PRECIOUS METAL PLATING

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0. Introduction

0.1 The precious metal plating started with the sole aim as a decorative finish has made inroads into the field of electroplating for improving corrosion resistance. Precious metals are characterised by their excellent chemical and physical properties. They are used in industry particularly where the requirements involve high chemical resistance, good electrical conductivity and/or low contact resistance. Ruthard (1) has published a comprehensive survey of the applications of the precious metals, including electroplated coatings, also covers the applications of these metals in bulk.

During the past two decades, there has been a rapid growth of the electrical, electronic, aircraft, missile and allied industries. The application and the use of electroplated precious metal coatings by the aforementioned industries have been the prime impetus for research and development of precious metal electroplating. With the emphasis on the reliability of electrical circuits, the precious metal deposition becomes important and may be expected to grow in the future.

The application of heavy coatings in particular, are growing rapidly today and rhodium, for example, may be plated in thickness of upto 0.001" (25 microns) for contacts. As the difficulties of depositing heavy coatings are overcome, these processes are opening the way to the replacement of mechanical cladding methods, as electrodeposition is frequently cheaper than hot pressing, rolling techniques. For example, watch cases are deposited with gold to a thickness of over 0.001" and in the chemical industry for the protection of large containers and apparatus, heavy silver plating is adopted.

TABLE I

CHEMICAL PROPERTIES AND APPLICATIONS OF PRECIOUS METALS

Metal	*Chemical properties*	*Applications*
Silver	Resistant to oxidation, sensitive to sulphide, soluble in nitric acid.	Electrical industry, chemical plant, jewellery.
Gold	Resistant to oxidation, sensitive to cyanide, soluble in aqua regia	Jewellery, dental and electrical industries.
Palladium	Forms reactive oxide, resistant to sulphide, soluble in nitric acid.	Alloying element in the electrical industry, catalyst.
Platinum	Resistant to oxidation, soluble in aqua regia.	Jewellery and electrical industries, temperature measurement
Rhodium	Forms reactive oxide, insoluble in aqua regia, high temperature resistant.	Alloyed with platinum for thermal elements, catalysts, electrodeposited coatings.
Iridium	Highest chemical resistance, forms volatile oxide.	Alloying element for hardening Pt, electrical and jewellery industries.
Ruthenium	Not highly oxidation resistant, very volatile oxide.	Ru alloys for pen nib tips, alloyed with Pt, for hardening.
Osmium	Not highly oxidation resistant, very volatile oxide.	As ruthenium.

Among the various precious metals in use in the industry, gold is widely used. Silver is used widely, next perhaps to gold. Silver tends to tarnish and is protected by a flash of rhodium. Of the platinum group of metals, rhodium has the widest applications due to its several desirable properties. Palladium is finding limited use in printed circuits in plating electrical contacts. Indium is used as a diffusion coating in aircraft engine bearings and as a 'doping' agent in electronic industries on metals like gold, silver, copper, tin, etc.

The persistent demand made by the electronic design engineers has stimulated the development of a number of precious metals processes that are commercially practical and which produce deposits to meet a wide range of end service requirements. These new processes are simple to operate and produce precision results. Today's technological advances with respect to developed and patented formulations are such that practically any design engineering problem can have tailor made for it a precious metal plating formulation that will do just about anything the metals themselves can do but with the tremendous savings that are possible when one substitutes a coating for the solid metal. Hence many of today's high speed communications are made possible through the use of plated coatings at a fraction of the cost of what would have been about a decade ago.(2)

1. Gold

1.1. In the last ten years, interest in and use of gold has expanded rapidly owing to the growing demands of the fast developing electronics, control communications, space and aircraft industries. Resistance to tarnish and corrosion to various chemicals, maintenance of low contact resistance, resistance to oxidation at high temperature, and good solderability after extended storage are the special properties of gold which have created the demand for gold.

Gold was one of the first metals to be plated by the use of an external source of current and was plated by Professor Brugnateli in Italy around 1805 (3). From 1850 to 1924 there was very little significant development in gold plating. In 1929 the first of the Bek patents (4) described the production of heavy gold alloy plating for jewellery. Kushner (5) published in 1940-42 a series of articles on gold plating.

