

## **Silver Plating; Past, Present and Future.**

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Silver plating has been with us for many, many decades. Changes to formulations required to service the electronics industry drove changes to formulations that had been around for some time. With the current requirements regarding legislation/environment and the new potential applications in the photo voltaic (solar) market driving changes this paper will 1) review past & present formulations and applications but 2) discuss the driving forces and new applications that are forcing formulation changes for the first time in many years regarding silver plating.

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## Introduction

Silver plating baths have been around for some 100 + years. Originally these solutions were produced from alkaline cyanide electrolytes by dissolving silver cyanide in a solution of sodium cyanide. With the discovery that potassium salts, because of their purity, produced “cleaner” baths came the use of silver potassium cyanide (known as the double salt) in making up baths. This eliminated the use of “dusty” silver cyanide, simplified replenishment and overcame the need to filter residues. The general properties and hazards from traditional silver baths can be seen below. (See table 1, Silver Plating Chemistries).

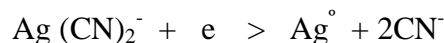
Silver            Colour – white as deposited (traditionally the whitest). Density, 10.5g/cm<sup>3</sup>.

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

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

Because of the tendency for silver cyanide plating baths to produce poorly adherent immersion coatings the use of a strike bath has always been necessary. Silver strikes are usually operated at room temperature and have a low silver content with a high cyanide content in order to cause a strike of adherent silver onto the base material. Plating times are very short in order not to produce powdery deposits.

The mechanism of deposition is from the complex silver cyanide ion as shown in equation



Traditionally these high cyanide (100 –150g/l KCN) silver baths used silver sheet anodes to form the complete replenishment circle. However dog bone shaped or corrugated shaped anodes were also very popular as are different types of silver grain (traditional, exploded, popcorn etc) used in baskets are now.

Originally silver was almost totally used for decorative applications. The rapid increase in the price of gold during the sixties/seventies saw the use of silver increase substantially, in the electronics market where its tendency to migrate, tarnish or give reduced electrical properties gave no performance problems.

When coupled with semi-metallic (decorative) or organic (decorative and electronic) brighteners silver cyanide based plating baths became very popular, due to their ease of operation, consistent satisfactory deposits and ease of effluent treatment, for both the decorative and electronics market .....and this is still the case today.

However, these simple silver baths developed further for the electronics industry during the seventies due to the need to produce very high speed plating silver solutions, in order to meet the needs of the electronics industry for semi conductor components on PCBs. The requirements

from the semi-conductor market for selectively silver plated lead frames saw a new generation of silver processes developed. These processes were originally claimed to be non-cyanide systems but were actually low cyanide systems. True, on make up there would be no free cyanide found but due to replenishment by salt only they did build up some free cyanide during their life.

Over recent years there have been many papers published regarding silver alloys, such as silver tin, silver copper etc. However none of these processes have made progress to become a useable manufacturing process.

Later silver was to be used as a lead free alternative for solderable finishes on PCBs. Processes containing silver nitrate with an organic solderable coating are readily available in the market but are almost strictly used in the PCB industry only.

Traditionally precious metal plating has not been considered a “polluter” to the environment. The high costs of the precious metals itself has acted to “police” precious metal plating in the past ensuring that precious metals are not lost into the various effluents. Silver processes have always been easily dealt with. The metal could be reclaimed from drag outs and cyanide containing effluents are easily treated. 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.

The focus of this paper will be to look at the recent applications and developments for the Low Cyanide and Non Cyanide systems. This paper will show the trends and current developments in eliminating potentially hazardous chemicals from both the plating bath and from the deposited metals and look at new applications for silver plating.

## **Innovations.**

### **Low Cyanide High Speed Silver Plating** (See table 2 & 3, Low Cyanide Silver Chemistries).

As the electronic industry emerged fully during the seventies the need to plate silver at high speeds became very apparent. High Cyanide bright silvers were being used in a large numbers for barrel plating parts extremely successfully. However these baths showed limitations when being used at high current densities on high speed reel to reel lines and selective spot lines in particular. The requirement to selectively plate silver spots onto lead frames required vastly different plating conditions and parameters, therefore a new range of silver plating solutions were developed to meet these new demands. The silver plating processes developed although still using the “double” salt silver potassium cyanide were very different from conventional silver cyanide baths.

These low Cyanide Silver plating processes have now been with us since the early seventies. Due to the fact they do not contain any free cyanide there is no capability to dissolve silver anodes. They therefore use DSA (dimensionally stable anodes such as platinised titanium. They contain **zero free cyanide** on make up and are silver replenished by the addition Silver Potassium Cyanide. Generally the baths have a finite life due to density build up and traditionally will have

around 20g/l Free Cyanide at the end of their life. The conductivity of the process is supported by either phosphate or nitrate chemistry to replace the cyanide.

