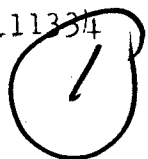


UNANNOUNCED

PB 111334



DTIC FILE COPY

Metallic Paints for
Printed Electronic Circuits
and Other Uses

by

Samuel Wein, Consultant

DTIC
ELECTE
DEC 01 1988
S D
CD

(Metallic Coatings on Non-Metallic Materials, V. 7)

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

19961126 135

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

1953

Distributed by
Business and Defense Services Administration
Office of Technical Services

~~Price: \$1.00~~

DTIC QUALITY INSPECTED 3

88 11 29 045

X21867

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 VII. METALLIC PAINTS
FOR PRINTED ELECTRONIC CIRCUITS AND OTHER USES

	<u>Page</u>		<u>Page</u>
<u>INTRODUCTION</u>	234	<u>II. COMMERCIAL METAL PAINTS</u>	
Decorative Finishes	234	(Continued)	
Luster finishes	234	Gold (Continued)	
Opaque finishes	234	Applied over Enamel	246
Color and Brilliance	234	Covering Power	247
Electrical Conductivity	235	Salvage of waste	247
Base Materials	235	Palladium	247
<u>I. TECHNICAL AND PATENT</u>		Platinum	247
<u>LITERATURE</u>	235	Silver	248
Mixing of paints	235	<u>III. METHODS OF APPLYING</u>	
Fluxes	236	<u>METAL PAINTS</u>	248
Degussa types	236	Surface Preparation	249
Barium	236	Stirring of Paints	249
Boron	236	Hand Brushing	249
Chromium	236	Dipping	249
Manganese	237	Spraying	249
Organic Solvents	237	Stippling	249
Metallic Constituents	237	Stamping	249
Aluminum	237	Silk Screen Printing	250
Antimony	237	Printing	251
Bismuth	237	Off-set process	251
Bronze	238	Transfer process	251
Cobalt	238	Drying	252
Copper	238	Firing the Paint	252
Gold	238	Kiln operation	252
Graphite	239	Maturing temperature	253
Indium	239	Precious Metal Products	254
Lead	239	Glass and Ceramic	
Molybdenum	240	Decorators	254
Nickel	240	<u>IV. PB-REPORTS</u>	255
Palladium	240	<u>V. REFERENCES</u> (listed	
Platinum	240	by author)	257
Rhodium	242	<u>VI. PATENTS</u>	260
Ruthenium	242	United States	260
Silicon	242	British	261
Silver	242	Dutch	261
Tin	245	Belgian	261
Uranium	245	Italian	261
<u>II. COMMERCIAL METAL PAINTS</u>	245	French	261
Copper	245	German	261
Gold	245	Japanese	261
Two-fire type	246	Russian	261

Accession For	NTIS DTIC Unannounced Justification	By	Distribution	Availability Codes	Level and/or Special



DTIC QUALITY INSPECTED 4

CHAPTER VII

Metallic Paints for Printed Electronic

Circuits and Other Uses

Introduction: Techniques developed in metallizing glass, ceramics, and similar materials by the application and firing of metallic paints have been greatly stimulated recently by the development of new uses in radio and electronics. While metallic films on glass have been used for hundreds of years, particularly gold and silver for decorative purposes, this chapter will consider in greatest detail materials and methods employable in the newer applications such as printed circuits.

Metallic paints are mixtures of metal powders or metal salts suspended in a liquid vehicle containing binders and thinners which must be fired at relatively high temperatures. The resultant coating is useful either to conduct electrical current or to provide an attractive decorative luster surface. The Mechanical Films described in Chapter VI are also suitable for electrical conductance but differ from Metallic Paints in that the binders used do not require high maturing temperatures.

These paints are commercially available in (1) finely divided powder form, (2) a paste form, mixed with a suitable organic vehicle to form more or less thin paint-like consistency, and (3) a prepared paint-like mixture, ready for use, requiring no additional thinners.

Decorative Finishes: Industry recognizes two types of metallic paint finishes.

1) Luster finishes when applied and fired on glass-like surfaces, will yield very thin films of brilliance. Base metals can produce luster colors but if the precious metal content exceeds a certain limit, metallic mirrors result which are known as bright gold, bright platinum, etc.

2) Opaque finishes of some precious metals after firing, remain matt and devoid of luster until burnished.

Color and Brilliance of Finishes: Gold and platinum are the only precious metals which in the form of oil paints yield specular films when fired on glass-like surfaces in the oxidizing atmospheres of pottery or glass industry kilns or lehrs. Silver, palladium and the other metals of the platinum group, in the same form and under like conditions yield, at best, lustrous finishes but not metallic mirrors. The results obtainable when these metals are heated in reducing atmospheres apparently have no practical value as commercial decorations or conducting films.

While platinum by itself can produce an acceptable bright metal film, when alloyed with gold it becomes whiter like silver and then has more sales appeal.

Palladium in combination with gold yields a white metal finish, "bright palladium," similar to platinum, but with a bluish grey tinge in color like chromium plate. When the wartime use of platinum for decorating pottery and glass was prohibited, bright palladium was substituted and later retained a popularity for decorative purposes.

Bright gold can be modified by the addition of other metals or luster pigments to yield metallic films of other than the gold color proper.

Such bright metal finishes are sold as bright green gold, bright white gold, bright copper, and bright bronze. All of these contain gold as the basic metal. The terms "bright copper" and "bright bronze" simply signify that the films obtainable with these items resemble in appearance and color the respective metals. Base metal paints alone, including copper and bronze, do not yield metallic films because their compounds cannot be reduced to the metallic state simply by heating in air such as is the case with precious metals.

Electrical Conductivity: Silver is used in metal paints for electrical and electronic applications, although metallic copper and aluminum are intrinsically lower in price, readily available in a similar powder form, compatible with the same binders and thinners, and are almost as good electrical conductors. The latter metals in powder form are too quickly oxidized or corroded in the atmosphere. Silver is one of the few metals that has the faculty of being highly conductive in either metallic, oxide, or sulphide form. Copper and aluminum are seldom used in metal paints for conductive coatings because their oxide or sulphide air corrosion products are very poor conductors.

Base Materials for Metal Paints: This chapter is concerned chiefly with products useful in the decorative, electrical, and radio industries based on fired metallic films. Other materials and applications are described in Chapter IX "Applications" while materials and methods of forming unfired conducting films of graphite or metallic powders have been described in Chapter VI.

In the listing of materials, methods, and applications of metallic paints, the following order will be followed:

- 1) Metal paints described in the technical and patent literature.
- 2) Metal paints commercially available.
- 3) The specific methods used in forming metal paints into decorative designs and "printed circuits".

TECHNICAL AND PATENT LITERATURE

The information in the literature on Metal Paints can be divided into variations in fluxes and in the principal metallic constituent. In each of these divisions materials will be treated in alphabetic order. Variations in treatment of the base materials will also appear in connection with discussions of coating materials.

Paints are usually mixed together in a porcelain jar pebble mill. The size of the particles produced depends on the number of revolutions given the ball mill, the initial size of particles, the relative weight and size of pebbles, and other operating factors. The grinding process must be carefully standardized not only to provide adequate covering power as in ordinary paints but also to obtain the uniform electrical properties needed in printed circuits.

FLUXES

A report distributed by the Office of Technical Services (#1) PB-100950, "Printed Circuits," prepared by the staff of the Engineering Electronics Section of the National Bureau of Standards, discusses the functions of ceramic and glass types of fluxes in providing adhesion and partial sintering of the silver particles during firing. The glass flux in finely powdered form consists of 10 to 15 per cent by weight in a silvering formation. Commercial ceramic glaze formulations are proprietary secrets apparently evolved from much older mixtures used in Germany. The ceramic fluxes used in Germany depends upon the employment, singly or in combination of compounds, of bismuth, titanium, barium, strontium, and manganese. The use of ceramic flux in small quantities increases the electrical conductivity and ability of the fired coating to accept soldering.

The DEGUSSA organization in a report distributed by the Office of Technical Services (#2) PB-85604, "Germany Radio Ceramics," and prepared by a British Intelligence Objectives Team in 1945, is said to have used bismuth resinate and manganese naphthenate fluxes in the formulation of their silver paints known as "Argalvan" (pages 210-228).

The proportion of these fluxes in the formulation was varied according to base material as follows:

<u>Base</u> <u>Material</u>	<u>% Bi₂O₃</u>	<u>% Mn₂O₄</u>	<u>Firing</u> <u>Temperature</u>
Mica	0.44	0.03	560-580° C
Glass	0.44	0.06	550-600° C
Porcelain	0.44	0.08	700-730° C

The bismuth resinate solution (containing 7.12% Bi₂O₃) was made as follows: Heat 600 grams high acid resin to 195° C and then add 1350 grams bismuth subnitrate gradually bringing into solution by stirring for 6 to 8 hours. To the cooled, crushed mass add 1300 grams nitro-benzene and sufficient turpentine to bring the total weight to 12000 grams.

The manganese naphthenate was a solution of 8.0% Mn₂O₄ in xylol, nitrobenzene, and turpentine.

For the series of silver paint known as "Poliersilber," the following flux was melted, quenched, and ball milled:

SiO ₂	(silica)	64.02
PbO	(litharge)	111.98
B ₂ O ₃	(fused boric acid)	23.98
Na ₂ CO ₃	(soda crystals)	17.303
TiO ₂	(titania)	10.56

Another flux believed to be a sodium alumino-titano-silicate and a solution of lead resinate were added in certain Poliersilber formulations.

Barium: Kretzer used a formula of barium with tin to which was added acids of the following elements, strontium, calcium, magnesium or aluminum. The formula was recommended for decorating glassware, enamel, etc.

Boron: Egly made a glaze of boracic acid or metallic borates to be metallized by conventional methods.

