Modern Trends & Developments in Plating with Platinum Group Metals

Steven Burling; Metalor Technologies, Birmingham, United Kingdom

This paper will show the trends and current developments in the plating of the Platinum Group Metals. Specifically metals such as Palladium (and Palladium Nickel), Rhodium, Platinum and Ruthenium will be covered showing how the development of modern formulations has led to applications in electronics, automotive, aerospace and medical industries as well as developments in the more traditional decorative market. The need to develop environmentally friendly products and how this has been approached will also be covered.

For More Information, contact.
S.Burling
Metalor Technologies (UK) Ltd.,
74 Warstone Lane,
Birmingham,
BN18 6NG
UK.

Tel: +44 121 236 3241
Fax: +44 121 236 3568
steven.burling@metalor.com

Introduction

Whilst not being the first choice for plating applications the use of the platinum group metals to provide a “white” technical or decorative finish has been appreciated by the industry for many years. The price of these metals has often, at various times, provided a barrier to more wider uses but they have still found their applications despite these price barriers.

This paper will show the trends and current developments in the plating of the Platinum Group Metals. Specifically metals such as Palladium (and Palladium Nickel), Rhodium, Platinum and Ruthenium will be covered showing how the development of modern formulations has led to applications in electronics, automotive, aerospace and medical industries as well as developments in the more traditional decorative market. The need to develop environmentally friendly products and how this has been approached will also be covered.

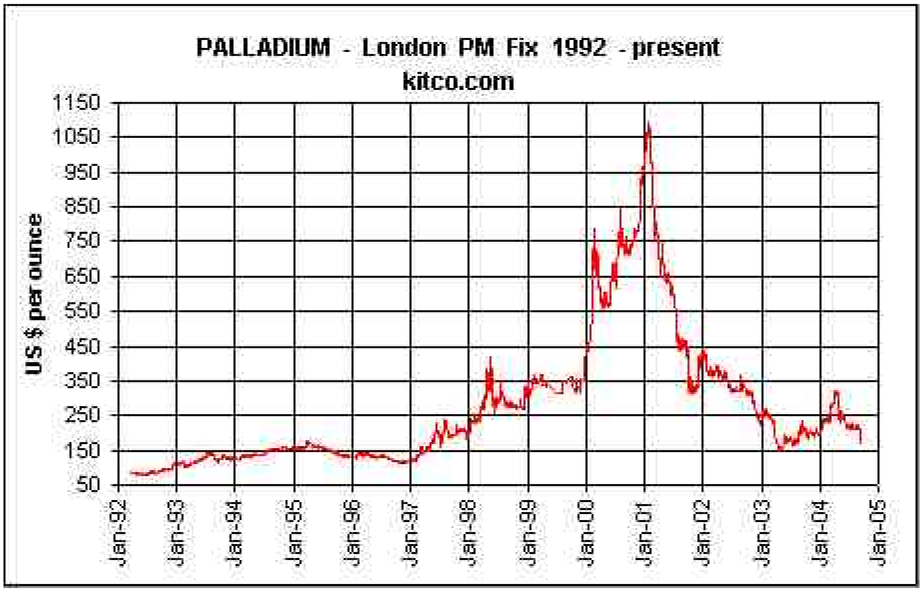
The Metals

Palladium	Colour – grey white as deposited. Density, 11.2g/cm3
	Matt – Semi bright for electronics and fully bright for decorative applications.
	Mostly alloyed with Nickel nowadays. Density, 11.2-11.5g/cm^3
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.
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.
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.

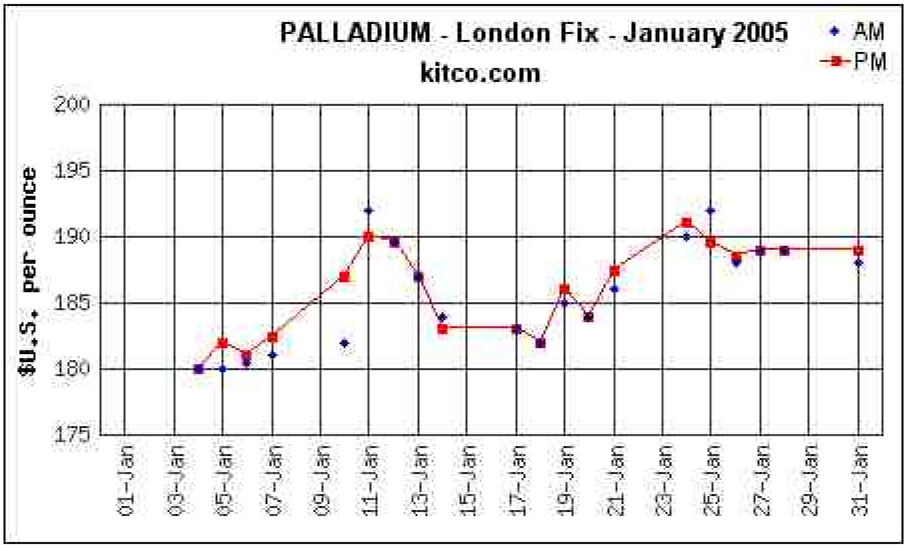
As detailed above price has always been a issue with these products maybe with the exception of ruthenium. A little examination of their price variability is therefore worthy of evaluation.

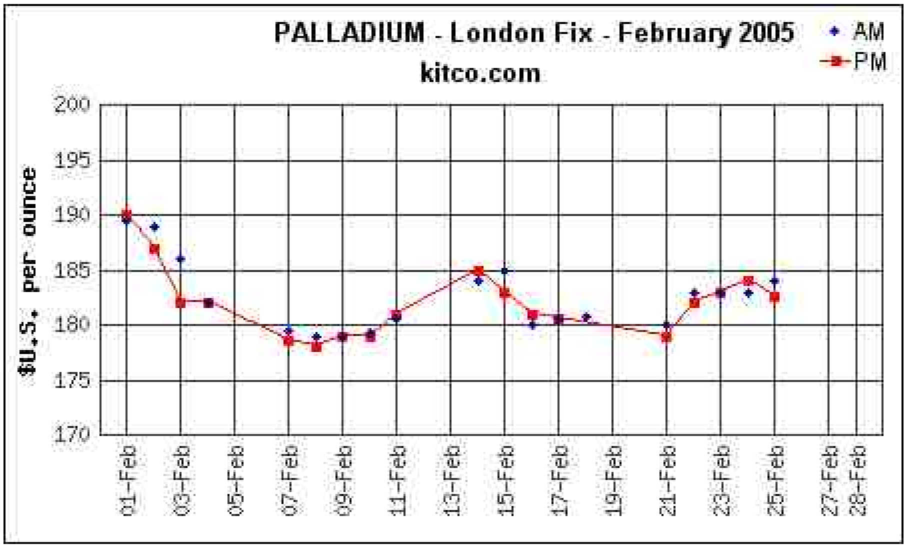
Palladium.