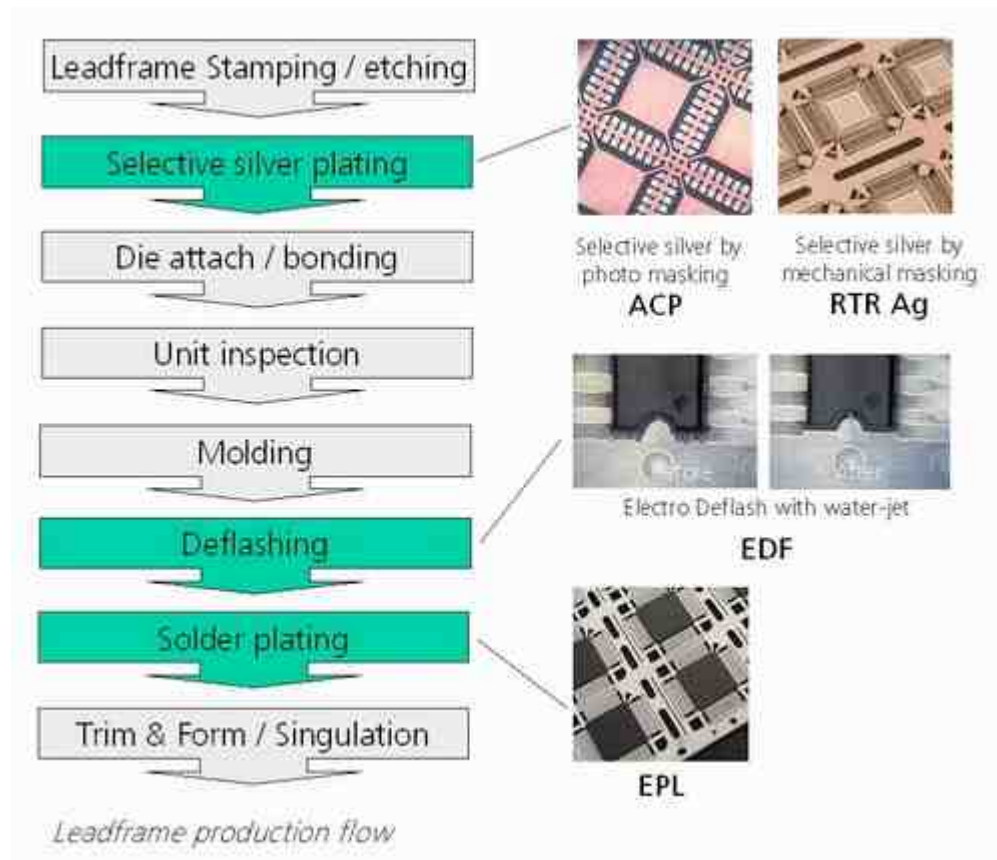
## FEATURES AND BENEFITS

Low Cyanide	:	Safer Working Environment
Low Cyanide	:	Reduced Health and Safety Costs
Low Cyanide	:	No need for Silver Strike in Pre-treatment
Low Cyanide	:	Reduced Environmental Impact
No other Pollutants	:	Reduced Environmental Costs
Extremely Fast Plating Rates	:	High Production Levels.

### Operating Parameters of Low Cyanide High Speed Silver Plating

<u>Usual Working values</u>		<u>Permissible Working Range</u>	
Content of Silver	65 g/l	Content of Silver	50.0 to 80g/l
pH-value	8.5.	pH-value	8.0 to 10.0
Working temperature	65°C	Working temperature	40 to 70°C
Cathode current density		Cathode current density	
Phosphate	20 A/dm <sup>2</sup>	Phosphate	up to 80 A/dm <sup>2</sup>
Nitrate	100 A/dm <sup>2</sup>	Nitrate	up to 250 A/dm <sup>2</sup>
Cathode current density		Cathode current density	
Phosphate	20 A/dm <sup>2</sup>	Phosphate	up to 800 A/ft <sup>2</sup>
Nitrate	100 A/dm <sup>2</sup>	Nitrate	up to 2500 A/ft <sup>2</sup>
Deposition rate		Deposition rate	
Phosphate	1.0 µm/10 seconds	Current Density	10 A/dm <sup>2</sup>
Nitrate	1.0 µm/2 seconds	Current Density	50 A/dm <sup>2</sup>

Examples of silver plating (and process sequence) on lead frame ([www.meco.nl](http://www.meco.nl)).