1.2. *Bright Baths*—In the early 1950's the electronics field began to expand rapidly and provided the long needed incentive for intensive research in gold plating. The period 1950-60 has been the marked increase in gold plating investigation. Deposits from the conventional cyanide gold bath are dull, coarsely crystalline and have poor resistance to abrasion. Bright baths of the high alkali free cyanide type and having pH ranges above 9 have been described by Rinker (6) and Nobel and Ostrow (7). A cyanide bath containing cobalt is said to give close grained deposit, harder than conventional gold bath. The gold deposit is claimed to have no cobalt in it(8). Ostrow(9) has described a bright bath with 0-2 g/l of free cyanide and operated at a controlled pH of 8.0-8.5. A neutral bath has been described by Volk (10). A cyanide bath for heavy gold plating has been described by Seegmiller and Gore(11). He uses Turkey red oil (0.5 ml/l) as the organic addition agent. Fischer and Schwarze (12) have described a bath containing condensation product of carbon disulphide and acrolein to gold and gold silver alloy baths. The development of low or no free cyanide solutions operating at less than 30°C and plating at 90-98% current efficiency was a still further development and improvement in the plating of printed circuits (13).

1.3 *Doped Alloys*—The above mentioned bright baths cannot give thick deposits. Hard bright gold formulation also utilizes a cold cyanide electrolyte along with a base metal. To meet some of the requirements in the semiconducter field, alloys of gold with Gr. III and V metals have been plated on a production basis (13). The incorporation of specific impurities in semiconducter, is known as "doping." A metallo-organic complex of antimony, as tartarte, has been added in amounts 7 to 15 mg/l in a phosphate bath (14). Potassium antimonate is also used(15). Doping of gold electroplates with antimony previously was produced in a manner that was unreliable and not reproducible. The new process (alloying) is the first one that gave transistor engineers a controllable electroplating doping method. The deposits are bright and contain upto 4% antimony(2). The alloy plate is heat fused to a germanium wafer to give a ternary alloy-gold-antimony-germanium alloy. Gold alloys containing 4-25% antimony have been recommended for sliding contacts such as connectors(14). The alloy deposits have good solderability and have additional merit in cryogenic and high vibration application because of the antimony content(2).

Silver has been alloyed to give a bright hard gold plating solution and the deposit is said to have hard wearing quality(16). The deposit contains app. 1 % silver. Rinker (17) has given a full description of the process.

1.4 *Acid Electrolytes*—There has been the most recent demand in the U.S. for bright gold deposit of higher purity and better corrosion resistance. All the usual alloying metals like silver, nickel, cobalt, etc., debase the gold deposit while hardening, brightening but resulting in a marked decrease in resistance to corrosion and high temperature. The equipments for "space probe" require electronic components of a very high reliability at increasingly high operating temperatures and the gold deposits should afford maximum base metal protection and maximum corrosion resistance. Success in achieving these objectives has been met with the recent introducton of 24 carat deposits, plated from acid electrolytes with non-discharging (organometallic) addition agents for brightness and levelling as well as for hardenng through preferred orientation(18)-. The baths are usually citrate type(19) or sulphamate type or phosphate type depending on the end use. Apart from the specific use in missile, these acid baths are used in plating printed circuits where the solution attacks on the resist used or the resistance of the coating to etching media are the major considerations. Further, acid gold bath can be used for plating gold on stainless steel and other passive metals directly without any intermediate layer. Acid gold deposits give perfect adhesion on passive silver and nickel deposits. Acid gold deposit has low diffusion coefficient and low porosity, which in practice enable a thinner coat to be used with equal efficiency. This acid gold bath permits simplified masking possible and this reduces cost in labour and in gold. The above facts have direct bearing on the printed circuit plating. The bonding agent of the copper laminate is not only unattacked by the acid gold solution but it is not at all weakened thus permitting narrower conductors. Furthermore even if the photo resist or screen resist is not perfect, it will not strip in the acid gold electrolyte. This allows much greater variation in applying resists, while maintaining consistently high quality of the finished plated circuit. Weisberg (18) has rightly said that the acid gold baths have at present answered all the most recent demands of the electronics industries on the gold plater and it is to be anticipated that there will be a period of quiet and refinement of existing baths before new properties are desired of gold.

