

## CHAPTER XI

### Metal Electrodes Deposited on Quartz Crystals by the Evaporation Process

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#### 11.1 INTRODUCTION

QUARTZ crystal plates used in radio sets and carrier filters are often plated with thin metal films for electrodes. The earliest method of depositing such films was a chemical method using silver. Coatings have also been successfully applied for some uses by spraying on gold or silver pastes and then reducing them to metal form by baking. Metal spraying has been attempted with much poorer results. Evaporation and condensation of the metal in a vacuum process has been developed which possesses many advantages over the chemical deposition method. The process did not originate in association with crystal development, but has found one of its important uses in that field.

Although the deposition of metal films by this process was known in the early nineteen hundreds, the process did not come to be seriously considered in our laboratories as a usable tool for any purpose until about 1915 when experiments were carried out on forming the anode or plate on the wall of the glass bulb of a three element vacuum tube of that period by evaporation of silver and other metals from an electrolytically plated wire. From that period on much work was done on the deposition and use of such films for other purposes, most of which were connected with research and development studies. By 1930, the techniques involved had been developed so as to handle many metals, and to plate on a variety of surfaces including those of ground quartz plates. When National preparedness got under way in 1940, the knowledge and techniques involved were utilized in the development of apparatus for the Western Electric Company to use in the large manufacturing programs for quartz crystals for military radio sets.

#### 11.2 THE METAL FILM ELECTRODE

The metal film type of electrode on crystals possesses several advantages over the solid plate electrode in close proximity. It provides the maximum piezoelectric coupling to the crystal. It prevents arcing between the crystal surface and the electrode when a crystal oscillator is operated at higher voltages than are preferred for maximum frequency stability. It allows of obtaining several different electrodes on one surface of a crystal by a division

of the film. It avoids frequency changes in a crystal that result from any shift of an electrode with respect to the crystal. It protects the crystal surface, reducing aging effects that might occur from erosion. It is readily adaptable for various types of contacts at nodal or near nodal points such as clamp type mountings, and soldered on wire supports. The metal film type of electrode also has disadvantages that appear in certain cases. Certain metals are subject to chemical action such as oxidation that may occur in air, or in holders made of certain materials, and such action will cause a frequency change. There are difficulties of mounting where friction might wear away the metal film. Adsorption of moisture is a variant also.

The metals more consistently used for coating quartz crystals are aluminum, silver and gold. Aluminum is commonly used where the crystal plates are held in clamp-type mountings, it being advantageous for resistance to wear. Silver is also extensively used for it can be easily soldered to for wire type mountings, and it is easier to apply than aluminum. Silver films can also be readily divided when several electrodes are required on one surface. Gold is used where resistance stability and resistance to corrosion are important. It is also an easy metal to deposit by evaporation.

### 11.3 DEPOSITION OF THE FILM

The evaporation of the metals in vacuum for plating quartz crystals is accomplished by heating small pieces of the metal to a temperature as high or higher than the melting point of the metal. Due to the very low vapor pressure of most metals at room temperature, it is necessary to elevate the temperature of the metal to considerably above the melting point to produce the vaporized material at sufficient rate to coat the crystals in a reasonable period of time.

Elevated temperatures are, however, not necessary for some metals. Fig. 11.1 shows the vapor pressures of a large number of metals over a wide temperature range. Metals such as cadmium and zinc have a vapor pressure of .1 mm of mercury and will therefore vaporize without melting in vacuum.

The elimination of absorbed gas from the surface to be plated is important. This gas may react chemically with the material being vaporized, and it also affects the adherence of the metal film to the surface. Most of the adsorbed gas is removed in the vacuum chamber. The apparatus must be capable of being pumped out to a pressure of  $2 \times 10^{-5}$  mm of mercury, and the pressure should be maintained at less than  $5 \times 10^{-6}$  mm while the metal is being evaporated. As applied to silver, for example, when crystals are plated in this pressure range, the metal films will be the typical silver color with a bright luster. It is known that for some applications, crystals can be plated with silver films considered passable at a pressure as high as  $1.5 \times 10^{-4}$  mm of mercury. At this pressure, the metal film will have a

grey appearance and the adhesion of the metal is not as good, although the electrical resistance of such films can be fairly low.

The removal of the adsorbed gas in the vacuum chamber is facilitated by heat. For many applications, crystals are sufficiently freed from gas by the radiated heat from the heater that evaporates the plating metal, but in some cases, this is not sufficient, and it is necessary to provide additional heat to raise the temperature of the crystals. This is particularly true for crystals to be used at high frequencies. They must be heated to at least 75°C.

It is very important also that all crystals to be plated be clean and free from dust, lint, fingermarks, or any foreign material. Such materials will

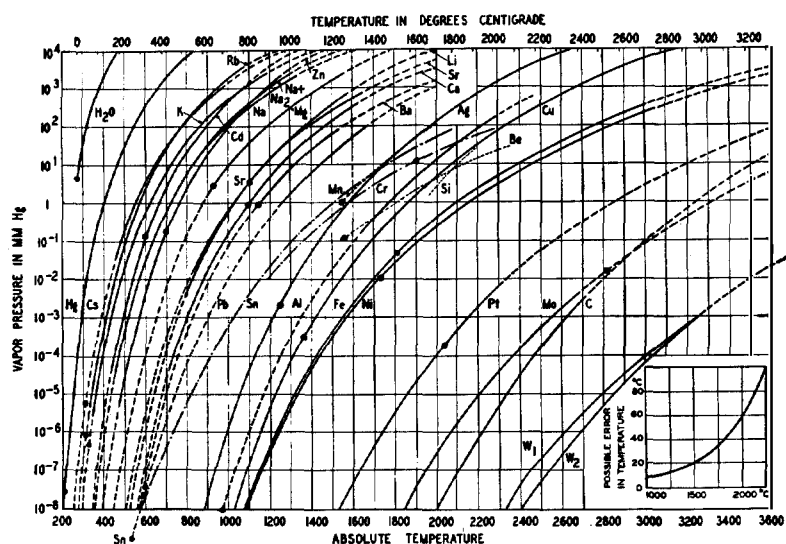


Fig. 11.1—Vapor pressures of a number of metals as a function of temperature

not only cause shadows and roughness, but will interfere with adherence of the metal films by virtue of being covered, and by virtue of their ability to release gases that interfere with the plating. The term cleanliness is comprehensive in the production of films of good adhesion, as it applies not only to vaporous material that can be observed by eye or with microscopic aid, but to any gas molecules that may be on the surfaces of the material to be plated or included in the deposited layer of metal.

The effect of lint and dust on a surface before plating is shown by the photograph in Fig. 11.2. Spots of various sizes, and holes in the plating are produced on one sample due to foreign material. The other sample was free from foreign materials when plated.

Foreign materials other than dust and lint will produce other types of flaws in the plating. Traces of grease, adsorbed gas, for example will produce discolorations of varying degrees when present on the crystals. In Fig. 11.3 are shown platings on a number of quartz crystals which were not properly cleaned. The presence of the foreign material renders the plating dark, and the degree of darkness is associated with the amount.