Chromium: Underwood recommended the following conducting glaze formulation: Feldspar 36.2%, flint 30.3%, whiting 15.0%, fluoride clay 13.0%, and

chromic oxide 5.5%. When this glaze was fired at 1200° F and cooled, hard soldering could be done on its surface.

Manganese: Rowland's form of metallic glaze was made up of: Ball clay 10%, aluminum hydrate (calcined) 37%, feldspar 37%, manganese dioxide 4%, chromic oxide 2%, iron oxide 2%, iron dichromate 8%. To this mixture was added 4% by weight of gum arabic and $\frac{1}{2}$ % benzoic acid, and water was added to a density of 1.3. The paste can then be applied to the given surface by means of a brush and fired.

ORGANIC SOLVENTS

In the formulation of Degussa "Argalvan" silver paints in the previously quoted Office of Technical Services report PB-85604 (2), a mixed solvent of nitrocellulose, ethyl alcohol, methylated spirits, benzyl alcohol, nitrobenzene, methyl cyclohexane, xylol, mono ethyl glycol ether, butyl acetate and citronella oil was used. A different proportion of these solvents, with nitrocellulose and ethyl alcohol omitted, was used as a thinner to obtain the desired viscosity.

METALLIC CONSTITUENTS

In the following listing of metallic paints, in alphabetical order according to the chief coating constituent, other fluxes and solvents will also be used.

Aluminum: Voight and Haeffner referred to the use of aluminum films on glass surfaces for infra-red heating.

Dykstra and Meyer deposited volatile aluminum films on high tension electrical knobs at 1250° to 1300°F.

Long made electrical resistors by causing finely powdered aluminum to be blown under pressure upon glass at 200° to 400°C.

Huysmans used mixtures of Senegal gum copal and aluminum sulphate with an added emulsion of calcium carbonate and powdered aluminum to ornament glass. Other metal powders, such as copper and magnesium, may likewise be used.

Antimony: Dykstra and Meyer sprayed molten antimony upon porcelain electrical insulator knobs held at 1250° to 1300° F. in a reducing atmosphere for four hours.

Bismuth: Hefter claimed improved adhesion by using colophonium or synthetic resins or the natural resins as binders with bismuth salts. Example 1, Rubber resin 12.5 grams, bismuth resinate 25 grams, oil of turpentine 62.5 grams. Example 2, Gutta percha 25 grams, bismuth oleate 25 grams, oil of turpentine 50 grams. Example 3, bismuth naphthenate 10 grams, oil of turpentine 90 grams.

Kerridge formed optical light filters by depositing bismuth from its sulphoresinate compound in an organic solvent. This compound applied to the surface of the glass decomposes on heating to leave a film of metallic bismuth. It is also claimed by the inventor that neutral light filters may be made from an alloy containing the metals gold and palladium or gold and platinum.

Bronze: Marelli formed a conductive refractory material by adding bronze powder as follows: Bronze powder 10%, powdered glass 50%, lead oxide 1%, refractory filler 1%, water 38%. This mixture was molded then heated to 320°C. and slowly cooled.

Cobalt: Davies treated ceramics with a solution of 1 to 10% cobalt powder, cellulose nitrate, amyl acetate and calcium borosilicate flux. This applied film is fired in an atmosphere containing nitrogen and 5% hydrogen as the temperature is slowly raised to 1100° - 1300° E. After tinning by immersion in a molten bath of an alloy of lead-tin (solder), wires may be attached by soldering.

Copper: Brenner mixed copper oxide, the necessary amount of carbon for its reduction, and ceramic materials. Hollow open articles were molded from this paste mixture, baked in a reducing atmosphere, then plated from an acid copper plating bath.

Hunt and Barrow coated porcelain insulators for electrical purposes with: Copper oxide 40 to 50%, zinc oxide 50 to 60%, mixed with enough water to make a thick paste. After a coating of sodium silicate was applied, the insulators were fired. A bright copper layer was formed by treatment in an acid bath containing powdered zinc, while rotating the insulator and brushing the surface.

Leibig immersed glass in molten cupric chloride for 4 to 5 minutes at temperatures near the softening point of the glass. For soda lime types of glass this temperature is about 650° C. The glass was then cooled and washed in concentrated hydrochloric acid solution. If a borosilicate glass was used, it was then steeped in a solution of either paraformaldehyde, urea or glycerine.

Fischer, Harnish and Russell formed metal sleeves by soldering to a porcelain surface which was metallized with: Copper oxide 80% and lead borate 20%. The surface was fired at 625° C., then plated with zinc and the metal sleeve or collar attached by soldering.

Gold: While paints of this metal are used very rarely in commerce for electrical or radio purposes, they are used where chemical vapors would effect silver, but not gold, and for other decorative purposes on glass.

Sauzay reported that practises of gold coating on glass, or mixing gold with glass were known to the Ancients.

Gold may be dissolved in aqua regia, then treated with potassium hydroxide or ferrous sulphate. The precipitate is filtered, a very small quantity of calcined borax is added, and then the mixture is made into a paste with spirits of turpentine. This paste is applied to glass by brush. On heating in a muffle furnace, the spirits of turpentine volatilize and the borax vitrifies. Thus the gold is firmly fixed on the glass and is burnished, first with blood-stone and then with agate.

Voigt and Hoeffner mixed gold sulphide with balsam of sulphur, using organic solvents such as benzene, with or without essential oils. Bismuth, boracic acid or phosphoric acid were added in combination as a flux.

Angenard employed a three solution formulation to apply gold to porcelain or glass to be fired at red heat.

Jira suggested the use of gold resinate with the following thinner: Acetophenone 5 to 20%, Fenchone 10 to 30% and nitrobenzene 10 to 25%.

Franceschini formed films of gold or platinum on glass, porcelain or terra-cotta by using gold chloride treated with balsam of sulphur or with oil of turpentine in which sulphur had been dissolved. The object was heated slightly, another coat applied to the surface, and then heated in a muffle furnace to form a bright metal layer suitable for plating with copper.

Malcolmson and Miner mixed gold chloride with terpene and sulphur, or with an alkali polysulphide. A paint was made by adding lavender, rosemary or other essential oils, to a thin consistency. This paint was applied to aluminum and fused into its surface at elevated temperatures (between 300° and 600° C.). An essential oil containing a saturated alcohol or ester such as terpenol with sulphur, was treated with gold chloride (10% aqueous solution) containing resins of bismuth, rhodium or chromium. The product so formed was then diluted to the desired viscosity with the oil for use as a paint.

Tomlinson formed films of gold on plate glass high in lime content by adding gold chloride and enough oil of rosemary to form a paste. The pasty mass was then thinned with about five times its weight of oil of lavender for application to glass surfaces and firing at 900°F.

Budnikoff formed metallic paints by boiling turpentine with 20% of sulphur on an oil bath with a reflux condenser and adding gold chloride. After some hours, a red brown liquid was formed which contained 0.4 to 14.6% sulphur, depending on the fraction collected, while about 50% of the turpentine remained as a resin. This compound, when further diluted may be used as a gold paint for glass, ceramics, etc.

Ballard added sulphur to gold compounds for decorative purposes on ceramic glass and the like surfaces.

Graphite: Paints of graphite may be used for films of high resistance and for subsequent treatment such as electroplating.

Werner applied graphite to porcelain or pieces of clay and subsequently heated them to 200 to 240° F.

Office of Technical Services report PB-26998 (3) deals with semi-conductors developed in Germany by the Rosenthal Porcelain Company. To a finely-ground, low-melting glass composition was mixed graphite in various proportions. This mixture was then sprayed upon porcelain and fused at 800° to 900° C. Resistors were made in two ranges, 50 to 100 ohms and 150 to 200 megohms. The resistivity produced was a function of the continuity of the graphite particles. This is also true when mechanical mixtures of graphite and resins are used for conducting surfaces.

Indium: An Indium Corporation of America alloy , consisting of 22.5 parts Indium to 77.5 parts of gold, has a working temperature of a little above 500°C. when used in coating metal with glass inserts. This is an ideal temperature, since exposure to any temperature above 600° C. would be destructive to glass - to - metal seals, whenever exposure to temperatures of 400° C. must be endured in service. Furthermore, the low vapor pressure of Indium prevents the unwanted contamination of adjacent parts which occurs when zinc is used in the brazing material.

Lead: Green and Blodgett coated borosilicate glass with a film of metallic lead derived from a mixture of a lead oxide with finely ground powdered glass of low melting point. A mixture containing 8% barium oxide and 61% lead

oxide was ball-milled for at least 24 hours to form an 80-mesh powder. A paint was then mixed in the following proportion: Powder 200 grams, Zapon varnish 100 grams, amyl acetate 150 grams. This paint was applied to the borosilicate glass and fused at elevated temperature. When the glass was cooled, reduction of the lead compound to the metallic lead may be accomplished by means of hydrogen.

Molybdenum: Lederer mixed molybdenum sulphide with amorphous sulphur to form a paste. This was formed into filaments or films, dried in air, and heated in the presence of a reducing gas (hydrogen), to form hydrogen sulphide and metallic molybdenum.

Nickel: Ward dispersed nickel flakes in the following binders: Natural or synthetic resins, cellulose derivatives, oils, paraffin, glyptals, aqueous solutions of gum tragacanth, sulphonated oils (castor, etc.). A typical mixture, easy to brush or spray, is: Nickel 100 parts, oil modified glyptal 2 parts, and mineral spirits 2 to 200 parts. The film is applied to glass and then baked at 400° C. for about 20 minutes to an hour. After the resin is carbonized, the metallic film will be found to adhere to the glass.

Palladium: This metal is lighter in weight and resembles silver in color. It is less costly but half as plentiful as platinum. Pure palladium is highly resistant to tarnishing, even when exposed to the vapors of sulphur, and, in this and other ways, resembles platinum in chemical properties.

Voigt and Haeffner suggested the use of palladium with printed circuits but gave no technical details.

Jira recommended a thinner for palladium resinate as follows: Acetophenone 5 to 20%, Fenchone 10 to 30%, and nitrobenzene 10 to 25%.