Another major area of use of the acid gold plating system is in the electronic components industry—especially in barrel plating of miniature components. Baths with small hole size present a rinsing problem, if cyanide solutions are used for gold plating. With the low pH solution these rinsing and handling problems are eliminated. Better uniformity of electrodeposit is obtained when plating electrically isolated metallic parts like transistor headers, and relay blocks, because the deposit is not attacked by the electrolyte during non-contact time.

1.5 *Electroless Gold Plating.*—In recent years plating by chemical reduction or more popularly known as electroless plating has become important since the throwing power of these solutions is 100 per cent and the deposit is uniform. The industrial use of this process has increased since the gold deposit is said to 99 .34 per cent fine. The brightness of the deposit depends on the basis metal and can be easily polished.

The electroless gold solution like nickel consists of gold salt in a solution with a buffer and a reducing agent. Amine complex or hypophosphite is used as reducing agent. A typical bath is given below (20):

Potassium gold cyanide	..	2 g/l
Ammonium chloride	..	75 g/l
Sodium citrate	..	50 g/l
Sodium hypophosphite	..	10 g/l

pH is maintained between 7.0 to 7.5 by the addition of ammonia. Stainless steel or glass containers are used and heated by means of water jacket. Temperature (92°—95°C) is to be controlled closely and chemical addition made when required. At 92°C the rate of deposition is 0.04 mil per hour. This process is suitable for small parts which cannot be easily handled for electroplating.

There are a number of proprietory processes which claim deposition speed and thickness as required.

1.6 *Characteristics of Gold Baths*—Ostrow and Nobel(21) have studied the characteristics of the deposits from various gold baths. They have studied typical baths and formulation of these baths are given in Table II.

They conclude that there is marked difference in the physical characteristics like reflectivity, thickness, porosity and hardness of the deposits.

TABLE II

FORMULATIONS OF GOLD BATHS

Constituents	*Standard Cyanide*	*Bek Process*	*Russian Gold*
Gold as potassium gold cyanide ..	1 oz./gal.	1.5 g/l.	5.0 g/l
Free Potassium cyanide ..	4 oz/gal	15 g/l	16 g/l
Pottassium carbonate ..	2 oz/gal	15 g/l	
Potassium phosphate dibasic ..	4 oz/gal	3.0 g/l	
Nickel as potassium nickel cyanide ..			
Potassium Cobalt Cyanide ..			10 g/l
Current Density Range ..	0-6 amp/ft²	0-20 amp/ft²	0-6 amp/ft²
Temperature ..	140°F	130°F	160°F

Constituents	*Volk*	*Bright Phosphoric acid type*
Gold as potassium gold cyanide ..	4.0 g/l	8.0 g/l
Nickel as potassium Ni. cyanide ..	0.5 g/l	
Nickel as Nickel sulphate ..		0.25 g/l
Monosodium phosphate ..	15 g/l	60 g/l
Disodium phosphate ..	20 g/l	
pH adjust with phosphoric acid ..	6.5—7.5	4.0 g/l
Current Density Range ..	0-15 amp/ft²	0-15 amp/ft²
Temperature ..	152°F	Room

Constituents	*Proprietary Bright Acid 23.9 K*	*Proprietary Neutral High Speed 23.9 K*	*Proprietary Bright Acid 24.0 K*
Gold Metal ..	8.0 g/l	4.0 g/l	4.0 g/l
Brighteners ..	Organic type	Organic type	Organic type
Alloying metal in deposit ..	Nickel	Nickel	
Current Density Range ..	0-20 amp/ft²	0-20 amp/ft²	0-20 amp/ft²
Temperature ..	120°F	room-120°F	room
pH ..	4.5	7.0	4.5

These differences depend largely on the type of bath used to produce such coatings. The metallography of the proprietary cyanide and acid gold baths indicates that there is difference in structure of the deposits. This does not mean that all cyanide baths will have a columnar structure nor will all acid type gold baths produce laminar deposits.

(*a*) *Hardness*—Hardness is an important characteristic of the gold deposit and generally determines the quality of the deposit. Ostrow and Nobel(21) have compared the hardness of different types of gold deposits and the figures are given in Table III.,

(*b*) *Porosity*—is probably the most important factor of a gold deposit, since the advantage of gold deposit as an overlay is lost without a pore-free deposit.