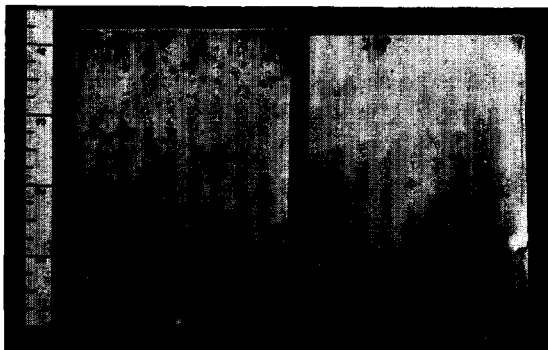


Fig. 11.2—Platings on mica, showing on the left hand piece the spots or holes caused by dust and lint

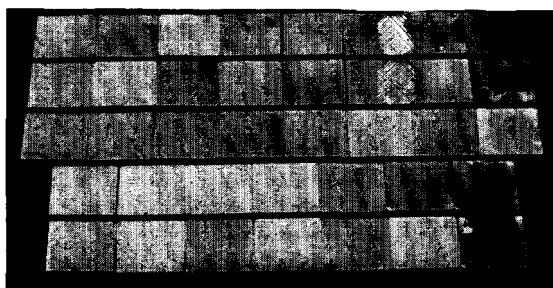


Fig. 11.3—A variety of discolored areas on plated quartz crystals showing the presence of foreign matter

When the same crystals were cleaned before plating, the discoloration of the patch type disappears as shown in Fig. 11.4. There are still differences as can be seen from the shades of the various crystals, and these differences can be due to different reflections with direction from the crystal axes, to different finishes, or other lesser causes.

In Fig. 11.5 are shown a number of crystals with platings that are clear and uniform indicating desired cleanliness.

The color of the plating is dependent upon the gases present, either on the surface or in the vacuum chamber. This is demonstrated by plating silver in different degrees of vacuum. In Fig. 11.6 are shown three crystals

plated with the same thicknesses of silver, but in different degrees of vacuum.

The white crystal, A, was plated in a vacuum of  $1.5$  to  $5 \times 10^{-5}$  mm pressure. The grey one, B<sub>1</sub>, was plated with a pressure of  $7$  to  $8 \times 10^{-4}$  mm and the black, C, was plated with a pressure of  $2 \times 10^{-2}$  mm. The effect of the small amount of gas upon the color is very marked. Poor adherence and high electrical resistance also become more pronounced with the increased air pressure.

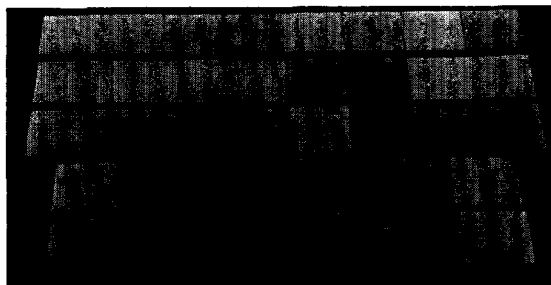


Fig. 11.4—The same crystals as in Fig. 11.3 but cleaned much better before plating. Discolorations remaining are due to different reflection coefficients resulting from different crystal surface structures beneath

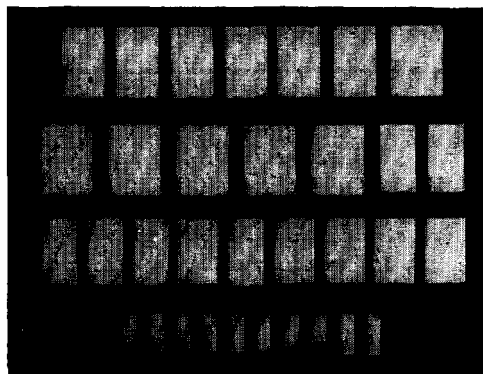


Fig. 11.5—Crystals that are perfectly clean give film surfaces that are clear and bright

In Fig. 11.7 are shown two crystals plated with silver which show a simulated finger mark in one case and a soapy water mark in the other.

For reasons of cleanliness in most cases, and for various other reasons in other cases, crystals are usually etched in hydrofluoric acid before plating. Certain radio crystals are etched 10 to 20 minutes in about 30% hydrofluoric acid, and certain filter crystals are etched 30 to 35 minutes in commercial (48%) hydrofluoric acid. The amount of etching necessary should be determined by those factors calling for etching-cleanliness determined by factory process, adjusting to frequency, aging, internal losses, etc., as too

much etching weakens adherence of the deposited metal film. They are then washed in running heated tap water at 180°F for one-half hour. If the tap water contains much mineral salts, they are given a final wash in hot distilled water to prevent the formation of water marks on the surfaces when dried. The crystals are oven dried at 250°F and inserted in the plating chambers of the machine preferably while warm to prevent condensation of moisture on the surfaces from a possible surrounding humid atmosphere.

To control thickness of deposit, it would appear logical to control time and temperature of vaporization of the metal. This is done as in the case of continuous plating of long rolls of material. However, accurate control of deposit thickness can be achieved otherwise in the case of batch plating of quartz crystals. Since the vapor to be deposited travels in straight lines in vacuum from source to recipient and usually stays where it first strikes

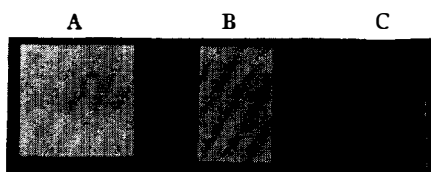


Fig. 11.6—Crystals, silver plated in different degrees of vacuum. A. Pressure  $1.5$  to  $5 \times 10^{-6}$  mm. B. Pressure  $7$  to  $8 \times 10^{-4}$  mm. C. Pressure  $2 \times 10^{-2}$  mm. Plating in all cases is 4 milligrams per sq. in.



Fig. 11.7—Crystals, plated, showing respectively a finger mark and a water mark

or condenses, the geometry of the plating arrangement becomes of primary importance in controlling thickness of deposit. By using a tungsten or molybdenum heater upon which are hung pieces of the metal to be plated which are in the form of U shaped wires, and operating until the metal is all evaporated, the thickness of plating can be controlled.

#### 11.4 EQUIPMENT

Figs. 11.8 and 11.9 show the arrangement of the heater, the plating metal and the plate for holding the crystals. The heater consists of two lengths of molybdenum wire held a few inches above the crystals to be plated. The metal to be plated is in the form of wire, and is cut into certain lengths and bent into U or hairpin shape. These are hung on the heater wire, and spaced uniformly. The uniformity in spacing with provision to retain that

uniformity is obtained by constructing the heater wire in a spiral or zigzag shape. The pieces of wire then are placed over the low points.

