Optical coatings in the 1940s: Coating under adverse conditions

By Philip Baumeister

Mary Banning Friedlander operating the knife switches that powered the evaporator at the Institute of Optics, University of Rochester, circa 1944. The glass plate that is the lid of the evaporator and the water-cooling coils of the oil diffusion pump are visible.

In the 1980s it is evident that the geographical locations of the institutions in North America that train optical engineers are quite diffuse, ranging from Quebec in Canada to as far south as Tucson, Ariz., and Puebla, Mexico. But in the 1940s, the lion's share of the training was in Rochester, N.Y. There were a few physics departments in the U.S. that trained optical physicists such as the University of California, Berkeley, the Johns Hopkins University, and Massachusetts Institute of Technology.

However, training in optical engineering was patently centered at the Institute of Optics of the University of Rochester, located in the same city as Eastman Kodak, Bausch and Lomb, Wollensak, and Ilex. The director of the institute, Brian O'Brien, had started depositing optical coatings for neutral density filters[1] in the late 1930s. He knew that he must expand the optical coating program when the U.S. launched into World War II in late 1941. The National Defense Research Committee would supply ample money to fund his program, but where would he find the personnel?

Professor O'Brien had heard from Professor Pfund at the Johns Hopkins University that a talented "hands-on" optical physicist would soon receive a doctorate. Her name: Mary Banning. And O'Brien was reassured that *this* optical physicist would remain on the staff. For if the physicist were a male, it was highly probable that a draft notice would arrive, at which time he would instantly vanish from the laboratory only to reappear toting an M-1 in the U.S. Army. It was later proven that Professor O'Brien's exploits in physiological optics (which won his election to the National Academy of Sciences) equaled his prowess in exempting the young lads on his staff from the draft.

Mary Banning arrived in Rochester in the summer of 1941. She quickly took charge of the coating operation. That she was "hands-on" is attested to by the adjacent photo, which shows her in the laboratory operating one of the deposition tanks. These are described later on.

Coatings—choice of technologies

Those of us who, today, can order and have delivered to our doorstep a finely crafted stainless steel box coater might find it difficult to understand the options that faced Mary Banning. First, it was by no means obvious that vacuum deposition was the best method of depositing coatings. There was an alternate method of depositing layers chemically—the acronym CVD (for chemical vapor deposition) is now used—that is described later. And many of the vacuum technologies that we take for granted today either did not exist or were in their infancy. This will become more obvious as we survey the equipment that she built.

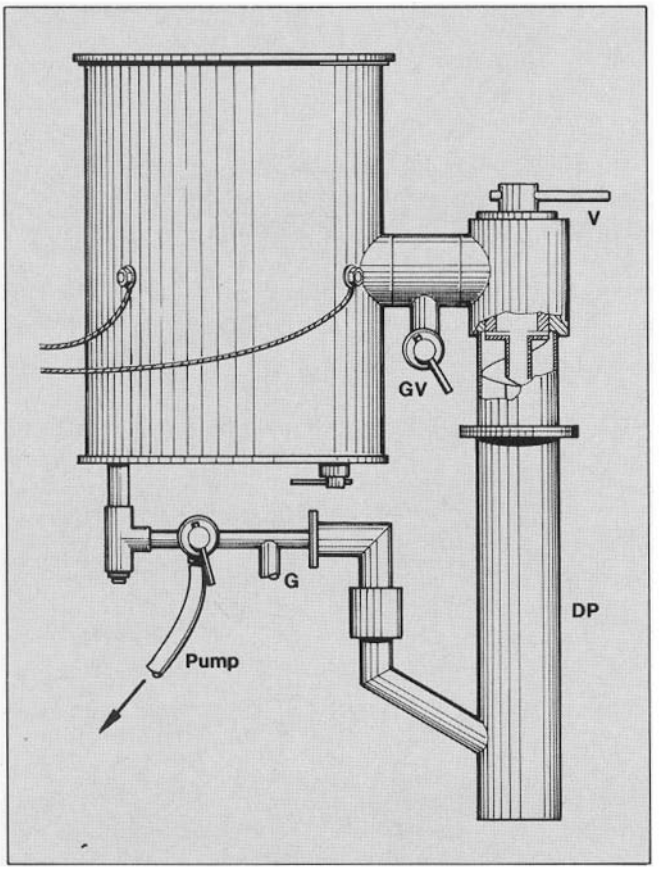

FIGURE 1. Elevation view of the exterior of the evaporator, showing the stopcock high-vacuum valve V, *the diffusion pump* DP, *the valve to the high-vacuum ionization gauge* GV, *the outlet to the Pirani gauge* G, *and the rubber hose to the mechanical vacuum pump (from Ref. 2).*