## 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

<u>Usual Working values</u>			<u>Permissible Working Range</u>		
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 <sup>2</sup>		rack	up to 1.2 A/dm <sup>2</sup>	
barrel	0.5 A/dm <sup>2</sup>		barrel	0.2 to 0.5 A/dm <sup>2</sup>	
Anodical current density			Anodical current density		
rack	0.25 A/dm <sup>2</sup>		rack	0.25 to 0.5 A/dm <sup>2</sup>	
barrel	0.5 A/dm <sup>2</sup>		barrel	0.25 to 0.5 A/dm <sup>2</sup>	
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 Silver plating from low and non cyanide processes will become more prevalent in the coming years despite their APPARANT higher cost NOW.

Which brings to current developments.....

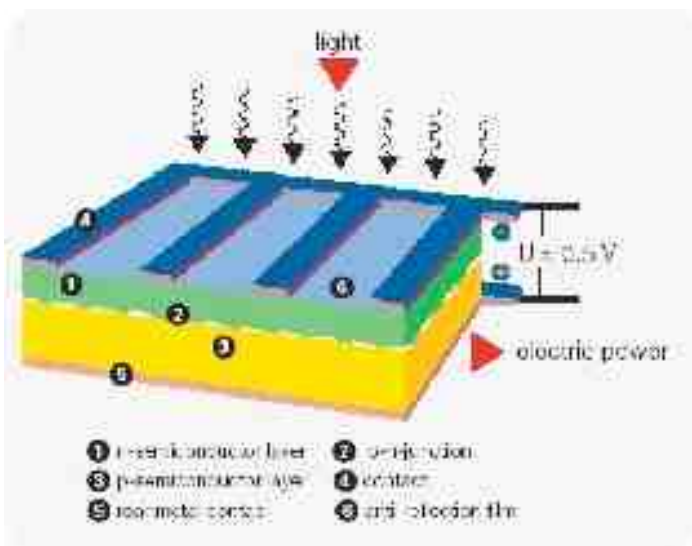
### Use of Silver Plating processes for Photovoltaic markets.

As we know there has been a great deal of discussion over the last decade regarding the objective of clean renewable energy sources to replace carbon based products. One such technology is to use silver as a conductor to transform solar energy into electricity via a silicon wafer. Over the recent years this market to manufacture these products has grown substantially.



Traditionally the silver conductor is applied by screen printing a silver paste onto the silicon wafer which has an anti reflective coating applied. On firing the silver paste will burn through the anti-reflective coating creating a bond to the silicon creating the circuit.

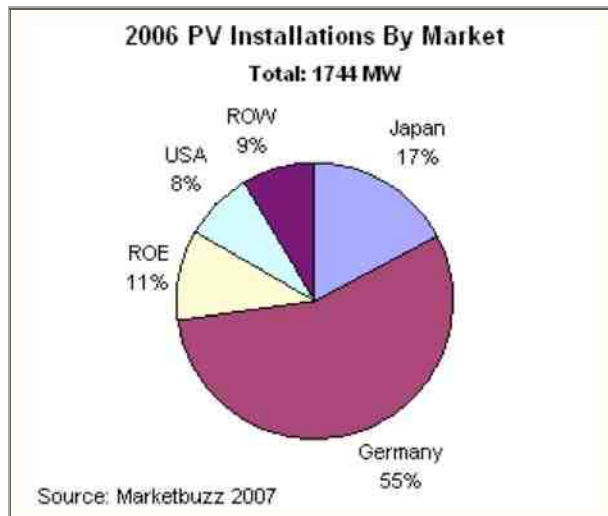
Information from [www.schott.com/photovoltaic/english](http://www.schott.com/photovoltaic/english).



## Market Information

World solar photovoltaic (PV) market installations reached a record high of 1,744 megawatts (MW) in 2006, representing growth of 19% over the previous year.

Germany's grid connect PV market grew 16% to 960 Megawatts in 2006 and now accounts for 55% of the world market. While Japan's market size barely advanced last year, Spain and the United States were the strong performers. The Spanish market was up over 200% in 2006, while the US market grew 33%.



World solar cell production reached a consolidated figure of 2,204 MW\* in 2006, up from 1,656 MW a year earlier. Japanese producers lost ground over the past 12 months, dropping from 46% to 39% share, to the benefit of Chinese cell manufacturers.

Polysilicon production rose 16% in 2006, which, when combined with aggressive PV industry procurement, allowed a marginally higher market growth rate than projected twelve months ago. Nonetheless, polysilicon supply issues will still constrain cell production in 2007.

**Estimates are that 270 tonnes of silver ink will be consumed in 2007. One third in Europe one third in Asia (mostly Japan) and one third in ROW (mostly USA).**

### **New process opportunity.**

Ideally the engineers designing this process would like a continuous, consistent, conductive silver layer as possible. Due to the technique of screen printing the fired films is not as continuous as needed.

