Precious Metal Plating and the Environment.

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Traditionally precious metal plating has not been considered a "polluter" to the environment. The high costs of the precious metal itself has acted to "police" itself in the past ensuring that precious metals are not lost into the various effluents. With the changes in legislation and the current perceptions regarding the environment, changes to the chemicals used in precious metal plating are now being seen.

This paper will show the trends and current developments in eliminating potentially hazardous chemicals from both the plating bath and from the deposited metals. All the precious plated metals will be discussed. The difficulties this could bring to both the decorative and industrial/electronic markets will also be discussed. The need to develop more environmentally friendly products and how this has been approached will also be covered.

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Introduction

Precious metal process developers and process users have never in the past been considered as major polluters. This is despite the Plating and Surface Coating industry attracting environmental concerns from both industry and legislative bodies. Due to the high cost of precious metals (and currently going even higher) users have always managed their systems to avoid excessive drag outs and loss of costly material. Mostly the precious metal types of chemistry avoided any use of heavy metals, toxic polluters (with the exception of cyanide) and other “nasty” elements. With the increase in legislation regarding the use of lead, cadmium, nickel, etc in deposition we now see more emphasis being placed in respect of legislation and this too is now impacting on precious metal plating.

This paper will evaluate the current situation regarding gold, silver, palladium, rhodium, platinum and ruthenium plating. In doing so this paper will evaluate

1) current situation

> **Materials used and their restrictions**
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> **Restrictions on metals, explosive/oxidising materials, poisons/toxic materials, precursors for drugs, complexors etc.**

2) where we are heading

> **New innovative processes**
>
> **New processes, utilising alternative processes,**

3) where we could go.

> **Food for thought.**

In examining the above we will look at

a) the solution chemistries for plating the metals above,

b) the deposited metals and their alloys,

c) transport issues,

d) legislative issues,

The Metals

Gold Colour – described as gold colour. Density, 19.3g/cm^3.

Bright, many colours for decorative applications Density 16.9-17.5g/cm^3.
Matt - Bright for electronic wearing application, Density 16.5-17.5g/cm^3.

HAZARD – CYANIDE, ARSENIC & SEMI METALS.

Silver Colour – grey white as deposited. Density, 10.5g/cm^3.

Matt – Semi bright for electronics and fully bright for decorative applications.
Bright for decorative applications.

HAZARD – CYANIDE, SEMI METALS (such as Antimony).

Palladium Colour – grey white as deposited. Density, 12.00g/cm^3.

Matt – Semi bright for electronics and fully bright for decorative applications.
Mostly alloyed with Nickel nowadays. Density, 11.2-11.5g/cm^3.

HAZARD – AMMONIA, DEPOSITED NICKEL IN PLATED JEWELLERY.

Rhodium Colour – grey white as deposited but whiter than palladium or platinum. Density 12.4g/cm^3.

Bright at thin coatings <0.2 microns for decorative applications and semi bright to matt for technical applications.

HAZARD – CORROSIVE, LEAD AS A BRIGHTENER.

Platinum Colour – grey white as deposited. Similar to palladium but less white than Rhodium. Density 21. 2g/cm^3.

Bright at thin coatings <0.2 microns for decorative applications and semi bright to matt for technical applications.

HAZARD – CORROSIVE, AMMONIACAL, ALLERGIES.

Ruthenium Colour – grey white as deposited. Similar - slightly darker than palladium but less white than Rhodium. Density 12.2g/cm^3.

Bright at thin coatings <0.2 microns for decorative applications and semi bright to matt for technical applications.

HAZARD –CORROSIVE, UNPLEASANT ORGANIC ADDITIVES.

Regarding the above we need to look at them in reverse order. In looking at these issues we will start with LEGISLATIVE ISSUES first. It is these issues which import the demands on the solution developers, followed by any transport issues. We can then look at the deposited metals and finally how this all impacts on the solution chemistry and the development.

We will then look at where we are currently, recent developments towards more environmentally friendly products for precious metal plating and finally postulate where we could be heading.

d) LEGISLATIVE ISSUES

COSHH is basically a risk assessment the user carries out on a product to incorporate hazard, usage, period of use and number of people using it. Based on this controls need to be in place to minimize the risk.

RoHS The RoHS Directive stands for "the restriction of the use of certain hazardous substances in electrical and electronic equipment". This Directive will ban the placing on the EU market of new electrical and electronic equipment containing more than agreed levels of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants from 1 July 2006.
Companies now need to confirm that electronic / electrical components do not contain specified hazardous materials eg Pb, Cd, Hg, and some organics.

WEEE (Waste electronic and electrical equipment) This is related to RoHS and is the End of Life Directive which related to the same hazardous materials as RoHS.

COMAH This is the license needed by companies using large amounts of hazardous materials eg Cyanide. It is this requirement that is impacting on customers pushing them into wanting to use lower free cyanide baths, 70g/l as compared to 150g/l.