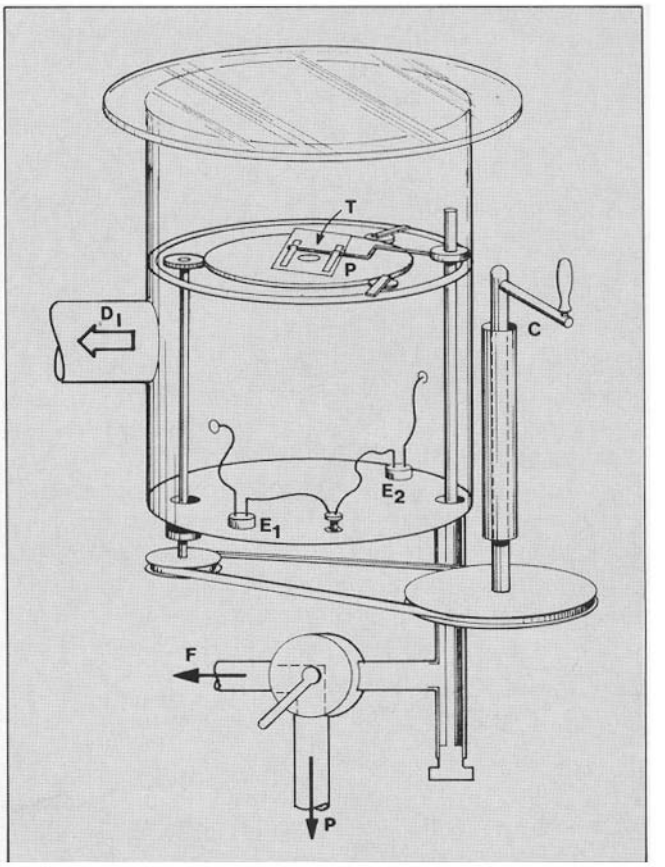

FIGURE 2. Isometric view of the evaporator, showing the top window W; the outlet D_1 to the diffusion pump; the plate P that is coated; the monitor test glass T; the hand crank C that rotates P during the deposition; and the evaporation sources E_1, E_2 (from Ref. 2).

Deposition apparatus: overview

Figure 1 and 2 show the tank in which the depositions were made. It was constructed of brass—yes, (almost) all brass. But why not steel? Remember that welding that produced pinhole-free joints was in its infancy in the 1940s. Furthermore, mild steel rusted and stainless steel was practically impossible to procure because of wartime shortages of critical materials. The objective was to produce a tank quickly for research and development; brass could be easily soldered to produce vacuum-tight joints.

The tank, as described in the final report[2] for the project, was a side-pumped cylinder that was about 320 mm (14 in.) diameter. The top was sealed with a 20-mm thick glass plate that seated against a rubber gasket. The glass plate is clearly seen in the photograph. The valve that connected the diffusion pump to the tank was a 80-mm (3-in.) stopcock. Do we remember those little conical glass stopcocks that we used in chemistry laboratories? If you scale that to 80 mm—with the solid "core" of steel and the outer sleeve made of brass—you get some idea of its construction. There was a pry-bar of half-meter length in the lab that supplied the extra torque to open or close that valve.

The diffusion pump oil was obtained from Distillation Products in Rochester and was a relatively recent innovation. Some of the coating tanks that had been built earlier at the Institute by O'Brien had used mercury in the diffusion pumps. These had the advantage that the working fluid did not oxidize if exposed to air at high temperatures, as does the oil. But the extra pumping speed offered by the oil was definitely an advance in the technology.

