

X21868

UNANNOUNCED

PR 111335

①

DTIC FILE COPY

Vacuum Coating Methods

by

Samuel Wein, Consultant

DTIC ELECTE  
S DEC 01 1988 D  
CD

(Metallic Coatings on Non-Metallic Materials, V. 8)

19961126 144

Prepared in Cooperation with  
the U. S. Navy, Bureau of Aeronautics  
Contract no. CC-3935

DISTRIBUTION STATEMENT A  
Approved for public release  
Distribution Unlimited

1953

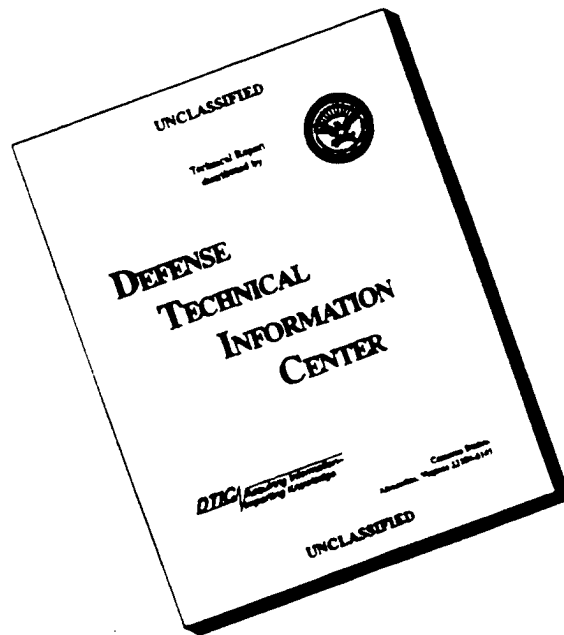
Distributed by  
Business and Defense Services Administration  
Office of Technical Services

DTIC QUALITY INSPECTED 3

~~Price: \$1.00~~

88 11 29 044

# DISCLAIMER NOTICE



**THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.**

Quotations from this report should credit the author. No responsibility is assumed for the completeness or accuracy of this report. Where patent questions are involved, the usual preliminary search is suggested. If a copyright notice appears in the document, the customary request for quotation or use should be made directly to the copyright holder. The author has assumed all responsibility for any infringement of any copyrighted material or statements which may appear herein.

The U. S. Department of Commerce is unaware of any secrecy restriction involving the material in this publication.

Mention of the name of any firm, product, or process in this report is not to be construed as a recommendation or endorsement but merely as a citation that is typical in its field. Commercial directories generally list names of additional companies and products.

CHAPTER VIII. VACUUM COATING METHODS

	<u>Page</u>		<u>Page</u>
<u>INTRODUCTION</u>	262	<u>PROCESSES</u>	
Advantages	262	(Continued)	
Disadvantages	262	Thermal Decomposition	
I. <u>APPLICATIONS</u>	262	of Salts	268
Materials Coated	262	Aluminum Coatings	268
Advertising Displays	263	Silicon Monoxide	
Condensors	263	Coatings	268
Microphone Diaphragms	263	III. <u>EQUIPMENT AND</u>	
Novelties	264	<u>OPERATION</u>	268
Optical Filters	264	Cleaning	269
Beam-splitting	264	Fill-in Coats	269
Phonograph Master Records	265	Evacuating system	269
Piezo-Electric Crystals	265	Protective lacquers	269
Resistor units	265	Production costs	270
Shields	265	Roll Coating	271
Static Grounding	265	Holding fixtures	272
Tin Cans	265	Equipment	
Window Glass	265	Manufacturers	273
II. <u>PROCESSES</u>	265	Metallizing firms	273
High Voltage	266	IV. <u>PB-REPORTS</u>	273
Arc	266	V. <u>REFERENCES</u> (by Author)	277
Thermal Evaporation	266	VI. <u>PATENTS</u>	280
Eddy Current Technique	267	United States	280
Getter Pills	267	Canadian	281

DTIC  
COPY  
INSPECTED  
6

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input checked="" type="checkbox"/>
Unannounced Justification <input checked="" type="checkbox"/>	
By _____	
Distribution _____	
Availability Codes _____	
Dist	Availability For Special _____
12	

DTIC QUALITY INSPECTED 4

## CHAPTER VIII

### Vacuum Methods

Introduction: Although methods of depositing thin films of metals in vacuum on glass, ceramics, plastics, as well as on metals have been known for more than 75 years, their use until recently has been chiefly in physical and chemical laboratories. They have been useful in the study of atomic structure, electron theory, and the production of metal films on miscellaneous surfaces for specialized purposes. Modern evacuating systems with their highly efficient associated devices have only recently brought these processes important practical and commercial uses.

Vacuum methods are useful because they permit:

(1) Extremely thin films to be formed (in the barrier types of photo-cells, films are used both as optical filters and as electrical conductors).

(2) Metals that ordinarily cannot be precipitated out of solution can be vacuum deposited.

(3) Metals can directly be applied to non-conducting surfaces without resorting to preliminary chemical and physical treatments.

(4) Materials can be coated with metals by this method which would be destroyed by high temperatures or chemically destructive compounds in some other processes.

(5) Semi-metallic elements such as tellurium, silicon and selenium can be deposited on any given surface in very thin layers.

(6) One metal can be deposited on another far removed from it in the electrochemical series. This would be difficult to accomplish by electroplating. For example, gold or platinum can be deposited on aluminum or magnesium.

The disadvantages in the use of vacuum processes are that they are comparatively slow and tedious, and that the equipment used is expensive and not easily adapted for mass production.

Applications: Vacuum metallization has been used for many applications; decorative, as well as practical and technical. Special surface finishes such as change in color, or brushed, hammered, or wrinkled effects can be produced without additional extensive operations. The better known applications of vacuum metallization to various base materials will be discussed before describing the methods employed.