Baker and others (22) have reviewed porosity testing in gold deposit. They broadly classify porosity into three general groups. One type called intrinsic porosity, is always present and is a basic parameter which is predicted by the nature of mechanism of

TABLE III

HARDNESS OF GOLD DEPOSIT

Sl. No.	*Type of Bath*	
1.	Bright Acid Proprietary Bath (23.90 K)	300 Vickers
2.	Bright Acid Proprietary Bath (24.00 K)	250 Vickers
3.	Bright Neutral Proprietary Bath (23.90 K)	200 Vickers
4.	Bek	100 Vickers
5.	Acid Phosphate Gold less than	100 Vickers
6.	Volk less than	100 Vickers
7.	Standard Cyanide less than	100 Vickers
8.	Russian less than	100 Vickers

NOTE: All the hardness values are approximations
METHOD: Scratch Type Test

electrodeposition. Intrinsic porosity is influenced by the type of bath, condition and kind of basis metal, bath temperature, c.d., etc. The other type of porosity, in the asplated coating, is the accidental or gross porosity due to the extraneous causes like dirt, metal inclusions, etc. The third type of porosity is that which results from corrosive attack by the environment. This is more pronounced in the case of composite coatings and is closely related to the electrochemical behaviour of the plated metal or metals and to the resistance to corrosion that these coatings exhibit when exposed to a given environment.

Porosity is usually evaluated by exposing the parts to atmospheres containing small amounts of sulphor dioxide and hydrogen sulphide, usually consecutively. There is an electrographic method (23) of testing porosity. The test methods depend largely on the surface conditions of the base metal. It is considered that bright gold deposits are less porous than those obtained from conventional cyanide solutions.

(*c*) *Solderability*—Gold plating is widely used in electrical and electronic designs for a variety of reasons, one of which is its reputation for good solderability. The literature contains very little information on solderability of gold plating. Foster(24) has done significant work on the subject of soldering to gold plating. He studied the ductility of alloys of gold in tin, in lead and in tin-lead (60-40). Metallurgical examination revealed that the soldered joint contained a hard and white crystal, probably some gold-tin compound, which causes the reduction in joint strength and which produces the crystalline appearance of solder joints. Harding and Pressly(25) have elaborately studied the inadequate joint strength and failures of the solder to wet the gold. They recommend that thin gold plating (approximately 10 millionth of a inch) is definitely a soldering aid and has no detrimental effect on the structure of solder joints. Thick gold plating (approx. 50 millionth and above) should be avoided when strength is important. Pure gold deposit should be chosen. The soldering operation should be precisely controlled to minimise soldering temperature and soldering tune.

2. Silver

2.1 Silver coatings are applied to a great variety of basis metals and alloys because of the unique properties that silver exhibits in the decorative, electrical, chemical and mechanical fields. Its pleasing appearance is the chief reason for its use on tablewares, decorative metal objects, etc. Silver is used in electrical and electronic circuits because of its high conductivity. The general insolubility of silver in most corrosive media makes it useful in the manufacture of chemical engineering equipments and surgical instruments. Silver deposits are used in mechanical field because of its high load-carrying and non-welding properties under marginal lubrication for the fabrication of bearings, thrust washers, and anti-fret surfaces in thicknesses from 0.0005" (0.013 cm.) to about 0.060 in. (0.15) compared to approximately 0.002 in. (0.052 cm.) maximum for most other applications. Silver

deposits are used in non-metallic materials in the manufacture of ornamental objects. Silver deposit in the silver coulometer forms the basis of international ampere(26).

2.2 *Silver bath*—Solutions and techniques for electro-deposition of silver are well established. The earliest patent for decorative silver plating is credited to Elkington and Bairratt, U. K. in 1838. Two years later, Elkington received a patent for silver plating. Strange enough, this patent describes essentially the present day silver bath, *i.e.*, the double cyanide baths with excess alkali cyanide. As in the case of gold bath, very little basic changes have been effected from the old cyanide baths used by jewellery and decorative industries. Current investigations devoted to silver plating are not so much concerned with finding radically new types of solutions though such work is in progress as they are with modifying the present cyanide bath in order (*a*) permit the use of higher current densities without sacrificing the appearance of the silver deposits, (*b*) improve the throwing power so as to secure better distribution of the deposit, (*c*) control the corrosion of silver anode and (*d*) apply mechanised equipment as plating apparatus, automatic filtration, anode and cathode agitation and more efficient racking or jigging methods. It is from these studies that we may expect the future progress in commercial silver plating (26).