Deposition apparatus: do-it-yourself

Virtually all of the appendages to the evaporation chamber were both designed and produced in-house. For example, a ground joint that was well lubricated with stopcock grease served to introduce rotary motion into the chamber so that the substrates could be rotated during

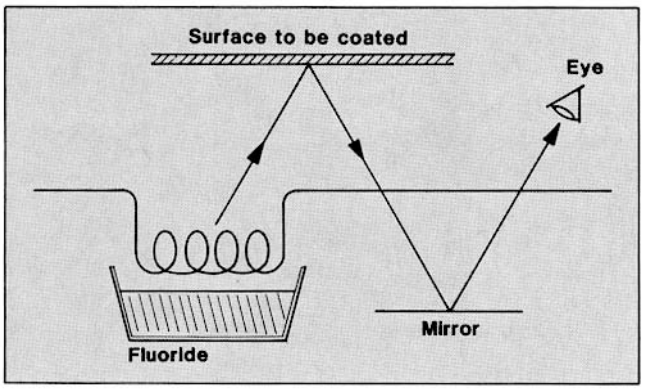

FIGURE 3. Schematic view of visual optical monitoring in reflection, in which the light from the coiled filament reflects from the surface (inside of the vacuum system) that is being coated, from a mirror and thence through the outer window of the vacuum tank (not shown) to the eye of the observer. The relative distances are foreshortened for purposes of illustration. Fluoride is the cryolite evaporation source that is heated radiantly by the filament (from Ref. 2, p. 33).

deposition. The Pirani gauge that measured the pressure (at the higher end of the scale) was made from a 25-watt light bulb. The ionization gauge (that functioned at relatively low pressures) was fabricated by punching a hole in a #45 radio receiving tube and attaching it to the vacuum system with a glass tube and Picein wax.

The substrates were glow-discharge cleaned prior to evaporation. The glow was powered by a 12-kV neon sign transformer. The high-voltage lead through in the side of the vacuum tank was fabricated from wax and glass rod. A low-voltage, high-current transformer heated the evaporation sources. The photo on page 10 shows the array of knife switches that powered various parts of the apparatus. The period from 1941 to 1946 witnessed research and development on methods of producing neutral density filters,[3] single-layer beam dividers,[4] and multilayer reflectors.[5] Some of the coating tanks were devoted to production. A substantial number of cube corners were coated with "back surface silver" and scores of mirrors were aluminized. Beam dividers for the optical system used in a submarine periscope were produced by CVD depositing a titanium film on glass plates.

The development of new coatings dovetailed with the production of coatings for instruments that the institute produced for the military services. In a letter to the author, Mary Banning mentioned the "terrible pressure we were working under. We worked usually on things that should have been done yesterday."

The same vacuum coating techniques were used as are in use today, with two exceptions: the variety of coating materials was quite limited, and the thickness of the layers was controlled by judging the color.

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Coating materials and techniques

Zinc sulfide was principally used for the high-index layers and either cryolite (a sodium-aluminum fluoride) or magnesium fluoride were principally used for the low-index layers. The attempts to evaporate silica from heated filaments were not successful. A variety of metals, including platinum, palladium, iron, nickel, and chromium, were deposited from heavy tungsten boats for use in neutral density filters.

Silver was deposited for second surface mirrors and was overcoated on its rear surface with copper to protect it from chemical attack. Highly reflective opaque layers of aluminum were obtained only when the pressure in the chamber vacuum was relatively low. This happened only when the chamber was free of small leaks and was relatively clean.

Multilayer dielectric coatings

An impressive accomplishment was the production of multilayers containing up to seven layers. Figure 3 shows how the thickness of a layer was determined during its deposition—this is termed *monitoring* in the trade. A fluorescent lamp was reflected from the "test glass" inside the vacuum tank. The deposition was terminated when the film on this plate reached the proper thickness, which was judged by its color. All of this was done while a hand crank was turned to rotate the substrates during deposition to obtain relatively good thickness uniformity across the substrates.

The report[2] chronicles the process that was used to determine the thickness of a layer as it was being deposited:

> Judgment of the proper color of the filters is difficult and constant practice is needed to insure reproducible results. However, it is quite possible to train an operator in a few days to make good filters. Cryolite appears yellow by reflected light when it is extremely thin; this is because it causes the glass to transmit more blue light than usual by destroying the blue reflection. With a slightly thicker film it appears pink, then magenta, then blue as the increased transmission moves to long wavelengths. . .

There are many uses for such coatings. They have been used as reflectors in Fabry-Perot interferometers and as color separation filters.

Zinc sulfide colors are easy to see, because they change the reflection from 4% to 30%. The first observable color is bluish white, which rapidly changes to brilliant white; yellow, magenta, and blue follow with increasing thickness. Cryolite films on top of a colored zinc sulfide film are extremely hard to see; except when both films are a quarter wavelength thick there is a characteristic paleness, a washed-out look, or absence of color that denotes the match is reached. A good operator can always tell this position.