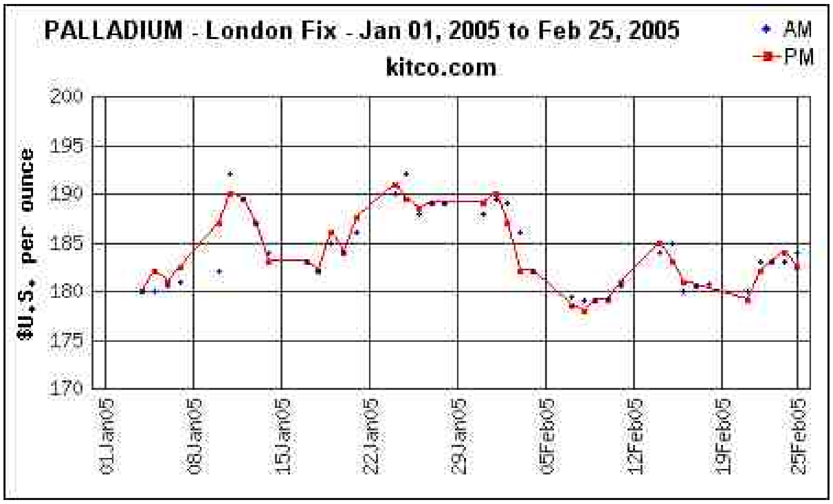
The most widely used of the Platinum group metals due to its applications in the electronic market.

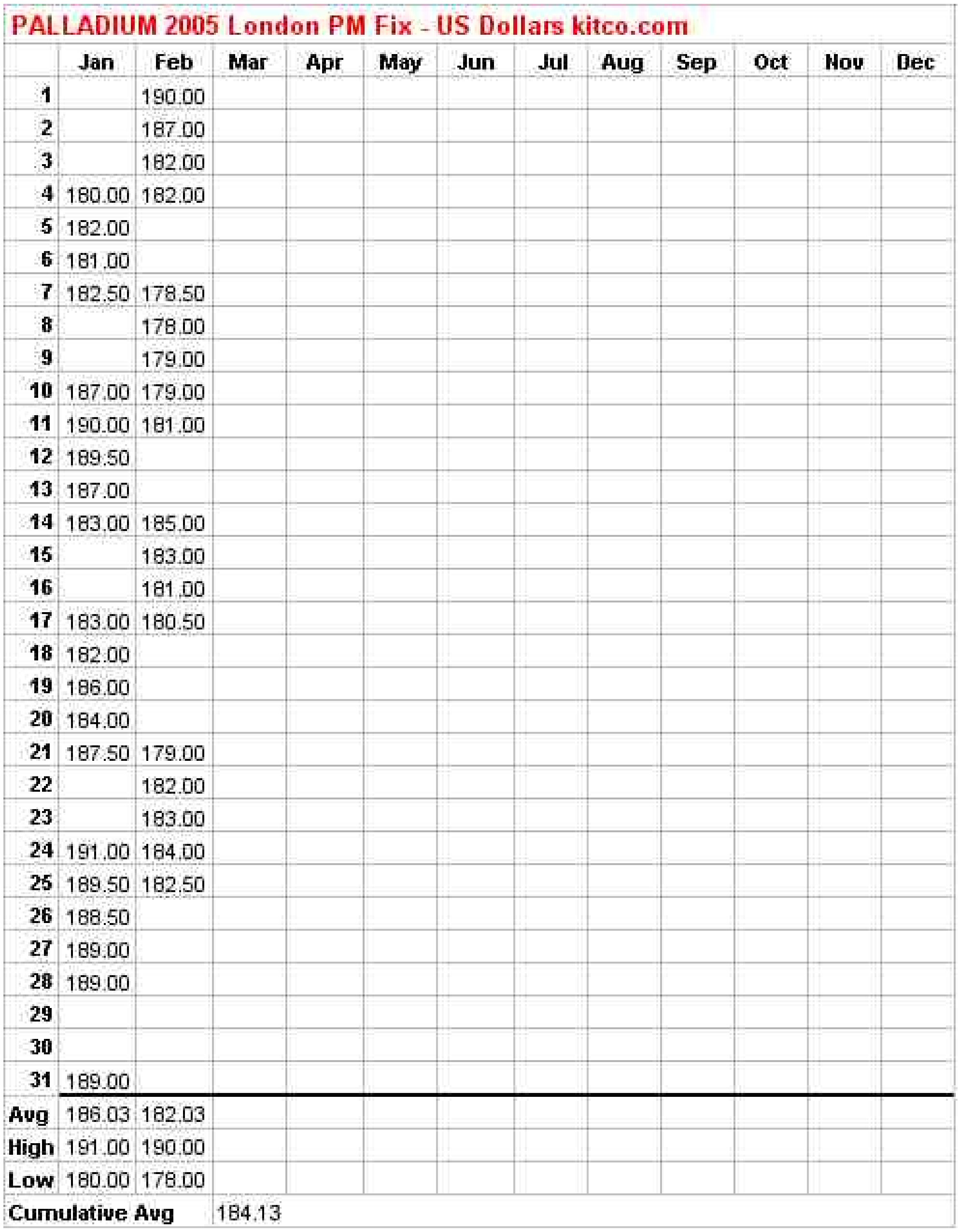



PALLADIUM - London PM Fix 1995 - 1999
kitco.com
US $ per ounce
450
400
350
300
250
200
150
100
Jan-95
May-95
Sep-95
Jan-96
May-96
Sep-96
Jan-97
May-97
Sep-97
Jan-98
May-98
Sep-98
Jan-99
May-99
Sep-99
Jan-00


PALLADIUM - London Fix - January 2005
kitco.com
AM
PM
$U.S. per ounce
200
195
190
185
180
175
01-Jan
03-Jan
05-Jan
07-Jan
09-Jan
11-Jan
13-Jan
15-Jan
17-Jan
19-Jan
21-Jan
23-Jan
25-Jan
27-Jan
29-Jan
31-Jan


PALLADIUM - London Fix - February 2005
kitco.com
AM
PM
$U.S. per ounce
200
195
190
185
180
175
170
01-Feb
03-Feb
05-Feb
07-Feb
09-Feb
11-Feb
13-Feb
15-Feb
17-Feb
19-Feb
21-Feb
23-Feb
25-Feb
27-Feb
28-Feb