COMAH is a regulation related to danger of accidents and applies to production, storage or transportation.
The regulations have 2 schedules 1 with specific chemicals, the other with generic hazards (eg Toxic) In the case of cyanide this will be "Very Toxic" but in a solution of <70 g/l free cyanide it becomes "Toxic" For each hazard there are 2 limits, which relate to the duty tarifs you have to pay. eg

	Level 1	Level 2
Very toxic	5 tonnes	20 tonnes
Toxic	50 tonnes	200 tonnes

The limit is the total amount of the material stored at any one time. So could be 4000 litres of solution (density 1.25) or 3000 litres and 1000Kg salt

REACH is a new requirement coming in during 2007 that requires manufacturers to register any materials and their use on a database. The introduction will be phased based on hazard and quantity produced. This will not effect all companies immediately as only Quantities above 1,000 tonnes will be involved initially. Eventually it will include quantities over 1 tonne/year but the phasing will be >1000 tonnes or great concern registered within 3 years, >100 tonnes within 6 years and 1-100 tons in 11 years.

REACH will have no effect on COMAH. The idea of COMAH is to reduce hazardous material but also to provide the Government with the money to sort out any accidents/spillages etc.

Nickel Allergy

Nickel Free is already well established and implemented in European Law. European legislation is already in place and restricts the use of Nickel in many / most jewellery applications.

In fact though people prefer to not use Nickel rather than simply strive to meet the Nickel emission regulations where failures in service can produce rejects /failures that fall foul of the trading laws in many member states. Also if the "Nickel Free" description is put onto the label this is hard to justify if there is Nickel present in the product regardless of whether Nickel is emitted or not.

Why do people want Nickel Free Plating ?

This question is often asked and the answer is very straightforward. Nickel has become the focus of attention as it is a proven allergen frequently used in decorative and functional articles worn in close and constant contact with the skin.
The Nickel plating processes used in industry have been established for a number of years and the metal was originally chosen because it possessed the properties required to ideally suit the application intended.

Effluent

In discussing the above we have yet to mention effluent. There are many local levels of allowed effluent levels but generally it can be said that limits are getting lower e.i if your nickel was 5ppm it is probably 2ppm now.

Traditionally in the past dilution has been a typical answer to the problem. If a limit of 2 or 5 ppm on nickel was allowed the user would simply dilute to achieve the correct level. With levels of allowable limits being reduced dilution is not longer an option for 1) cost reasons – simply water is becoming more expensive and 2) the total allowable limit in a period (of nickel as an example) is also being implemented.

It can be seen from above that all these legislative issues have a direct cost to the user. However it is often overlooked when costing comparisons to the "Non Hazardous" systems are made.

c) TRANSPORT

Transport issues are becoming more a factor in development of precious metal plating processes. The movement of hazardous materials is becoming more and more difficult (and expensive).

Both from a legislative perspective and also from carriers who are finding the restrictions more cumbersome.

Regulations are different for

Road
Sea
Air

More and more transport companies are restricting the volumes and types of material they will handle. Typically Cyanide causes the most problems but even moving materials such as silver nitrate are becoming more restrictive due to the oxidising nature of the material. Cost issues such as training of drivers to deliver hazardous materials, to administer the procedures required, for the licenses required, cost of personal protective equipment and insurance requirements (having done risk assessment) have persuaded many transporters not to deliver hazardous materials.

There can also be restrictions during the transport process that may lead to delays. For Example during bad weather ferries used in shipping can be delayed. Therefore users often have to have increased stocks, which in turn leads to higher costs (stocking, limits/permits, insurance etc).

Accidents and spillages related to cyanide, particularly in the mining industry and in the transportation of hazardous waste have been reported. In some areas local authorities have taken drastic action to curtail use and transportation of cyanide materials. E.g. China, one country where legislation is becoming very prohibitive.

As a result, in China, in some areas, the use of cyanide is becoming so prohibitive that new companies are looking to set up with non cyanide processes. Overall they claim no extra costs due to reduced set up costs concerning licenses/permits effluent etc

It can be noted that in plating worldwide accidents have been few due to the prudent nature of the people involved. However it only takes one slip and............................

b) DEPOSITED METALS

Having decided to set up precious metal plating, observed all the legislation, arranged the transport, looked into the effluent requirements what do we now face in depositing the metals.

Removal of the “unwanted deposits” can be challenging but can be achieved. Some with less difficulty some with more difficulty. The removal of lead from certain baths and processes was quite straightforward to precious metal platers. Removal of cadmium from some gold processes and nickel from decorative hard golds whist still maintaining a light stable colour more challenging. In the case of replacing the nickel from Jewellery items affected by the nickel allergy legislation this involved a new process sequence. Bright nickel was substituted by bright acid copper with a thin diffusion barrier of palladium prior to the gold plating. Unfortunately this had the side effect of introducing another ammoniacal process stage.

a) SOLUTION CHEMISTRIES

Gold Chemistries.

