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ALUMINUM OXIDE SELF-SUPPORTING FILMS

Self supporting thin films of Al_2O_3 are produced by anodization of aluminum foil and by selective removal of aluminum metal to expose the Al_2O_3 film. The process consists of 5 steps, as follows (Fig. 1):

1. Foil preparations
2. Anodization
3. Oxide removal
4. Metal removal and cleaning
5. Mounting

1. Foil Preparation

The most suitable material for producing Al_2O_3 self-supporting films is 0.003-inch-thick aluminum foil of 1145 alloy (99.45% Al, 0.55% Si and Fe, 0..05% Cu, 0.05% Mn, 0.03% others), H-19 temper (strain hardened, extra hard), bright finish (approaching mirror finish). It is cut into 4-inch by 6-inch flat sheets, with the mill marks running in the 6-inch directions.

These specifications may be altered to suit specific purposes. However, when other alloys are used impurities become trapped in the film, making it unsuitable for certain applications; softer tempers weaken the structural rigidity of the foil, making it more difficult to handle; and since the film is an exact replica of the foil surface, rough surface finishes produce rough films.

The sheet is formed into a channel by sharply bending the long edges at 90 degrees, so that the final dimension of the flat foil surface is 3-1/4 inches by 6 inches, with two strips 3/8 inch by 6 inches running perpendicularly to that surface and imparting structural rigidity to the foil Figs. 2 and 3).

Using flat clips which do not strain or distort the surface, the foil is immersed for one minute in a 30 g/1 solution of "Ridoline 53" at room temperature, and thoroughly rinsed with running hot and distilled water. Ridoline 53 is a nonetching alkaline cleaner manufactured by Amchem Products, Inc., Ambler, Pennsylvania. Other cleaning and deoxidizing agents may be used, as long as they leave a clean hydrophilic surface, they do not dull the specular finish of the foil, and they can be completely removed during the rinse.

The foil is kept wet, and anodized immediately following the water rinse.

2. Anodization

The foil is connected to the positive terminal of a dc power supply, and a cathode plate is connected to the negative side of the supply. The cathode may be made of aluminum or other conductive material which does not dissolve into or contaminate the anodizing solution.

Foil and cathode are then immersed into an anodization bath of 3% by weight solution of ammonium citrate in a glass or plexiglass tank; care must be taken that the clips holding the foil are free and clear of the solution and that the foil alone is immersed (Fig. 4).

Aluminum oxide is formed in ammonium citrate at the rate of 13.7 A^o/volt, and the film thickness is therefore determined by the positive voltage applied to the foil. As the full voltage is applied, a high initial current starts to flow, which decays to a saturation value after a period of time. Both saturation current and time are a function of voltage value; typically, for a 1000 A^o film the saturation current is approximately 15 $\mu A/cm^2$ and the time necessary to reach this current is about one hour; higher or lower voltages will result in proportionately higher or lower currents and times. The value of the initial current is obviously limited by the capability of the power supply and does not appear to affect film characteristics.

The gas bubbles which are formed during anodization tend to stick to the cathode and to the foil; occasional mechanical agitation disperses them, speeds up the process, and avoids formation of pinholes in the oxide.

When the anodization is completed the foil is washed with distilled water and rinsed with alcohol; at this juncture it may either go directly to the next step in the process or be stored indefinitely for future use. However, care must be taken not to scratch the delicate surface oxide during handling.

3. Oxide Removal

The aluminum oxide film becomes self-supporting when the aluminum foil upon which it was grown is etched away with hydrochloric acid during the metal removal step. Since Al_2O_3 formed in ammonium citrate is impervious to HCl, the oxide must be removed over a selected area on one side of the foil, and this is done using a 50% by weight solution of sodium hydroxide and a mechanical mask to define the area of oxide removal and to protect the remaining oxide. The mechanical mask consists of a rubber ring 3-inch OD × 2-1/2-inch ID × 1/8-inch thick cemented to a metal ring with the same diameters and thick enough to support the rubber when it is pressed against the foil to form a seal. This mask diameter can be used for relatively thick films, but it must be reduced for films thinner than 500 A^{o}. Other shapes and sizes may be used as needed, provided that their areas are compatible with the film thickness.