The heater is still a strong wire at the temperature the wire pieces melt. The melted metal, by means of surface tension, pulls itself into a globule and hangs to the heater wire which it wets. It is essential that a large number of small globules be formed, rather than a few large globules, as

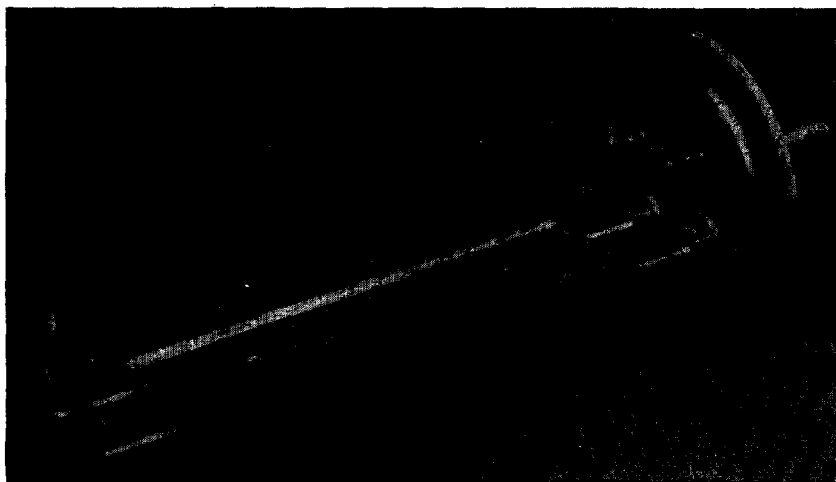


Fig. 11.8—Removable tray from a standard design of plating machine showing molybdenum heater wires upon which are hung U shaped pieces of wire of the metal to be plated. The crystals are placed close together upon the flat surface beneath the wires.

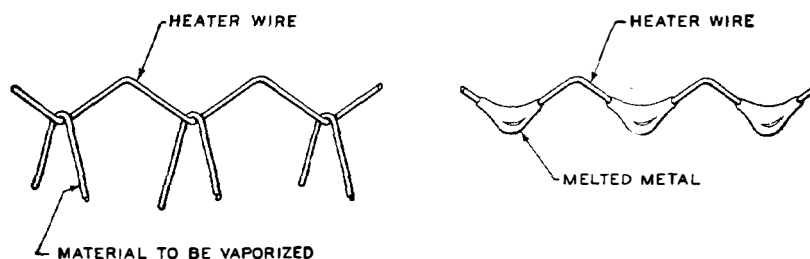


Fig. 11.9—Diagram showing the pieces of metal wire hanging upon the heater wire before melting, and after melting. In the latter case, the surface tension pulls the wire into a globule which hangs on the heater wire until fully evaporated.

with the latter, the melted metal may drip onto the crystal plates below. As an example, in the machine depicted herein, the heater wire is wound on a  $\frac{1}{16}$ -inch diameter mandrel on a lathe, with  $24 \pm \frac{1}{2}$  turns per 4 inches. They are then cut into  $13\frac{1}{2}$ -inches lengths (81 turns) and each end straightened for  $3\frac{1}{2}$  turns for mounting in the supporting binding posts above the tray. There remain about 74 turns or "wells" as the low spots are called.

The following are material and heater wire data for producing some typical specific weight films of silver, gold and aluminum.

*Silver.* Plating 4 milligrams per square inch. 5900 Ångstrom units or about .02 mil thick.

Heater wire .020-inch diameter molybdenum with 24 wave wells per 4 inches. Two heaters required 2 inches apart. One and three-quarter inches above tray. Silver wire .010-inch diameter is cut into two lengths,  $\frac{1}{2}$  inch and  $\frac{1\frac{1}{2}}{3}$  inch, and then bent into hairpin shape with a total of 75 pieces attached to each heater wire. Starting at one end attach 25 pieces  $\frac{1}{2}$ -inch long. Then 25 pieces  $\frac{1\frac{1}{2}}{3}$ -inch long, then 25 pieces  $\frac{1}{2}$ -inch long. One piece is placed in each heater well.

*Gold.* Plating, 3 milligrams per square inch, 2400 Ångstrom units or about .01 mil thick. Heater wire .015-inch diameter tungsten. Two heaters required 2 inches apart. One and three-quarter inches above tray. Six wave wells per inch. Gold wire 24 K., .010-inch diameter,  $\frac{5}{8}$ -inch long pieces bent into hairpin shape, with a total of 22 pieces attached to each heater wire is used.

Starting at one end attach 8 pieces at three wells spacing, then 6 pieces at four wells spacing, then 8 pieces at three wells spacing.

*Aluminum.* Plating, 1 milligram per square inch. 5700 Ångstrom units or about .02 mil thick.

Heater wire .020-inch diameter molybdenum. Two heaters required 2 inches apart. One and three-quarter inches above tray. Eleven wave wells per  $3\frac{7}{8}$  inches. Aluminum wire, 2SH grade, .016-inch diameter cut into two lengths and then bent into hairpin shape with a total of 36 pieces attached to each heater wire is used.

Starting at one end attach 12 pieces  $\frac{7}{16}$ -inch long, then 12 pieces  $\frac{1\frac{9}{16}}{4}$ -inch long, then 12 pieces  $\frac{7}{16}$ -inch long. One piece is placed in each heater well.

It should be pointed out that the material to use for a heater wire is dependent upon the metal that is being deposited. It is essential that the metal to be vaporized either wet the heater wire or amalgamate with it, otherwise the globules of melted metal will not remain in the wells.

Silver can be evaporated 100% from molybdenum wire. Due to the tendency of aluminum to alloy with molybdenum and tungsten, it is necessary to operate at a higher temperature as compared to silver or gold. Normally 92% evaporation is obtained. To obtain 100%, the necessary temperature would be excessively high.

Table I with the legend and Table II are a resumé of the work of W. C. Caldwell, Department of Physics at Iowa State College, who investigated the adaptation of various materials in wire form for use as heater elements for the evaporation of a large number of metals together with the melting temperatures and temperatures at which rapid evaporation is produced.



In Fig. 11.10 are given graphs to show the thickness of deposited films in terms of weight per unit area.

### 11.5 PLATING MACHINE

In Figs. 11.11, 11.12, and 11.13 are shown photographs of plating machines that have been developed. Fig. 11.11 is the front view of a single chamber machine. The removable plating element or tray shown in Fig. 11.8 slides into a chamber at the top of the machine. The chamber is evacuated by means of two types of pumps, a rotary oil sealed pump, and an oil vapor pump. The pumps and the vacuum chamber with necessary valves and gauges are constructed in a unit. A control panel, showing in Fig. 11.11,

TABLE I\*

	Aluminum, 659-1800°C	Antimony, 630-1380°C	Barium, 850-1140°C	Beryllium, 1350-1530°C	Bismuth, 271-1470°C	Cadmium, 321-767°C	Cobalt, 1480-2900°C	Columbium, 1950-2900°C	Copper, 1083-2310°C	Germanium, 959-2700°C	Gold, 1063-2600°C	Iron, 1535-3000°C	Lead, 327-1613°C
Tungsten, 3370-5900°C	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>3</sub> 1 R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>3</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>3</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>		W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> 3 R <sub>2</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>
Tantalum, 2850-4100°C	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>2</sub> E <sub>2</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> 1 R <sub>1</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>3</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> R <sub>2</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>3</sub> 1 R <sub>1</sub>
Molybdenum, 2620-3700°C	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>3</sub> R <sub>3</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>3</sub> 1 R <sub>1</sub>
Columbium, 195-2900°C	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>2</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>2</sub> R <sub>3</sub>	2	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>		W <sub>1</sub> E <sub>2</sub> R <sub>2</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>2</sub>	W <sub>3</sub> 1 R <sub>1</sub>
Platinum, 1773-4300°C							W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>					W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	
Iron, 1535-3000°C	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>2</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> 1 E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>1</sub> R <sub>3</sub>		W <sub>1</sub> E <sub>3</sub> R <sub>2</sub>		W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Nickel, 1452-2900°C	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>2</sub> R <sub>3</sub>		W <sub>1</sub> E <sub>3</sub> R <sub>2</sub>		W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Chromel, 1350°C	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>1</sub> R <sub>3</sub>		W <sub>1</sub> E <sub>3</sub> R <sub>2</sub>		W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Silver, 960-1950°C	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>2</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>		W <sub>2</sub> E <sub>1</sub> R <sub>3</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>							W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>