Materials Coated: The technical and patent literature includes reports of vacuum metallization of fabrics and textiles (cotton, wool, silk) as well as paper, wood, linen, jute, hemp, leather, gelatin, mica. etc. by vonBose, Pfanhauser and Sommer, and others. Synthetic resins (plastics) including cellulose nitrate, acetate, cellulose acetate-butyrate, cellulose propionate, polystyrene, methyl methacrylate (Lucite, Plexiglas), polyethylene, polyvinylidene chloride, nylon and most of the thermosetting materials have been coated by this method.

Cellulose acetate is coated on one side with films of metals for electrical, radio packaging, and display purposes. Products include sequins, greeting cards, and theatrical stage settings and costumes.

Among the manufacturers which offer the metallized plastic in such form as festoons, fringed, cut-outs, streamers, pompons and stamped out geometric designs are included:

Coating Products, Inc.  
 136 W. 21st. St., New York City  
 Dorrie Process Co.  
 60 Greenpoint Ave., Brooklyn, N.Y.  
 Hy-Sil Mfg. Co.  
 28 Spring St., Revere 51, Mass.  
 Leedel Products, Inc.  
 351 W. 35th St., New York City  
 Metal Films Corp.  
 200 Fifth Ave., New York City  
 Mirro-Plex, Inc.  
 160 Fifth Ave., New York City  
 Sprague Martin Vacuum Plating Co.  
 45 W. 53rd. St., New York City  
 Vacuum Metallizing Co.  
 32 Greenpoint Ave., Long Island City  
 Walco Bead Co.  
 37 W. 37th St., New York City  
 Wrapture, Inc.  
 619 W. 130th St., New York City

Advertising displays have been made by placing text and illustrations in a suitable box containing a light that flashes on and off periodically. When the light is off, the observer sees his face reflected from the coated mirror surface on a glass plate within the box. When the light is on, the message at the back of the box can be seen because the glass plate then transmits light.

Condensors made by vacuum coating with zinc, aluminum, and other metals on paper have been described by Anonymous (1), and The Office of Technical Services, PB-Reports #421, 466, 18908, and 39361 and Godley and Balsbaugh.

A recently developed product termed the "Solite" condenser, made by the Solar Mfg. Corp., uses a deposit of between 25 to 100 millimicrons thickness of aluminum on Kraft paper (Cornell).

Wehe vaporized zinc on Kraft paper for use as radio condensers. Such condensers are not only smaller in size for a given value in terms of capacity, but claim the added advantage of self healing of punctures through the insulation. An excellent mechanical set-up for vacuum coating is shown by Wehe.

Microphone diaphragms made of duraluminum coated with gold are located between two small chambers containing granular carbon. The carbon granules are in electrical contact with a gold film on the duraluminum diaphragm, by means of a technique developed by the Western Electric Company.

Novelty products have included chessmen, buttons, toys of all types, trumpets, trophy cups, flower pots and vases, jewelry cases, plaques, radio housings, card boxes, razor blade dispensers, religious articles, flashlight reflectors, Christmas ornaments, nameplates, light switches, shields, custom jewelry, etc. etc.

Optical Filters: Semi-transparent films of metals are used in optical filters having unique transmission characteristics dependent on the metal deposited, and are also used as optical filters which must simultaneously serve as electrical conductors, as in the case of the conducting medium for the barrier type of photo-cell.

Such filters may be formed of a single metal or an alloy. Alloys are used where transmission of a specific color is required and where the required characteristics cannot be obtained with a single metal. The following table shows the colors transmitted by certain metals:

<u>Metal</u>	<u>Color</u>
Silver	Blue-Violet
Chromium	Brown
Aluminum	Blue
Gold	Green
Copper	Green
Selenium	Orange

Any two or more of these metals applied to a glass surface as successive films will produce a transmission color equal to the product of the transmission of the component metals.

It is well known that a coating of a metallic fluoride on an optical lens will reduce or eliminate reflection at the glass-air interface if the coating has the proper thickness. This is a most important application of vacuum coating techniques.

In spectrophotometers, semi-transparent films which will transmit all colors to an equal degree are employed to attenuate one source of light without affecting the color response. An alloy of chromium and platinum has such a characteristic. Another use of semi-transparent films is in interferometers employed to examine minute contractions and expansions in industrial machines.

Strong at the California Institute of Technology, proved that a coating of metallic fluoride will reduce the internal reflection in multiple lenses as well as the light reflected from the surface, and would increase the transmission. By transmitting more light for a given light source and a given aperture, a coated camera lens has a greater effective speed than an uncoated one.

Strickland, Turner, Richards and Miller reported the transmission values of thin films on glass in several papers.

Beam-splitting, as in binocular microscopes or in color cameras, is another use of thin metallic layers for optical purposes. For example, a thin film of an alloy of aluminum and copper will reflect red and blue light but will transmit green light, the aluminum reflecting the blue and the copper reflecting the red.

Phonograph Master Records made in wax, insoluble metallic soaps, or other materials must be electroplated with a suitable hard metal and then backed up to a desired thickness for use as a "stamper". To accomplish this electroplating process, Edison, sputtered gold on the master record (wax), then backed the thin shell with copper by electroplating. Russell used palladium because it is harder than gold and is not affected by chemical action between the palladium surface and the resinous material with which it is in contact during the molding process.

Piezo-electric crystals are coated with metals to make better or more intimate electrical contact, according to Hulburt, and Kingsley.

Resistor units, according to Richtmyer, Zworykin, and Holbruck, are coated with metals for electrical contact purposes.

The electrical resistance of such films is higher than for massive metal. Extremely thin layers show almost infinite resistance up to a finite thickness at which the resistance drops tremendously (according to Richter). Probably the agglomerate structure of the film contributes to this. The resistivity of an evaporated aluminum film 0.00002 mm. thick is  $2 \times 10^{-5}$  ohm-cm. as compared to  $2.8 \times 10^{-6}$  ohm. cm. for massive metal. In spite of their extreme thinness, metal films act as a partial barrier to water vapor. In general, however, they are more valuable for their excellent optical properties than for other physical properties.

Shields for high frequency oscillators are made by forming thin films of metals on plastic and other materials.