The foil is laid on a flat smooth surface, the ring is placed on it and clamped down with moderate pressure, and NaOH is poured into the mask until it completely covers the metal area to be exposed (Figs. 5 and 6). After a period of time which is a function of film thickness, the NaOH is rapidly washed off in running water and the foil is immediately placed into the HCl bath. Typically, a 5-minute exposure is sufficient for 1000 A^{o}; in general it is more desirable to overexpose than to underexpose the film because if the Al_2O_3 is not completely removed the HCl will not completely etch away the metal and will leave an imperfect film.

An alternate masking method is to cover the oxide with a chemically resistive coating except in those areas in which the metal is to be etched away, and to remove this coating after exposure to NaOH. More elaborate film shapes are then possible, but the process also becomes further complicated by the additional step needed to remove the resistive coating. One such coating, "Tech-Pen Ink" manufactured by Mark-Tex Corp., Englewood, New Jersey, adequately withstands 50% NaOH for ten minutes, and is readily dissolved in trichloroethylene; it is applied through a hypodermic needle as a mask for dots and it is used in conjunction with the mechanical mask to produce 2-1/2-inch-diameter films with 2-mm-diameter metal dots supported in their center.

4. <u>Metal Removal and Cleaning</u>

The metal is etched away in a 900 cc bath of HCl diluted with water, to which has been added two drops of wetting agent such as "Aerosol" or Dupont "Zonyl A."

As the metal is being removed and the film becomes exposed it becomes more and more fragile. It is therefore important that vibrations, currents or violent etching action be avoided at this and following steps. The etching action can be maintained at a moderate level by using suitably diluted HCl and periodically cooling the bath to room temperature; the dilution ratio will be dictated by the thickness of the film, and is 1:1 for 1000 A^{o} films;the bath temperature does increase significantly if the HCl is not cooled between etches or after dilution; the foil must be kept vertical in the etch so that the escaping gas does not exert too much pressure on the film; poor wetting action during drainage of the HCl will lead to film rupture due to high surface tensions, but too much wetting agent will generate excessive foam and result in high pressures being exerted on the film; the bath level must be kept below the height of the anodized portion of the foil to avoid unnecessary etching action.

After the exposed metal has been removed, the etching action stops and the HCl is drained from the bath; it can be reused several times until the alloying metals insoluble in HCl begin to leave residues on the film. The bath is then filled with 95% ethyl alcohol, drained, refilled for a second alcohol rinse and redrained. The foil is carefully removed from the bath and taken to the mounting station.

The bath consists of a 1000 cc beaker modified with a bottom drain tube which is preferably located near the wall to prevent vortex formation; the drain is connected to the common arm of a three-way valve; the second arm of the valve is connected to another 1-liter beaker, similarly modified with a drain, which is used to contain the alcohol rinses and which is mounted higher than the bath to allow gravity feed of the rinse; the third arm of the valve is connected to the waste disposal. Thus, at one position of the valve the bath will drain into the waste disposal, and at the other position the rinse will flow into the bath. Using such an installation it becomes possible to fill and empty the bath very smoothly, avoiding currents which can rupture the film. The flow rates into and out of the bath can be controlled with additional needle valves when circumstances warrant it (Fig. 7).

5. Mounting

At the mounting station the foil is supported horizontally at both ends leaving the film completely exposed. The mounting ring is coated with a potassium silicate solution and raised very slowly and steadily until it comes into contact with, and is cemented to the film; the silicate is allowed to dry and the excess film is cut away.

The mounting step is the most precarious portion of the process, and the design of the mounting ring contributes significantly to the operation's success; the outside ring diameter should be smaller than that of the film; if it must be larger, a raised rim around its inside diameter will make it easier to contact the film before the ring touches the foil; the mounting area should be free of burrs, scratches and dust; machining marks should be concentric, and sharp edges should be broken.

The film is cemented to the mounting ring with a solution of 1% KASIL No. 1 and 1% Aerosol in distilled water. KASIL No. 1 is a potassium silicate with a 2.50

weight ratio (SiO_2/K_2O), 29.8° Be, manufactured by the Philadelphia Quartz Company of California, Berkeley, California. There is some indication that the shelf life of such dilute solutions of silicates is limited, and a fresh solution should therefore be mixed every month, or whenever inadequate cementing occurs. The cement is applied with an artist's brush so as to form a continuous raised bead around the mounting hole taking care to insure complete wetting of the mounting area.