Rosenblatt described the preparation of three palladium solutions which can coat glass and ceramic surfaces. In preparing these solutions, palladium di-o-toluidine nitrate and palladium di-ammonium nitrate are caused to react with naphthol and acetic acid, aniline hydrochloride, or naphthylamine hydrochloride to form precipitates which are soluble in benzol or methyl and amyl alcohol.

Platinum: This metal is used instead of silver when greater resistance to chemicals of higher melting point, or ease of assembly by brazing are necessary.

Voigt and Haeffner, in printed circuit patent applications, referred to the use of platinum films on glass without giving technical details.

Johnson dissolved 100 parts of nitro-hydrochloric acid, evaporated to dryness, and added 25 parts litharge. The finely ground mixture was made into a thin paste-like consistency by the addition of an essential oil, such as lavender.

Brown dissolved sulphur in spike oil and mixed in a solution of platinum chloride in ether. Such a mixture may be applied to glass surfaces and fired.

Parsche mixed iron and copper sulphates with ochre or whiting in the proportions of 1 part metal salts to 2 parts of ochre. After this preliminary coating was fired at 750° F., a platinum film was made up of: Platinum chloride 50 grams, litharge 1 gram, and lead borate 1 gram, plus sufficient essence of lavender to make a thin paint-like mixture. This was applied to the preliminary coating and fired at 1000°F.

Rheinberg formed platinum films on glass with this solution: Collodium dissolved in methyl alcohol, 3 parts; platinum chloride dissolved in industrial alcohol, 3 parts; industrial alcohol, 3 parts; and bismuth chloride (1% solution), 1 part. All parts were by volume. A stronger bismuth chloride solution should be made up in industrial alcohol containing 5% hydrochloric acid. This should then be further diluted with industrial alcohol just before use, since very weak solutions of bismuth will not keep well. Rheinberg found that the bismuth compounds were better than the various lead salts he tested. The recommended temperature for use with Crown glass is 600° to 650° F. and the time is 3 minutes.

McKelvey and Taylor deposited platinum upon glass from a mixture of 1 part platinic chloride prepared by evaporating a 10% solution to dryness. The solution was then moistened with a few drops of absolute alcohol, ground finely in an iced mortar with 10 parts lavender oil. The latter was added gradually in small quantities. This solution was applied to the slightly warmed surface to be platinized as a thin film, then first carefully heated to drive off the volatile material, and finally heated to an incipient red heat to burn off the carbonaceous material and fuse the platinum into the glass. This method was not recommended for the preparation of reflecting surfaces, but was of value for the production of films on glass to which metal was to be attached, as by soldering.

Budnikov formed reaction products of either phosphorous-sulphur compounds, chlorine-phosphorous-sulphur compounds, nickel sulphide, or a mixture of these with chlorine compounds or alkali polysulphides. These were then mixed with gold or platinum salts and used to coat ceramics or glassware.

Smede and Shand formed a so-called "mahogany" metallic glaze as follows: Compound I - Albany slip 85%, feldspar 5%, iron oxide 3%, manganese oxide 2%, flint 5%. To the foregoing there was added: Compound II - platinic chloride 4.3%, oil of lavender and spike. Fire at 450° to 800° C. A modified and simple formulation for platinum films made by these inventors consisted of: Lavender oil 7.85%, platinic chloride 4.3%, gold chloride 3.1% and bismuth chloride 3.0%.

Bahrtdt used complex platinum compounds with alkyl halides or their derivatives containing sulphur with $Pt(CH_3)_3Cl$ the preferred compound. The platinum compound was applied to the surface of a material, warmed to about 150° to 180° C., and finally heated in a muffle furnace.

Marboe formed platinum mirrors under the same conditions as with copper mirrors, by decomposing an acetyl acetate compound. The compound may be prepared, according to the method described by Werner, by dissolving 1 part platinous potassium chloride in 8 parts hot water, and mixing with a solution of 3 parts (1:3) potassium hydroxide and then heating until the solution turns yellow. Acetyl acetone (2 parts) is then added and the mixture heated and stirred constantly for about 15 minutes. The fine yellow powder that forms is collected by filtration. An increased yield may be obtained by the addition of potassium hydroxide (1 part) to the filtrate and heating again and then repeating this process. The yellow powder obtained is washed well with water and dried.

Rosenblatt described the preparation of five complex platinum nitrate solutions which can form metallic films. In preparing these solutions di-metatoluidine platinum nitrate, platinum di-ammonium nitrite, platinum di-pyridine nitrite, platinum potassium nitrite, and platinum di-ortho-toluidine nitrite are caused to react to form salts or solutions soluble in benzol that can be diluted later with gasoline. The platinum potassium compound, however, is soluble in either ethyl alcohol or dioxane and is only slightly soluble in benzol.

Rheinberg used gun cotton dissolved in methyl alcohol as a binder for platinum chloride or chloro-platinic chloride. The mixture was applied to a glass surface and fired at temperatures between 500° to 740° C. The firing temperature can be reduced, if necessary, by adding a lead or bismuth salt, as follows: Collodion (6% dissolved in methyl alcohol), 3 parts; platinic chloride (12% solution using commercial alcohol as the solvent), 3 parts; ethyl alcohol, 3 parts; and bismuth chloride (1% solution using commercial alcohol as the solvent), 1 part. All parts are by volume.

Becker, Christensen and Kleimack mixed platinum chloride with oil of rosemary or oil of lavender and a little powdered glass. This is applied and fired at 400° to 800° C.

Jira suggested the following thinner for use with platinum resin-ate paint: Acetophenone 5 to 20%, Fenchone 10 to 30%, nitrobenzene 10 to 25%.

Rhodium: Voigt and Haeffner mentioned this metal in their patent specification for printed circuits on glass without giving technical details.

Rosenblatt formed rhodium films on glass using ammonium rhodium nitrite $(\text{NH}_4)_3\text{Rh}(\text{NO}_2)_6$ or $(\text{NH}_4)_2\text{NaRh}(\text{NO}_2)_6$ in suspension in o-toluidine. After the addition of alpha-naphthol and a few drops of acetic acid this suspension is boiled. The color gradually becomes dark reddish. The solution may be dissolved in benzol and then gasoline without causing precipitation of the reaction product.

Ruthenium films are also mentioned by Voigt and Haeffner for use on glass for printed circuits without giving technical details.

Rosenblatt described the preparation of sodium ruthenium nitrite for forming metallic films. The product of its reaction with acetic acid and either meta- or ortho-toluidine is soluble in benzol and can be further diluted with gasoline.

Ruthenium nitroso chloride is sold on special order by Baker & Company.

Silicon: Hyde vaporized and condensed silicon tetrachloride on a hot glass surface under reducing conditions to form a thin film with conducting properties. Such a film is iridescent in appearance and adheres tenaciously to the glass surface.

Silver: Of the precious metals used, metallic silver is used to the greatest extent, primarily because it is least expensive, has by far the best electrical conductivity, is easily compounded, is easily applied on glass and ceramics.

Voigt and Haeffner used silver films on glass surfaces for printed circuits but gave no technical details.

Chablin and Hemeque mixed a paste of silver chloride and spirits of turpentine, apply to a glass or porcelain surface, dry and fired. When cool, the film is plated from an acid copper bath

Marino coated a surface with a film of silver fluoride, exposed this first to illuminating gas and then to the vapors of carbon disulphide at 50° C to form silver sulphide. To enhance the adherence of the silver sulphide film it is subjected to the action of a rapidly rotating wire brush of brass, zinc, or copper.

An Anonymous writer reported in Glasshutte the following paste formulation: (1) silver chloride 31 parts, lead borate 3 parts, potassium nitrate 3 parts, and sodium borate 1.5 parts. (2) silver chloride 31 parts, lead acetate 1.5 parts, sodium carbonate 1.5 parts, potassium nitrate 4 parts, boric acid 4 parts, sodium borate 4 parts. An essential oil is added until a convenient paste is obtained. The silver chloride is reduced with zinc and acid, thoroughly washed, dried, and kept in the dark. If the acid for the reduction is sulphuric acid, the first compound is used, if hydrochloric acid is used the second formula is found to give better results.

Yunoki and Nakazawa made a metal paint of: Solvent 0.0 part, silver oxide 0.1 part. The solvent is made up of: minium 0.1 part, borax 2.2 part, and bismuth 0.5 part. The paint is then applied to the glass surface and fired at 380° C.

Muller formed a solution of 100 grams silver nitrate dissolved in about half a liter of water. The solution so obtained was precipitated by the addition of an excess of a sodium hydroxide solution. This precipitate was then washed until it is practically free from excess alkali, and collected upon a filter. This gave about 70 grams of silver oxide, which in the moist condition was then ground up with 60 c.c. mucilage or dissolved gum and the intimate mixture treated with 20 grams of glacial acetic acid, while actively stirring. It will be noted that this quantity of acid is about half of the calculated amount to convert the silver oxide present to acetate. The suspension was then diluted to the consistency of a thick cream with water and applied to the glass surface which was then heated to about 350° to 900° C. The silver compound was converted to metallic silver and the glue was decomposed.

Smith found that the addition of lead borate to silver powder gave better adherence and a more stable film of metal formed on the glass. A eutectic compound is formed with a melting point of 300° C if equal parts by weight of lead borate and lead fluoride are added. Barium fluoride when used as the flux in a metallizing composition, combined with lead borate or barium borate will produce as good or better results than lead borate alone. Barium borate alone or with lead borate as the flux may likewise be used. A typical formulation suggested by Smith is: powdered silver 65%, lead borate 3.5%, bismuth subnitrate 1.5%, and lavender oil 30%. To such a mixture may be added about 10% lead fluoride, barium fluoride, or barium borate. A commercial compound consists of silver carbonate 12 parts, 1 part of either flux, and sufficient lavender oil to form a paste. In the place of silver carbonate for better results, the equivalent weight of oxide may be used with borosilicate types of glass. This paint is fired onto the glass surface at 620° C for half an hour and cooled gradually.