Static Grounding: Goss formed platinum films on glass to ground static charges.

Tin cans have been coated so that contamination of the material by tin is eliminated. Alloys of silver have been used for this purpose.

Window Glass has been coated with semi-transparent films so that those inside a building can see out, but those on the outside cannot see in.

Processes: In successful commercial vacuum metallizing, lower per unit processing costs are generally realized compared to other metal film formation processes. In most instances this results either through the utilization of cheaper base materials, lesser amounts of plating metal, cheaper handling techniques, or elimination of many costly operations.

Each complete process may be broken down into the following four major step sequence:

- 1) Cleaning the surface.
- 2) Coating the object with lacquer and baking to provide a suitable base or undercoat upon which to evaporate the metal.
- 3) Evaporation of the metal to produce the metallic film by high vacuum methods.
- 4) Coating with lacquer and baking to protect the thin metallic film against abrasion and general service abuse.



The four commonly employed methods of vacuum coating of metals on given surfaces are carried out in an evacuated chamber or in the presence of an inert gas at low pressures.

1) High Voltage: Gardner and Case described one variation of the high voltage or "Cathode sputtering" method as follows: "A base plate of metal or glass is covered by a bell jar with the joints made tight by wax or rubber cement. If an aluminum base plate is used, it may serve as the anode. The connection for evacuating is brought out through the base plate and the pressure is reduced to approximately 0.001 millimeter of mercury. The cathode, a very thin sheet or wire grid of the metal to be deposited, and the surface to be coated are placed parallel, and approximately 25 mm. apart. A 10,000 volt transformer (1/8 kw. is satisfactory) furnishes the current. It is advisable to rectify the current, either by means of a vacuum tube or by means of a mechanical rectifier driven by a synchronous motor. If no rectifier is used, the anode should preferably be of aluminum".

2) Arc: Metals in the form of thin gauge rods or "pencils" are brought together, a suitable source of power is applied between them, an "arc" is formed, and the evacuated chamber is soon filled with the vapor of the metal forming the arc. Sometimes a voltage differential is applied between the cathode of the arc and the work in order to attract the metal ions over to the surface to be coated.

3) Thermal Evaporation: This method was first suggested by Edison and thereafter developed in detail by Zworykin, Trautman, Saeger, Edwards, Williams, Williams and Ruedy, Alexander, Gardner, Biggs, Walker, Burkhardt and Reinecke, Siebertz, and Lenz. It is commonly used today because of its simplicity and because the required equipment is inexpensive.

In the early days, Edison used filaments of carbon, molybdenum or tungsten. Nichols of the Bureau of Standards used a coil of tungsten about 1/4 mm. in diameter, clamped by strips of iron to heavy (1 mm.) tungsten wires. The material to be coated is placed on a glass plate and supported on a clamp which can be raised or lowered. If the surface to be coated is too close to the material used as the coating, the film will not be uniform, being thickest in the center. Also, the heat from the filament may break the glass if it is thick and too close to the filament.

One can watch the progress of evaporation by looking up towards the filament from the bottom of the tube. This is especially convenient when semi-transparent deposits are required. When the filament is heated the metal to be evaporated will assume a vapor or gaseous condition, which soon condenses on the glass, plastic or other surface as well as the inner wall of the bell jar.

Henderson evaporated nickel which had been electroplated onto a tungsten wire in a technique designed to secure especially uniform films. Pfund evaporated bismuth from a tungsten spiral in a similar method.

Berghaus and Burkhardt made crucibles of cast molybdenum or tungsten. When heated in a vacuum system and the presence of an inert gas, such as argon, helium, nitrogen or hydrogen, the metal will distill and by means of an electrical charge, the particles will be attracted to the specific place where they are deposited.

Farkas decomposed chromium chloride as by heating a filament whose surface had been treated with the compound. This took place in an evacuated chamber. Simultaneously with this decomposition of the metal salt, there were introduced the vapors of pyrogallol. In this fashion, the reducing action of pyrogallol took place at once, forming a metallic film of chromium.

Wires of tungsten, iron, nickel and chromel are stretched between two electrical contacts and wound into conical baskets or in the form of a helical coil. Among the suppliers of tungsten and other metals for this purpose are:

Callite Tungsten Corp., Union City, New Jersey  
Sylvania Electric Products, Inc., Towanda, Penna.

4) Eddy Current Technique: The use of eddy currents for "Exploding" magnesium within vacuum tubes is a common practice. This method forms a mirror-like deposit on the inner wall of the evacuated bulb. The method is fast, but for some purposes the investment for equipment to produce the eddy current may be too expensive. "Getter pills" using alloys of different proportions between magnesium and aluminum, with a small percentage of barium are commonly used in the vacuum tube art and are also employed for making front surface mirrors. This idea is covered by patents to Case and Macksoud.

Getter pills are usually made up to individual requirements according to coating desired. Some typical getter pill alloys formulated by the King Laboratories, Inc. are shown in the table below.

Getter Pill Composition

<u>Barium</u>	<u>Magnesium</u>	<u>Aluminum</u>	<u>Flash Temp. Deg.C.</u>
42 3/4	5	52 1/4	1025-1075
37 1/2	25	37 1/2	850-900
43 3/4	12 1/2	43 3/4	900-950
25	55	20	700-750
42	9	49	925-1000
35	50	15	900-950
37 1/2	37 1/2	25	750-800
43	20	37	850-900
45	--	55	1125-1175
50	--	50	1125-1175
60	--	40	1000-1075
70	--	30	950-1025
75	--	25	925-1000

The lower the temperature values in the column at the right the lower will be the temperature at which the evaporation of the magnesium is practically complete and at least a trace of barium is detectable in the deposit. The higher figure gives the temperature of practically complete barium deposition. In the case of alloys containing no magnesium, the lower figure gives the approximate temperature at which the barium begins to deposit and the higher value is the value required for complete evaporation.

The magnesium will usually begin to distill at least 50 degrees lower than the lower values given in the table. It is recommended that where the "flashing rate" be fast, the getter be raised to a temperature at least 50 degrees higher than the upper figures given in the chart.