It is also very important that the mounting ring and the film be maintained perfectly parallel as they come into contact with one another; the cementing must occur evenly around the entire edge of the ring, or else stresses will be caused which will rupture the film. A microscope rack and pinion movement is used as a raising mechanism and a ball joint is used as an alignment fixture for the ring (see Figs. 8 and 9).

After the silicate dries, the excess film is cut away with a scalpel and loose fragments are collected on a small cotton ball dipped in alcohol. If cutting is attempted before the silicate is completely dry, the film will become detached and will rupture.

The mounted film is bakeable and can be stored indefinitely.

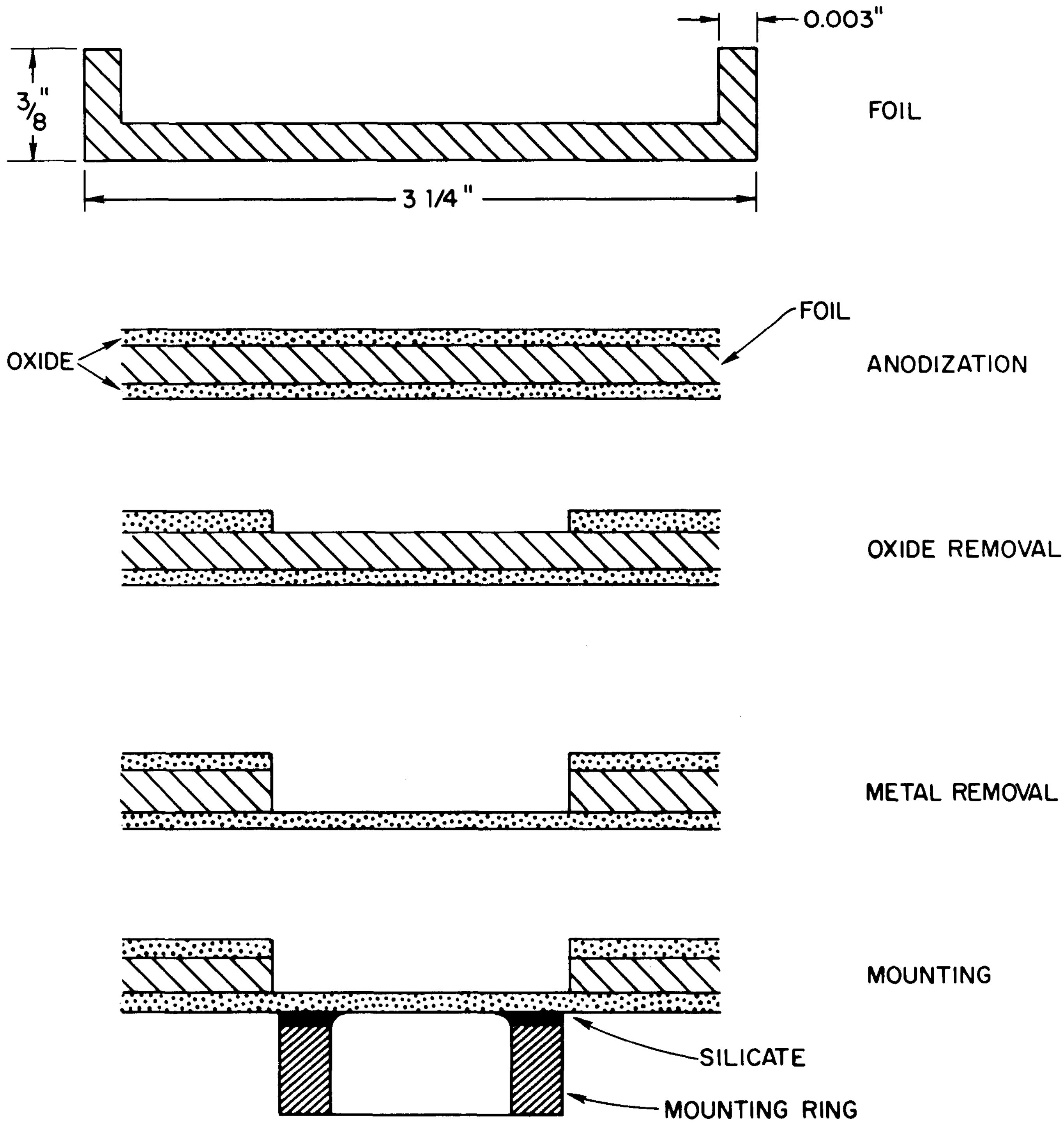

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FIG. 1 - PROCESS SCHEMATIC

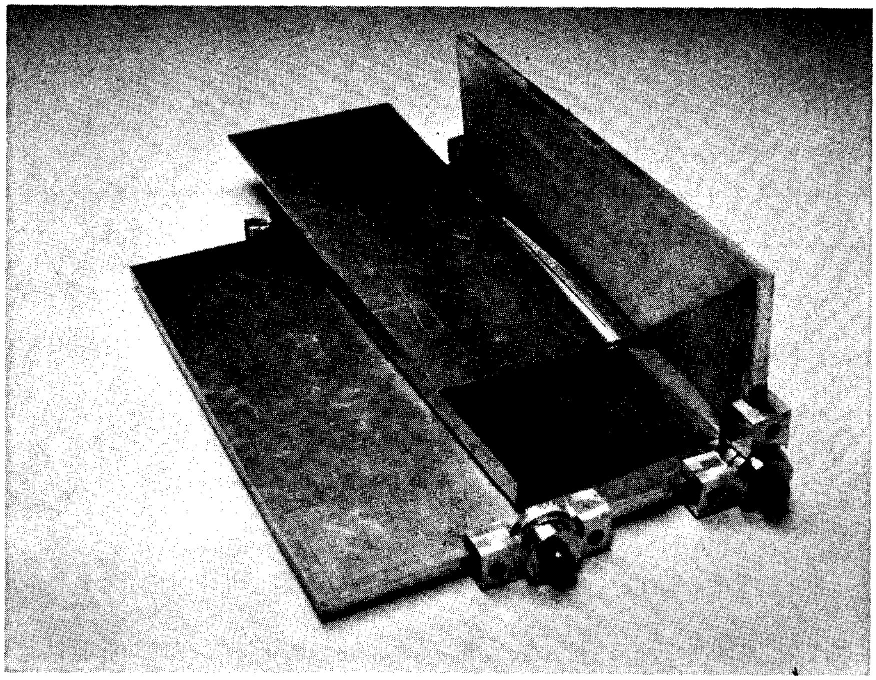

FIG. 2--Foil bending brake assembled