Dol'nikov mixed fine silver oxide with a solution of resin in turpentine and powdered mica. Such paints may be applied to a given surface, dried and fired at 325° C. These paints are used as the conducting medium for electrical condensers.

Kollmar used the following formula: Powdered silver 20 grams, bismuth nitrate 1 gram, and resinic acid 4 grams, and 75 grams of a 50% resin solution in oil of turpentine is added. This proportion may be applied to glazed porcelain, dried, and fired at 730° C.

Gallup mixed silver powder (325 mesh) with molten wax, applied this to a surface and baked first at 200° to 300° C for 15 minutes, then at 400° to 600° C for one-half to one hour. The film so formed is usually used in a specially designed photoelectric cell accredited to Essig.

Jira used the following thinner for silver resinate: acetophenone 5 to 20%, Fenchone 10 to 30%, and nitrobenzene 10 to 25%.

Weyl experimentally observed that it is possible to reduce silver ions on a silicate glass by hydrogen gas at a temperature as low as 80° to 100° C.

Burke used the following formula for silver paint: silver oxide 16 ounces, bismuth subnitrate 1 ounce, mercuric oxide 1.5 ounces, and tung oil 2 ounces. Gum turpentine is used as the thinner.

Murray suggested the following formula: silver oxide 76%, raw linseed oil 4%, lead silicate 12%, and mineral spirits 8%. This paint requires firing at 450° C.

Fredenburgh formed geometric designs in silver by means of a rubber stamp or printing press on glass incandescent lamps using a compound of: silver oxide 70% and lead borate 30%. The lead borate when heated to 400° to 500° C readily fuses into a colorless glass which adheres to the glass surface, whereas the silver oxide when heated to between 250° to 300° C is completely decomposed into metallic silver and oxygen.

The above solids may be mixed with 50% gum dammar and either 50% raw linseed oil, or preferably 35% of glycerol, 15% linseed oil. In order to print this paint it must be tacky and have a heavy body. Gum dammar is employed to do this, whereas the linseed oil is used to dilute (thin) the mix. Glycerol serves the same purpose. Castor oil has been used also but by far the best results with greater brilliance are obtained by using gum dammar and linseed oil. Because the viscosity of the vehicle is so high when the gum dammar is used, it is preferable to add before milling a quantity of benzol to 1 part by weight of the vehicle. After completing the milling operation, the resulting ink fluid should be heated, preferably on a steam bath, until the benzol is evaporated, the ink being constantly agitated by stirring during this operation.

If the printing is to be performed by rubber stamps, it may be found desirable to employ glycerol as the vehicle. In such a case, the consistency thereof to enhance the milling operation may be adjusted by adding methyl alcohol. The fluid or ink, after thorough ball milling is preferably placed in a vacuum oven and heated to about 60° C to remove the alcohol. Generally the temperature and pressure should be maintained at such values as will satisfactorily effect the removal of the alcohol without harming the other ingredients of the ink. With a batch of 300 grams mixed in the proportions given, the temperature should be about 60° C and the heating continued for about 30 minutes, the pressure being adjusted accordingly.

The formulation of several types of Degussa silver paints is completely described in the Office of Technical Services (2) PB-85604 report, mentioned previously in discussion of fluxes and organic solvents. Silver resinate used in "Argalvan" solutions are formed from mixtures of 5 parts resin (high acid value) and 8 parts of silver carbonate. The resin is heated to 126° to 135° C before adding silver carbonate in small amounts awaiting the subsidence of the reaction before making further additions. The temperature must not be allowed to rise excessively. After completing additions in four or five hours, the temperature is held for a further half hour at 126° to 135° C. The powdered resinate cake has a silver content of approximately 56%.

The formulas for bismuth and manganese fluxes, solvents, thinners, thickeners, sulphur resins, for several typical silver paint mixtures, and for the preparation of silver carbonate and other metal paints are also given as used by Degussa organization in 1945.

Uranium salts have been described by Hufford and Scott, which produce uranium oxide films by evaporation from tetraethylene glycol solutions. This compound improves spreading qualities, polymerizes on heating, and is removed by burning off above 600°C. (See MDDC-1515).

Tin: Ward formed conducting films of tin on glass by exposure to the boiling vapors of tin chloride.

When tin chloride vapors are condensed on glass, and subsequently hydrolyzed, an iridescent film of variable conductivity may be obtained according to Biggs. Littleton also patented the use of tin.

Stong heated glass or ceramics to 700°C for 10 to 20 seconds. During this increase in temperature period, the surface is exposed to the vapors of boiling stannic chloride. Stong called this process "iridizing", because the surface usually becomes iridescent. Subsequently films of platinum or silver may be formed thereon.

Ward formed alloys of nickel and tin on glass and similar surfaces as follows: Example I - tin 50 parts, nickel 50 parts, ethyl cellulose 2 parts, toluol and alcohol 63 parts. In the formulations, flake types of nickel and tin powders are used. If water soluble methyl cellulose is used in the place of ethyl cellulose, 30 parts water is used instead; this is Example II. Example III uses - tin 50 grams, nickel 50 grams, urea resin 7.5 grams, butyl alcohol 20 grams, and xylol 20 grams. Example IV - tin 60 grams, nickel 50 grams, short oil modified glyptal resin 5 grams, and toluol 25 grams. Example V - tin 50 parts, nickel 50 parts, camphor 7.5 parts, and toluol 50 parts. The film may be applied to the given surface by any convenient means, then baked at 400°C for about 20 minutes to an hour.

COMMERCIAL METAL PAINTS

Commercial literature on metal paints does not reveal compositions of metals, fluxes, or solvents, but offers much information on methods and end products in which they are used.

Information received from several of the manufacturers is presented in condensed form in the alphabetical order of the metallic constituents. More complete instructions for use of the many varieties of metallic paints may be obtained from the industrial concerns engaged in this business.

Copper: The Hanovia Chemical & Mfg. Co. makes for general work Types "R", "P", and series 1, 4, and 10 bright copper or gold bronze finishes for brushing on glass and pottery.

Gold: The Hanovia Chemical & Mfg. Co. makes a series of bright gold paints ranging from a low viscosity mobile liquid to a viscous mass having a brown color, adhesiveness similar to that of varnish or lacquer, and transparency when spread thinly on clear glass.

Coatings of bright gold, applied by any of the usual methods, dry chiefly by evaporation of the solvents, leaving a glossy incrustation which is resistant enough to a light touch, but susceptible to being damaged by careless or repeated handling. This is more or less true of all unfired ceramic decorations which do not require a great deal of abrasion resistance since they are only intermediate phases of the decorating process.

In dry air and at normal temperature, bright gold decorations should dry within less than one hour. This is of special importance where the decorated ware is handled in periodic kilns. Use of tunnel kilns or lehrs involves less handling. Complete elimination of manual handling is possible where bright gold is applied by machines which may be constructed so as to automatically place the decorated pieces on the conveyors. Mechanical conveying affords the possibility of quickly drying ware by infrared rays from lamps suspended over the conveyor. This also shortens the period during which the decorations remain tacky and are apt to attract dust and fuzz.

A "Two Fire Type of Bright Gold" will adhere to clean and dry glass surfaces when directly applied and fired. A "Two Fire" type of bright gold was formerly used for the decoration of glass and still is preferred for certain purposes where the newer types are not applicable. This yields good results only on glass that has been subjected to so-called "mud treatment" which involves an extra fire and may be described as follows:

A thin paste is made of calcined copper sulphate with a suitable binder, such as corn starch, barytes or powdered chalk, and a sufficient quantity of water. The copper sulphate may be partly replaced by yellow ochre. The paste must be mixed very uniformly and must be kept stirred while being used.

The pieces to be gilded are dipped into this mudding mixture, the consistency of which is to be so adjusted as to allow a rather heavy homogenous layer of the mud to be deposited on it. After drying, the "mudded" pieces are fired to dull red heat and allowed to cool. They are then thoroughly washed and cleansed, and, when again dry, are ready to be gilded.

The following two recipes for mudding mixtures were stated by Mr. Rhiel to have been used with good results for a number of years. Formula I - copper sulphate 2 parts, barytes 3 parts. Formula II - copper sulphate 2 parts, yellow ochre 2 parts, corn starch 1 part.

The "mudding" process not only increases the sticking power of the gold, but also materially improves its color and brightness on the reverse side of the glass.

Bright Gold for Use over Fired Enamel Colors: If bright gold is to be fired on top of enamel colors or fusible enamels, these must be fired to maturity before the bright gold is applied. On unfired colors, bright gold turns black. But even on fired colors, most types of bright gold listed for application on ceramics and glass cannot be used. Since a coating of fired enamel color is many times thicker than a bright gold film, the latter, if applied over color, has ample chance to sink into the color when both are reheated to a temperature necessary for the maturing of the gold. As a result, the gold decorations may become dull and lusterless.

Some types of bright gold may be applied on any color that has been fired to maturity on glass or ceramics. However, when the decorated pieces are then refired to mature the gold, it is still advisable to regulate the firing cycle so that the peak temperature remains some ten or twenty degrees Fahrenheit below the maturing temperature of the color on which the gold has been applied. This will prevent the dulling of the gold film.

Bright gold compounds made by Hanovia Chemical & Mfg. Co. are graded according to their fine gold content. Grade "0" is the highest, grade 14 the lowest grade listed. Grade 9 is the standard for pottery, grade 10 the standard for glass.

Covering Power of Gold Paints: Metallized film thicknesses on glass and ceramics being used today vary from 0.000004" up to 0.005", depending on (1) the end application and (2) the method used. Thinner films are economical because they cover more area for a given weight of metal, 1 gram of gold in the form of a paint applied in a 0.000004" film will cover 800 square inches. To estimate the number of pieces that can be painted with one bottle containing 10 grams standard bright gold, take the number of square inches of area covered by the design on one piece and divide this figure by 8000. Thus, one bottle may decorate 4550 dinner plates of 9" diameter each 1/16" wide edge line of gold, at a cost of about 4/10ths of a cent per plate for gold.