Kemet Laboratories, Inc. likewise make a series of getter pills for similar purposes.

An interesting study of getter pills is accredited to Ehrke and Slack.

Thermal decomposition of volatile iodides, hydrides, and carbonyl compounds at elevated temperatures to form films of boron, titanium and carbon for atomic energy applications and research in Great Britain is briefly described (p.10 - 11) in PB-107963.

The merits of various methods of vacuum coating of thin films for atomic energy research in Great Britain and special applications is also compared by Jacques. Cathode sputtering and thermal evaporation of a large number of metals and alloys including 12 references are cited. (See PB-107963, pp 22-26).

Aluminum does not tarnish as easily as silver because it is protected by films of aluminum oxide (50 to 100 Å) formed when it is exposed to air. In spite of this natural protective film, evaporated aluminum coatings are mechanically and chemically too delicate for many mirror applications. Therefore, it is necessary to coat the front surface aluminum mirrors with a transparent, durable material.

Silicon Monoxide Coatings: Because of its excellent physical properties, the use of silicon monoxide was considered for protective films. Silicon monoxide can be evaporated directly onto the reflector surface; but the evaporation is difficult and the resulting films have doubtful qualities because of loose structure and inadequate adhesion to the mirror material.

Haas and Scott obtained hard, adherent films of silicon monoxide by another method. Silicon was evaporated onto the aluminum surface and then oxidized to silicon monoxide by anodizing. The evaporation of silicon, which usually presents difficulties, was successfully carried out from thick (approximately 0.8 mm.) tungsten boats heated electrically by a current of approximately 400 amperes. For anodizing, an ammonium tartrate bath with 3 percent tartaric acid, at a pH of approximately 5, was used. The thickness of the protective film can be determined by observing the interference colors produced by the evaporated silicon, and it can be controlled by the voltage used in anodizing. This process produced hard, adherent silicon monoxide films with good mechanical and chemical properties according to Haas and Scott. Photographs and diagrams of the vacuum apparatus are provided in an article by Scott, and Godley

Quartz may be evaporated upon glass and other surfaces according to Ogle and Weinrich.

The following three basic work-handling techniques have been developed for applications of high vacuum metallization:

- 1) Objects are held stationary within the vacuum chamber where coating is required on one side only.
- 2) The objects are held by rotating jigs within the vacuum chamber. This method is used for irregularly shaped objects which require coatings over their entire surfaces.

3) Continuous lengths of material fitted on a rewinding mechanism within the vacuum chamber as in the case of continuous rolls of plastic sheets and fabrics.

Cleaning: Application of the undercoat is preceded by a thorough cleaning of all surfaces. Washing with a suitable detergent is usually adequate for plastics. The undercoat seals the pores, which otherwise would provide gas traps and cause interference by outgassing during the evacuation procedure. It also eliminates surface irregularities, which would be exaggerated optically by the evaporated bright metallic film deposit, only a few millionths of an inch thick.

The formulation of the undercoat depends upon the nature of the object to be coated. Certain lacquers will adhere well to cellulose acetate but not to polystyrene, therefore lacquer selection is extremely important and should be referred to the lacquer manufacturer.

Fill-In-Coats: Inasmuch as the appearance of a metal coating is dependent upon the surface characteristics of the base upon which it is deposited, it may be necessary to employ fill-in coats of lacquers or varnishes to obtain high gloss, and hence highly reflective surfaces. Solvents may be employed also to cause reticulation of the surface of the base plastic in order to obtain wrinkled and brushed finishes. All commercial techniques of applications of these fill-in coats may be employed. The formulation of these fill-in compositions must be done with particular care taken in order to insure complete dryness. The plastic compositions and the fill-in coating must have a low enough vapor pressure to allow the vacuum system to produce a pressure of 0.5 micron or less. Most of the plastic compositions fall into this category, and, in general, this is not too stringent a limitation on commercial production.

The Evacuating System: In actual practice vacuum is created by two sets of pumps: (1) the roughing system in which a mechanical pump evacuates the system down to about 75 microns, and (2) the oil diffusion pump with which the pressure may be brought down to that actually required between 0.5 to 5.0 microns for the evaporation of metals.

Protective Top Lacquers: Metallized objects require a transparent coat of lacquer in order to protect the metal deposition against general service abuse and also to provide the medium for introducing color effects. Among the commercial firms producing lacquers for both the undercoat as well as the top coat for use with all sorts of base materials are:

Doran Products Co.  
Newark, New Jersey  
Schwartz Chemical Co.  
328 W. 70th St., New York City

The lacquers may be applied to the given surface by several convenient methods, for example: (1) dipping in a diluted solution, (2) spraying, and (3) centrifugal means applicable to small pieces in order to obtain fast drying.

The metallic film will not need protective coatings when there will be no subsequent handling. Tarnish-free reflective surfaces can then employ a coating of aluminum.

Range of Colors: Variations in color tones of the metallic finishes are obtained by dyeing the top coat lacquers. A range of metallic appearances can be had by this technique, varying from tones of gold through copper, and virtually including all colors of the total spectrum.

The Distillation Products Co. described a typical system which would require approximately 1500 square feet of operating space. It would consume, on an average, \$3.00 power per hour. When kept in full production it would use approximately \$7.00 worth of raw materials per hour.

The production capacity of these complete high vacuum systems is gaged by the productivity of the vacuum chamber. Under most favorable conditions, three cycles per hour can be obtained. The number of pieces that can be loaded into the vacuum chamber per cycle is a function of the volume occupied by the object. In the instance of a vacuum chamber 48" in diameter by 48" long, the following are typical cases:

Assuming small objects such as #30 ligne novelty buttons, to be the work involved, 12 riser-rods can be loaded per station, and there are eight stations per holding fixture. This would then require 288 riser-rods per hour. Forty buttons per riser-rod loading would accumulate 11,000 per hour. For this volume, automatic riser-rod loading and unloading devices would be desirable. Otherwise a total of 27 workers would be required to handle all of the pieces involved.