Gold, is the major product used for the electronic and decorative market. It is deposited from a "mildly acidic, generally nickel or cobalt brightened, gold potassium cyanide bath". Although nominally a "cyanide" bath the gold potassium cyanide is stable at a the pH of 4.0 – 5.0 and in effect causes very little effluent and toxicity problems. However it is still "Toxic" and carries that stigma.

Gold. There have been a number of processes used in the decorative market that are alloyed with cadmium to produce a 12/14/16/18K alloy deposit. The diving force for these products was always cost. Typically parts would be over plated with 1micron of a 23.5K hard acid gold deposit. Often these solutions also contained free cyanide. The Cadmium is necessary to give these low carat deposits corrosion resistance , without the Cadmium the Copper easily tarnishes and the deposit colour degrades. Cadmium is one of the metals mentioned above that is now very restricted by legislation. As like Lead it can have significant health impacts and so most legislation that restricts lead also restricts the use of Cadmium.

Gold. Again for the decorative market there is the "nickel free" legislation. Here there is a great misconception. Generally it is understood that products have to be free from nickel a) in the top layer (usually gold, but could also be rhodium, or silver when a white colour is required) and b) in the under layer. In fact the directive actually states that an "emission" swab test has to be passed. In this case goods can be marked as "passing" the emission test. For example gold plated 5 microns over 5 microns bright nickel would certainly pass the swab test. However in this case goods could not be marked at "nickel free". Public perception has therefore dictated that goods should be greater than the legislation.

Gold process using Sulphite are available but have distinct drawbacks. Particularly in electronic interconnection, their ability to gall and cold weld was documented in the 70s and 80s. They do not form "colour golds " as per the acid hard golds so are also limited in decorative fields. New complexes of gold have been reported in the late 90s and early 00s but as yet no real commercial practices can be found .

See table 1) Gold Plating Solutions

Silver Chemistries.

Silver as a plated metal offers the greatest challenges regarding the replacement of cyanide. For platers cyanide is a most useful complex to work with. It forms a most forgiving suitable complex for electrodeposition and despite its hazardous nature is very easy to work with. Silver brighteners for this application are well established and dealing with cyanide effluent is also well established. For these reasons silver plating is actually looked on as a low cost/low maintenance plating process when the silver metal costs are excluded.

Standard silvers usually contain 150g/l free cyanide and low cyanide versions 70g/l. There are also solutions used in high speed plating that start with 0g/l free cyanide but build up to around 20g/l by the end of their life.

Silver electrolytes based on fluoborate, halides and thiosulphate have been mentioned in the literature since the 1930's. In the 1970's, papers on the use of silver succinimide started to appear. Several Patents were issued on cyanide free processes based on some of the above complexes; "A coherent, continuous, matte deposit" was claimed from the formulation below.

1976US Patent.	
Silver chloride	12 g/l
Sodium Thiosulphate	36 g/l
Sodium Sulphate	11 g/l

"A mirror bright, stress free deposit" was claimed from this patent.

1978 US Patent.	
Silver succinimide	22 g/l
Succinimide	11 g/l
Conducting salt	30 - 40 g/l
Brightener	

In the 1990's, more papers were presented offering production processes based on silver succinimide or silver MSA and potassium Iodide. Several reviews in the last few years have expressed reservations over such processes and the take up by industry was limited. A review in 2002 of two "commercial" non cyanide processes showed problems:

- Poor colour of deposit – yellowing
- Poor adhesion over bright nickel
- Immersion deposits – contamination

There have been other processes on offer in the US and Europe but the acceptance has been low, mainly due to cost and approvals.

With more stringent requirements regarding transport, storage and usage of silver cyanide products and processes the time is right for a new truly non cyanide process, capable of utilising silver anodes (cost issue), to be brought to the market.

See table 2) Silver Plating Solutions

Palladium/Palladium Nickel Chemistries

The Technology of Palladium-Nickel deposition and it's specific function is relatively new, about 25 years. Originally Palladium-Nickel has been developed for the spectacle industry as a barrier layer either under gold, or as a final finish. The utilisation in the electronic field emerged in volume later despite some early successes by entreprenurial electronic accounts.

The chemistry of the Pd/Ni baths traditionally uses the ammonia under different forms for complexing the nickel and allowing the co-deposition to attain the required percentage on the finished item (mostly connectors). The presence of ammonia and its inherent volatility gives strong vapours around the electrolyte cell. The solution to removing the smell is to invest in high cost extraction equipment which will add to the cost of the process. The working conditions are therefore a little inconvenient due to the frequent requirement to adjust the pH as necessary. On some lines usages up to 50 litre (NH_3) in 24 hours has been known in order to maintain the speed of the process at a high working temperature. In parallel, if we use hydrochloric acid in the proximity a white vapour of Ammonium Chloride can be generated in the workshop, which can be uncomfortable. Therefore, the object to eliminate ammonia from the system is largely justified in terms of working environment and therefore the elimination of the risk of respiratory irritation.

Existing Processes.