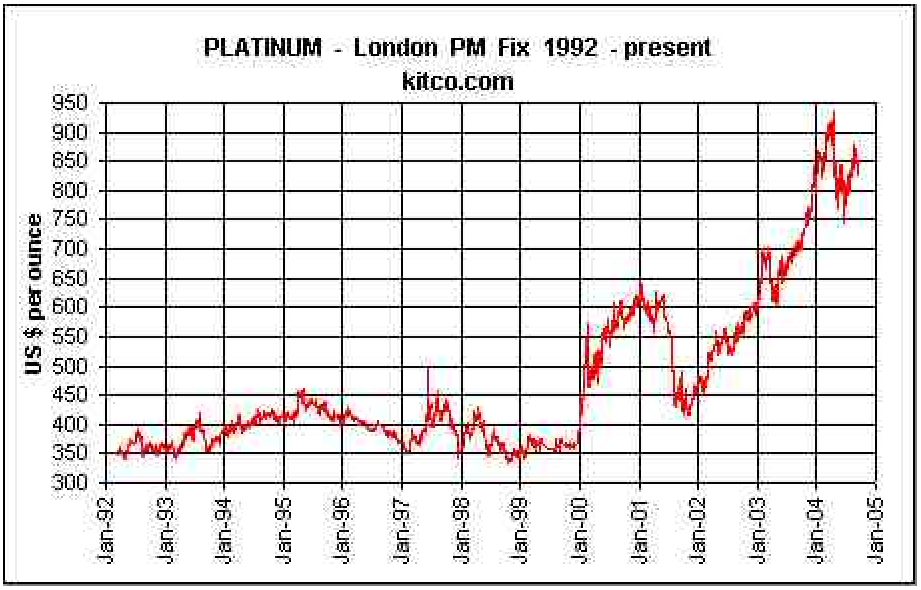

PALLADIUM - London Fix - Jan 01, 2005 to Feb 25, 2005
kitco.com
AM
PM
$U.S. per ounce
200
195
190
185
180
175
170
01Jan05
08Jan05
15Jan05
22Jan05
29Jan05
05Feb05
12Feb05
19Feb05
25Feb05



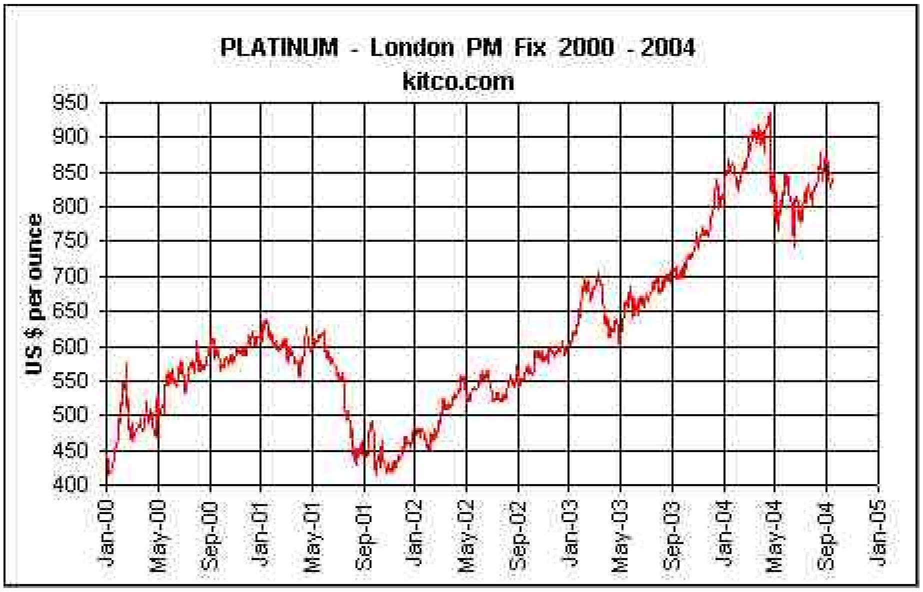
PALLADIUM 2005 London PM Fix - US Dollars kitco.com

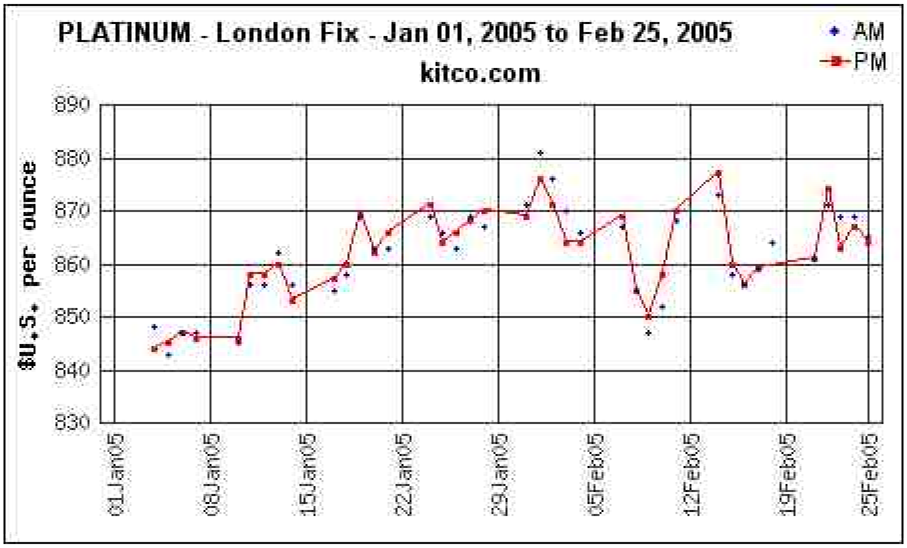
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1		190.00										
2		187.00										
3		182.00										
4	180.00	182.00										
5	182.00											
6	181.00											
7	182.50	178.50										
8		178.00										
9		179.00										
10	187.00	179.00										
11	190.00	181.00										
12	189.50											
13	187.00											
14	183.00	185.00										
15		183.00										
16		181.00										
17	183.00	180.50										
18	182.00											
19	186.00											
20	184.00											
21	187.50	179.00										
22		182.00										
23		183.00										
24	191.00	184.00										
25	189.50	182.50										
26	188.50											
27	189.00											
28	189.00											
29												
30												
31	189.00											
Avg	186.03	182.03										
High	191.00	190.00										
Low	180.00	178.00										
Cumulative Avg			184.13									