Salvaging Gold Waste for Refining: Gold waste accumulations, emptied bottles or jars, rags, paper, brushes, etc., should be carefully collected and periodically shipped to a gold refinery.

The Hanovia Chemical Mfg. Co. reports 1000 well drained but not washed gold paint bottles contain enough gold to warrant its recovery as a separate lot. The refining of a lesser number of bottles is hardly profitable because of freight and refining costs. Smaller lots should, therefore, be thrown in with other or richer refuse.

It will also pay to save rejected and broken gold decorated ware, fired and unfired, until about 10 barrels are filled.

Waste material that also contains silver, platinum or palladium is processed by refineries for a small or nominal service charge with payment for the metal based on the market prices prevailing the day the shipment is received.

Bright Palladium: The Hanovia Chemical & Mfg. Co. grades #62 or #65 are for use on glass and pottery, BM-#78 is for machine banding on glass, #65-X is for spraying glass or pottery, and "ST-#163" is for hand stamping pottery or glass.

Platinum: Hanovia liquid bright platinum is essentially a solution in volatile oils and other solvents, of organic platinum and gold compounds of resinous character to be painted on glazed ceramic surfaces and heated. Besides the precious metals, this compound contains some base metal and organic compounds which serve as fluxes to fix the metal firmly on glass and ceramic surfaces.

This paint is available in different degrees of fluidity ranging from the consistency of a thin varnish to that of heavy molasses. A low viscosity type #05 is used for producing thin conductive films on porcelain, glass and other ceramic materials. Application is by means of a camel's hair brush or, if properly thinned, by spraying. The surface to be covered must be clean and dry. No more liquid platinum should be applied than is necessary to make the coating level out evenly. At room temperatures, the coating will dry in one hour sufficiently for careful handling. To speed production, the drying time may be reduced by passing the coated objects through a warm zone. General directions on firing are the same as for other ceramic coatings.

Silver: The DuPont Company makes a series of air drying silver paints. These may be baked at 572°F to expedite the drying of the film formed. An "F" formula series, number 4132 to 5052, has varying characteristics in electrical conductivity, flexibility, moisture and scratch resistance, static shielding, and ability to take soldering directly. They are varied to suit the following base materials: Bakelite, canvas, cellulose, acetate, ceramics, gelatin, glass, mica, paper, plastics, porcelain, wood, fabrics, steatite, etc. and for these methods of application: brush, dip, screen stencil, spray, squeegee, etc. They require different thinner solvents: butyl acetate, pine oil, turpentine, toluol, water, etc. and types of solder to be used in joining. Information on methods of application and use of these paints may be secured direct from the E. I. du Pont de Nemours & Company, Inc.

A report on "Electronic Miniaturization," distributed by the Office of Technical Services (4) PB-100949, describes the use of duPont #4731 paint (or its equivalent) applied by dipping, brushing, or screen printing. After allowing to dry in air, fire for 5 minutes at 700°C. The coating may either be copper plated and connections attached by regular 63 lead - 37 tin solder, or connections may be attached directly without an intermediate plating if 95 tin - 5 silver solder is used with poly-pane resin flux.

Linick Chemical Co. makes a type "CSL" paint that is a silver suspension in a binder with butyl acetate as the thinner. It is intended for use with paper, glass, porcelain, wood, steatite, and plastics. A suitable sealer such as shellac or varnish should be applied first when treating porous base material. After the film is applied by any method, it is allowed to air dry for 10 to 12 hours at room temperature or warmed to 100°C for speedier drying.

Metaplast Corporation. makes a series of silver paints for coating various kinds of plastics and other materials by screen printing, spraying, and other methods. Among thinners and solvents employed are amyl acetate, cellulose acetate, carbitol acetate, cellusolve, xylol, butyl, acetate, or methyl cellusolve.

METHODS OF APPLYING METAL PAINTS

The following pages will be concerned with methods of preparation of the metal films on given surfaces and their conversion into decorative designs and printed circuits.

The techniques of making printed circuits and their utility in radio and other electronic equipment has been described in a report by the Office of Technical Services (1) PB-100950 - "Printed Circuits" - previously cited. More compact electronic devices can be produced in lighter-weight, higher powered equipment while retaining the advantages of mechanized production processes. The advantages inherent in printed circuit production processes are largely based upon the system of metallizing non-conductors to form electrically conducting patterns, and especially, with screen-process printing and special silver-pigmented paint. At this time the screen process seems to be best suited of all coating processes for this application, although other methods including dipping, brushing, decalcomania transfers, etc. also deserve mention.

The history, as well as the technical and patent literature on applications of printed circuits to electronic uses will be discussed in Chapter X (Applications), of this series.

Surface Preparation: The surface prior to the formation of the metal film should be cleaned by caustic soda or equivalent commercial cleaners and then washed with running water. Once the surface has been cleaned, it must not be touched by hands or other sources of grease or dirt.

Stirring of Paints: Before and during use, the metal paint must be thoroughly stirred in order to avoid separation of the solids from the vehicle. A convenient method of keeping the paint stirred is to roll the covered container on its side on a set of mechanical rolls. This method of stirring avoids undue exposure to the air with loss of solvent.

Hand Brushing: It is important to use an appropriately shaped, good quality camel's hair brush, or its equivalent, of the correct size for the type of work. Use mechanical holders and an arm rest to assist the hand employed for brushing. By so doing, fatigue is minimized and better applications with faster production results.

Dipping: This method requires a fairly rapid drying, limpid paint that yields a uniform cohesive coating. The portion of the glass or ceramic part requiring metallizing is submerged in the paint with masking paint, masking tape, and other means of blocking utilized if required.

Spraying: This technique is used where large surfaces are to be covered, since they reduce labor costs by fast rates of production compared to brushing methods. However, loss of precious metallic paints by this method is generally too costly unless equipment for its complete recovery is provided.

Spray guns for 20 pounds pressure with ease of cleaning and control of the volume conical or flat shape, and the pressure of the spray should be provided.

The covering power depends upon the method of application; the maximum is obtained on large flat sheets and is about 10 square feet per troy ounce. Much of the paint can be lost on spraying small objects so that the coverage may be as little as 3 square feet per troy ounce.

Stippling: Thick metallic paints are usually reduced to the consistency of thin molasses by heating as in a shallow dish on an electric hotplate to exclude the risk of fire. The thickened metal paint is spread on a glass slab by means of a palette knife or spatula. A sponge, thoroughly washed and dried and cut to the desired size, affords a convenient tool for picking the metal paint up from the slab and applying it to the given surface. As the sponge becomes saturated with the metal paint, the impression will appear increasingly blurred. The sponge should then be washed in the same solvents recommended for cleaning brushes.

For better uniformity during a longer run of a given stippled pattern steel wool has been successfully substituted, because it retains its spring almost indefinitely and does not absorb enough metallic paint to require frequent cleaning.

Stamping: The metallic paint is reduced in consistency as for stippling. The procedure for hand stamping is as follows: Spread the metal paint on a glass slab using a printer's knife or spatula. Then roll it out to a

thin layer by means of a rubber roller. The operator picks the metal paint up from the thin film with his rubber stamp and dabs it to the given surface. It is advisable to make a few preliminary tests in order to determine whether the metal paint on the slab has the right "tack." If it is too soft or "open," the metal paint may squash and yield blurred instead of clean-cut stamps; in that case it should be allowed to set until it works properly. If the metal paint is too stiff or tacky, the stamps will be more or less dotted with pin-holes. It is also important to see to it that the metal film on the slab has the correct tackiness because if it is very thin, not enough metal paint is applied to the surface to be coated and the work will appear discolored after firing. Too thick a film, on the other hand, will cause squashing the same as if the metal paint were too soft.

After the metal paint is picked up from the slab a new portion should be taken and spread again from its supply vessel. If the metal paint becomes too tacky, as is shown by increased suction when lifting the rubber stamp from the ware, the addition of a small amount of fresh metal paint will help to restore its original consistency.

Silk Screen Painting: This process is adapted to glass and ceramic printing, is really a modern development of the arts of stencilling which dates back to the early Egyptians and Orientals. It has been only within the last decade, however, that the screen process technique has been commercially developed, first for paints, inks, and dyes, and now as described by Remington for metallic paints for application to glass and ceramic surfaces.

Early screen process stencils were probably made by blocking out, or filling mesh of the screen with a varnish or some other suitable medium, so that the color could be pressed or "squeegeed" through the open or unvarnished portions. Similar modified or improved processes, such as the Keyline, glue block lacquer process, glue-Tusche, and glue-sized screens are employed today. However, the utilization of a coarse silk screen with a thin paper stencil on the under side was a very important improvement.

It has only been within comparatively recent years that the silk screen process has been generally used for the application of metallic paints. The process lends itself exceptionally well to printing flat surfaces as well as round or irregular surfaces.

The heart of silk screen printing method is the screen plate itself. Whether it is to be used on a machine for forming designs (decorations) or printed circuits on round or irregular surfaces, or on a table for flat pieces, the constructional details of the silk screen are essentially the same.

The preparation of photographic screen stencils is based on the discovery made many years ago that a colloid, such as glue, gelatin, or gum arabic containing a bichromate is rendered insoluble in water when exposed to a source of light. Hence, if a film of colloid is exposed to a source of light through a negative, those portions of the colloid that will be affected by the light will become insoluble and those portions of the film that have not been affected by the light are completely soluble in water and washed out in running water.

The modern "silk screen" stencil employs photographic methods to form designs with far better or sharper lines on the surface to be decorated or the printed circuit to be formed.