The foregoing method might seem somewhat primitive to those who, like the author, are accustomed to entering the desired thicknesses into a process control computer, which then sets the wavelength of the monochromator for monitoring and subsequently terminates the deposition at the proper thickness. But the success of Banning's procedures is well documented.

Figure 4 shows the transmittance versus wavelength of some coatings that are now termed quarterwave stacks. We should remember that in 1941 this coating was relatively new, having been published[6] only a few years earlier. We can use a shorthand notation to list the design as follows: H represents a zinc sulfide layer whose optical thickness is $\lambda_0/4$ at a reference wavelength λ_0 of 520 nm. L represents a cryolite layer of the same optical thickness. The designs whose transmittance curves are shown in Fig. 4 are the following:

air HLH glass	(three layers),
air HLHLH glass	(five layers),
air HLHLHLH glass	(seven layers).

The transmittance at the "tuned wavelength" steadily decreases—from 33 to 15 and finally to 8%—as more LH pairs are added to the three-layer stack.

There are many uses for such coatings. They have been used as reflectors in Fabry-Perot interferometers[7] and as color separation filters.[8] Figure 5 shows the transmittance of a 7-layer filter in which each of the layers is three quarter-waves in optical thickness. The result is that the spectral width of the attenuating region in the visible is much narrower than its counterpart in Fig. 4. The coating in Fig. 5 reflects the green strongly and hence appears "minus green" (or magenta) in transmittance.

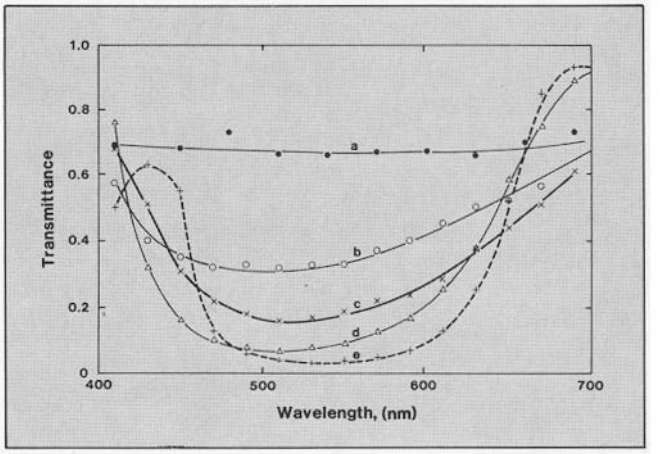

FIGURE 4. Measured transmittance of a single layer of zinc sulfide layer (a) and multiple layers deposited on a BK-7 glass substrate. H *and* L *represent layers of zinc sulfide and cryolite, respectively. Both have an optical thickness of $\lambda_0/4$ at a reference wavelength λ_0 of 520 nm. The designs and corresponding curves are as follows: (b)* air HLH glass, *(c)* air HLHLH glass, *(d)* air HLHLHLH glass, *(e)* air HLHLHLHLH glass *(from Fig. 17 of Ref. 2).*

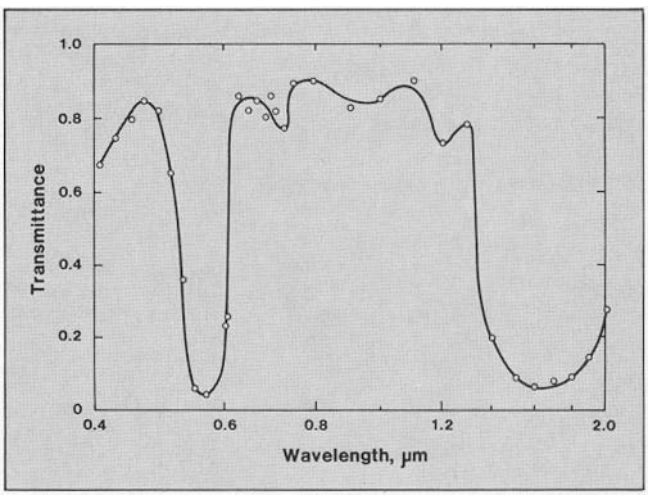

FIGURE 5. The same design as the curve in Fig. 4(d), with the exception that each layer has an optical thickness of $3\lambda_0/4$ at a reference wavelength of 570 nm (from Fig. 24(b) of Ref. 2).