TABLE I (continued)

	Magnesium, 651-1110°C	Manganese, 1260-1900°C	Nickel, 1452-2900°C	Platinum, 1773-4300°C	Selenium, 200-688°C	Silver, 960-1950°C	Strontium, 752-1150°C	Tellurium, 452-1390°C	Thallium, 303-1650°C	Thorium, 1845-3000°C	Tin, 231-2270°C	Titanium, 1800-3000°C	Vanadium, 1715-3020°C	Zinc, 419-907°C
Tungsten, 3370-5900°C	M <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> 3 R <sub>3</sub>	W <sub>1</sub> 4 R <sub>2</sub>	W <sub>3</sub> 1 R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> R <sub>1</sub>	W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Tantalum, 2850-4100°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>3</sub> 1 R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	5 E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Molybdenum, 2620-3700°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> 1 R <sub>1</sub>	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Columbium, 1950-2900°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>		W <sub>3</sub> 1 R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>
Platinum, 1773-4300°C			W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>											
Iron, 1535-3000°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	M <sub>3</sub> E <sub>2</sub> B			W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>		W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>
Nickel, 1452-2900°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> B			W <sub>2</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	5 E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>		W <sub>3</sub> E <sub>3</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>
Chromel, 1350°C	M <sub>3</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>2</sub> B			W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>	W <sub>3</sub> 1 R <sub>1</sub>		W <sub>1</sub> E <sub>1</sub> R <sub>1</sub>			W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>
Silver, 960-1950°C					W <sub>1</sub> E <sub>1</sub> R <sub>2</sub>		M <sub>3</sub> E <sub>3</sub> R <sub>1</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>	W <sub>1</sub> E <sub>3</sub> R <sub>3</sub>		W <sub>3</sub> 1 R <sub>3</sub>			W <sub>1</sub> E <sub>3</sub> R <sub>2</sub>

Legend for Table 1†

W<sub>1</sub> The metal wets the filament well.W<sub>2</sub> The forces of wetting are not large. Drops of the metal may occasionally fall from the filament.W<sub>3</sub> The metal will not adhere to the filament.M<sub>3</sub> The metal is not melted.E<sub>1</sub> Evaporation of the metal takes place readily.E<sub>2</sub> Evaporation of the metal proceeds slowly.E<sub>3</sub> No evaporation of the metal takes place.R<sub>1</sub> No reaction of the metal with the filament.R<sub>2</sub> Reaction of the metal with the filament proceeds slowly usually without much effect on evaporation.R<sub>3</sub> Reaction of the metal with the filament results in burning out the filament.

B The filament burns out due to heating the metal to nearly the melting point of the filament.

\* W. C. Caldwell, *J. Appl. Phys.*, Vol. 12, 1941, pp. 779-781.

† Ibid.

## Notes

1. In some cases where the metal does not wet the filament, the surface tension is such that the globule of molten metal is supported mechanically by the spiral filament. Although evaporation occurs, the occasional dropping of molten metal from the filament is an undesirable characteristic.

2. In an attempt to evaporate columbium, wire with a diameter of .030 inch was used. Apparently the heat transfer from filament to the columbium was not efficient enough to melt the columbium, but fine columbium wire wrapped tightly about the filament should melt quite easily.

3. Iron is difficult to evaporate because it forms low melting point alloys. However, if several turns of tungsten are wrapped tightly about a short length of iron wire, the iron can be successfully evaporated. An iron-tungsten alloy is formed along the whole length of the helix, but a core of tungsten is left unaffected so that the filament is maintained intact. Differential evaporation of iron from the molten tungsten-iron alloy probably takes place. Nickel can be evaporated by this same procedure.

4. Due to its low vapor pressure, platinum evaporates very slowly. If very fine platinum wire is wrapped tightly around a tungsten filament, the efficiency of heating is adequate to melt and to evaporate the platinum.

5. A shell of some refractory compound of strontium separated the molten strontium from the filament so that the wetting properties could not be examined.

TABLE II.\*—*Satisfactory Filament Materials for the Evaporation of Various Metals*  
(Listed in order of merit)

Metal	Filaments
Aluminum.....	Tungsten, tantalum, molybdenum, columbium
Antimony.....	Chromel, tantalum, tungsten
Barium.....	Tungsten, tantalum, molybdenum, columbium
Beryllium.....	Tantalum, tungsten, molybdenum
Bismuth.....	Chromel, tantalum, tungsten
Cadmium.....	Chromel, columbium, tantalum
Cobalt.....	Columbium
Copper.....	Columbium, molybdenum, tantalum
Germanium.....	Tantalum, molybdenum (other filaments not tried)
Gold.....	Tungsten, molybdenum
Iron.....	Tungsten
Lead.....	Iron, nickel, chromel
Magnesium.....	Tungsten, tantalum, molybdenum, columbium
Manganese.....	Tungsten, tantalum, molybdenum, columbium
Nickel.....	Tungsten
Platinum.....	Tungsten
Selenium.....	Chromel, iron, molybdenum
Silver.....	Tantalum, molybdenum, columbium, iron
Strontium.....	Tungsten, tantalum, molybdenum, columbium
Tellurium.....	Tungsten, tantalum, molybdenum, columbium
Thallium.....	Nickel, iron, columbium, tantalum
Thorium.....	Molybdenum
Tin.....	Chromel
Titanium.....	Tungsten, tantalum
Vanadium.....	Tungsten, molybdenum
Zinc.....	Tungsten, tantalum, molybdenum, columbium

\* Ibid.

contains the meters for the gauges and heaters, the controls for the heaters, and the switches for general operation.

Fig. 11.12 is a side view of the same machine.