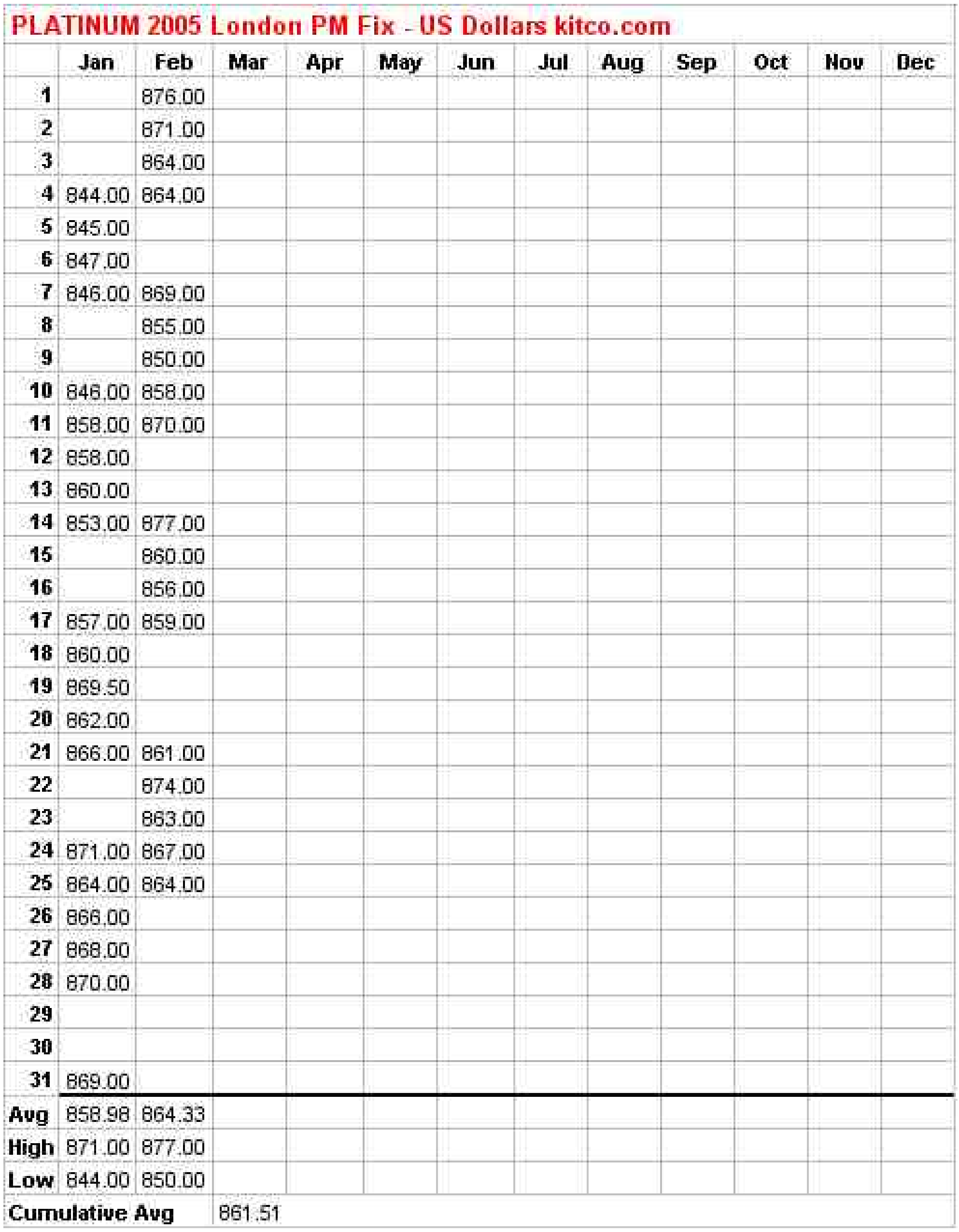
Platinum, our next metal of the group has also had interesting period particularly since the new millennium..



Generally it can be seen that Platinum has mostly risen continuously since the millennium.



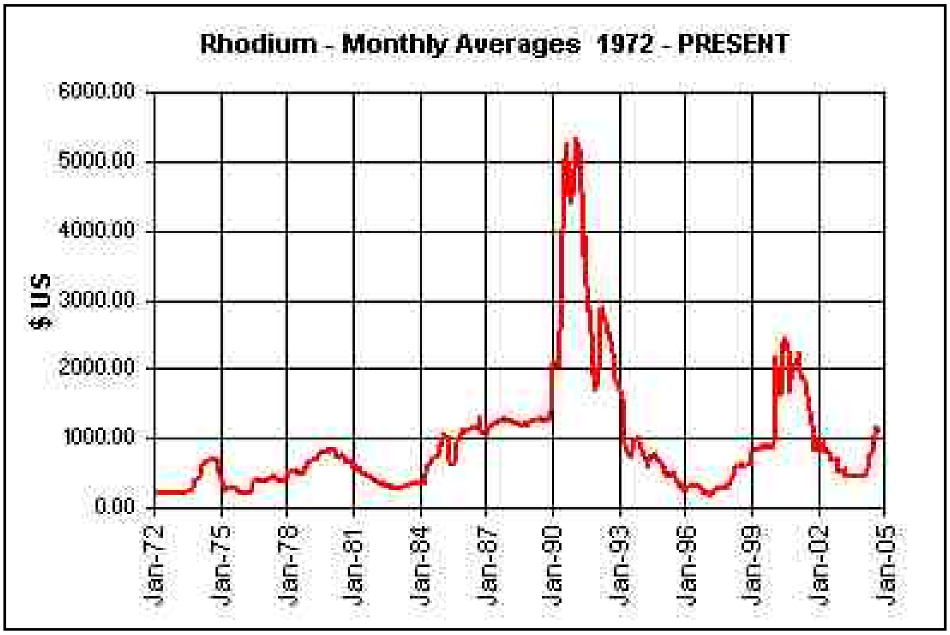

PLATINUM - London Fix - Jan 01, 2005 to Feb 25, 2005
kitco.com
AM
PM
$U.S. per ounce
890
880
870
860
850
840
830
01Jan05
08Jan05
15Jan05
22Jan05
29Jan05
05Feb05
12Feb05
19Feb05
25Feb05