Zahn in his book "Silk Screen Methods," page 81, gives a method for forming the screen stencil photographically;

- 1) A wooden frame of the given size is made.
- 2) Silk is stretched under tension by any convenient means such as by nails or special glues over the frame.

- 3) The silk is now sensitized with bichromated gelatin and dried in a dark room.
- 4) A photographic negative is now placed against the surface of the sensitized silk and exposed to a source of light. The photographic negative has on it the specific design of the decorative figurine or the form of a printed circuit.
- 5) When the negative is taken away, the sensitized silk is "developed" as by allowing tap water to run over its entire surface. In this fashion the portion of the sensitized gelatin that has been exposed to light will become insoluble in water and will not wash out. On the other hand, that portion of the sensitized gelatin which has not been exposed to light through the photographic negative will wash out in the water.
- 6) The silk screen so formed is now placed in a mild air draft and allowed to dry.

It is beyond the scope of this book to describe further technical details of screen printing or "serigraphy" as it is sometimes called. This method of printing with stencils ranks with relief, intaglio, and planography as one of the four basic methods of printing. For additional information references should be made to the following books and technical sources:

Zahn, "Silk Screen Production," page 81.

Swiggett, Mod. Pl., Aug. 1951.

Hiett, "Screen Process Production," page 29.

Brunetti & Curtis, Bureau of Standards Circular #468, Nov. 15, 1947.

Kosloff, "Screen Process Printing," 1950, 193 pages. Signs of the Times Pub Co., Cincinnati, Ohio.

Middleton, "Silk Screen Process," 1950, 136 pages, Blanford Press, Ltd., 16 W. Central St., WCl, London, England.

Beigeleisen & Busenmark, "Silk Screen Printing Process," 2nd ed., 1941, 225 pages, McGraw-Hill Book Co., 330 W. 42nd St., New York 18, N. Y.

Screen Process Printing Association (International), 3325 So. Michigan Ave., Chicago 4, Illinois.

Printing: Although the literature (patent and technical) refers to printing methods, as the use of a letter press or its equivalent, yet there is no mechanical device available to accomplish this, although considerable discussion is heard in the industry concerning it.

Offset Printing: The recesses of an etched metal are filled with metal paint, picked up with a suitable roller or tissue paper, and transferred to the nonmetallic surface. This method has been commonly used in the United States and abroad to reproduce designs, floral, and geometric, for glass and ceramic surfaces with marked results.

The Transfer Process: This process produces designs on given surfaces by picking up the metal paint from a master plate, applying to revolving, smooth rubber composition roll and transferring thence to the object being coated.

In another procedure a rubber roll with protrusions on its surface makes the desired print.

A third method of transfer printing fills in an etched-out design of a steel plate with a suitable printing ink, then transfers it to a printing paper by contact and aided usually by light brushing. The paper is then peeled off with it all of the paint left in the crevices of the steel plate placed in contact with the object to be coated. On wetting with water, the paper is then released, leaving a surprisingly well defined print on the object.

Drying: While the manner in which the painted coating is dried is important, it should be varied to obtain best results for the type of paint and base material used. For example, one manufacturer specifies a three-hour drying at 60°C for a silver paint which is manufactured for use on thermo-plastic surfaces.

Longer drying times may be advantageous to secure better adhesion and electrical conductivity.

Firing the Metallic Paint: After the base material is coated or decorated by any of the methods discussed, it is heated to the so-called "maturing temperature" of the metal paint. During this process, the essential oils volatilize leaving a thin film of metal.

Kiln Operation: It is necessary to quickly dispose of fumes originating from the metal painted surface, and to forestall the entrance into the firing chamber of reducing fuel gases or fumes since otherwise dull streaks, greyish white scum, or a burn appearance of the coating may result.

Two requirements necessary for good results are therefore required. First, the firing chamber must be efficiently ventilated and, second, cracks or holes through which fuel gases might enter must be sealed before each firing.

In a periodic or muffle type kiln, the fumes will usually find a ready escape if the door is left open, or at least partially open, during the smoking-off period. Where this cannot be done, a smoke pipe should be installed in the ceiling of the kiln to be closed by a damper when the temperature has reached about 840° to 900°F (450° to 480°C). An air intake is then opened into the bottom part of the front.

For ventilation of tunnel kilns or lehrs, a forced draft system utilizing preheated air is required. Free circulation of air and complete combustion of the organic matter in a kiln is required to obtain an adherent metal film; therefore, pieces must not be spaced too closely. Organic matter of the metal films should be completely destroyed and dissipated at dull red heat if ventilation is adequate. This can be readily observed either by leaving the door open or through a peephole in the door. Heating is continued with the door closed, until the maturing temperature of the paint has been reached. The heat should then be shut off and the kiln allowed to cool down to ordinary room temperature with the kiln door kept closed or at least only gradually opened after every trace of red heat color has disappeared.

Continuous kilns are advantageous because the pieces require a minimum amount of handling and are discharged in good annealed condition. A pilot plant

with a continuous belt furnace designed specifically for use with printed circuit materials is described in Bureau of Standards Technical Report #1551.

If heat at the beginning of the firing cycle increases too rapidly, a crust containing carbon may form on top of the metal film. This is hard to burn off because the flux also acts prematurely. For most glass and ceramic products this is of little consequence, except that too rapid firing may also result in the crazing or blistering of the metal film. The maturing temperatures of metal films on glass and ceramics are generally high enough to destroy all traces of carbon. Some glasses with lower maturity temperature may result in a dark gold film color on the reverse side of glass and some times minute holes may form by escaping carbon dioxide gas. Troubles occur most frequently on gold bands near the top of tumblers or other tall objects where the glass may heat up too quickly.

To prevent these defects decorated ware should travel through a comparatively long pre-heating zone where it slowly and gradually acquires the temperature necessary for the complete elimination of all organic constituents of the metal paint before the maximum heat zone is entered. Glass decorating kilns, called "lehrs" are especially constructed to take care of this requirement. The actual duration of the pre-heating period depends on factors such as the following: (1) the pre-heating of bulky articles of pressed glass must be slower than that of thin stem glasses of similar composition; and (2), objects of hard glass can be pre-heated more quickly than the same type of objects in softer glass. As a general directive, it may be said that for a given type of glass, the peak temperature in the fire box will have to be raised if the belt speed is increased, it must be lowered if the belt speed is reduced.

Maturing Temperature: The term "maturing temperature" has been described as the degree of heat which is necessary to accomplish a perfect bond between the metal paint and the surface to be decorated. Different types of glass as well as of ceramics require different peak temperatures for their satisfactory and permanent decorations with metal paints.

The degree of maturity may change even for one and the same type of product according to firing conditions, such as type and size of kiln, rate of temperature increase, bulkiness of objects, etc. The following table lists, for the principal ceramic and kindred bodies, the approximate degree of temperature at which bright gold matures when fired in periodic kiln. The temperatures are only intended as comparative values to be varied according to the factors previously discussed.

Ceramic Product	Deg. C	Deg. F	Cone
Vitrified China (European, Oriental)	800	1472	015
Vitrified China (American Hotel China)	770	1418	016
Vitrified China (American Dinnerware)	740	1364	017
Semi-Porcelain (Terra Cotta)	740	1364	017
Belleek, Bone China	710	1310	018
Quartz Glass	680	1256	019
Resistance Glass (Pyrex, etc.)	650	1202	020
Lime Glass	590	1094	022
Heavy Lead Glass	530	986	---
Thin Lead Glass	500	932	---
Quartz (Rock Crystal)	550	1022	---
Mica	540	1004	---

The equivalence in cones given in the last column is based on the old tables established by Seger and his successors. They are only approximate. For a study of the modern use of pyrometric cones, we recommend the publication by Edward Orton, Jr., American Ceramic Society, Columbus 2, Ohio, "The Properties and Uses of Pyrometric Cones."

Properly fired silver should adhere tenaciously to glass or ceramic surfaces with a tensile strength of approximately 3000 pounds per square inch.

Precious Metal Suppliers: The following lists some of the producers of precious metals or compounds covered in the chapter:

American Platinum Works, Newark, New Jersey.
Baker & Co., Inc., Newark, New Jersey.
Drakenfeld & Co., 45 Park Place, New York, N. Y.
E. I. du Pont de Nemours & Co., Inc., Wilmington, Dela.
Fulton Gold Refineries, 71 Fulton Street, New York, N. Y.
Handy & Harmon, 82 Fulton Street, New York, N. Y.
Hanovia Chemical & Mfg. Co., 1 Central Ave., E. Newark, N. J.
Kastenhauber & Lehrfeld, 21 W. 46th St., New York, N. Y.
Metaplast Corp., Long Island City, N. Y.
Platinum Chemicals, Inc., 53 So. MacDonald St., Mesa, Ariz.
Precimet Laboratories, 64 Fulton St., New York, N. Y.

Glass and Ceramic Decorators: The United States Census of Manufacturers for the year 1937 gives a listing of business done by decorators of glass and ceramics. The following lists some of the firms engaged in the manufacture of decorative applications of metal paints:

Atlas China Co., Inc., 137 - 5th Avenue, New York, N. Y.
Baker China Studio, 219 Monmouth St., Trenton, N. J.
Belmont China Co., 1441 Etruria, East Liverpool, Ohio.
Benedict Mfg. Co., East Syracuse, N. Y.
Bernthal Co., 137 - 5th Avenue, New York, N. Y.
Bruick Industries, 7127 $\frac{1}{2}$ Van Nuys Blvd., San Francisco, Calif.
Burke Industries, 5007 N. Clark St., Chicago, Ill.
Canonsburg Pottery Co., Box 110, Meadow Lane, Canonsburg, Penna.
Canterbury Silversmiths, Inc., 617 - 62nd St., Brooklyn, N. Y.
Chicago Silver Co., 226 So. Wabash Ave., Chicago, Ill.
Ciske & Dresch, 17 No. Wabash Ave., Chicago, Ill.
DeLite Mfg. Co., 128 W. 24th St., New York, N. Y.
DeLuxe Decorating Works, 12 W. 18th St., New York, N. Y.
Eastern China Co., 522 E. 81st St., New York, N. Y.
Emerald Glass Co., 3020 Roswell, Los Angeles, Calif.
Empire State Glass Decorating Co., 197 Grand St., New York, N. Y.
Friedman Silver Co., 366 - 5th Ave., New York, N. Y.
Gunner Mfg. Co., 31 Forest St., Attleboro, Mass.
Holt & Co., 362 - 5th Ave., New York, N. Y.
Imperial Glass Corp., Bellaire, Ohio.
Johnson China Co., Inc., 1150 Southard St., Trenton, N. J.
Kass China Co., 909 Vine St., East Liverpool, Ohio.
Keystone Silver Co., 804 Sansome St., Philadelphia, Penna.