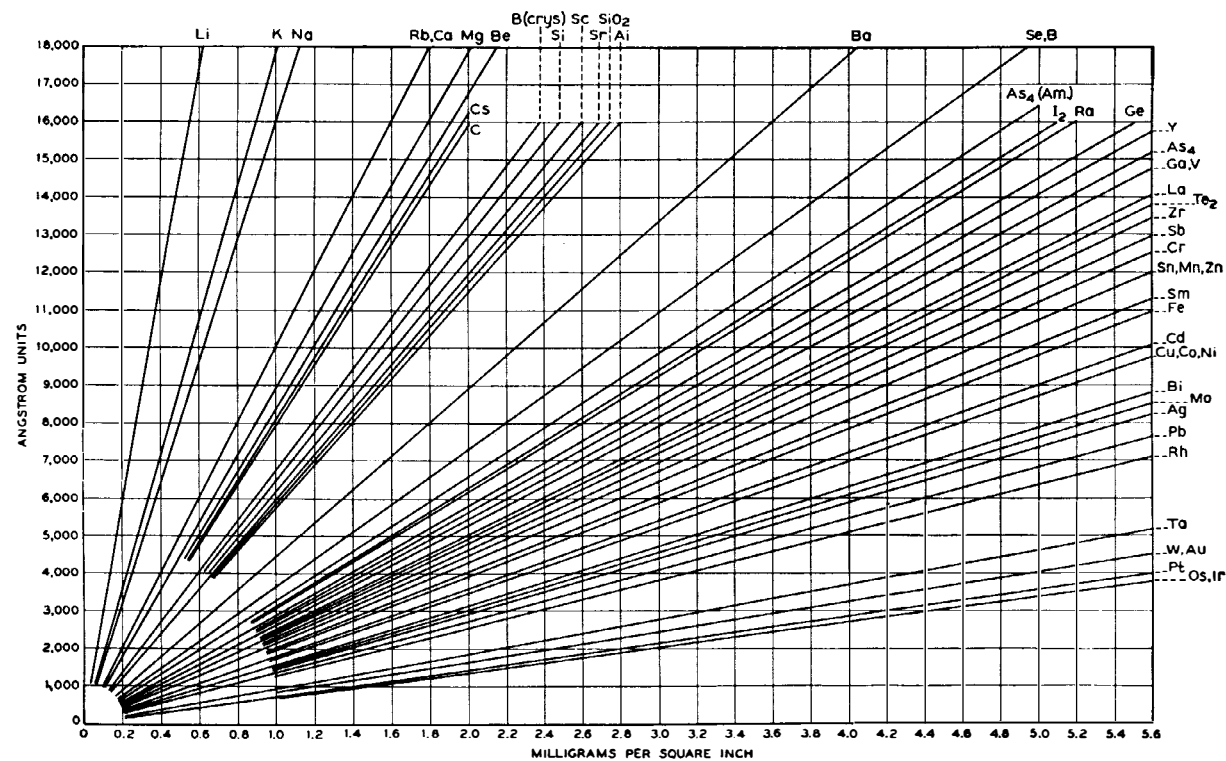


Fig. 11.10—Graphs showing the thickness of evaporated films in Ångstrom units as a function of mg per square inch of deposited metal. 1000 Ångstrom units equals  $3.937 \times 10^{-6}$  inches.

Fig. 11.13 is a front view of a six-chamber machine designed for factory production. The six chambers are grouped in threes with separate sets of pumps so that one group can be plating while the other is being loaded, or to operate at half capacity when vacuum leak troubles develop in one group, or to operate at half capacity when that is sufficient for the production

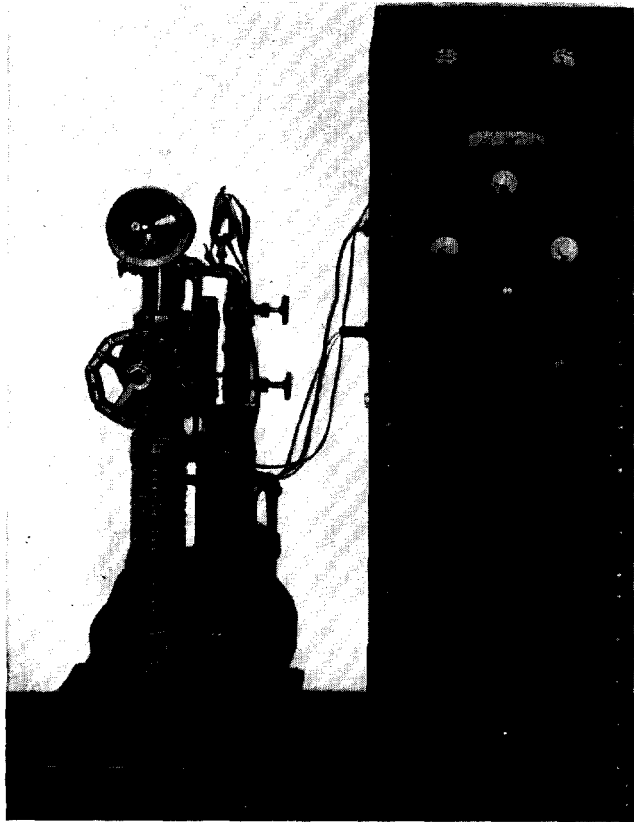


Fig. 11.11—Single chamber plating machine with control panel

involved. The control panel is built into the machine as shown in the photograph.

In Fig. 11.14 is shown the piping arrangement of the machine. The vacuum chamber lies horizontally at the top. The removable plating element or tray of Fig. 11.8 is in place. The chamber is sealed by means of a black gum rubber gasket without cordage that is mounted against the flange on the tray head. It is lightly lubricated with a low vapor pressure grease.

A vacuum tight seal is produced by atmospheric pressure when the chamber is evacuated.

The plating chamber or chambers are connected through a large tube or manifold with the oil vapor pump that stands in a vertical position. The outgoing gases from this pump are removed near its base by a pipe leading

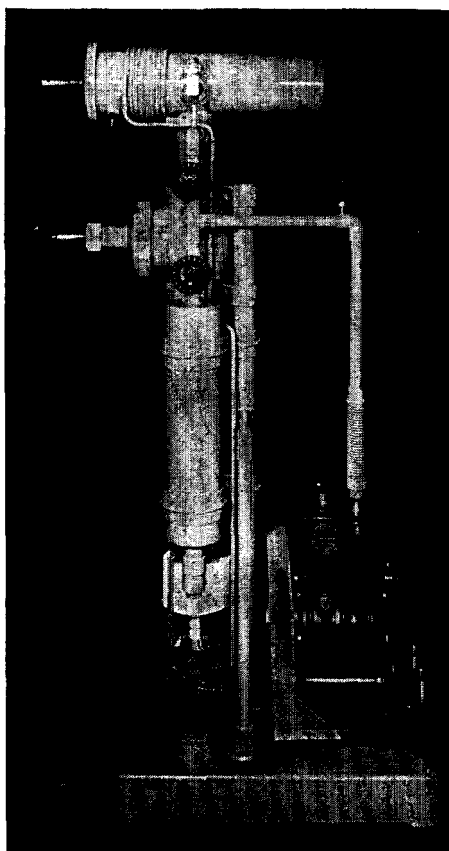


Fig. 11.12—Side view of single chamber plating machine

to a volume tank, which tank acts as a vacuum reservoir if the rotary mechanical pump is shut down for a period.