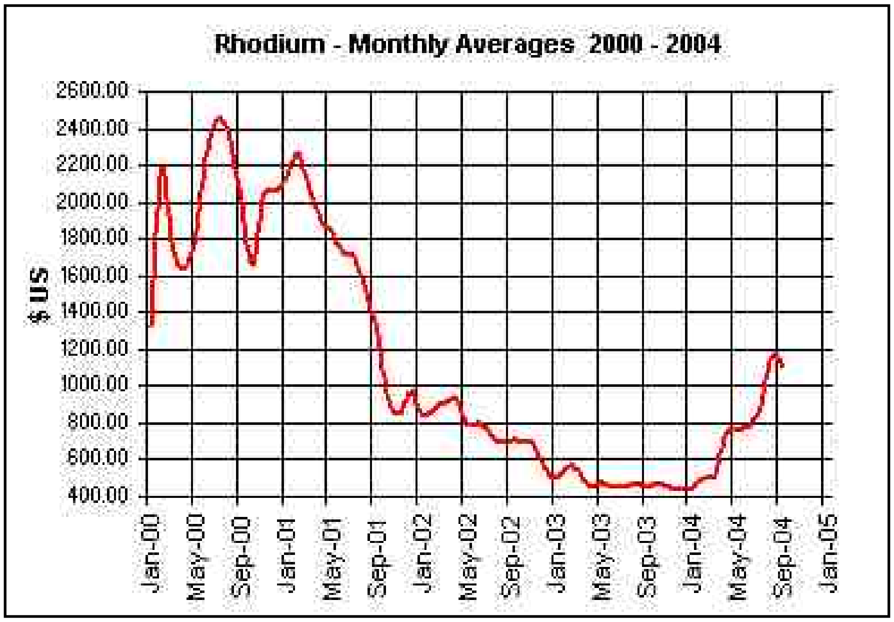


PLATINUM 2005 London PM Fix - US Dollars kitco.com

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1		876.00										
2		871.00										
3		864.00										
4	844.00	864.00										
5	845.00											
6	847.00											
7	846.00	869.00										
8		855.00										
9		850.00										
10	846.00	858.00										
11	858.00	870.00										
12	858.00											
13	860.00											
14	853.00	877.00										
15		860.00										
16		856.00										
17	857.00	859.00										
18	860.00											
19	869.50											
20	862.00											
21	866.00	861.00										
22		874.00										
23		863.00										
24	871.00	867.00										
25	864.00	864.00										
26	866.00											
27	868.00											
28	870.00											
29												
30												
31	869.00											
Avg	858.98	864.33										
High	871.00	877.00										
Low	844.00	850.00										
Cumulative Avg			861.51									

Rhodium is the second most commonly used platinum group metal due to its ability to give a "white" deposit for the decorative market, particularly costume fashion item.





There were as with Palladium specific reasons for the hike in price at the end of the 80's and during the early 90s related to the ability to refine the ore. Basically old inefficient refineries were closed and the new ones did not function appropriately at first.

Consumption

Users and potential users of Platinum Group Metal processes have often claimed that increases in their usage in the plating industry could lead to increased prices for the metal. In fact their usage as part of the overall consumption would not be significant as to make any real difference in the raw metal price. As with all precious metal processes the price of the raw metal is controlled by the metal markets and usage outside of plating is significantly higher. The table below shows the supply of platinum and palladium in 2002/2003. It can seen that the consumption in plating is not as significant in comparison.

Supply By Region ('000 oz)

		South Africa	Russia	North America	Other	Total
Platinum	2002	4450	980	395	145	5970
	2003	4670	1050	295	225	6240
		South Africa	Russia	North America	Other	Total
Palladium	2002	2160	1930	990	170	5250
	2003	2310	2950	940	250	6450
		South Africa	Russia	North America	Other	Total
Rhodium	2002	485	90	28	9	612
	2003	545	140	20	15	720

The applications.

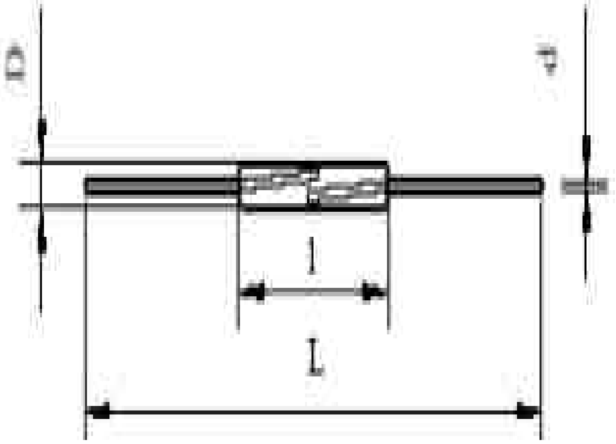
Amongst the precious metals, with gold and silver consuming much of the market, applications for the platinum group metals have been consigned to specific applications where they are technically or commercially superior.

We see all of the platinum group metals used in the decorative market where their grey-white colour can give a protective finish that cannot be provided with other metals.

Industrially palladium and in particular palladium nickel dominates the other metals as detailed below.

Palladium & Palladium Nickel. Its major application area is in the electronic market for such applications as connectors, semi conductor wafers & contacts used mostly in telecommunications. Pure Palladium is mostly used for automotive contacts.

Rhodium is still widely used for reed blades in automotive and security applications



Rhodium or Ruthenium Plated Tip of the blade

Platinum's major contribution is in extending the life of turbine blades both industrial and in aerospace applications. It is also used in many precious metal plating applications as part of the dimensionally stable anode (DSA) – platinised (plated) titanium.

Ruthenium. Reed blades, Electrical components manufactured in Molybdenum

Molybdenum, by buffering silicon against damaging thermal expansion whilst providing a contact of low electrical and thermal resistance, has an important part to play in determining the reliability of semiconductor devices. By selecting appropriate surface coatings such as

Ruthenium, the bulk properties of molybdenum can be used to full advantage without the problems associated with the chemistry and metallurgy of its surface.

Aerospace companies are increasing their research and development efforts looking at the ways in which ruthenium's incredibly high melting point, temperature stability, corrosion resistance and hardness can be used in aircraft turbine blades. Adding ruthenium to turbine blade coatings could mean higher temperatures which mean more efficient burning of fuel, reducing its consumption and the emission of CO_2.

The Chemistries.

1) Palladium & Alloy Chemistries.

1.1 Pure Palladium.

Palladium processes have been used in electroplating processes as 1) originally a cheap alternative to gold, 2) as a bondable, solderable and high temperature electronic contact material, but 3) really came to prominence as an alloyed coating with nickel for the electronics industry in the 80s and 90s. Palladium nickel particularly found a niche in the mobile telecommunications boom of the 90s where it's cost advantage over gold pushed it to prominence.

Palladium solutions based on Palladium Diammine Dinitrite ("P" salt) $(Pd(NH_3)_2(NO_2)_2$ and Palladium Bromide ($PdBr_2$) were brought to prominence in the 60s but have mostly been replaced by more modern alternatives. Palladium "P salt is" still used today (but not so widely). Both palladium for rack and barrel applications have mostly been replaced by ammoniacal products utilising either palladium diammine dichloride ($Pd(NH_3)_2Cl_2$),tetrammine dichloride $(Pd(NH_3)_4Cl_2$ or tetrammine sulphate$(Pd(NH_3)_2SO_4$. High speed reel to reel palladiums have also until recently, been mostly based on the above ammoniacal solutions, both chloride and sulphate.

