

PREPARATION OF CARBON FILMS BY USE OF A GLYCERIN SUBSTRATE

WALTER J. HUMPHREYS. From the Department of Zoology, University of California, Berkeley, California

While carbon films are highly desirable for supporting specimens for electron microscopy, the difficulty in preparing them prevents their routine use in many laboratories. The usual method employed is to coat the grids with a plastic film which is then coated with carbon in an evaporator, followed by removal of the plastic with a suitable solvent (6). Satisfactorily removing the plastic film without damaging the carbon film, however, is arduous. Stripping carbon films from glass slides (2) or from cleaved mica surfaces (3) is tedious, and getting such films properly spread on grids and adequately attached to the grid bars presents other difficulties.

It was reasoned that an ideal way to prepare grids coated with carbon would be to float them on the surface of a water-soluble liquid, the surface of which would serve as the substrate for the deposition of evaporated carbon. The liquid substrate could be removed by floating the grids on the surface of distilled water. Necessary properties of such a liquid would be a low vapor pressure, high solubility in water, and a surface tension strong enough to support the grids. Glycerin was

found to serve the purpose adequately; it has a vapor pressure of about 0.2μ Hg at room temperature, it is very soluble in water, and its surface tension is sufficient to support grids. The idea of casting films onto liquid surfaces is not new. In 1948 Hast (4) recommended evaporation of metals onto glycerin as a method for producing very thin metal films.

First attempts to use this principle were only partially successful. Grids were suspended on the surface of small individual droplets of glycerin on a microscope slide and placed in an evaporator for coating at a pressure of 0.3μ Hg. Due to traces of water in the glycerin, which is hygroscopic, bubbles formed in the glycerin and on bursting they often flipped the grids from the surfaces of the droplets. To avoid this problem, the procedure described below was adopted.

A grid punch is used to make a series of holes spaced about $\frac{1}{8}$ inch apart in a thin strip of celluloid. Thin celluloid rulers do very well for this. The celluloid strip is clamped in a holder which keeps it clear of the resting surface when the holder is set down. A suitable holder is a stack of micro-

scope slides, bound together by Scotch cellophane tape, between the middle two slides of which one edge of the celluloid strip is slipped. A small glass rod is used to suspend a film of glycerin across each hole in the strip, care being taken to avoid excessive amounts of glycerin so that it does not spread laterally from the hole's edge. A grid is placed on the surface of each film of glycerin, smooth surface up. Placement of the grids is checked with a dissecting microscope in order to make sure that the entire lower surface of each

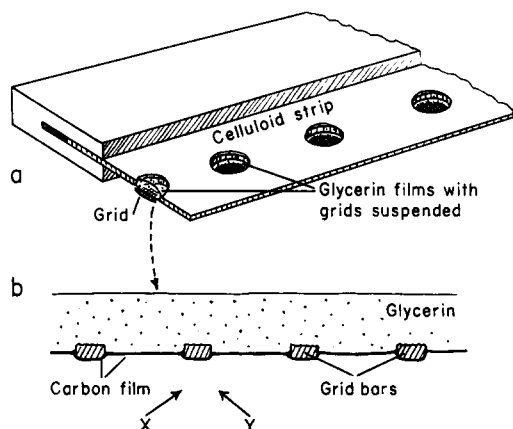


FIGURE 1 *a*. Diagram showing how grids are suspended from films of glycerin. The grids as shown would be coated from below. To coat the grids from above, the holder is inverted, after the glycerin is degassed, so that the grids rest on top of the glycerin.

b. Diagram of a cross-section of a grid, illustrating how the glycerin surface in contact with the grid bars serves as a substrate for carbon deposition. The grid as shown would be coated from below. To avoid the possibility of having areas shadowed from the carbon source by the grid bars, the carbon is applied in two coats from opposite directions which are indicated by the arrows, *X* and *Y*.

grid is in proper contact with the glycerin surface. The upper surfaces of the grids should be free of glycerin. The holder with the celluloid strip is inverted so that the grids are suspended from the lower surfaces of the glycerin films (see Fig. 1 *a*). The strip with the grids can then be placed in the evaporator and coated with carbon from below at a pressure of 0.3μ Hg. Since the bubbles leave the top surface of the glycerin film, the grids are not displaced. If it is inconvenient to coat the grids from below, the holder with the strip containing the suspended grids can be placed in the evaporator, taken to the above pressure, allowed to

bubble, and then be turned over so that the grids lie on the upper surface of the glycerin films. With this procedure the grids are not thrown from the glycerin even if further bubbling occurs. Carbon can then be deposited on the grids from above. Coating the grids from above has the advantage of permitting judgement of the thickness of the carbon film deposited, by the use of a piece of white porcelain spotted with a drop of vacuum pump oil, the difference in darkening between the oil drop and the porcelain being used as an index of thickness (1).