A more representative case would involve larger objects such as toy pistols, of such size that would permit seven pistols per riser-rod and six riser-rods per station. This would accumulate 1000 units per hour. This volume would necessitate a total of seven workers.

The cost of operating this production unit has been calculated at current rates and includes power consumption, consumable materials and personnel. The minimum personnel required for continuous production includes one man to operate the vacuum chamber, one for each of the two dipping machines and one for general equipment handling. The combined cost of power and materials for continuous production is \$11.28 per hour. The only tools required are spring clips to hold the work, on which costs vary according to the complexity of the clip.

Production rates depend upon the dimensions of the coated object. Typical examples are size 10" x 6" x 1", 144 load pieces per load, 432 pieces per hour; size 2½" x 1½" x 1", 2880 pieces per load, 8640 pieces per hour; size 2 ¾" x 2 ¾", 3456 pieces per load, 10,368 pieces per hour in the 48 x 48 inch chamber.

Table 1

A Comparison of Methods For Producing Small Ornamental Metallized Plastic Articles

<u>Technique</u>	<u>Vacuum Metallization</u>	<u>Silver Reduction</u>	<u>Electroplating</u>
Appearance	Excellent	Excellent	Very good

Table 1 - Continued

<u>Technique</u>	<u>Vacuum Metallization</u>	<u>Silver Reduction</u>	<u>Electroplating</u>
Utility*	Very good	Very good	Excellent
Unit Cost	\$.03	\$.07	\$.14
Remarks	Physical details maintained. Service utility of finish dependent upon protective lacquers used. Brightness of finish unaffected by aging.	Physical details maintained. Service utility of finish dependent upon protective lacquers used. Brightness of finish affected by aging.	Physical details blurred. Service utility of finish excellent. Brightness of finish may be affected by aging.

\* Evaluation of the factors that determine the functional value of the item, including permanence of finish under service conditions, weight, protection, afforded to the plastic item, etc.

Table 2

Coating Cost Comparison

	<u>Silver Reduction</u>	<u>Vacuum Metallization</u>
Production volume per day	300 gross pieces	300 gross pcs.
Initial capital equipment invest.	\$20,000.00	\$28,000.00
Labor required	28 man days	9 man days
Total direct costs	\$.013 per unit	\$.003 per unit.

Recent advances in vacuum coating plant and techniques are discussed by Holland.

Roll Coating: Continuous lengths of plastic films and synthetic fibre fabrics can be metal coated on one or two sides as needed. In many lightweight transparent film applications such as tinsel foil for packaging, one-side metal coatings without protective topcoats are satisfactory.

A plan lay-out for vacuum coating of films is described in detail by Schneider. It consists of the following steps:

- 1) Degasify the film.
- 2) The vacuum metal distillation unit.

Such a unit as described by Schneider with a capacity of 1500 feet of 20 inch wide and 0.0075 inch thick acetate film will coat with

aluminum at a rate of at least 20 feet per minute and will require about 15 minutes to reach the operating pressure. Allowing time for loading and unloading, the cycle will be approximately 1½ hour per 1500 foot roll.

The estimates in Table 3 indicate the cost of operation of the equipment per square foot of coated acetate sheeting. The electrical costs were figured on the basis of \$.05 per kilowatt hour and the water at \$.20 per 1000 gallons. Since the data in this table have allowed a considerable proportion of the cost as a contingency factor, the figures should be regarded as maximum rather than minimum. Also, where electric rates are lower than \$.05 per kilowatt hour, the figure given will be correspondingly reduced.

Table 3

Estimated Cost of Metallizing by Roll Coating  
0.0075" Acetate Film

120 kw. hours on the coater per 1500 ft. roll, and 37 kw. hours per roll on the degasifier, making a total of 157 kw. hours per roll at a cost of	\$ 7.85
Water consumed by the coater itself per roll is approximately 210 gallons or	.06
Water consumption on the degasifier per roll is again approximately	.06
The crucible material may run as high as \$5.00 per sheet	5.00
Operator cost, approximately	6.00
Maintenance, supplies, and other contingencies	6.03
Total cost per roll	\$ 25.00
1500 feet of 20 inch wide acetate is 2500 sq. feet per roll; therefore, the cost per square foot of metallizing is	.01
The cost of material per square foot varies between \$.046 and \$.048; \$.05 per square foot is allowed as an outside figure	.05
Total cost of metallizing one square foot of acetate sheet	\$ .06

Holding Fixtures: A stationery holding fixture that is basic in principal in all devices intended to hold plastic objects for one side coating as for ornamental Christmas bells, is inserted into individual cups retained by the fixture wall. The cups align the plastic bells so that the center axes of the bells are directed inward towards the sources. This

completely masks the outside of the bell and permits metallization of the plastic bell interior only. The fixture is held in a dolly ring. This makes for ready loading by the operator.

Inasmuch as the most economical methods utilize dipping techniques for application of the fill-in coats and top-coat lacquers, such an operation is recommended.

The work carrying rack throughout all operations is the "riser-rod" to which the individual plastic pieces are attached by spring clips. The angle of attachment is predetermined to eliminate any accumulation of lacquers in reverse-curved horizontal sections. The loaded riser-rods are then transferred into an automatic dipping machine. Here a chain conveyor, with special attachments to hold the riser-rods, carries the work into the lacquer bath. Under controlled conditions of extraction-angle and rate, with fixed viscosity of the lacquer, the pieces are withdrawn free of flow-marks and tears. The chain conveyor carries the work into the oven tunnel. Here controlled temperature forced drafts dry the coatings for approximately one hour. The dried coated work is removed by the operator and loaded into the station-holding fixture.

Manufacturers of Vacuum Metallization Equipment include:

Distillation Productions Industries, Rochester 3, New York.  
National Research Corporation, Cambridge 42, Massachusetts.  
Radio Corporation of America, Camden, New Jersey.  
Stokes Machine Company, Philadelphia, Pennsylvania.