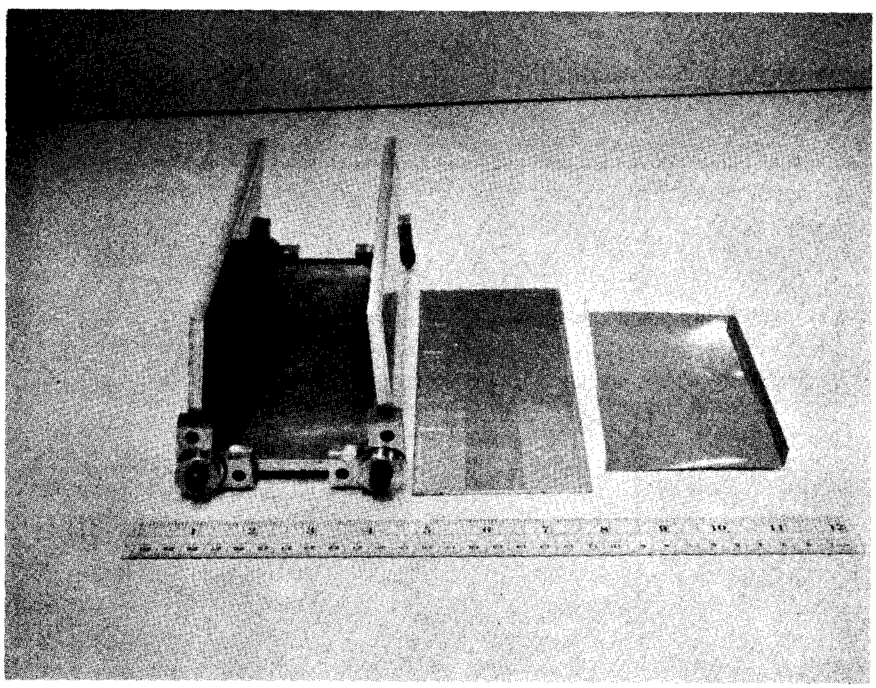

FIG. 3--Foil bending brake disassembled

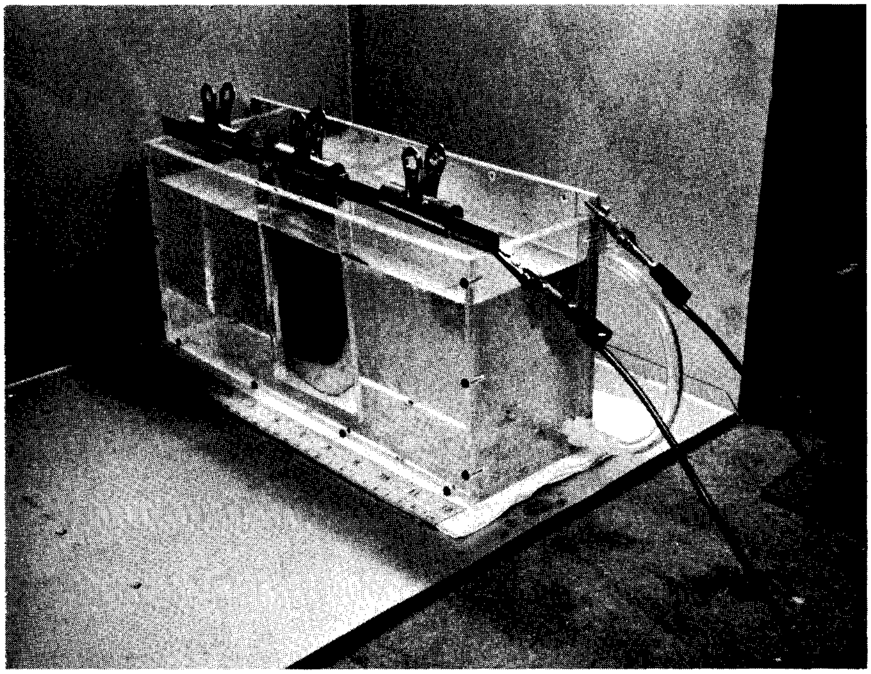

FIG. 4--Anodization bath with cathode and one foil in place

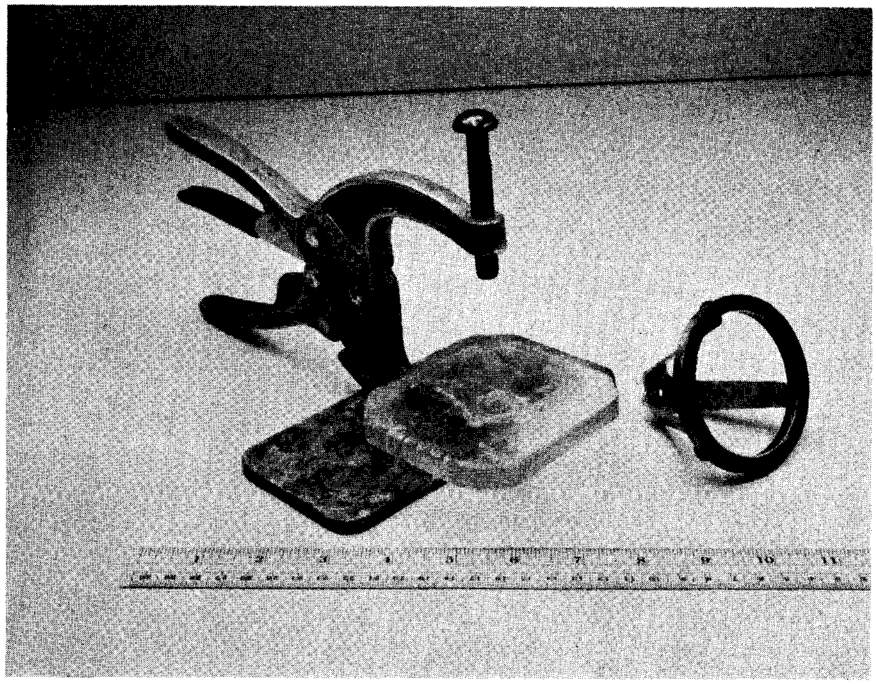

FIG. 5--Oxide removal mask and clamp

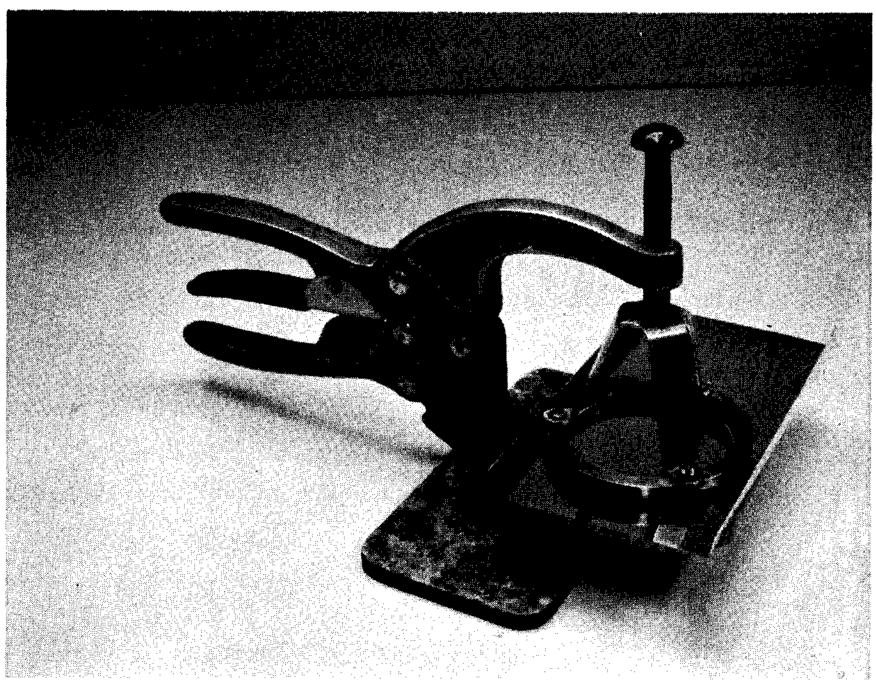