2.3 Attempts are made constantly to replace the conventional cyanide solution with less poisonous chemicals. Iodide, sulphite, thiourea, thiocyanate, thiosulphate, ferrocyanide solutions have been studied. In recent times fluoboric acid, pyrophsophoric acid and sulphamic acid plating baths have been investigated(23).

Bright silver baths are prepared by adding a number of additives to the silver solution. Carbondisulphide and its derivatives, thiosulphates, mercaptans, salts of selenium and tellurium, xanthogenates, etc., are used as additives. Antimony and bismuth are also used.

2.4 *Heavy Silver Deposit*—In the late forties requests from industries arose for heavier silver deposits for steel-backed, silver plated bearings and similar applications. The heavy silver plating is used in modern aircrafts. The silver deposit for this purpose was required to be fine grained and free from excessive nodules in thickness (prior to machining) upto approximately 0.06" (0.15 cm.). After machining, a thin layer of lead-tin or lead-indium is deposited on the silver to improve seizure resistance under load conditions. The adhesion of silver deposit to the steel is of great importance and a number of tests like heating to about 540°C (if without copper undercoat) ultrasonic inspection, radiography, etc., are in vogue to test the adhesion. High current densities are used with special solution composition, pH, temperature and better jigging.

In the electrical industry, silver deposits are used in switch gear manufacture. The use of silver plated contacts is decreased owing to the susceptibility of this metal to sulphur attack. If silver is used, it is covered with a thin flash of rhodium. Hard silver deposit is also applied to HF components including coils and wave guides in order to give a high surface conductivity. There is considerable literature on the hardness of silver deposit. Antimony as a salt of tartarate has been used as hardening agent(27). Raub and Engel(28) have investigated the addition of lead and bismuth in silver. Such a solution gives a silver deposit having hardness of 180 Kg/mm^2 (29). Organic addition agent (condensation product of acroelin with carbon disulphide) is also used(30).

In the assembly of electronic equipments the problems of contact potential (due to dissimilar metals) sometimes presents a situation which affects the performance of the equipment. Marsh(31) has drawn the important role played by the silver electrodeposits in mitigating the same.

2.5 *Tarnishing of silver deposit*—Tarnishing of silver deposit is one of the most serious problems in the jewellery and electrical industries. Although a number of methods have been suggested for the prevention of tarnishing of silver, there is no method which has really solved the problem. Lacquering is one of the suggested method. As a temporary protective dilute solutions of greases, petroleum jelly or waxes are employed. As in the case of other metals silver can also be coated with a film by immersion in chromic acid or acidified dichromate solutions. This film has some protective value. In order to avoid discolouration of the silver by the film, the composition and the immersion time must be controlled. Yampolksy has suggested the use of a solution containing 1% $K_2Cr_2O_7$ at pH of 3.0 to 4.5 at 15°—25°C for 20 minutes(32). Baeyens and Melse (33) have investigated chromate passivation of silver for electrical applications. They found that a metal complexing agent

was necessary to the hexavalent chromium solution to maintain a defined relationship between the pH value of the solution and the metal solution potential. Goldie (34) has made a comparitive study of the various chromating processes.

Oxide films of some metals are coated to prevent tarnishing. Such films of the Oxides of metals of the third and fourth group of the periodic table which migrate to the cathode under the influence of electrophoresis to form a protective film. A very thin film of rhodium or palladium or gold is also used to prevent tarnishing.