Valves 2 and 3 are placed at the inlet and outlet respectively of the vapor pump so that this pump may be maintained under vacuum while trays of crystals are changed in the plating chambers. While the oil in the vapor pump is hot, letting air in will produce harmful chemical action, hence the provision for sealing it off when the vacuum is let down. After the trays are changed, the rotary mechanical pump evacuates the chambers through

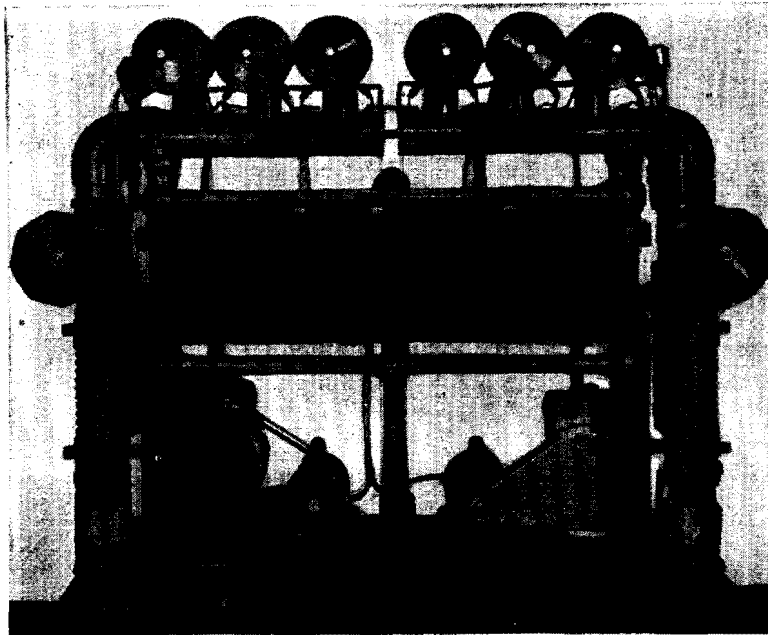


Fig. 11.13—Production model plating machine embodying six chambers

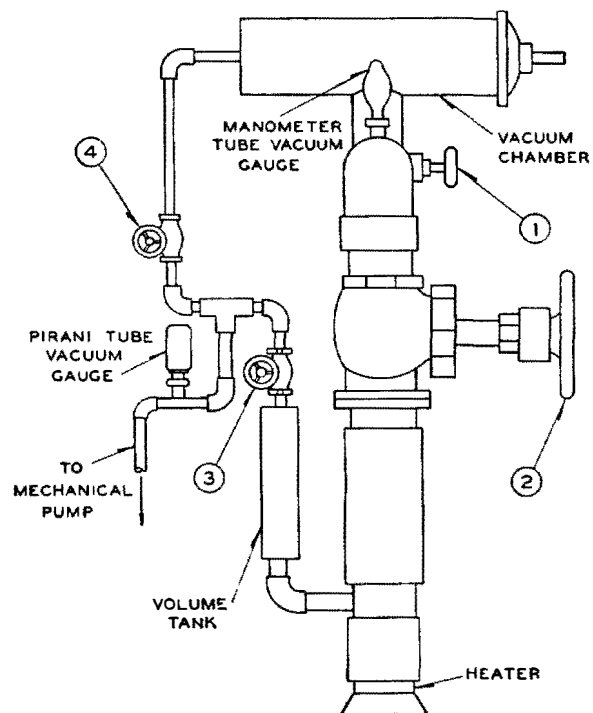


Fig. 11.14—Piping arrangement of the plating machine

a separate pipe and valve 4 until the vacuum is low enough to use the vapor pump again. Valve 4 is then closed and valves 3 and 2 are opened.

Two vacuum gauges are provided, a Pirani gauge to determine when the rotary mechanical pump has produced sufficient vacuum to start the vapor pump, and a manometer tube vacuum gauge to determine when the vapor pump has produced sufficient vacuum to start the plating.

Valve 1 is provided to break the vacuum prior to removing trays from the plating chambers.

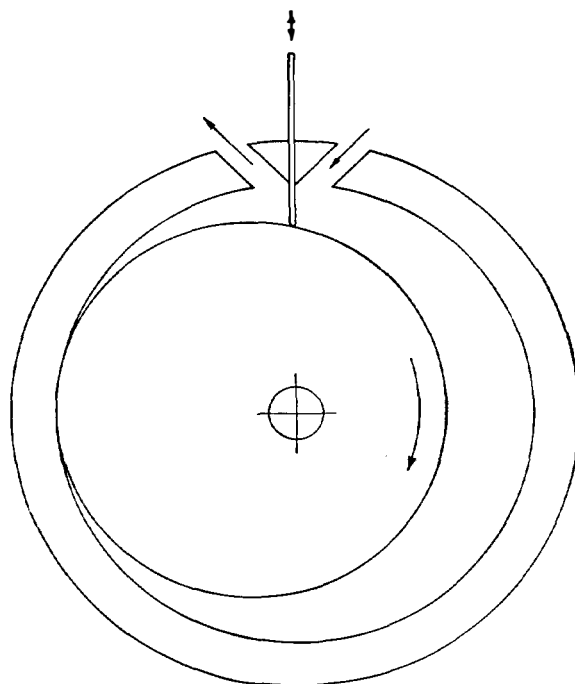


Fig. 11.15—Schematic design of the rotary mechanical pump

Water cooling is provided to carry away heat from the vapor pump and from the plating chambers. A pipe is wound around the outside of the pump and the chambers for this purpose. This pipe is not shown in Fig. 11.14, but may be seen in Figs. 11.11 to 11.13.

#### 11.6 PUMPS

The backing pump or forepump may be any kind of a pump that will produce a vacuum of  $1 \times 10^{-3}$  mm. The commercial rotary type pump diagrammed in Fig. 11.15 has been found to be a very satisfactory pump for this purpose.



It consists of an oil-sealed rotating cam working against a slide partition. Gas to be removed flows in a port on one side of the slide, is compressed by the rotary cam and driven out at atmospheric pressure through a vent on the other side of the slide. The slide keeps the incoming and outgoing gases from mixing. There is also a check valve at the exhaust vent to prevent gases from returning to the pump.

To obtain a still better vacuum a water cooled oil vapor pump is used, located between the forepump and the main manifold. This pump is visible in Figs. 11.11 and 11.13 standing in a vertical position underneath the large valve.

At the bottom of the pump is a reservoir of low vapor pressure oil which is heated by an electric heater.

This oil is a highly refined petroleum product with a vapor pressure of  $10^{-7}$  mm of mercury and must not be heated if oxygen is present in the system in excess of  $10^{-2}$  mm of mercury, as "burning" and severe darkening of the oil will result necessitating cleaning the pump internally and inserting new oil.

In operation the vaporized oil rises under slight pressure up a central tube and discharges downward through suitably arranged jets. It condenses to liquid again on the water cooled cylinder wall and returns to the oil reservoir. Baffles inserted above the jets prevent upward diffusion of oil vapor into the manifold and plating chambers.

The oil vapor projected downward by the jets carries the gas molecules to the lower end of the pump where they are pumped out through the tube connected to the rotary mechanical pump.

### 11.7 VACUUM GAUGES

The two vacuum gauges mentioned operate on different principles and are of different design. The Pirani gauge utilizes as its principle of operation the fact that the cooling of a hot wire in a partial vacuum is dependent upon the amount of gas present to carry away the heat. The gauge therefore employs a heated wire in a tube that is connected to the pipe line in which the vacuum is to be measured. The effect of the gas in carrying away heat and changing the wire's resistance is measured by means of a Wheatstone bridge. To eliminate effects of ambient temperatures upon this wire, a similar wire is employed in one of the other arms of the bridge, this second wire being in a well sealed evacuated vessel. The two wires are heated by alternating current that is supplied to the bridge and the unbalance is indicated by an A.C. microammeter. When the pump has reduced the pressure in the pipe to its inlet as far as it can, the heat losses in the two wires are equal, the bridge is balanced, and the ammeter reads zero. Before this vacuum is reached, however, the larger amount of gas in the con-

nected tube carries heat away from the wire faster than in the other, which is evacuated and sealed, and the bridge is unbalanced. It is possible to calibrate the ammeter readings against gas pressure, but that is not necessary in this application. The gauge here is used only to determine when the pump has produced sufficient vacuum for starting up the vapor pump, and that occurs when the vacuum has reached the limit this gauge will register.