For best results, the carbon should be deposited in separate thin layers vaporized from different angles until the desired thickness is obtained. In evaporators in which it is possible to rotate the grid holder while the carbon is being evaporated, this is recommended. When this is not possible, the bell jar can be removed after a thin first coat of carbon is deposited, the holder rotated 180° from its original orientation, and a second coat of carbon deposited until the combined thicknesses of the two layers is the thickness desired. This is done to avoid the possibility of the grid bars' shading the glycerin surface from the carbon source, thereby causing a lack of carbon deposition in some areas (see Fig. 1 *b*). For the same reason, the grids should be placed on the glycerin so that the smoother surface faces the carbon source.

In coating plastic substrates, rapid deposition of carbon is often used because prolonged exposure to the heat radiated from the carbon arc can damage the plastic. With a glycerin substrate no such problem exists, and it is possible to deposit the carbon very slowly if one wishes to do so. In our laboratory very slow evaporation is preferred because the resulting films are mechanically stronger, and they seem to conduct heat and electrical charges better. Bonding of the carbon atoms that make up the film may be better when a slow evaporation is used. Another explanation could be that the films made by slow evaporation are thicker than their optical densities would indicate. Although two carbon films may have the same optical density, there is evidence that the one made by slow evaporation may be much thicker than the one made by rapid evaporation (5).

After the films are formed, the celluloid strip is slipped from the holder, gently placed on the surface of distilled water, and moved around until most of the glycerin is dissolved. One end of the

strip is then slowly pushed beneath the water until it is submerged. Surface tension holds the grids on the surface of the water, and the remaining glycerin dissolves. To insure complete removal of the glycerin, most of the water is drained or siphoned off and the grids are floated up on a fresh volume of water. They are then removed from the surface of the water for drying.

Care must be taken in removing the grids from the water surface. A convenient way is to pick them up on a screen made from a piece of nylon netting having a mesh just small enough to prevent the grids from falling through the openings.

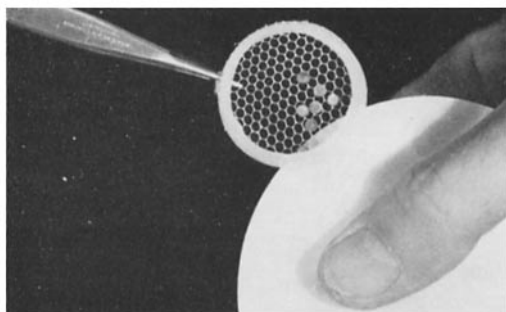


FIGURE 2 Nylon screen used to remove carbon-coated grids from the surface of water. The screen is held in a vertical plane and the edge of a piece of filter paper is touched to the back of the screen at the bottom of each grid. This removes most of the water with minimal stress on the film.

A screen of this type is easily made by clamping a piece of the netting between two small hoops similar to those used for embroidery. After the grids have been lifted from the water surface, the screen is held vertically and a piece of filter paper is placed against the netting on the side opposite to that on which the grids rest. Touching the edge of a piece of filter paper near the bottom of each grid draws off most of the water from its wet side (see Fig. 2). With care, only one side of the carbon film ever gets wet. Keeping the other side dry avoids getting contaminants from the water on that surface. The screen with the grids is then placed flat on a piece of filter paper for complete drying, after which they are ready for use.

Carbon films made in this way are very clean, provided the grids, celluloid strip, glycerin, forceps, water, etc. were clean. New commercially available grids should be cleaned thoroughly

before use. Ultrasonic cleaning in a special ammoniated cleaning solution¹ followed by sonication in two acetone rinses is an excellent way to clean either new or used grids. Grids to be coated should be flat, but if they are slightly dish-shaped the concave surface should be placed in contact with the glycerin.

Advantages of this technique are several: (1) Manipulation of the grids is minimal, (2) sources of contamination are reduced, (3) the surfaces of the carbon films are as smooth as the surface of the glycerin substrate, and (4) the intimate contact of the carbon film with the grid bars makes them more stable mechanically and provides better thermal and electrical conduction from film to grid.

Because of the brittleness of pure carbon films, any deformation of a grid will break the film in some of the open areas. This hazard is reduced if rigid grids, such as those made of titanium, are used.

The vapor pressure of glycerin, about 0.2μ Hg at room temperature, limits one to the use of a pressure of about 0.3μ Hg for vaporizing the carbon. Lowering the vapor pressure of the glycerin by cooling it with a cold finger in the vacuum chamber would allow one to vaporize the carbon at lower pressures.

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¹ L and R No. 112 Waterless ultrasonic instrument cleaning solution (ammoniated), L and R Mfg. Co., Kearny, New Jersey.

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