3. Rhodium

3.1 Rhodium, one of the metals of the platinum group, has great stability and resistance to corrosion characteristic of that group. It is a metal too hard to be worked by the craftsman. However, in the electrodeposited form the physical properties of the noble metal are of practical value to science and industry at relatively a small cost. Even though a few references to electrodeposition of rhodium are found in the literature prior to 1915, this metal was never used to any extent for plating purposes until 1930. In general, it may be said that only acid electrolytes will give a bright, white deposit and at the same time show good throwing power. These faliry strong acid solutions are phosphates, phosphates-sulphates and sulphates. Before the current application and developments in the electronic field, the major use of rhodium plating was in the jewellery and decorative fields where only flash coatings are used (0.000001"—0.000010"). In the past ten years the industrial use of rhodium has increased tremendously with applications running the gamut from thin jewellery flashes to 0.001" for use on electrical contacts subject to severe friction and corrosion. The wear resistance of rhodium electroplates 0.00001" or less in thickness seems to be about midway between that of nickel and chromium. The hardness, good reflectivity and wear resistance have been used to great advantage on search light reflectors—the first commercial application. Its wear resistance combined with its freedom from corrosion and high conductivity, also makes rhodium extremely valuable for electrical contacts. Depending on the application, thickness of rhodium electroplate on electrical contacts ranges from 0.000005" to 0.0001" with light duty contacts frequently plated with 0.0000015" or rhodium over 0.0005" silver(35). Increased interest in rhodium deposits for industrial purposes is shown by issue in June 1960 of a Ministry of Aviation U.K. Process specification on Rhodium Plating, DTD 931. This provides users and electroplaters with a comprehensive guide to the factors involved in the successful use of rhodium (36).

Rhodium deposit is characterised by high tensile stress and porosity. Hence, a thick flash coating is used. There are commercial

TABLE IV

RECOMMENDED THICKNESS OF RHODIUM COATINGS

Sl. No.	*Class No.*	*Typical Application*	*Minimum thickness on agreed significant surfaces, in.*
1.	Rh 15	Tarnish resistance	0.000015
2.	Rh 25	Reflectors, anti-tarnish	0.000025
3.	Rh 100	Light mechanical loading, for reliability of electrical contacts after long idle periods	0.000100
4.	Rh 200	Medium mechanical loading-sliding contacts	0.000200
5.	Rh 400	Heavy mechanical loading-sliding contacts	0.000400
6.	Rh 800	Very heavy loading-conditions in special applications only	0.000800

processes which off-set these two defects. Compressive stress introduced by these manufacturers reverses the inherent tendency affording an integrally bonded, more tenacious adherence than possible heretofor(37). Selenic acid or magnesium sulphate and sulphamate are usually added as stress reducing agent.

3.2 Rhodium can be deposited directly onto copper, brass, bronze nickel, nickel-silver, phoshpor bronze, beryllium-copper as well as gold and platinum. Because of the acid content of the bath and the position of rhodium in the electrochemical series, it cannot be plated directly on to iron, steel, zinc, aluminium, lead or tin and therefore a preliminary deposit of silver is usually need on these metals(38).

3.3 Rhodium is particularly indicated as the desirable coating for electrical contacts and slip rings because of its extreme hardness and good electrical conductivity (39). Rhodium is ideal for printed circuitry. Rhodium electrodeposits in grid wires in vacuum tubes suppress secondary electron emissivity. The use of rhodium in semi-conductor applications is finding every-increasing acceptance. Rhodium is also used as a tarnish-resistant coating over silver conductors in R.F. Circuits. Many applications for selective area deposition of rhodium are easily processed. The recommended thicknesses of rhodium coatings, for specific applications are given in Table IV (38).

4. Palladium

4.1 It is only recently that electrodeposited palladium has become of industrial importance though the oldest practical formula for palladium plating bath is given in a patent by Pilet(40) which is analagous to his formula for a platinum plating bath. Stevens has described the development of an electrolyte based on tetramnine palladous bromide(41). Palladium has many of desirable properties characteristics of the platinum group of metals, amongst which are excellent resistance to tarnishing and corrosion and low electrical contact resistance. Although wrought palladium is very soft, the electro-deposited palladium possesses a relatively high hardness 300-400 DPN. These properties render electro-deposited palladium attractive for many applications in the electrical industry and particularly in the field of printed circuitry. The deposit is easily soldered. Electro-deposited palladium has, however, a fairly high electrical resistivity and is therefore not normally suitable for R.F. application(42).