3 catagories of process:
- Systems “high ammonia” with Chloride.
- Systems “low ammonia” with Chloride.
- Systems "low ammonia without Chloride.

Work to replace ammonia in palladium nickel baths was completed in the early part of this millennium and the new innovative process will be explained further in this article.

See table 3) Palladium & Palladium Alloy Plating Solutions

Rhodium Chemistries

Rhodium baths are mostly formed around complexes of Rhodium Sulphate and some Rhodium Phosphate. They always contain sulphuric acid. In the past lead has been, and still is, used as a brightener/whitener for the rhodium plating processes. There are no real issues with this being used as the amounts are only ppm in the plating process so would be ppb in the deposit if at all. However again producer perception is dictating that lead should not be used. The bath itself is acidic but at a low level where even though classed as corrosive does not cause great difficulties. Because of the very very high price of Rhodium mostly these products are used in limited quantities and often fall under the volume level to create difficulties both in use and in transport.

See table 4) Rhodium Plating Solutions

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Platinum Chemistries.

Solutions based on Chloroplatinic Acid ($H_2PtCl_6.6H_20$) or Platinum Diamino Dinitrite $Pt(NH_4)_2(NO_2)_2$ along with solutions based on Sodium Hexa Hydroxy Platinate ($Na_2Pt(OH)_6$) have been widely available for some years. Solutions using these basic products are known to have their limitations regarding the thickness that can be achieved, particularly the Chloroplatinic acid based and therefore baths made from these chemicals can also have limited life spans.

Products based on the Platinum Diamino Dinitrite (known as Platinum P salt) also had the disadvantage of needing to be operated in a strong ammoniacal presence at elevated temperatures requiring constant additions of ammonia. If allowed to run at lower levels low plating efficiencies are seen.

As well as the use of ammonia there is the potential danger that Platimum P salt can become explosive if it becomes completely dry and there are a significant number of people who are sensitive to platinum, particularly dust. Platinum salts have a high sensitising potential, Platinum dust has a WEL of 5 mg/m^3. Soluble Platinum compounds have 0.002 mg/m^3
Again physical controls are needed with health monitoring of workers for sensitisation.
causing severe allergic reactions in some people.

See table 5 Platinum Plating Solutions.

Ruthenium Chemistries.

Not a great deal has changed with Ruthenium plating baths in recent years. Despite offering significant cost advantages over the other Platinum Group Metals usage of this metal as a plating process is minimal. Its main usage is, Industrially, in plating reed relays, plating of molybdenum shims and for the production of a dark(grey/black) bright finish for the decorative market.

The industrial chemistries are either simple, based on Ruthenium Trichloride or complex based on Ruthenium Sulphamate. Generally Ruthenium deposits are very stressed when deposited therefore the coatings are either very thin or use complexed systems to reduce the internal stress and build thicker layers.

In decorative plating its use is almost exclusively to produce a dark (grey black) finish on costume jewellery items usually in combination with two colour golds or gold/rhodium. Current work has been almost entirely related to the decorative processes in order to remove the Phenol and Pyridene compounds used to produce the dark grey/black deposits.

See table 6) Ruthenium Plating Solutions

Innovation.

This paper will concentrate in demonstrating on three areas where the most significant changes are being made or have the potential to be made. All are being used in production environments.

Replacement of Cadmium in gold plating baths

Replacement of Ammonia in Palladium Nickel Baths

Replacement of Cyanide in Silver Baths.

The Replacement of Cadmium in gold plating processes.

The restriction of Cadmium by our industry is a clear example of how proactive and responsible the finishing industry is . It can clearly be noted that from data received that the use of Cadmium (before any restrictions) in our industry represents only a small percentage of the Cadmium that we are exposed to in our daily lives. 70% of the world's cadmium supply is used in batteries. However Cadmium Free processes have been developed for the watchcase industry and these are being used , particularly for Japanese manufacturers of watches where the use of Cadmium is proactively restricted.

Operating Parameters of Cadmium Free 18K Gold Plating

Parameter	**Unit**	**Range**	**Optimum**
Gold	g/l	2.5 - 5.0	4.0
Copper	g/l	15-25	20
Free Cyanide	g/l	7-12	10
Additive	ml/l	3-5	4
Wetting Agent	ml/l	1-5	2
pH	-	9.5-10.5	10
Temperature	^{O}C	50-70	60
Solution Density	^{O}Be	10-15	12
Agitation	m/min	3-6	4
Current Density	A/dm^2	0.5-1.5	0.8

18K cadmium Free deposits have passed Artificial Sweat Tests ,Salt Spray tests and thermal cycling tests applied to watchcase and watch strap parts by leading Japanese manufacturers.
The 18K cadmium Free is being used successfully in production in Southern China where many of the leading watch case and strap plating companies are located.

The innovative processes incorporate the use of a semi metal and organic additive that ensure a true 18K alloy is produced , this true alloy formation is the key to successes in the corrosion tests applied as no discrete areas of Copper are noted hence only the properties of the true alloy are exhibited.