FIG. 6--Foil in oxide removal assembly

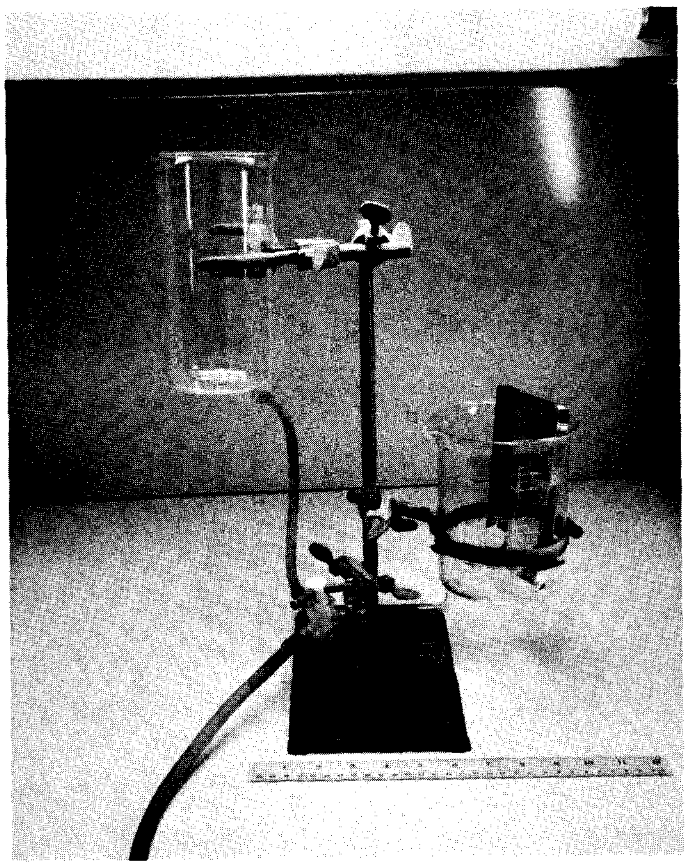

FIG. 7--Metal removal and cleaning bath

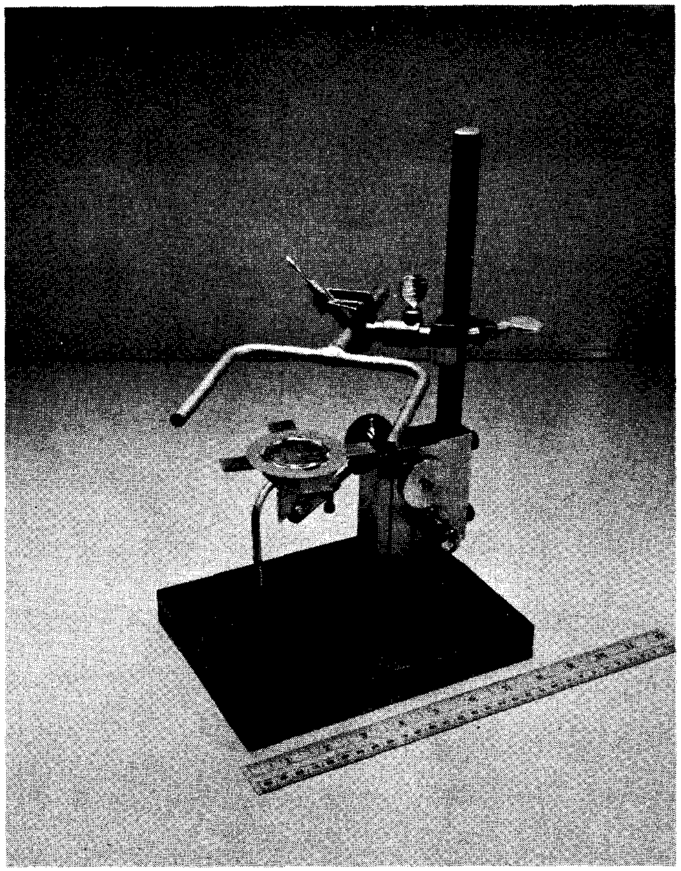

FIG. 8--Mounting assembly with mounting ring in place

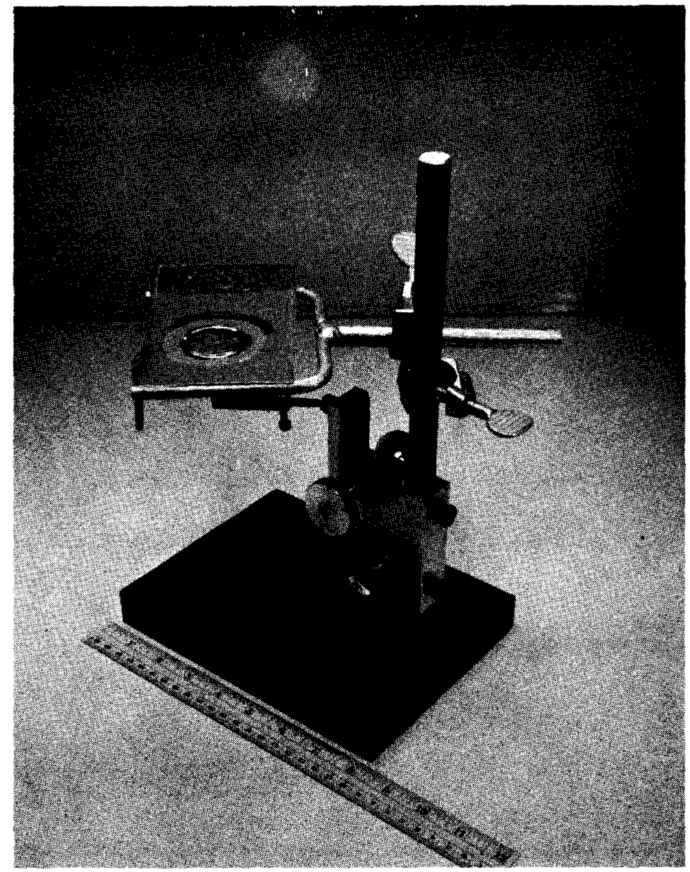

FIG. 9--Mounting assembly with mounted film