plate, washing in isopropyl alcohol, immersion in a one percent solution of acetone semicarbazone to react with the iodine) all proved fruitless. The last hypothesis assumed that the latent image formed on the surface of the thick iodide layer and that this greater thickness of iodide reduced the effectiveness of the silver as a halogen absorber. As a test of this hypothesis, a thin gelatin coating containing acetone semicarbazone was applied to the iodized plate,

prior to exposure and Becquerel development, to act as a halogen acceptor -- with no gain in exposure efficiency. Since all hypotheses were rejected we cannot account for the lower speed found for thick layers developed by the Becquerel phenomenon.

## **ALTERNATIVE DEVELOPING METHODS**

### **Physical Development**

When this daguerreotype study was first undertaken it was hoped that a newly announced (23), improved physical developer could be used to develop daguerreotype plates. Physical development seemed feasible for this purpose because Waterhouse (24,25) in 1898 and 1899 published a series of papers on his daguerreotype studies in which physical development was successfully used for developing daguerreotype plates. Despite all this, all attempts at using the newly announced physical developer for developing daguerreotypes were unsuccessful. A more careful reading of Waterhouse's papers uncovered some qualifications: 'When developing by this method it will be found desirable to heighten the sensitiveness of the plates with an organifier to which may, with advantage, be added a little erythrosin to make the plates orthochromatic ... The plate is exposed moist' (24). And in another of his papers, he states, ' ... my results would seem to show that the underlying silver of the plate which is generally supposed to perform the role of sensitizer or halogen-absorbent when a daguerreotype plate is developed with mercury, is quite unequal to the task when an ordinary wet [plate] or dry [plate] developer is used, and some additional organic sensitizing is necessary to shorten exposure; and this is the case even when the developer contains free silver in the form ready for deposition.' (25)

In addition, an abstract from a German paper seems to confirm the difficulty of physically developing daguerreotype plates: 'Metallic vapor deposits of high purity cannot be developed with conventional photographic physical developers, but can be developed with metallic vapors and with solutions used for enlarging colloidal particles. Examples are given of mercury vapor and of a liquid developer containing silver nitrate, formaldehyde and ammonia.' (26)

### **Chemical Development**

For the sake of completeness, chemical development was tried using a pyrogallol formula published by James and Vanselow (27) and designed for developing silver iodide emulsions. The formaldehyde was omitted from the formula. Results with chemical development were also unsuccessful.

### **Silver-salt-diffusion Development**

In a recent patent describing a direct application of the Daguerreotype process (28), a number of developer formulae are given which will develop a daguerreotype surface and transfer a negative image onto a baryta-receiving sheet. Although these were not tried, they do hold promise and might lead to a better understanding of the relationship between plate sensitivity and developing method. Even the notion of transferring the image onto a paper support seems to have research applications.

### **CONCLUSIONS**

1. The sensitivity of iodized daguerreotype plates varies with thickness of the silver iodide layer and depends upon the method of development.
2. Maximum sensitivity, when the Becquerel phenomenon is used for development, is obtained when the silver iodide layer is about 30 nm thick. At this thickness it will appear yellow-tinged-with-red.
3. Sensitivity diminishes with iodide thicknesses between 30 and 90 nm and rises again to a maximum at a thickness of 110 nm whereupon the plate will again appear yellow-tinged-with-red, but more saturated than the 30 nm layer. The sensitivity of the plate at this second maximum is 1/12th that of the first.
4. Sensitivity correlates with spectral reflection density at 424 nm for iodide thicknesses up to 50 nm, but above that thickness, there appears to be an inverse correlation between absorption and sensitivity (Becquerel development).
5. For both mercury and Becquerel development, thinner iodide layers (about 30 nm) result in characteristic curves of higher overall slope than do thicker layers (110 nm).
6. Development method affects both the hue of the image and the maximum brightness of the highlights. Mercury development produces significantly brighter highlights compared with those produced by Becquerel development. After gilding, the midtones of a mercury image are brownish; in a Becquerel-developed image, they are bluish.
7. In agreement with early reports, sensitivity maxima were observed at thicknesses of iodide that were yellow or yellow-tinged-with-red (30 and 110 nm). With mercury development, these were approximately the same at the midpoint of the characteristic curve although contrast was

much lower for the thicker layer; with Becquerel development, the thinner coating was much more sensitive than the thicker, having a threshold speed equal to the thicker mercury-developed coating but with much higher contrast.

8. Why Becquerel development is less efficient for thick layers than for thin is not known, but it does not seem to be caused by either the Herschel effect, adsorbed iodine on the iodide crystal, or by the absence of a halogen acceptor at the crystal surface.

## SUMMARY

This paper deals with a study of a curious phenomenon observed while a daguerreotype plate is sensitized by fuming with iodine. As this sensitizing process continues, the surface of the plate is seen to go through a series of colors quite unrelated to the color of silver iodide. The objectives of this study are threefold: (1) to measure the thickness of the silver iodide layer for a series of plates that have been exposed to iodine fumes for various lengths of time and therefore have different colors, (2) to determine if interference or scattering is the cause of the observed colors, and (3) to measure the photographic speeds of a series of plates, each of which is differently colored.

In Part I, a series of differently colored iodide layers was prepared, each layer stripped from its silver support and its thickness measured by two different techniques, X-ray fluorescence analysis and spectral absorbance (Bouguer's law). The results of the methods were in good agreement; thicknesses were found to range between 15 and 230 nm.

In Part II evidence is presented indicating that both interference and scattering are taking place. The scattering is due to the optically rough surface which is seen (on scanning electron micrographs) to become rougher with increasing iodide thickness. The evidence for interference is qualitative since quantitative agreement between observed and calculated reflectance curves was not found. This disagreement was probably due to choosing a theoretical physical model having a plane parallel-sided layer which is not representative of the rough iodide layer found in daguerreotype plates.

Experimental evidence suggests that silver iodide layers less than 90 nm are discontinuous and therefore even such thin "layers" can scatter light. It was found that diffuse reflectance, and therefore scattering, increased with iodide thickness, levelling off at a thickness of about 75 nm.

This study has shown that the colors seen on iodized daguerreotype plates are not due to a single, clear-cut cause but instead represent a very complex optical problem involving interference, scattering, and possibly absorption.

In Part III, the photographic speed of the iodide layer was found to depend upon both its thickness and the method of development, that is, whether it was developed with mercury or by making use of the Becquerel phenomenon. The maximum speed of a plate was found when an iodide layer 30 nm thick was developed by the Becquerel phenomenon: this maximum speed is roughly equivalent to an exposure index of 0.0008 or 60 seconds at  $f/4.5$  on a bright, sunny day. Thick iodide layers (110 nm) result in characteristic curves of much lower contrast than obtained with thin layers (30 nm).

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