Innovation.

Palladium Nickel Process Without Ammonia.

Baths without ammonia allowing an ideal of Pd/Ni have been strongly expected for some time. The development effort has been to replace the nickel ammoniacal complex. A new idea, very simple, has been developed. That was to develop a Palladium/Nickel bath to operate in the same pH range 4.0 - 4.5 as nickel solutions. This bath should be capable in one operation to achieve an adherent deposit of any 80/20 Pd/Ni alloy directly onto substrate such as nickel. This bath to be ammonia free and containing neither chlorides nor strong acids.

These new baths of Pd/Ni are based on an organic complex. The main progress has been in the realisation synthesis of the new organic complexes with palladium and in the identification of the new organic brightener. This brightener having a specific effect on the brightness of the Pd/Ni deposits even when these are used at very high current density (over 50 A/dm^2). The deposits obtained through this new process are therefore bright, white and functional.
The whole process of gold on Pd/Ni on Ni can now be completed using baths with a pH around 4.0, without chloride. With the new Pd/Ni process there is no corrosion of the copper as commonly seen with ammonia baths. Neither is there attack of the stainless steel due to the lack of chlorides. As well as offering an exceptional white bright deposit, this Pd/Ni deposit offers other qualities, typical of a Pd/Ni. Good adherence on different substrates, good ductility, absence of porosity and good resistance to corrosion. In effect, until now with ammonia baths, the ammonia vapours disturbed the ability to increase the temperature of the bath in favour of very high speed deposits, therefore achieving even higher productivity and obtain the optimum deposit characteristics.

Properties of the deposit from the new Palladium Nickel process.

Appearance	Bright and white
Ductility	Good (180° ϕ 5 to 8mm)
Hardness	390 HV (100gf)
Contact Resistance	< 10 mΩ
Wear Resistance	British telecom, pass
Density of the Deposit	11.1 g/cm^3
Speed of Deposition (@ 42 A/dm² 70°C) (@ 56 A/dm² 70°C)	24.8 mg/A.min 9.4 µm/min 12.5 µm/min
Porosity	Good
Corrosion Resistance 0.6 to 3µm on copper	Passes the CASS TEST
Nitric Acid SpotTest	Passes the test

Operating Parameters of Ammonia Free Palladium Nickel Plating

Parameters	**Unit**	**Medium Speed**		**High Speed**	
		Range	**Optimum**	**Range**	**Optimum**
Palladium	G/l	7 - 15	12	18 – 23	20
Nickel	G/l	4 – 12	11	9 – 15	11
Palladium Nickel HS Replenisher Brightener	ml/l	4 - 8	6	4 - 8	6
Palladium Nickel Complexing agent	ml/l	67- 81	74	67 - 81	74
Current density	ASD	10-30	20	25 - 56	42
Deposition speed	mg / amp min				
20 ASD		14 – 18	16.0		
42 ASD				23 - 27	24.8
Deposition Speed Time to deposit 1 micron.	Sec.				
20 ASD			26		
42 ASD					7
pH	-	3.5 - 4.5	4.0	3.5 - 4.5	4.0
Temperature	^{0}C	55 - 75	60	60 - 75	65
Solution Density	^{0}Be g/ml	10.8 – 33.5 1.08 – 1.30	17.8 1.14	10.8 – 33.5 1.08 – 1.30	17.8 1.14
Anodes		Platinum or Platinised Titanium			
Agitation	-	Vigorous to very vigorous	very strong (maximum)	Vigorous to very vigorous	very strong (maximum)

Innovation

Cyanide Free Silver

This new innovative generation of Cyanide Free Silver plating processes contains **zero cyanide** and therefore offers significant environmental and safety benefits as it saves the ever increasing cost of controlling these toxic materials allowing a lower cost operation from environmental viewpoint.

The bath is made by utilising a complex of Silver MSA with new patented complex to replace the cyanide. The bath is straightforward to make up and utilises a wetting agent and brighteners as with traditional cyanide silver baths. It will also dissolve readily silver anodes avoiding some of the cost issues with other non cyanide baths where additions of silver have to be made with salts.

Of course there are no other components with any environmental issues so the entire process is seen as a “green technology” and is the future of Silver electrodeposition.

FEATURES AND BENIFITS

Non Cyanide : Safer Working Environment

Non Cyanide : Reduced Heath and Safety Costs

Non Cyanide : No need for Silver Strike in Pre-treatment

Non Cyanide : Reduced Environmental Impact

No Pollutants : Reduced Environmental Costs

No Carbonates : Increased bath life

Fully Analysable : Easy to Operate

Operating Parameters of Cyanide Free Silver Plating

Usual Working values			**Permissible Working Range**		
Content of Silver		30.0 g/l	Content of Silver		28.0 to 35.0 g/l
pH-value		10.0	pH-value		9.8 to 10.2
Working temperature		20°C	Working temperature		17 to 22°C
Cathodic current density			Cathodical current density		
	rack	1.0 A/dm^2		rack	up to 1.2 A/dm^2
	barrel	0.5 A/dm^2		barrel	0.2 to 0.5 A/dm^2
Anodical current density			Anodical current density		
	rack	0.25 A/dm^2		rack	0.25 to 0.5 A/dm^2
	barrel	0.5 A/dm^2		barrel	0.25 to 0.5 A/dm^2
Deposition rate			Deposition rate		
	rack	0.6 µm/min		rack	up to 0.6 µm/min
	barrel	0.3 µm/min		barrel	up to 0.3 µm/min

Future

Clearly legislation is not going to be relaxed anywhere, anytime regarding the use of hazardous processes.