Among the firms which do vacuum metallizing for other industries are:

J. B. Products Corp., 1745 No. Ashland Ave., Chicago 22, Illinois.  
Precision Optical Co., 1001 E. 163rd. St., Bronx, New York.  
Process and Instruments, Inc., 60 Greenpoint Ave., Brooklyn 22, N.Y.  
Sprague Martin Vacuum Plating Co., 45 W. 53rd. St., New York City.  
Steinfield, J. S., 135 Eastern Parkway, Brooklyn 17, New York.  
Vac Art Corporation, Bay City, Michigan.  
Worcester Moulded Plastics Co., 14 Hygia St., Worcester 8, Mass.  
Zenith Optical Co., 123 W. 64th St., New York City.

U. S. Department of Commerce, Office of Technical Services, has the following PB reports dealing with either the methods or their many applications resulting from processes described in the present chapter. Orders for reports which are available in printed or mimeographed form should be directed to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., accompanied by check or money order made payable to the Treasurer of the United States. Orders for other types of reproduction (microfilm, enlargement print, photostat) should be forwarded directly to the:

Library of Congress  
Photoduplication Service  
Publication Board Project  
Washington 25, D. C.

accompanied by check or money order made payable to the Chief, Photoduplication Service.



PB-421 - "Manufacture of metallized paper fixed capacitor units by the Robert Bosch Co., Stuttgart, Germany." Fred E. Henderson, 1945, 5p. Mimeo. \$.10.

PB-466 - "Report on Robert Bosch (Manufacture of metallized paper capacitors.)". S. J. Borgars and others, 1945, 4p. Mi. \$1.25 Ph. \$1.25

PB-4158 - "German vacuum evaporation methods of producing first surface mirrors, semi-transparent mirrors, and non-reflecting films." John R. Whipple, 1945, 43p. Mi. \$.50. Ph. \$3.00. Mimeo. \$1.25.

PB-4666 - "Report on German manufacture of searchlight reflecting surfaces." C. W. Hansell, 1945 3p. Mi. \$.50 Ph. \$1.00.

PB-1292 - Synder, C.L. - "Specialized ceramic products; their use in German communication equipment" 1945. 40p. Mi. \$.50 Ph. \$3.00 (FIAT-Fr 278).

PB-6588. - "Metallized-glass attenuators and miscellaneous R. F. test accessories." Polytechnic Institute of Brooklyn, 50p. Mi. \$.50. Ph. \$4.00.

PB-7667 - "Anti-Reflection Coatings for photographic lenses." A. G. Handy, 1943. 3p. Mi. \$.50. Ph. \$1.00.

PB-7667s. - "Centrifugal lens coating process (Leitz method)." I. Archavsky and others, Oct. 1945. 9p. Mi. \$1.00 Ph. \$1.00. Supplement to PB-7667.

PB-18220.-"Research on evaporation of films." Sept. 1944. 12p. (in German). Mi. \$.50. Ph. \$1.00.

PB-14956 - Borchers, H. "Deposition of Metals from the Gaseous Phase, especially by Decomposition of Carbonyls, and Application of the Resulting Products. July, 1945, 5p., Mi. \$.50, Ph. \$1.00. (Text in German).

PB-18908 - "Robert Bosch G.M.b.H., Stuttgart, and sundry dispersal sites." J. G. Osborne, Dec. 1945. 27p. diags. Mi. \$.50. Ph. \$2.00.

PB-22715 - "Preparation of thin films through thermal evaporation in high vacuum, investigation of their physical and chemical properties and development of suitable evaporation apparatus." Auwarter (in German). Sept. 1944, 2p. Mi. \$.50 Ph. \$1.00.

PB-22937 - "The production of end reflector mirrors in the German Optical industries." W. R. Knowlton, Sept. 1945, 8p. Mi. \$.50, Ph. \$1.00.

PB-22942 - "Investigation of Processing Equipment and Materials used by the German firms in the manufacture of lenses and prisms for

- military optical instruments." A. J. Devlin and R. F. Kleeth, Oct. 1945. 17p. Mi. \$.50. Ph. \$2.00.
- PB-22943 - W.R. Knowlton. "The production of partial reflecting mirrors in the German optical industries." Sept. 1945. 4p. Mi. \$.50. Ph. \$1.00.
- PB-22945 - "Some German developments on inorganic films of optical thickness." Sept. 1945. 18p. graphs. Mi. \$.50. Ph. \$2.00.
- PB-32597 - "Low reflection treatment of glass surfaces" First and Second progress reports. Apr-Aug. 1942." Llewellyn Richards and William C. Miller, June 1942. Mi. \$1.00. Ph. \$2.00. 9p.
- PB-32598 - "Low reflection treatments of glass surfaces." First and Second progress reports. Apr.-Aug.1942." Llewellyn Richards and William C. Miller, June 1942. Mi. \$1.00. Ph. \$2.00.
- PB-36006.- "Reflection-reducing films produced by the evaporation process." U.S. Bu. of Ordnance. Nov. 1942. 4p. Mi. \$1.00 Ph. \$1.00.
- PB-39361 - "Metallized paper capacitors, July 1945." S.J. Borgas and others. Feb. 1946. 76p. photos, drawings. Mi. \$2.00, Ph. \$6.00 Mimeo. \$2.00.
- PB-40294. - (BIOS-441). - "The platinum metal industry in Germany", July 1946. 71p. E. C. Rhodes and others. Mi. \$2.00.. Ph. \$5.00. (Photographs do not reproduce well).
- PB-52418. - "The preparation of thin boron films." R. W. Dodson and H. Russell, Jr. June 1944. 12p. drawings, table. Mi. \$1.00. Ph. \$1.00.
- PB-73416 - Siemens-Schuckertwerke A.G., Berlin, "Method of Producing Aluminum Surfaced Mirrors" 1940-1941. 15 frames (in German) Mi \$1. Ph. \$1.50 Micro FIAT-reel J236 - Frames 7044-7058 only.
- PB-77739 - D.O. Hendrix. "Methods of Making Triple Mirrors." Third Progress Report. July 1943, 7p., Mi. \$1. Ph. \$1.
- PB-78221 - "German methods of rhodiumizing, aluminizing, anti-reflection surface coatings, and allied subjects." K. M. Greenland and others. Mar. 1947. 32p. photos, drawings. Mi. \$1.00 Ph. \$3.00.
- PB-78591 - "Coatings of low and high reflectivity for optical surfaces." Luther B. Lockhart, Jr. Sept. 1944. 52p. graphs, tables. Mi. \$2.00 Ph. \$4.00.
- PB-78594 - "Survey of two-coat reflection-reducing films." L. B. Lockhart, Jr. Jan. 1945. 36p. graphs. Mi. \$1.00 Ph. \$3.00.