This gauge is useful in the pressure range of .1 to .001 mm pressure. Above .5 mm pressure, the heat loss in the measuring tube becomes approximately constant. It does not therefore unbalance the bridge at atmospheric pressure to the extent of damaging any instruments or other elements in the circuit or the gauge.

The other gauge is known as a manometer gauge and is a standard Western Electric Company D-79510 type tube and can be used to measure a pressure of  $10^{-4}$  mm or lower. It is connected to the manifold near where the plating chamber is located. It contains a thermionic cathode, a grid and a plate, arranged in the usual form for amplifying tubes. Its connection and operation, however, are totally different. The grid is maintained at a potential of about 100 volts positive with respect to the cathode. The current flowing is regulated at about 20 milliamperes by regulating the current through the cathode. This regulation is accomplished automatically by utilizing a relay in the lead to the grid which reduces the cathode heating current when the grid current is high and increases it when the grid current is low. The electrons while flowing to the grid inside the tube will strike gas molecules occasionally, ionizing them. The number of strikes will be proportional to the density of the gas molecules. The plate is maintained at a negative potential of about 8 volts with respect to the cathode. The ionized gas molecules with their positive charges will be attracted to the plate, where, upon striking they give up their charge. The current flowing from the plate to the cathode, outside the tube, will then be a measure of the gas pressure inside.

The determination of the gas pressure in the tube is based upon the ratio of the positive ion current to the electron current. For pressures less than  $10^{-4}$  mm the positive ion current is directly proportional to the pressure of the gas in the tube for any set of given plate and grid potentials and geometry of the tube.

For the particular tube used in these designs, if the electron current is maintained at 20 milliamperes, the pressure in millimeters of mercury of the gas is equal to the positive ion current times five, the positive ion current being amperes, or  $\text{pressure} = 5 i_p$ , gives a figure that is the pressure in mm Hg.

The manometer must not be operated until suitably low gas pressures for operating the vapor pump are reached.

After the manometer has been subject to atmospheric pressure for a short

period, a noticeable amount of gas adheres to or is absorbed by the three elements. Upon evacuation, to the operable level, this gas begins to come off. The manometer will indicate higher than correct pressures until this gas is driven off.

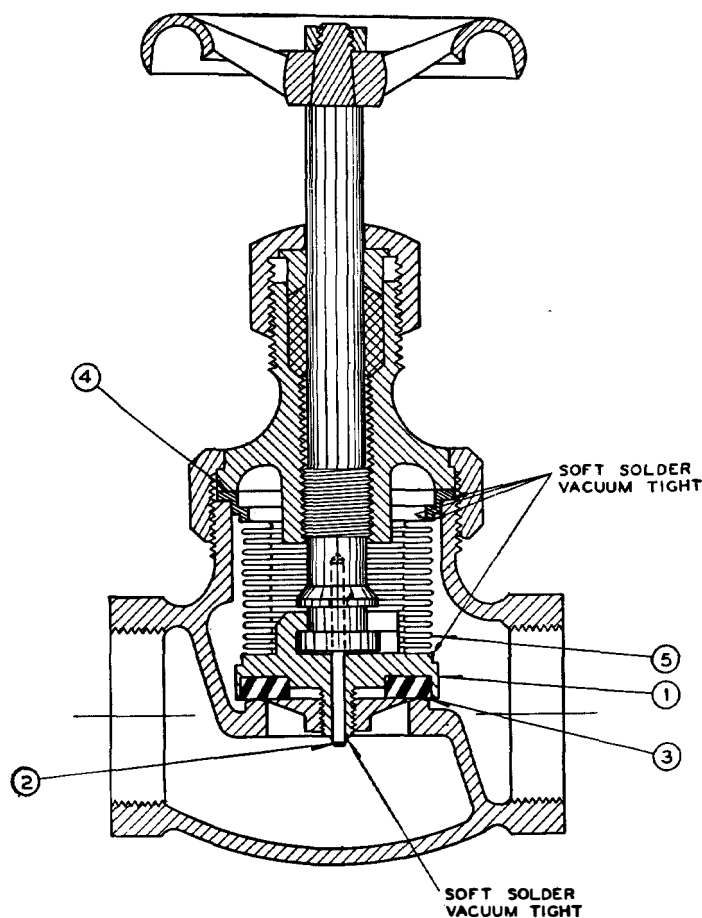


Fig. 11.16—Globe valve modified for vacuum line use

### 11.8 VALVES

Valves in a vacuum system are generally a source of trouble. A very minute leak can prevent attaining the vacuum necessary for plating. To avoid leaks, valves were reconstructed with sylphon bellows to maintain the seal. Commercial valves with sylphon bellows usually require modification to make them suitably tight for vacuum use.

Fig. 11.16 shows a standard  $1\frac{1}{2}$ -inch globe valve that has been modified.

The guides usually cast to and as an integral part of the gasket holder 1 are machined off and the upper edge of the gasket holder cut to accommodate the sylphon bellows. The gasket supplied with the valve is removed and the entire surface of the gasket holder on the gasket side coated with a layer of soft solder. A new gasket 3 of black gum rubber, Koroseal or Neoprene is inserted. A .125-inch diameter pin 2 is inserted extending into the valve stem and soldered at the end. This keeps the gasket holder in proper alignment with the valve seat replacing the guides that are removed. A brass ring 4 is provided and the sylphon 5 soldered to it, and to the gasket holder as shown. The flange of the brass ring 4 is soldered to the globe. The sylphon used for this type  $1\frac{1}{2}$ -inch valve is 2 inches O.D. 1.3 inches I.D. with twelve live convolutions.

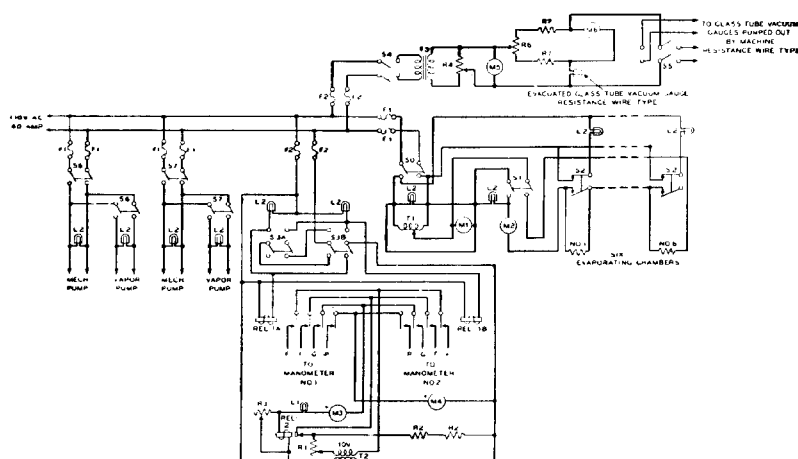


Fig. 11.17—Circuit diagram for the 2 x 3 chamber machine of Fig. 11.13

### 11.9 CIRCUIT DIAGRAM

The circuit diagram for the control and measuring panel of the multi-chamber machine is given in Fig. 11.17. Each pair of pumps, mechanical plus its associated vapor pump, is interlocked so that a vapor pump cannot be started until after the mechanical pump circuit is closed. Each pump has its own indicator to show when in operation. The Pirani gauge is supplied with A.C. by a transformer, and the voltmeter and ammeter used are of the rectifier type. Either Pirani gauge may be switched to the gauge circuit.