Cost issues which appear to have been the biggest stumbling block are being eroded day by day as the “real” cost of using hazardous materials are being realised.

Clearly though gold plating with its major reliance on GPC based solutions will need to be reviewed in the near future. For the electronic industry any restriction on the use of GPC based products would create major problems. Only connectors plated in solutions based on GPC offer the good wear properties required for a connector. The fact of depositing the alloyed element from a complex of gold, cyanide and the brightening metal (usually 0.2% Co or Ni) is what gives the deposit its good wear properties. Many papers have been written in the early seventies explaining the poor wearing properties from deposits from pure golds mostly sulphite type gold.

With the expected difficulties in use of cyanide based products (even as complexed as gold) in the future means that alternatives have to be considered.

Palladium Nickel as an alternative to gold has already been discussed above and offers an immediate solution without adding new issues. Mostly the Palladium Nickel is over plated with gold from a GPC based solution. Perhaps as the thickness is so small a sulphite based system could be potentially used in the future.

Alternatively new gold systems (or re-engineered gold sulphite systems) based on new complexes will have to be used. Papers have been written regarding the use of gold from new complexes and have been presented in the past but as yet no current systems are commercially available.

With the thicknesses of gold plating on connectors being used being reduced maybe a reengineered sulphite process would be acceptable. One certain difficulty will be getting the connector industry to accept a new standard.

Clearly Silver plating from non cyanide processes will become more prevalent in the coming years despite their APPARANT higher cost NOW.

Conclusions & Summary

Respect for toxic materials within the industry has minimised accidents and injuries. Improvements in effluent treatment and treatment of air emissions has reduced environmental impact.

Plating can be hazardous to your health.
Plating can be hazardous to the environment.

Our industry is constantly striving to become more environmentally responsible, legislation is making this more of a compulsion than a choice.

Alternative non/less hazardous processes are available. NOW!

- **"Ammonia Free"** Palladium Nickel
- **"Nickel Free** " Precious Metal processes
- **"Cyanide Free"** Precious Metal processes
- **"Cadmium Free"** 18K Alloy Gold Plating

R&D efforts continuously strive to further enhance the safety and environment awareness in our industry. With the increasing use of organic materials, at the same time there is the drive to be more environmentally friendly. Care has therefore to be taken in the choice of organics and in fact a number of products that could have been used in the past are now prohibited. Work has already removed the small amounts of Cadmium used in precious metal plating and continues with the removal of Lead, Phenols & Pyridenes etc.

Although solution costs may appear to be higher, We need to remember that the cheapest is not always the wisest investment ,nor in the big picture the most economical purchase.

Increased tightening of environmental legislation will mean that processes will have to be changed irrespective of the cost implications.

Table 1 Gold Chemistries.

Gold	Type A	Type B	Type C	Type D	Type E
Basis	Potassium Cyanide	Potassium Cyanide	Potassium Sulphite	Sodium Sulphite	Sodium Sulphite
Type	Rack Barrel High Speed	Rack Barrel High Speed	Rack	Rack	Rack
Application	Electronic Decorative	Electronic Decorative	Electronic	Electronic	Electronic
Gold Conc	2-15g/l	2-15g/l	10g/l	10g/l	10g/l
Base Electrolyte					
Sulphite			35g/l	30g/l	30g/l
Oxalate/Citrate	100g/l	100g/l			
Temperature	35- 55°C	35- 55°C	55°C	52°C	45°C
pH	4.0-5.0	4.0-5.0	9.5	7.3	7.2
Density	12°Be	9°Be	9°Be	12°Be	18°Be
Additive	Organic	Organic	Arsenic	Thallium	Arsenic or
					Thallium
Concentration	5ml/l	5ml/l	50 mg/l	15 mg/l	15-30mg/l
Metal Brightener	Nickel	Cobalt	None	None	None
Concentration	1-2g/l	1.2g/l			
CD A/dm2	0.5 – 25	0.5 - 25	0.1 - 0.3	0.1-1.0	0.1-1.0
Brightness	Bright	Bright	Bright	Semi	Bright
	Reflective	Reflective		Bright	
Hazard Bath Additive	Toxic None	Toxic None	None Poison	None Poison	None Poison

Table 2 Silver Chemistries. (SPC = Silver Potassium Cyanide)