PB-78595 - "Reflection-reducing coatings for optical surfaces."  
Peter King and L. Lockhart. Mar. 1944. 28p. graphs, tables.  
Mi. \$1.00 Ph. \$2.00.

PB-78596 - "Reflection-reducing coatings for transparent  
plastic surfaces." Peter King. Jan. 1943. 13p. photos,  
tables. Mi. \$1.00 Ph. \$1.00

PB-79240 - Elliott, E. R. "German Optical Mirrors and Reflectors"  
Nov.-Dec.-1946. 27p. Mi \$1 Ph. \$2 (BIOS-FR-1342).

PB-79599. - "Protective coating of mirror surfaces with an  
oxide of silicon." J. E. Tausz and M. Tausz. May 1947. 11p.  
drawings. Mimeo. \$.50.

PB-92745. - "Studies on the structures and behavior of thin  
evaporated films of silver, aluminum, silicon, and germanium."  
George H. Hass. Dec. 1947. 12p. photos, drawings, graphs.  
Mi. \$1.75. Ph. \$2.50.

PB-92821 - "Silicon monoxide protected front-surface mirrors."  
Proj. 8-23-02-002 (XR 750). Geo. H. Hass and Noel W. Scott.  
Oct. 1947. 30p. photos, drawings, graphs, tables. Mi. \$2.00.  
ph. \$3.75. Mimeo. \$.75.

PB-99479 (Army) Engineers Research and Development Laboratories,  
"Aluminum-oxide protected evaporated aluminum mirrors and  
reflection-type interference filters using aluminum oxide as  
dielectric." G. Hass. June 1948. 11p. Mi. \$1.75, Ph. \$2.50.

PB-99756 (Army) Engineer Research and Development Laboratories.  
"Preparation of hard oxide films on evaporated aluminum surfaces  
and application of such films." George Hass. July 1949. 34p.  
Mi. \$2.25, Ph. \$5.00.

PB-101267 - "Production of surface mirrors by the vaporization  
of metal in a high vacuum," Grunewald and Eber, Apr. 1942.  
20 frames. (Text in German and English). Mi. \$1.75, Enl. Pr. \$3.75.

PB-105191 - "Symposium on vapor deposition of metals," Research  
and Development Board. May 1950. 76p. Mi \$3.50, Ph \$10.00.  
J. R. Townsend.

Order from British Information Services, 30 Rockefeller Plaza,  
New York 20, New York. PB-107963. "Thin films symposium at  
Harwell, March 1951", 51p. 1952, \$1.70.

References to the Literature

This portion of the chapter reviews in alphabetical order the names of those investigators and inventors whose names are mentioned throughout the text.

Alexander, P. P.

U. S. Pat. #2,038,402 Apr. 21, 1936

U. S. Pat. #2,047,350 July 14, 1936

U. S. Pat. #2,051,798 June 20, 1936

U. S. Pat. #2,100,045 Nov. 23, 1937

U. S. Pat. #2,153,786 Apr. 11, 1939

U. S. Pat. #2,440,135 Apr. 20, 1948

Anonymous

Electronics, March 1947, p. 174

Berghaus, B. & Burkhardt, W.

U. S. Pat. #291,590 May 18, 1943, "APC"

Biggs, O. H.

U. S. Pat. #2,064,369 Dec. 15, 1936

Burkhardt, W. & Reinecke, R.

U. S. Pat. #2,148,045 Feb. 21, 1939

U. S. Pat. #2,148,046 Feb. 21, 1939

Cartwright, A. E. & Strong, J.

American Phys. Soc. Vol. 13, p. 10, 1938

Case, T. W.

U. S. Pat. #1,584,728 May 18, 1926

Cornell, J. I.

Tele-Tech, January 1947, p. 98

Distillation Products Co.

Rochester, N. Y.

Edison, T. A.

U. S. Pat. #484,582 Oct. 18, 1892

U. S. Pat. #526,147 Sept. 18, 1894.

U. S. Pat. #767,216 Aug. 9, 1904

U. S. Pat. #865,688 Sept. 10, 1907

Edwards, W. H.

U. S. Pat. #2,058,429 Oct. 27, 1936

U. S. Pat. #2,067,907 Jan. 19, 1937

Canadian Pat. #362,808 Jan. 19, 1937

Ehrke, L. & Slack, C. M.

Jour. App. Phys. Vol. 11, p. 129, 1940

- Farkas, C.  
U. S. Pat. #945,504 Jan. 4, 1910
- Gardner, B. C.  
U. S. Pat. #2,107,784 Feb. 8, 1938
- Gardner, I. C. & Case, F. A.  
Bur. of Stand. Circ. #389, Jan. 1931
- Godley, P. & Balsbaugh, J. C.  
Electronics, April 1947, p. 113
- Godley, P.  
Iron Age, April 1, 1948.
- Goss, J. H.  
U. S. Pat. #2,346,483 April 11, 1944
- Haas, G. H. & Scott, H. W.  
Office of Technical Services, PB-Report #92,821, Oct. 1947
- Henderson, F. E.  
Office of Technical Services, PB-Report #421,1945
- Holbruck, R. H.  
U. S. Pat. #2,057,431 Oct. 31, 1936
- Holland, L.  
British Plastics, Vol. 27, p. 97, 1951
- Hulburt, E. O.  
U. S. Pat. #1,848,630 Mar. 3, 1932
- Kemet Laboratories, Inc.  
Cleveland, Ohio
- King Laboratories, Inc.  
205 Oneida Street, Syracuse, N.Y.
- Kingsley, T. G.  
U. S. Pat. #2,097,488 Nov. 2, 1937
- Lenz, C.  
U. S. Pat. #2,304,834 Dec. 15, 1942
- Macksoud, M. E.  
U. S. Pat. #2,164,332, July 4, 1939
- Metal Hydrides, Inc.  
Beverly, Mass.
- Nichols, W. H.  
Private Communication