Chemical vapor deposition

The chemical vapor deposition technique was used to expose heated glass to a mixture of water vapor and titanium tetrachloride vapor

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl.$$

A solid film of titanium dioxide formed on the glass surface. The process was to heat the glass to about 200°C in a

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furnace. The hot glass was held over a dish of liquid titanium tetrachloride. A white cloud of titania "smoke" appeared when a jet of compressed air (that supplied the water vapor) was directed at the dish containing the liquid $TiCl_4$. No wonder that this process was called "fuming" in the literature at that time.

Regardless of whether it is termed fuming or the more modern CVD, hard, durable beam dividers with about 65% transmittance were produced in this manner. Banning noted that one of the casualties of the war was the chemical hood in which this work was done. It succumbed to the ravages of the hydrochloric acid vapor.

Trivia—and coatings after the war

One of the women technicians who operated the coating equipment became engaged. There is an apocryphal story that one day she accidentally ran her engagement ring across the glass plate that sealed the coating tanks, introducing a substantial scratch into the glass. (Extraneous note: Presumably this was accidental and not for the purpose of testing whether the Moh hardness of the stone in her ring was 10 or lower—perhaps zircon?) The glass continued in service for many years after that, but with the precaution that the scratch was always placed *up*—on the nonvacuum side of the plate where the surface is in compression. A scratch on the vacuum side would be in tension, causing the plate to crack and implode.

After the war ended in 1945, Banning remained at the institute to write a report[2] and publish[3–5] some of the results. She left the institute in the summer of 1946. After she married a year later and had family responsibilities, she found that her publications had established her reputation; she continued as a coating consultant for many years.

The brass evaporation tank suffered an ignominious fate. It was used strictly for "service" and was not under the supervision of any of the faculty. A result was that it suffered sad neglect in the 1950s. When the author arrived at the Institute of Optics in 1959, the joints on the tank has been smeared with numerous layers of Glyptal varnish to plug leaks into the vacuum.

But the worst was yet to come. In the early 1960s there was a graduate student in the physics department who felt that it was too much bother to open a can and brush on some Glyptal varnish to fix the leaks—he switched to a can of white spray paint. Soon afterwards the tank leaked permanently—little surprise! And so that noble deposition tank, which had served so well to advance our knowledge of coating, was relegated to the junkyard when the physics department assumed control of that part of the building in 1963.

In the era since the department of Mary Banning in 1946, the Institute of Optics has not fared well in keeping full-time faculty who are interested in optical coatings—there are none on the faculty today. Harry Polster, who worked as an assistant professor in the early 1950s, published some nice papers on all-dielectric bandpass filters that probed the effects of absorption in the layers on the bandwidth. But a few years later he left the institute for Perkin-Elmer, where he excelled as an instrument designer. The author followed Polster's footsteps and left for industry in the 1970s.

Acknowledgments

Mary Banning Friedlander, who now lives in Milwaukee, reviewed the article and supplied the photograph. Brian O'Brien who resides in Woodstock, Conn. contributed some recollections. Neither could locate Banning's coworker, Fred Paul, who contributed to the coating tank design.[9] Jack Coté (Santa Rosa, Calif.) produced the drawings.

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References

1. B. O'Brien, "Method and apparatus for producing thin wedges," U.S. Patent 2,160,981 (1939).
2. M. Banning, "The evaporation of thin films," Rep. Contract OEMsr-160, Sec. 16.1 Natl./Def. Res. Comm. (Institute of Optics, University of Rochester, Rochester, N.Y., March 1, 1945).
3. M. Banning, "Neutral density filters of Chromel A," J. Opt. Soc. Am. 37, 686 (1947).
4. M. Banning, "Partially reflecting mirrors of high efficiency and durability," J. Opt. Soc. Am. 37, 688 (1947).
5. M. Banning, "Practical methods of making and using multilayer filters," J. Opt. Soc. Am. 37, 792 (1947).
6. C. Cartwright and A. Turner, "Multilayer films of high reflecting power," Phys. Rev. 55, 1128A (1939)
7. J. Stone, "Refinements in the preparation and theory of multilayer films," J. Opt. Soc. Am. 43, 927 (1953).
8. A.F. Turner, "Some current developments in multilayer optical films," J. Phys. Radium 11, 444 (1950).
9. M. Banning and F. Paul, "A convenient type of vacuum chamber for the evaporation of optical films," Rev. Sci Instrum. 15, 152 (1944).