Palladium is appreciably cheaper than other precious metals (with the exception of silver). Taking into account the densities of the metals, palladium has an intrinsic cost, on a volume basis of approximately one-sixth that of rhodium and approximately one half of that of pure gold. In the telephone industry Palladium plating is used in the instrument used for subscriber trunk dialling system in the exchanges. Though there was a proposal to use palladium plating for printed circuitry, gold is preferred. Because of its comparatively cheapter cost and resistance to tarnishing and corrosion, palladium may easily replace gold in the near future in the electronic industry.

5. Platinum

5.1 Inspite of the large number of platinum plating solutions which has been suggested, the electrodeposition of this metal has not been successfully introduced as has that of rhodium. About 30 years ago a great deal of interest was being taken in platinum plating and a number of papers and patent specifications appeared describing improved electrolytes and their methods of operation. The successful rhodium plating developed a little later, was a serious competetor to platinum. For the past four or five years again the interest in platinum plating has developed. Use of platinum deposit for electrical contacts, on titanium in chemical industry, and in high tempera-

TABLE V

PROPERTIES OF SOUND PALLADIUM ELECTRO DEPOSIT (43)

Hardness VPN	300 — 400
Specific Gravity	11.9
Specific Resistance at $0^{\circ}C$ Cm	10.7
Electrical Conductivity per cent I.A.C.S.	16
Weight deposited per amphrgon	1.99

ture electronic equipment has been established (23).

A number of baths have been developed—phosphate, diamimna-dinitrite, alkaline, chloroplatinic acid, sulphato-dinitro-platinite (23). Excepting for a limited use, platinum plating is not popular as the other precious metals in the platinum group are equally effective.

6. Ruthenium

6.1 Ruthenium has very little application in industry at present although it can be electrodeposited in a satisfactory form from aqueous solutions. Thin bright deposits of ruthenium may be obtained by electrodeposition. A typical formation is given below:—

Ruthenium (as nitrosyl sulphamate)	5 g/l
Free Sulphamic Acid	10 g/l
Current Density	2 A/dm^2
Temperature	70°C

The rate of deposition is 0.0001 in. per hour. A flash undercoat of gold is desirable when plating silver, copper, or nickel or alloys based on these metals. For plating the more reactive metals like iron. zinc, aluminium or magnesium, a substantial undercoat of nickel, copper or silver plus the gold flash is required. The hardness achieved from a sulphamate both is above 900 DPN, but this can be increased to 1300 DPN by modification of the electrolyte. Adherent ruthenium coatings may be produced on ceramics, refractories and a number of metals by thermal decomposition of an applied ruthenium— organic compound such as phenol. The organic product is applied to the surface to be coated. The article is then heated under reducing conditions to volatalize the organic compound and reduce the coating to metal. Possible applications for these processes include thin film resistors and electrical contact surfaces on refractory components (44).

7. Iridium

7.1 The electrodeposition of iridium from an aqueous electrolytes is inherently difficult. More satifactory coatings can be obtained with a fused cyanide electrolyte, which is first charged with iridum by a.c. electrolysis and then operated at 6000°C with a soluble iridium anode. Adherent iridium coatings may be produced on ceramics, refractions and on a number of metals using the liquid-bright process.

8. Standard Specification

8.1 Standard specifications are essential to achieve uniformity of production and to give a guarantee to the consumer about the quality of the precious metal deposit. Indian Standards Institution have published standards on silver plating for commercial use and engineering purposes. Standards for gold plating should be processed. Precious metal plating has progressed well in the country and the situation with regard to specifications is not satisfactory as it pertains to industrial applications. Specification for plating as well as methods of test have to be published early and should not lag behind the technological development in the field.

9. Conclusion

9.1 Developments in precious metal plating have been stimulated by an increasing sophistication on the part of users. About ten years ago the problems of precious metel deposition were in the main process problems. very often in the form of poor adhesion or stressed deposits. Improvement in plating technique, increasing industrial experience and the availability of a useful volume of technical literatures have gone far towards meeting practical difficulties of this nature. It now appears that precious metal plating in general is entering a second phase of development, in which the mechanical and electrical properties of the coatings are coming under close scrutiny by engineers and physicists in relation to specific applicational requirements and against the background of ever-increacing emphasis on reliability of components and performance.

This situation imposes stringent demands on the precious metal plater. which must be successfully met if the deposits are to function satisfactorily in their critical roles.

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