- Ogle, J. C. & Weinrich, A. R.  
U. S. Pat. #2,432,538 Dec. 16, 1947
- Olsen, L. O. Smith, C. S. & Crittenden, E.C.  
Jour. App. Phys. Vol. 16, p. 425, 1945
- Pfanhauser, W. A. F.  
U. S. Pat. #1,758,531 May 13, 1930
- Pfund, A. H.  
Phys. Rev. Vol. 35, p. 1434, 1930
- Richards, L. & Miller, W. C.  
Office of Technical Services, PB Report #32,598, June 1942
- Richter, K.  
Kolloid. Zeit. Vol. 61, p. 208, 1932
- Richtmyer, F. K.  
U. S. Pat. #1,388,373 Aug. 23, 1921
- Russell, A. G.  
U. S. Pat. #1,986,536 Jan. 1, 1935  
U. S. Pat. #1,994,668 Mar. 19, 1935
- Saeger, C. M.  
U. S. Pat. #1,940,814 Dec. 26, 1933
- Siebertz, K.  
U. S. Pat. #2,164,595 July 4, 1939
- Schneider, M.  
Mod. Plast. Apr. 1950, p. 135
- Scott, Noel W.  
The Military Engineer, Mar.-Apr. 1949, p. 93-95
- Solar Mfg. Co.  
See Cornel, J. I.
- Sommer, L. A.  
U. S. Pat. #2,074,281 Mar. 16, 1937
- Strong, Prof. J.  
Procedures in Experimental Physics.
- Strickland, W. P.  
Jour. Soc. Mot. Pict. Eng. Vol. 49, p. 27, 1947
- Trautman, O. C.  
U. S. Pat. #1,700,002 Jan. 22, 1929
- Turner, A. F.  
Photo. Tech. Vol. 2, p. 48, 1940  
Chem. Abst. Vol. 35, p. 3403, 1941

- vonBose, J.  
U. S. Pat. #1,661,517 Mar. 6, 1928
- Walker, B. F.  
U. S. Pat. #2,303,871 Dec. 1, 1942
- Wehe, H. G.  
Bell Laboratories Record, Vol. 27, p. 317, 1949
- Williams, R. C.  
U. S. Pat. #2,079,784 May 11, 1937  
U. S. Pat. #2,151,457 Mar. 21, 1939
- Williams, R. C. & Ruedy, J. E.  
U. S. Pat. #2,239,452 Apr. 22, 1941
- Zworykin, V. K.  
U. S. Pat. #1,682,457 Aug. 28, 1928

United States Patents

484,582	Oct.	18,	1892	Edison, T. A.
526,147	Sept.	18,	1894	Edison T. A.
767,216	Aug.	9,	1904	Edison, T. A.
865,688	Sept.	10,	1907	Edison, T. A.
945,504	Jan.	4,	1910	Edison, T. A.
1,388,373	Aug.	23,	1921	Richtmyer, F.K.
1,584,728	May	18,	1926	Case, T. W.
1,661,517	Mar.	6,	1928	vonBose, J.
1,682,457	Aug.	28,	1928	Zworykin, V.K.
1,700,002	Jan.	22,	1929	Trautman, O. C.
1,758,531	May	13,	1930	Pfanhauser, W. A. F.
1,848,630	Mar.	3,	1932	Hulburt, E. O.
1,940,814	Dec.	26,	1933	Seager, C. M.
1,986,536	Jan.	1,	1935	Russell, A. G.
1,994,668	Mar.	19,	1935	Russell, A. G.
2,304,834	Dec.	15,	1942	Lenz, C.
2,038,402	Apr.	21,	1936	Alexander, P. P.
2,047,350	July	14,	1936	Alexander, P. P.
2,051,798	June	20,	1936	Alexander, P. P.
2,057,431	Oct.	31,	1936	Holbruck, R. H.
2,058,429	Oct.	27,	1936	Edwards, W. H.
2,064,369	Dec.	15,	1936	Biggs, O. H.
2,067,907	Jan.	19,	1937	Edwards, W. H.
2,074,281	Mar.	16,	1937	Sommer, L. A.
2,079,784	May	11,	1937	Williams, R. C.
2,097,488	Nov.	2,	1937	Kingsley, T. G.
2,100,045	Nov.	23,	1937	Alexander, P. P.
2,107,784	Feb.	8,	1938	Gardner, B. C.
2,148,045	Feb.	21,	1939	Burkhardt, W. & Reinecke, R.
2,148,046	Feb.	21,	1939	Burkhardt, W. & Reinecke, R.
2,151,457	Mar.	21,	1939	Williams, R. C.
2,153,786	Apr.	11,	1939	Alexander, P. P.

2,164,332	July	4,	1939	Macksoud, M. E.
2,164,595	July	4,	1939	Siebertz, K.
2,303,871	Dec.	1,	1942	Walker, B. F.
2,239,452	Apr.	22,	1941	Williams, R. C. & Ruedy, J.E.
2,346,483	Apr.	11,	1944	Goss, J. H.
2,432,538	Dec.	16,	1947	Ogle, J. C. & Weinrich, A. R.
2,440,135	Apr.	20,	1948	Alexander, P. P.
2,251,510	Aug.	5,	1941	Berghaus, B. & Burkhardt, W.
2,256,771	Sept.	23,	1941	Berghaus, B. & Burkhardt, W.
2,305,758	Dec.	22,	1942	Berghaus, B. & Burkhardt, W.

Canadian Patent

362,808 Jan. 19, 1937 Edwards, W. H.