Lenart Import Co., 225 - 5th Ave., New York, N. Y.
Levy Brothers China Co., 79 - 5th Ave., New York, N. Y.
Lith-O-Ware Products, 2450 So. Ashland Ave., Chicago, Ill.
Lotus Glass Co., Barnesville, Ohio.
Mesik Mfg. Co., 247 E. 23rd St., Los Angeles, Calif.
National Silver Deposit Ware Co., 44 W. 18th St., New York, N. Y.
New England Ceramics, Inc., Torrington, Conn.
Pacific China Decorating Co., 83 Metropolitan Ave., Brooklyn, N. Y.
Pavel & Co., F., 15 W. 16th Street, New York, N. Y.
Prill Silver Co., 53 W. 56th St., New York, N. Y.
Revere Silversmiths, Inc., 306 - 5th Ave., New York, N. Y.
Rockwell Silver Co., 24 Randolph Ave., Meriden, Conn.
Royal China & Novelty Co., 2715 Archer Ave., Chicago, Ill.
Royal China, Inc., 15th St., Sebring, Ohio.
Rulon-China Decorator Co., 78 Wall St., Trenton, N. J.
Schultz Co., A. G. 423 E. Lombard St., Baltimore, Md.
Senegal Potteries, Inc., 225 - 5th Ave., New York, N. Y.
Sinaco Co., Inc., 381 - 4th Ave., New York, N. Y.
Soria & Simon Co., 403 E. 62nd St., New York, N. Y.
Soriano Ceramics, Inc., 20-21 Steinway St., Long Island City, N. Y.
Stein Importing Co., 712 So. Olive St., Los Angeles, Calif.
Stetson China Co., 666 Lake Shore Drive, Chicago, Ill.
Stouffer Co., J. H., 902 So. Wabash Ave., Chicago, Ill.
Tatler Decorated Ceramics, Trenton, N. J.
Tolpin Art Studio, 3122 Lawrence Ave., Chicago, Ill.
Vogue Ceramics Industries Co., 9 E. 26th St., New York, N. Y.
Weissman Co., Inc., 189 W. Martin St., E. Palestine, Ohio.
World Hand Forged Mfg. Co., 338 Wythe Ave., Brooklyn, N. Y.

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-1292. Synder, C. L. "Specialized Ceramic Products; Their Use in German Communication Equipment." 1945, 40p. Mi. \$.50. Ph. \$3.00. (FIAT - FR-278).

PB-12537. Lorenz, C. A. G. "Method of Depositing Solderable Metallic Layers on Ceramics." Oct. 1944, 6p. (Text in German). Mi. \$.50. Ph. \$1.00.

PB-19435. Shuck, W. and Heintz, G. "Methods of Setting Up Electrically Conductive Layers on Electrically Non-Conductive Plastics, Especially Lead Electroplating." Dec. 1944, 6p. (Text in German). Mi. \$.50. Ph. \$1.00.

PB-26998. "German Developments in Semi-Conducting Materials (resistors, thermistors, varistors, etc.)." Jan. 1946. Odarenko, T. M. 109p. Mimeo. \$2.75.

PB-39353. Ward, C. O. L. and others. "Resistors and Fixed Capacitors Produced in Germany." April 1946, 85p. drawings. Mi. \$2.00. Ph. \$6.00. Limited supply of Mimeo. \$2.25.

PB-49209. Taylor, J. E. and others. "German Research on Rectifiers and Semi-Conductors." Sep. 1946, 51p. diags. table. Mi. \$2.00. Ph. \$4.00. (BIOS - FR-725).

PB-40291. "The German Radio Component Industry." Oct. 1945, 71p. F. McGinnety. Mi. \$2.00. Ph. \$5.00. (BIOS - FR-563).

PB-60903s2. "Degussa Formulae Relating to Enamels." May 1946. 25 frames, Mi. \$2.00. Enl. Pr. \$5.00. (BIOS - FR-788).

PB-85604. "German Radio Ceramics," Borgas, S. J. and others. 353p. diagrams, drawings, tables. Microfilm \$7.00. Photostat \$36.00. (Pages 210-228 Photostat \$4.25).

PB-100949. "Electronic Miniaturization," U. S. National Bureau of Standards, Electronics Div., Engr. Electronics Section. (NAer. 00685). Final report to Bureau of Aeronautics, Dept. of the Navy, Dept. of National Defense. Prepared by the Staff of the Engineering Electronics Section. Sept. 1949. 189p. photos, diagrams, drawings, graphs. Mimeo. \$4.75.

PB-100950. "Printed Circuits." U. S. Bureau of Standards, Electronics Div., Engr. Electronics Section. Final Report. NBS Project No. 01-36-522. Jan. 1950. 99p. photos, drawings, graphs, tables. Mimeo. \$1.75. NAer 00686.

PB-103988. "Report on Research Work for Improvements in the Manufacture of Ceramic Liquid Gold." Y. Tosaku and N. Kenji. 13 frames. Mi. \$1.75. Enl. Pr. \$3.75. (In Japanese). English abstracts included. (PB-103988s) 1p. Mi. \$1.25. Ph. \$1.25.

PB-107405. "Study of Automatic Printed Circuit Techniques." L. Balamuth & others. Apr. 1950, 175p. Balco Research Laboratories, Newark, N. J. Mi. \$6.50. Ph. \$22.50.

PB-107508. "Influence of a Transverse Magnetic Field on the Conductivity of Thin Metallic Films." E. H. Sondheimer. May 1950, 13p. Mi. \$1.75. Ph. \$2.50. M.I.T. Research Lab. of Electronics.

PB-107510. "Printed Circuit Techniques: An Adhesive Tape-Resistor System," B. L. Davis, Feb. 1952, 88p. Available from Supt. of Documents, U. S. Government Printing Office, Washington 25, D. C. Price: \$.30. (National Bu. Stds. C-530).

The following report is available now only in Atomic Energy Commission depository (reference) libraries, but is scheduled to be published as

"National Nuclear Energy Series," Div. IV, vol. 14B, Part II, Paper 16.1, by the McGraw-Hill Book Company 330 W. 42nd Street, New York 18, N. Y. MDDC-1515, Hufford and Scott.

REFERENCES TO THE LITERATURE

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

Angenard, L. P.

U.S. Pat. #43080, June 14, 1861. U.S. Pat. #46062, Jan. 31, 1865.

Anonymous

Glasshutte, vol. 45, p. 297, 1915.

Ballard, K. H.

U.S. Pat. #2,383,704, Aug. 28, 1945. Chem. Abst. vol. 39, p. 5428, 1945.

Bahrtdt, A.

German Pat. #595,356, Apr. 9, 1934.

Becker, J. A., Christensen, H., and Kleimack, J. J.

U.S. Pat. #2,418,461, Apr. 8, 1947.

Biggs, O. H.

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

Brenner, R. E.

French Pat. #652,748, Sept. 21, 1927. Chem. Abst. vol. 23, p. 3785, 1929.

Brown, M. W.

British Pat. #3148, Sept. 15, 1874.

Brunetti, C. and Curtis, R. W.

National Bu. of Standards' Circular 468, "Printed Circuit Techniques," Nov. 15, 1947. Price: \$.25. (Order from the Supt. of Documents, U. S. Government Printing Office, Washington 25, D. C.)

Budnikoff, P. P.

Zeit. Angew. Chem. vol. 35, p. 653, 1922. Russian Pat. #3433, Aug. 31, 1927; Chem. Abst. vol. 17, p. 1117, 1923; Chem. Abst. vol. 22, p. 4750, 1928.

Burke R.

Private Communication.

Chablin, L. & Hemeque, M.

British Pat. #580, Mar. 10, 1856.

Davies, D. A.

British Pat. #593,256, May 28, 1945.

Degussa

See Office of Technical Services, PB-85604.