Silver	SPC	SPC	SPC	SPC	SPC	MSA + Ag
Application	Industrial Decorative	Decorative	Industrial	Industrial	Industrial	Industrial
Type	Rack	Rack	Rack	High Speed	High Speed	Rack
	Barrel	Barrel	Mid HS			Barrel
Silver	36g/l	36g/l	50g/l	65g/l	65g/l	30g/l
Cyanide	150g/l	150g/l	70g/l	0-20*g/l	0*-20g/l	0g/l
Complexant	-	-	-	-	-	120g/l
Additive	-	-	-	-	0-5ml/l	-
Brightener	Organic	Antimony	Selenium	Selenium	Selenium	Organic
Temperature	25ºC	25ºC	40-60ºC	40-60ºC	40-60ºC	20ºC
Current Density	1.2A/dm^2	1-2A/dm^2	1-7.5A/dm^2	10-50A/dm^2	50-200/dm^2	1.1A/dm^2
Plating Rate	1 micron 1 minutes	1 micron 1 minutes	1 micron 10 seconds	1 micron 4 seconds	1 micron 2 seconds	1 micron 1 minutes
Agitation	Moderate	Moderate	Vigorous	Vigorous	Vigorous	Moderate
Hazard	Toxic	Toxic	Toxic	Toxic	Toxic	None

*** Made up at 0g/l free cyanide but builds up to 20g/l during bath.**

Table 3 Palladium & Palladium Nickel Chemistries

Palladium	P Salt	Ammonia Chloride	Ammonia Chloride	Ammonia Sulphate	Ammonia Chloride Nickel	Ammonia Sulphate Nickel	Ammonia Sulphate Cobalt	Non Ammonia Nickel
Application	Industrial	Decorative Flash	Decorative Industrial	Industrial	Industrial Decorative	Industrial	Industrial	Industrial Decorative
Type	Rack	Rack	Rack	R2R	Rack	Rack	R2R	Rack
Type	Barrel	Barrel			Barrel	R2R		Barrel
Type					R2R			R2R
Palladium	10-12g/l	2g/l	10g/l	25g/l	6-20g/l	10-25g/l	35-45g/l	4-25g/l
Nickel	-	-	-	-	10-20g/l	9-15g/l	-	9-13g/l
Cobalt	-	-	-	-	-	-	6-10g/l	-
C/Salt	15g/l Nitrite				50g/l	50g/l	40g/l	25g/l
Complexant	-	-	-	-	-	-	-	72g/l
Additive	-	-	50ml/l	35g/l	20m/l	20m/l	-	-
Brightener	-	2ml/l	10ml/l	50ml/l	10ml/l	10ml/l	5-20ml/l	6ml/l
Brightener	-	10ml/l	-	13.5ml/l				
W/Agent	-	5ml/l	-	-	-	-	0.5-5m/l	-
Temperature	30ºC	25ºC	40ºC	50ºC	35-55ºC	35-55ºC	50ºC	65-70ºC
pH	8.0	8.0	7.00	7.5-8.0	7.5-8.5	7.2-8.2	7.0-7.5	4.00
Density		4ºBe	12ºBe	12ºBe	8-20ºBe	8-20ºBe	24ºBe	17ºBe
Current Density	0.7A/dm^2	0.5A/dm^2	2A/dm^2	25 A/dm^2	1-50A/dm^2	3-50A/dm^2	5-70A/dm^2	1-70A/dm^2
Plating Rate	1 micron 9 minutes	0.2 micron 1.5 minutes	1 micron 3 minutes	6 micron 1 minute 25 A/dm^2	Variable R/B/HS	1 -5 microns minute		1 micron in 10secs 28 A/dm^2
Agitation	Moderate	Moderate	Vigorous	Vigorous	Moderate	Vigorous	Vigorous	Vigorous
Hazard	??????	Ammonia	Ammonia	Ammonia	Ammonia	Ammonia	Ammonia	None

Table 4 Rhodium Chemistries

Rhodium	Sulphate	Phosphate	Sulphate	Sulphate	Sulphate	Sulphate	Sulphate
Application	Industrial	Decorative	Decorative	Decorative	Decorative	Decorative	Decorative
Rhodium	5g/l	2g/l	2g/l	2g/l	2g/l	2g/l	2g/l
Sulphuric Acid	45g/l	36g/l	20g/l	25g/l	30g/l	20g/l	20g/l
Phosphoric Acid	-	20g/l	-	-	-	-	-
Additive	Sulphamate	-	-	-	-	Acid	-
Brightener	-	Lead	None	Lead	Organic	Organic +	Organic
Temperature	55ºC	40ºC	40ºC	25ºC	30ºC	25-30ºC	25-30ºC
Current Density	1.1A/dm^2	1-5A/dm^2	1-5A/dm^2	1-5A/dm^2	0.5-3A/dm^2	0.5-3A/dm^2	0.5-3A/dm^2
Plating Rate	1 micron 9 minutes	0.25 micron 8 minutes	0.25 micron 3 minutes	6-8mg A/minute	5 mg A/minute	6-12mg A/minute	6-12mg A/minute
Agitation	Strong	Vigorous	Vigorous	Moderate	Moderate	Moderate	Moderate
Hazard	Corrosive	Corrosive	Corrosive	Corrosive	Corrosive	Corrosive	Corrosive