In general it can be seen that in order to achieve a stress free/crack free deposit of pure palladium in rack and R2R applications the parameters have to be controlled quite tightly as well as maintaining the correct additive level which can be quite daunting in pure palladium processes. Studies of the properties of the deposited palladium have been the subjects of many reports. One such produced in 1999 by the Xiamen university (who have a reputation for palladium chemistry work) showed the complexity of additives needed to control a palladium bath to give the above required properties(1). Additives used consisted of a synthesised mixture of nicotinic acid and nicotinamide with weight ratio 1:10 0.2g/l (NANA), pyridine-3-sulphonic acid (PSA) 0.2g/l, α-furane formic acid (FF) 3.0-5.0g/l and cetyl trimethyl ammonium bromide (CTMAB) 10mg/l. For these reasons and for cost implications palladium has been replaced by palladium nickel wherever possible.

The benefits being,

1) Ease of control of the process (comparatively).
2) Improved quality of deposit (mostly).
3) Cost.

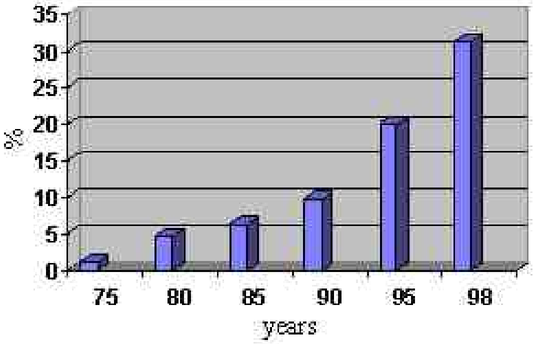
See Table 1) Operating conditions of various palladium make ups

1.2. Palladium Nickel.

The Technology of Palladium-Nickel deposition and it's specific function is relatively new, about 25 years. Originally Palladium-Nickel was developed for the spectacle industry as a barrier layer either under gold, or as a final finish(2).

The utilisation in the electronic field emerged in volume later despite some early successes by entreprenurial electronic accounts. We notice that, at the beginning of this technology, customers were reticent to replace a gold coloured metal to any pm alloy with a grey deposit colour.

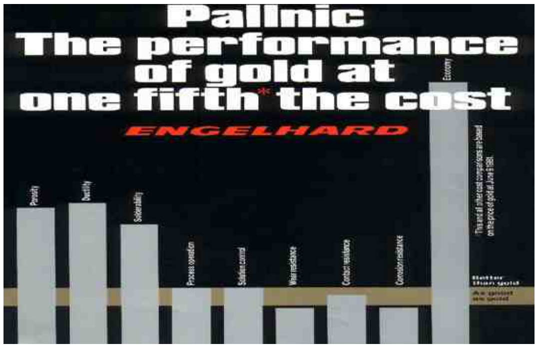
Since this time, the performance of PdNi has proved that it could satisfy the high performance expected from the user of precious metal in Interconnection Technology.
In fact, this type of deposit shows the quality required in the field of connectors, P.C.B. and lead frames. It has been proven that Pd/Ni is equivalent and in some cases an improved product compared to an acid gold deposit. Globally, industry has validated this process technology and has been shown to give reliable and constant results over many years.



Percentage of Connector Manufacturers/Platers using Pd/Ni in the Connector Markets

Palladium Marketing.

Traditionally, up until recently, Pd/Ni systems have been sold as a lower cost equivalent of hard gold plating systems. However, recent changes to the palladium price have meant that for a time this was longer true.
If we examine advertising literature from the early eighties (July ’81), we can see that the cost factor was the major benefit in marketing these processes.



However, there we also see some technical benefits of the process, such as better porosity, ductility and solderability. These benefits were rather lost in the “cost argument”: Volatile changes to the palladium pricing since 1997 have meant that gradually the “cost argument” was overtaken to the point where first palladium was more expensive than gold to plate and then palladium nickel at an 80/20 alloy. Currently palladium nickel is substantially lower cost than gold again.

Technical Discussions.

The chemistry of the original Pd/Ni baths uses the ammonia under different forms for complexing the nickel and allowing the co-deposition to attain the required percentage on the finished connector.

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.

Earlier Processes.

3 catagories of process:

- Systems “high ammonia”
- Systems “low ammonia”
- Systems "low ammonia without chloride"

The basic chemistry of these 3 systems is very similar due to the requirement of ammonia to complex the nickel.

Systems “High Ammonia”.

The largest source of ammonia in the system is the complex of nickel used to maintain the alloy. The conducting salts are frequently ammonia salt but practically they do not produce any ammonia odours. The nickel is consistently readjusted which implies a constant addition of ammonia. Most replenishments to this type of bath contain free ammonia to ensure the complete formation of the ammine complex. To increase the productivity of these baths, operation at 55°C implies a loss of ammonia due to evaporation. The greater the extraction effect the more ammonia will be lost and therefore more ammonia added to the bath. In these conditions, the daily addition of ammonia in a reel to reel line is important to assure satisfactory conditions of the alloy by maintaining the current Pd and Ni percentages in the deposit.

Systems “Low Ammonia”.

System with low ammonia were the first step in the suppression of ammonia in the bath as compared to more traditional systems. The chemistry of the baths is very similar to that employed in the strongly ammonia baths. The principle difference is in the replenisher solution containing nickel. The nickel is replenished in the form of a simple salt or in a very low ammonia containing complex. In the system, the ammonia complex is formed in the bath (in situ). This implies regular analysis of the bath to maintain the minimal amount of ammonia, generally 30 g/l. Practically this means that the complex must be formed rapidly in order not to have occasional problems with the quality of deposit in certain reel to reel plating lines.

Systems “Low Ammonia Without Chloride”.

A number of systems would contain ammonia with chloride. High chloride contents can provoke the corrosion of stainless steel, a material usually employed in production plants. The corrosion of these elements can provoke contamination of the bath by dissolving iron. The deposits will become stressed and the solution unstable. There now exists some electrolytes totally without chloride and with low levels of ammonia. These electrolytes run successfully and can be successful also in a brush head if used with care. The low ammonia without chloride offers the advantage of no corrosion of the equipment. Some manufacturers choose to replenish the nickel to the bath in this form of an ammonia complex to maintain the ammonia level within reasonable limits.

Sytems utilising Palladium as alloyed with cobalt(3) were also reported in the late 90s and early into 2000/2001. As yet they have not found extreme favour in the market which prefers to concentrate on Palladium nickel.

Process Without Ammonia.

Baths without ammonia allowing an ideal of Pd/Ni have been strongly expected for some time. The development effect has been to replace the nickel ammoniacal complex. A new idea, very simple, has been developed. That was to develop a Pd/Ni bath to operate in the same pH range 4.0 - 4.5. 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 should not have the current properties of the ammonia free bath and containing neither chlorides nor strong acids.

These new baths of Pd/Ni are based on an organic complex(4). 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.