- Dol'nikov, L. M.
Russian Pat. #551,132, June 30, 1939. Chem. Abst. vol. 35, p.3014, 1941.
- du Pont & Company, Inc., E. I.
Electrochemical Division, Wilmington, Del.
- Dykstra, L. J. and Meyer, E. M.
U.S. Pat. #2,274,955, Mar. 3, 1942, Ceram.Abst. May 1942, p. 105.
- Egly, G.
U.S. Pat. #1,103,353, July 14, 1914.
- Fischer, E. H., Harnish, J. D., and Russell, R.
U.S. Pat. #2,434,555, Jan. 13, 1948.
- Franceschini, F.
Ind. Silicati, vol. 10, p7,1932. Jour. American Ceram. Soc. vol. 11,
p. 436, 1932. Chem. Abst. vol. 27, p. 2628, 1933.
- Fredenburgh, M. N.
U.S. Pat. #1,538,890, May 26, 1925.
- Gallup, J.
U.S. Pat. #2,162,808, June 20, 1939.
- Green, R. L. and Blodgett, K. B.
Jour. American Ceram. Soc. vol. 31, p. 89, 1948.
- Hanovia Chemical & Mfg. Co.
1 Central Avenue, East Newark, N. J.
- Hefter, A.
U.S. Pat. #2,081,234, May 25, 1937.
- Hunt, M. H. and Barrows, G. M.
U.S. Pat. #1,987,683, Jan. 15, 1935.
- Huysmans, G. L.
Brit. Pat. #199,802, Mar. 28, 1922. Chem. Abst. vol. 18, p.315, 1924.
- Hyde, J. F.
U.S. Pat. #1,964,322, June 26, 1934.
- Indium Corp. of America
60 East 42nd St., New York, N. Y.
- Jira, J. W.
U.S. Pat. #2,281,843, May 5, 1942. U.S. Pat. #2,357,473, Sept. 5, 1944.
Chem. Abst. vol. 36, p. 5714, 1942. Chem. Abst. vol. 39, p. 396, 1945.
- Johnson, J. H.
Brit. Pat. #1989, Aug. 10, 1864.
- Kerridge, F. E.
Brit. Pat. #599,675, Nov. 22, 1943.
- Kollmar, M.
German Pat. #708,405, June 12, 1941. U.S. Pat. #2,351,974, June 20, 1944.
Chem. Abst. vol. 37, p.3240, 1943. Chem. Abst. vol. 38, p. 5654, 1944.
- Kretzer, H.
Dutch Pat. #75, Dec. 15, 1913.
Chem. Abst. vol. 8, p. 2469, 1914.
- Lederer, Anton
U.S. Pat. #1,079,777, Nov. 25, 1913.
- Leibig, E. C.
U.S. Pat. #2,075,446, Mar. 30, 1937.
- Linick Chemical Co.
29 East Madison St., Chicago, Illinois
- Littleton, J. T.
U.S. Pat. #2,118,795, May 24, 1938.

- Long, B.
Jour. Soc. Glass Tech. vol. 21, p. 428, 1937. Glasstech. Ber. vol. 16, p. 187, 1938. U.S. Pat. #2,119,680, June 7, 1938. U.S. Pat. #2,236,911, Apr. 11, 1941.
- Malcolmson, W. J. and Miner, R. V.
U.S. Pat. #2,398,712, Apr. 16, 1946.
- Marboe, E. C.
U.S. Pat. #2,430,520, Nov. 11, 1947.
- Marelli, G.
Italian Pat. #390,008, Mar. 29, 1941. Chem. Zentr. (20), vol. 1, p. 2149, 1943. Chem. Abst. vol. 24, p. 177, 1945.
- Marino, P.
U.S. Pat. #1,041,126, Oct. 15, 1912.
- McKelvey, E. C. and Taylor, C. S.
Jour. American Chem. Soc., vol. 42, p. 1364, 1920.
- Metaplast Corp.
Long Island City (1), N. Y.
- Muller, J. H.
U.S. Pat. #1,922,387, Aug. 15, 1933. Chem. Abst. vol. 27, p. 5167, 1933.
- Murray, A. F.
Tele-Tech, June 1947, p. 58.
- Parville, L.
French Pat. #279,952, Sept. 24, 1896. U.S. Pat. #602,227, Apr. 12, 1898.
- Parsche, F. C.
U.S. Pat. #1,183,109, May 16, 1916.
- Quinn, A. C.
U.S. Pat. #2,415,036, Jan. 28, 1947.
- Rheinberg, J.
Joint Meeting Phys. Soc. & Opt. Soc., London, Nov. 26, 1920, p. 28.
Brit. Pat. #156,472, Sept. 16, 1920, Chem. Abst. vol. 15, p. 1791, 1921.
- Rhiel, W.
See Hanovia Chemical & Mfg. Co.
- Rosenblatt, E. F.
U.S. Pat. #2,166,076, July 11, 1939. U.S. Pat. #2,328,101, Aug. 31, 1943.
Chem. Abst. vol. 33, p. 8367.
- Rowland, D. H.
U.S. Pat. #2,264,152, Nov. 25, 1941.
- Sauzy, A.
Wonders of Glass Making, 1872, p. 159.
- Smede, L. and Shand, E. B.
U.S. Pat. #1,852,093, Apr. 5, 1932.
- Smith, R. D.
U.S. Pat. #1,999,529, Apr. 30, 1935. U.S. Pat. #2,075,477, Mar. 30, 1937.
U.S. Pat. #2,103,598, Dec. 28, 1937. Chem. Abst. vol. 29, p. 4145, 1935.
Chem. Abst. vol. 32, p. 1888, 1938.
- Stong, G. E.
U.S. Pat. #2,475,379, July 5, 1949.
- Tomlinson, T. L.
U.S. Pat. #1,372,253, May 22, 1921. Brit. Pat. #163,606, June 23, 1920.
Chem. Abst. vol. 16, p. 150, 1922.
- Underwood, J. W.
U.S. Pat. #2,282,106, May 5, 1942.

- United States Government, Census, 1937.
 Superintendent of Documents, Washington 25, D. C. Chem. Abst. vol. 33,
 p. 9477, 1939.
- Vatter, H.
 U.S. Pat. #2,139,431, Dec. 6, 1938.
- Voigt, J. F. and Haeffner, J. A.
 Belgian Pat. #116,121, June 18, 1895. Italian Pat. #39,072, June 18,
 1895. U.S. Pat. #617,375, Jan. 10, 1899.
- Ward, T. W. H.
 U.S. Pat. #2,280,135, Apr. 21, 1942.
- Werner, E.
 Sprechsaal, vol. 63, p. 223, 1930. Ber. vol. 34, p. 2592, 1901.
- Weyl, W. A.
 Glass Ind. vol. 26, p. 557, 1945.
- Yunoki, S. and Nakazawa, Y.
 Japanese Pat. #38,689, May 21, 1921.

UNITED STATES PATENTS

43,080	June	14,	1861	Angenard, L. P.
46,062	Jan.	31,	1865	Angenard, L. P.
602,227	Apr.	12,	1898	Parville, L.
617,375	Jan.	10	1899	Voigt, J. F. and Haeffner, J. A.
1,041,126	Oct.	15,	1912	Marino, P.
1,079,777	Nov.	25,	1913	Lederer, Anton
1,103,353	July	14,	1914	Egly, G.
1,183,109	May	16,	1916	Parsche, F. C.
1,372,253	May	22,	1921	Tomlinson, T. L.
1,538,890	May	26,	1925	Fredenburgh, M. N.
1,852,093	Apr.	5,	1932	Smede, L. and Shand, E. B.
1,922,387	Aug.	15,	1933	Muller, J. H.
1,964,322	June	26,	1934	Hyde, J. F.
1,987,683	Jan.	15,	1935	Hunt, M. M. and Barrows, G. M.
1,999,529	Apr.	30,	1935	Smith, R. D.
2,064,369	Dec.	15,	1936	Biggs, O. H.
2,075,477	Mar.	30,	1937	Smith, R. D.
2,075,466	Mar.	30,	1937	Leibig, E. C.
2,081,234	May	25,	1937	Hefter, A.
2,103,598	Dec.	28,	1937	Smith, R. D.
2,118,795	May	24,	1938	Littleton, J. T.
2,119,680	June	7,	1938	Long, B.
2,139,431	Dec.	6,	1938	Vatter, H.
2,162,808	June	20,	1939	Gallup, J.
2,166,076	July	11,	1939	Rosenblatt, E. F.
2,236,911	Apr.	11,	1941	Long, B.
2,264,152	Nov.	25,	1941	Rowland, D. H.
2,274,955	Mar.	3,	1942	Dykstra, L. J. and Meyer, E. M.
2,280,135	Apr.	21,	1942	Ward, T. W. H.
2,281,843	May	5,	1942	Jira, J. W.
2,282,106	May	5,	1942	Underwood, J. W.

2,328,101	Aug.	31,	1943	Rosenblatt, E. F.
2,351,974	Jun.	20,	1944	Kollmar, M.
2,357,473	Sep.	5,	1944	Jira, J. W.
2,383,704	Aug.	28,	1945	Ballard, K. H.
2,398,712	Apr.	16,	1946	Malcolmson, W.J. & Miner, R.V.
2,415,036	Jan.	28,	1947	Quinn, A.C.
2,418,461	Apr.	8,	1947	Becker, J.A.; Christensen, H. & Kleimack, J.J.
2,430,520	Nov.	11,	1947	Marboe, E.C.
2,434,555	Jan.	13,	1948	Fischer, E.H.; Harnish, J.D. & Russell, R.
2,475,379	Jul.	15,	1949	Stong, G.E.

BRITISH PATENTS

580	Mar.	10,	1856	Chablin, L. & Hemeque, M.
1,989	Aug.	10,	1864	Johnson, J. H.
156,472	Sep.	16,	1920	Rheinberg, J.
3,148	Sep.	15,	1874	Brown, M.W.
163,606	Jun.	23,	1920	Tomlinson, T. L.
199,802	Mar.	28,	1922	Huysmans, G. L.
599,675	Nov.	22,	1943	Kerridge, F.E.
593,256	May	28,	1945	Davies, D. A.

DUTCH PATENT

75	Dec.	15,	1913	Kretzer, H.
----	------	-----	------	-------------

BELGIAN PATENT

116,121	Jun.	18,	1895	Voight, J. F. & Haeffner, J. A.
---------	------	-----	------	---------------------------------

ITALIAN PATENTS

39,072	Jun.	18,	1895	Voight, J. F. & Haeffner, J. A.
390,008	Mar.	29,	1941	Marelli, G.

FRENCH PATENTS

279,952	Sep.	24,	1896	Parville, L.
652,748	Sep.	21,	1927	Brenner, R. E.

GERMAN PATENTS

595,356	Apr.	9,	1934	Bahrtdt, A.
708,405	Jun.	12,	1941	Kollmar, M.

JAPANESE PATENT

38,689	May	21,	1921	Yunoki, S. & Nakasawa, Y.
--------	-----	-----	------	---------------------------

RUSSIAN PATENTS

3,433	Aug.	31,	1927	Budnikoff, P.P.
551,132	Jun.	30,	1930	Dol'nikov, L.N.