Table 5 Platinum Chemistries

Platinum	CPA	P Salt	SHP	Sulphamate	Phosphate	Sulphate
Application	Industrial Flash Rack	Industrial Aerospace Rack	Industrial Aerospace Rack/R2R	Industrial Decorative Rack	Decorative Rack	Decorative Rack & Barrel
Platinum	2-10g/l	5-10g/l	10-20g/l	6-20g/l	2-10g/l	2-5g/l
Conducting	-	Phosphate	Hydroxide	-	-	-
as Phosphate	-	100g/l	-	-	-	-
Hydroxide	-	-	-	-	-	-
Sulphamic Acid	-	-	-	20-100g/l		-
Phosphoric Acid	-	-	-	-	Acid/Density	-
Sulphuric Acid	-	-	-	-	-	30g/l
Temperature	45ºC	85ºC	80ºC	65ºC	45ºC	25ºC
pH	<1.0	8.5-9.0	8.0		1.0	1.0
Current Density	1-2A/dm^2	2 - A/dm^2	0.7A/dm^2	2-10A/dm^2	1-2A/dm^2	0.5-2.0A/dm^2
Density Be	-	7-16ºBe		-	5-30ºBe	Acid level
Plating Rate	Limited	3-5 micron 1 hour	I micron 10 minutes		1 micron 10-30 min	1 micron 12 minutes
Agitation	Vigorous	None	Moderate	Moderate	Moderate	Moderate
Hazard	Corrosive	Ammonia	Caustic	Corrosive	Corrosive	Corrosive

Table 6 Ruthenium Chemistries

	Trichloride	Sulphamate	Sulphamate	Sulphamate	Sulphamate
Application	Industrial	Decorative	Decorative Black	Industrial	Industrial
Ruthenium	5g/l	5g/l	5g/l	10g/l	5-10g/l
Acid	Hydrochloric	-	-	-	-
Additive	-	-	-	-	Sulphamate
Additive	-	-	-	-	Nickel 2g/l
Temperature	65ºC	70ºC	70ºC	70ºC	70ºC
pH	<1.0	1.6	1.8	1.6	1.7
Current Density	Variable	1.0 A/dm^2	2.0 A/dm^2	1.0 A/dm^2	1.0-3.0A/dm^2
Plating Rate	- -	1 micron* 18 minutes	1 micron* 8 minutes	1 micron* 12 minutes	1 micron 18 minutes
Agitation	Vigorous	None	Moderate	None	Moderate
Hazard	Corrosive	None	None	None	None

References

1.Nickel allergy :The European Directive and its consequences on Gold Coatings and White gold Alloys. P.Bagnoud.S.Nicoud.P.Ramoni Gold Technology18 (1996) 11-19.

2.Alternatives to Nickel in Electroplating Processes
F.Simon Trans IMF .1997.75.(3)

3.Control of Nickel emission in Jewellery and related Items
R.V.Green & J.F.Sargent Trans IMF .1997.75.(3)

4 Nickel Free Plating Technology. S.J.Hemsley & J.F.Sargent
Singapore Surface Finishing Society Seminar October 1997

5.Alternatives for Nickel in Electroplating Processes
F.Simon Plating & Surface Finishing Nov 1994

6. New Non Cyanide and Non Sulphite Gold Playing Process
Dr F Simon W Kuhn, Degussa Gavanotechnik GmbH

7. www.metalor.com
MetPall III : Ammonia Free Palladium Nickel
MetAulloy 18K CDF : Cadmium Free 18K Gold
MetSil 100 CNF : Cyanide Free Silver

8. A New Technology : Palladium Nickel Ammonia Free.
S.A. Burling, Engelhard-CLAL UK Ltd., L. Chalumeau, J. Gonzalez, C. Leclere,
M. Limayrac, Engelhard - CLAL Paris, S. J. Hemsley, Engelhard -CLAL (Singapore) Pte.Ltd
SurFin 2001 Nashville, USA.

9. Applications of Palladium and Palladium Alloys ; Stewart J Hemsley
Singapore Surface Finishing Seminar : October 2005

10. International Cadmium Association

11. Environmental Processes Developments for Decorative Electroplating
Stewart J Hemsley, Metalor Technologies, Singapore Pte Ltd. ISF Seminar Mumbai India 2006.

12 Modern Trends & Developments in Plating with Platinum Group Metals.
Steven Burling; Metalor Technologies, Birmingham, United Kingdom. SurFin 2005 St Louis USA.

13 Novel & Innovative Non - Cyanide Silver Process. A Report on Commercial Plating Experiences. Sascha Berger & Gerhard Hoffacker. Plating & Surface Finishing March 2005.