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

Properties of the deposit obtained

See Table 1 Operating conditions of various palladium (and palladium alloys) at various make ups.

2. 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.

In the 50s patents were applied for(5) regarding the heating of P Salt with an aqueous solution of sulphamic acid. The resulting bath produced from this compound claims to offer stress free deposits.

In general there is a great deal of experience in the manufacture of the “P” salt complex. Work over many years established that care must be taken when manufacturing the “P” salt in solution (the only non hazardous method of transporting the material) in order to maintain the highest efficiency of the concentrate.

During the dissolution of the “P” salt the shift towards the low efficiency complex is irreversible therefore great care must be taken to dissolve the “P” salt to maintain the quality of the concentrate.

$$Pt(NH_3)_2(NO_2)_2 \xrightarrow{NH_3} [Pt(NH_3)_3(NO_2)_2]\,[NO_2] \longrightarrow [Pt(NH_3)_4][NO_2]_2$$

It is therefore known that “P” salt should be dissolved by gentle means using minimal amounts of excess ammonia. Long storage and high ammonia content in the dissolved “P” salt will shift the equilibrium towards the lower efficiency species and that high pH during plating with high current densities also speeds up this shift towards the lower efficiency species.

Platinum solutions based on the Hexa Hydroxy Platinate to not suffer with these problems. Papers have been produced comparing the differences of these systems (along with the use of Tetrammineplatinum Hydrogen Phosphate ($[Pt(NH_3)_4]HPO_4$) in the plating of turbine blades where the platinum coated blade is further baked in alumina to form a superior diffused corrosion resistant coating (especially in sea environments)(6).

In decorative applications the primary requirement is to produce a “white” or as white as possible coating. Generally the “whiteness” from Platinum deposits is not as good as Rhodium but for marketing people a small difference is acceptable as it can be called platinum plated/coated etc. See table 5. Whiteness comparisons of the platinum group metals as deposited using the L*a*b. colour space method.

See Table 2 Operating conditions of various Platinum at various make ups.

3. Rhodium Chemistries.

Not much has changed with Rhodium chemistries over the past twenty five years however the knowledge in manufacturing the concentrates has evolved. Mostly the formulation of products for the industrial applications has remained static. What has changed is the control over the method of manufacture.

In the manufacture of Rhodium concentrates it is well known that concentrate can contain many differing polymers of Rhodium Sulphate. The effect of these identifying and attempts to quantify these polymers have also been the subject of some papers particularly from Russia and the Ukraine(7).

However it is in decorative applications where, as far as plating goes, the vast majority of Rhodium is used. Development have been in two areas.

3.1 The manufacture of “purer” and more consistent concentrates .

In order to produce pure concentrates the process of making Rhodium Sulphate (or Phosphate) undergoes any number of precipitation and re-dissolutions.

Generally Rhodium “black” is dissolved in hot concentrated Sulphuric acid to form the starting liquor or as more recently Rhodium Trichloride in solution is used as the primary liquor. In order to remove any harmful contaminants from Rhodium liquor Potassium (or ammonium) Hydroxide is then added to the liquor to precipitate Rhodium Hydroxide. The resulting Rhodium Hydroxide is washed and then re-dissolved with concentrated sulphuric acid. The supernatant liquid containing any impurities is then disposed of. In order to produce a consistent concentrate the manufacturing process goes through a precipitation - dissolution process a number of times. In this process potassium hydroxide is used. Potassium as an hydroxide is used as it is purer than Sodium, despite being more expensive, and Ammonia is not liked for environmental reasons. Also Potassium has been found to be the most efficient product in this precipitation process. Small levels of potassium (1-2g/l) can be found in the concentrate as Potassium Hydroxide is used in the manufacturing process but has no effect on the plating solutions formed.

3.2 The use of organic additives to increase the “whiteness” of the deposit.

In decorative applications the primary function of the Rhodium deposit is to give a bright white finish in a variety of decorative applications but mostly related to the costume jewellery industry. The use of organic additives in assisting the production of whiter deposits but also in maintaining the whiteness of the deposit as the bath ages (contaminated with nickel and organic pollutants from masking) has been the subject of recent developments(8&9). Traditionally both lead and selenium have been used to assist in a) the whiteness as with lead and b) the brightness as with selenium. Neither were ideal and in the case of selenium had the effect of reducing the "whiteness" . Products using lead even in extremely values (less than 10ppm) are now frowned upon for environmental reasons.

If we examine a number of different rhodium solutions with and without additives (both lead and organic (and different organic systems) we can see the differences as expressed in their "whiteness" using the L*a*b. colour space method. See table 5

The L*a*b colour space method(10)

Examining Colour

An infinite number of colours surround us in our everyday lives. We all take colour pretty much for granted and it has a wide range of roles in our daily lives. A colour expression often though means ten different colours to ten different people. If you show the same plated item to different people you are bound to get different answers describing the colour. Colour is a matter of perception and subjective interpretation. Even if they are looking at the same plated item different people will draw on different references and experiences to express colour in different words. Words for expressing colour have always changed with the times. Words like "electric" to describe a colour could not have been used before the invention of electricity. Adjectives such as "bright", "dull" and "deep" are often used to improve the description. Therefore verbal expression of colour is still not accurate enough. How then shall colours be expressed to avoid misunderstandings?

If there was a standard method by which colours could be accurately expressed and understood colour communication could be smoother, simpler and exact. Such precise colour communication could if applied to rhodium plated items eliminate colour related problems. The Principles of Colour are. Hue, Lightness, Saturation. By creating scales for hue, lightness, and saturation, we can measure colour numerically.

History of expressing colours numerically.

Various people in the past have devised methods, often using complex formulas, for quantifying colour and expressing it numerically with the aim of making it possible for anyone to communicate colours more easily and more accurately. For example, in 1905 the American artist A. H. Munsell(11) devised a method for expressing colours which utilised a great number of paper colour chips classified according to their hue (Munsell Hue), lightness (Munsell Value), and saturation (Munsell Chroma) for visual comparison with a specimen colour. Later, after a variety of further experiments, this system was updated to create the Munsell Renotation System, which is the Munsell system presently in use. In this system, any given colour is expressed as a letter/number combination (H V/C) in terms of its hue (H), value (V), and chroma (C) as visually evaluated using the Munsell Colour Charts. Other methods for expressing colour numerically were developed by an international organisation concerned with light and colour, the Commission Internationale de l'Eclairage (CIE).

The two most widely known of these methods are the Yxy colour space, devised in 1931(12) based on the tristimulus values XYZ defined by CIE, and the L*a*b* colour space, devised in 1976(13) to provide more uniform colour differences in relation to visual differences. Colour spaces[;] such as these are now used throughout the world for colour communication.