A single indicating circuit is also provided for the two high vacuum manometer gauges.

The plating chambers are operated one at a time. Their heaters are permanently connected in series, with a short circuiting switch for each.

When a short circuiting switch for a chamber is opened, a connected switch closes and lights an indicator lamp.

#### 11.10 OPERATION

The crystals, after etching, washing and drying as described in paragraph 11.3, are placed on the tray for plating. If after the etching and washing operation, the crystals are stored for a time exposed to ordinary room atmosphere, or subjected to packing and shipping before plating, they are cleaned just prior to plating by immersion in carbon tetrachloride C.P. for a few minutes, then washed with hot distilled water, and dried. While still warm they are placed on the plating tray in any desired order using only a flat smooth type of tweezers in their handling.

When the edges are not to be plated, the crystals may be in contact with neighboring crystals. When edges are to be plated, the crystals are placed on the tray parallel with the heater wires and separated  $\frac{1}{4}$  inch so the adjacent edges will be exposed to the evaporated material.

Water is started in circulation through the cooling coils on the machine.

The trays are inserted in the vacuum chambers, and the chamber heads supporting the trays pressed firmly against the flanges on the evaporation chambers to bring the lubricated rubber gasket into good contact. Valve No. 1 is the air inlet valve.

An actual plating operation for silver is as follows:

Close valve No. 1

Close valve No. 2

Open valves No. 3 and No. 4

Turn "Mech. Pump" Switch to "on"

When the mechanical pumps have pumped out the system until the A.C. Microammeter *M-6* reads zero turn vapor pump switch to "on." The circuit is arranged to prevent operation of the vapor pump switches unless the mechanical pumps are in operation.

Close valve No. 4

Open valve No. 2

Allow pumps to operate until a pressure at least as good as  $2 \times 10^{-5}$  mm Hg is attained before heating the wires to which the silver is attached.

Close plating regulator input switch—*SO*.

Adjust plating current regulator transformer *T-1* to zero.

Close unit switch *S2* controlling the heater wires in the evaporation chamber. Plating is carried out in one chamber at a time.

Close plating regulator output switch *S1*. When starting and stopping operation of the heater wires, the plating regulator input switch only is operated and the chamber unit switch controlling the set of heater wires in use is kept to "on."

The plating operations are controlled by a time-current schedule and this

must be strictly adhered to or negative plating results will be obtained such as improper quantity or poor distribution of the metal, or melted silver dripping from heater wires and falling on crystals.

While the silver is melting on the heater wires and being evaporated, enough gas may be liberated to cause an increase in pressure to an allowable maximum, of  $1. \times 10^{-4}$  mm Hg. If the pressure reaches the maximum, the plating regulator input switch is thrown to "off" and the evaporation chambers permitted to pump out until the pressure is again  $2 \times 10^{-5}$  mm Hg or close to that value. The lower the pressure at start of evaporation the greater the pressure working range before the maximum is reached.

Apply 5 amperes, regulating the current via transformer T-1 until constant. Increase current .5 ampere at 20 second intervals up to and including 10 amperes. Increase current 1 ampere at 15 second intervals up to and including 14 amperes. The final current insures that all of the silver attached to the heater wires has been evaporated.

The time-current schedule is repeated for each of the plating chambers.

This completes the deposition of the silver on one major surface on the crystals. The crystals are then permitted to cool for twenty minutes in the machine, continuing evacuation, before removing the trays, then

Close valves Nos. 2 and 3 to keep air away from the warm oil in the vapor pump.

Open valve No. 1, admitting air into the chambers to atmospheric pressure.

The crystals are then removed and turned over for plating the second major surface and the heater wires are reloaded with silver as before. After reinserting the loaded trays into the chambers, the operation for plating the second major surface is as follows:

Close valve No. 1.

Open valve No. 4 and again pump out the system until the meter M-6 again reads zero.

Close valve No. 4.

Open valve No. 3.

Open valve No. 2.

The plating time-current schedule is repeated for operation of the heater wires and operation of the valves repeated for repetitive platings.

The procedure for depositing gold and aluminum films is the same as for the deposition of silver films with the exception of changes in the time-current schedule that controls the flowing of the metal on the heater wires and evaporation. The following is the time-current schedule for these two metals.

*Gold.* Three mg per square inch in weight. Apply 10 amperes through heater wires and maintain the maximum current for about 40 seconds.

The maximum current should be approached over a period of 10 seconds to permit the gold to melt into globular form on the wires without dripping off.

*Aluminum.* One mg per square inch in weight. Aluminum alloys readily with both tungsten and molybdenum heater wires. It clings tenaciously and flows on the surfaces. Also because aluminum sometimes does make poor thermal contact with the heater wires, it is melted with a sudden application of heat. Apply 40 volts, 15 amperes for 3 seconds. To melt any pieces of aluminum that may have escaped melting by the first heat application: Apply same power for 1 second. Apply same power for 2 seconds twice. The power is shut off and the heaters permitted to cool for 20 seconds between heat applications.

Apply 5 amperes for 5 minutes. This flows the aluminum over the heater wires and distributes the metal evenly.

Apply 15 amperes over a 5 second period. Turn off power.

Apply power increasing from 15 to 16 amperes over a 5 second period.

Apply 16 amperes for 7 periods of 10 seconds each.

As the current decreases during the last power applications, it is maintained at 16 amperes by regulation of the transformer *T-1*.

Sufficient cooling should be permitted between power applications to maintain the vacuum below  $5 \times 10^{-5}$  mm Hg.

The plated material should be free from spots or blisters and have typical aluminum appearance.

When the machine is not in operation, the chambers should be kept closed and the machine pumped out.

This can be accomplished by closing valve No. 1.

Open all other valves and operate the mechanical pump for a short period of time.

Close valve No. 3.

Close valve No. 4.

Stop operation of mechanical pump.

Keeping the machine pumped out is important to avoid condensation of humid air in the system or potent vapors from materials in use at nearby work locations. A good location for performing metal plating work of this kind is in an air conditioned space, but where this is not possible a general contribution to obtaining low pressures consistently in the apparatus is to install a tank of nitrogen adjacent to the machine connecting it to the air inlet valve number one. Nitrogen at one pound pressure is then used to reduce the chambers to atmospheric pressure at all times and allowed to flush continuously through the valves and chambers when the machine is opened during plating operations.

If nitrogen is not obtainable, it is also helpful to let air into the machine after first passing it through a suitable drier tube.