[;] *Colour space(14) Method for expressing the colour of an object or a light source using some kind of notation, such as numbers*

The L*a*b* colour space method.

The L*a*b* colour space (also referred to as CIELAB) is presently one of the most popular colour space for measuring object colour and is widely used in virtually all fields. It is one of the uniform colour spaces defined by CIE in 1976 in order to reduce one of the major problems of the original Yxy colour space: that equal distances on the x, y chromaticity diagram did not correspond to equal perceived colour differences. In this colour space, L* indicates lightness and a* and b* are the chromaticity co-ordinates. Figure 1 shows the a*, b* chromaticity diagram. In this diagram, the a* and b* indicate colour directions: +a* is the red direction, -a* is the green direction, +b* is the yellow direction, and -b* is the blue direction. The centre is achromatic; as the a* and b* values increase and the point moves out from the centre, the saturation of the colour increases. Figure 1 is a view of this solid cut horizontally at a constant L* value.

The method of Colour Measurement using the Minolta Chromameter CR200

This procedure relates to standard white plate calibration.

Absolute colour measurements are made in L* a* b* co-ordinates in the Munsell colour system.

L* = Light/Darkness
+a* = Red. -a* = Green
+b* = Yellow. -b* = Blue

Equipment.

Minolta Chromameter CR200, Measuring Head, AC adaptor and White calibration plate.

4. Ruthenium Chemistries.

If not much has changed with Rhodium then the same can be said for Ruthenium. Despite offering significant cost advantages over the other Platinum Group Metals usage of this metal as a plating process is minimal. As described above its main usage is 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.

Conclusions.

The platinum group products have their place in today's modern electroplating market. Their uniqueness in offering "white" functionality for the decorative market and unique properties for the industrial market guarantees their usage. Work continues in looking at removing the more hazardous systems, as has occurred with Palladium Nickel where non ammoniacal systems are gaining prominence. Work continues to look at replacing platinum P salt type systems and an improved black deposit from the Ruthenium systems without resorting back to phenol or pyridene type compounds.

Until the use of Palladium Nickels in the early 80s the world of precious metal plating had been relatively organic free. With the advent of Palladium Nickel plating the use of organic additives and brighteners came about. Some Palladium systems now use even more complex organic products and with the move away from Ammonia type systems one can see this increasing. Most Rhodium systems for the decorative market now use an organic to a) increase whiteness or b) stabilise whiteness over a long period of time. Even gold system developments are now looking at their use with organic materials.

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.

Applications to use both Platinum and Palladium Nickel in electroforming applications for decorative and industrial applications have arisen in the last few years. With the use of modern additives and the historical application technology available there is hope that these application demands can be met without the use of hazardous materials.

Table 1. Palladium & Palladium Alloys

	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

Table 2. Platinum type products

	CPA	P Salt	SHP	Suphamate	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

Table 3. Rhodium type products

	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

Table 4. Ruthenium type products

	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

** Limiting thickness at 0.25 - 0.5 micron without significant stress.*

Table 5 Comparison of the white/grey/black using the L*a*b Colour Space

	L	a	b
Ruthenium “Normal”	61.85	0.37	1.27
Ruthenium “Black”	54.62	0.16	0.01
Rhodium “Black”	57.00	0.33	-0.30
Rhodium “White 1”	77.87	0.48	-0.13
Rhodium “White 2”	80.42	0.01	0.70
Rhodium “White 3”	79.47	-0.25	2.02
Rhodium “White 4”	75.30	0.68	0.71
Rhodium “White 5”	75.19	0.70	0.43
Rhodium “White 6”	78.86	0.16	-0.01
Platinum	74.40	0.28	1.99
Palladium	72.91	0.31	2.14

Normally we look at “Whiteness” it is the L value that is mainly used to quantify the Whiteness. However for the decorative market it is important to understand the a and b values also. A and B values are responsible of the shade and they are comparable if the “whiteness” is exactly the same, otherwise the colour opinion will be only a personal opinion by the final customer. Still the case with many customers.

References

1) Study on Some Properties of the Electrolyte Solution in the Electrodeposition of Palladium. Fang-zu Yang, Shu-Kai Xu, Ling Huang, Zhen-liang Li, Shao-min Zhou; Chemical Dept, Inst Physics Chem, State Key, Laboratory for Physical Chemistry of the Solid Surface, Xiamen Univ, Xiamen 361005 P.R. China.
Patent Specification. No 22070/59, the patent office London 26/06/1959 – Low Stress Platinum Coatings and Composition.

2) The Replacement of Gold Plating by Palladium Nickel on Connectors. P Wilkinson, Engelhard Ltd, Cinderford, UK. Institute of Metal Finishing, Annual Technical Conference, April 1986, Bournemouth, UK.

3) Pd/Co – A Successful Scale-up to the Production Environment. G.F.Breck, C.A.Dullaghan, J.Maisano and J.A.Abys, Lucent Technologies, Bell Laboratories, Murray Hill, NJ. AESF Annual Technical Conference, SurFin 2001, Nashville, USA.

4) Ammonia-Free Palladium-Nickel – A New Technology. S Burling Engelhard-Clal UK, C Leclere & J Gonzales Engelhard-Clal France & S Hemsley Engelhard-Clal Singapore. J Gonzales. AESF Annual Technical Conference, SurFin 2001, Nashville, USA.

5) Patent Specification 22070/59, London Patent Office, June 26th 1959, Low Stress Platinum Platings and Composition.

6) Developments in Platinum Electroplating: P & Q Salt Solution Optimisation. S.E.Hadian & Dr Gabe. Institute of Polymer Technology & Materials Engineering, Loughborough University, Loughborough, UK. AESF Annual Technical Conference, SurFin 2000, Chicago, USA.

7) Sulphate Complexes of Rhodium (III) in Electrodeposition Process. LB Khar'kova, VL Pekhn'o and SV Volkov. Vernadski Institute of General and Inorganic Chemistry, National Acadamy of Sciences of the Ukraine, Kiev, Ukraine. Russian Journal of Applied Chemistry Vol 72, No 4, 1999.

8) S. Dorner and L. Froels Galvanotechnik.49.539 (1948).

9) Baker, US Pat 2,057,475 (1936).

10) Bright "white" Rhodium Plating of Decorative Components S.Burling & D.Markey, Engelhard-Clal UK, G.Bolli, Engelhard-Clal Italy and S.Hemsley, Engelhard-Clal Singapore. AESF Annual Technical Conference, SurFin 2000, Chicago, USA.

11) A.H.Munsell (1905) Method of expressing colours.

12) & *13) CIE (1931) Method of expressing colours. *CIE (1976) Method of expressing colours.

14) Minolta Handbook (1993) P colour contamination.