There are therefore now moves to apply a plated coating. The technique is to fire a thinner coating of a narrow track width silver screen printed coating which is then used as the seed layer. The silver plating then can be applied very easily to this screen printed coating, plating 10



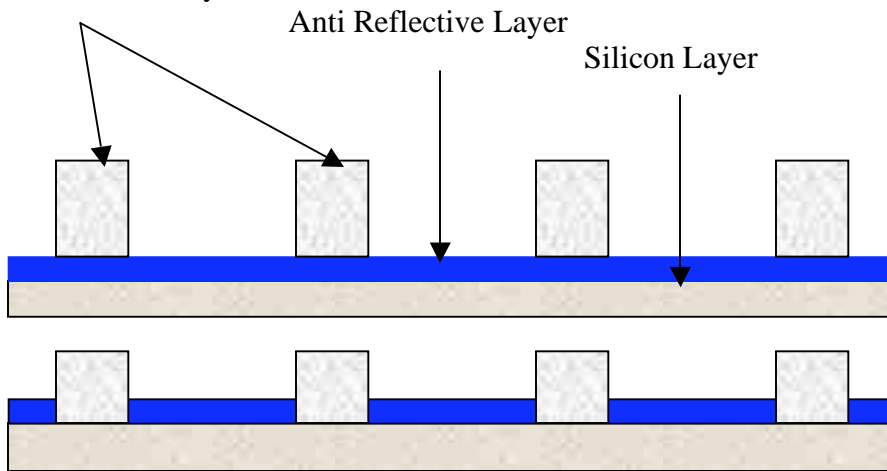
microns of a continuous pure silver layer. Efficiency increases in the transfer of solar energy collected to electricity makes this application of this technology very interesting to design engineers.

Issues such as 1) handling of the thin wafers, in order to achieve realistic plating production times and 2) the new inks required in order to, achieve a fine dense, thin, narrow layer all are both areas current being developed. Clearly though a new a process technology involving plating will develop.

Schematic of the process

a) Traditional (Schematic license – Actual screen printed layer is curved)

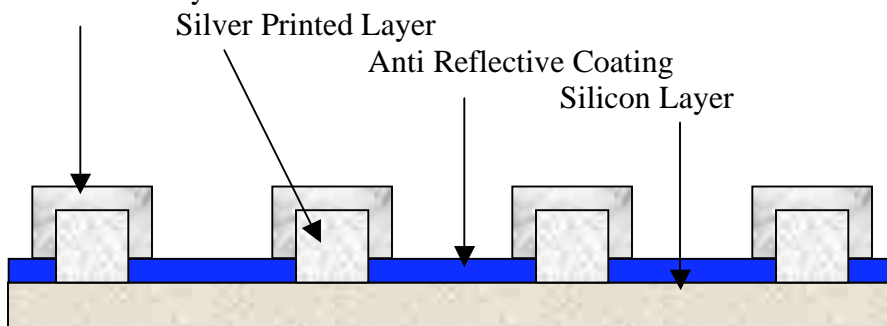
Silver Printed Layer



In this traditional method the screen printed silver layer fires through the anti reflective layer and becomes the total silver conductor layer

b) New method (Schematic license – Actual screen printed layer is curved as is plated layer)

Silver Plated Layer



In this new method the thinner, narrow, screen printed silver layer fires through the anti reflective layer and is then over plated with 10 microns of silver. This total combination then becomes the total silver conductor layer

## Conclusions & Summary

Silver plating has been with us for some time and will continue to be a useful deposited metal. Respect for toxic materials within the industry has minimised accidents and injuries and silver cyanide plating has its part to play for some time still. Improvements in effluent treatment and treatment of air emissions have reduced environmental impact. However.....

**Plating can be hazardous to your health – therefore should be treated with respect  
Plating can be hazardous to the environment –hence the need for “greener “ chemistries.**

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

**With the requirements from this new area it is possible that the alternative non/less hazardous processes, available now, will be the chosen processes rather than conventional cyanides.**

- **“Low Cyanide – High Speed” Silver Processes.**
- **“Cyanide Free” Silver Processes.**

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.

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.

**New opportunities are offering themselves in the photovoltaic market for silver plating. Handling issues both in terms of production output and environmental concerns are being overcome. Silver plating will therefore pay a part in this exciting emerging technology.**

**Table 1 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	25°C	25°C	40-60°C	40-60°C	40-60°C	20°C
Current Density	1.2A/dm <sup>2</sup>	1-2A/dm <sup>2</sup>	1-7.5A/dm <sup>2</sup>	10-50A/dm <sup>2</sup>	50-200/dm <sup>2</sup>	1.1A/dm <sup>2</sup>
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 2 Low Cyanide (Phosphate Type) Silver Chemistries.**

PARAMETER	UNIT	RANGE	OPTIMUM
Silver	G/l	55 - 75	65
Conducting Salts	G/l	110 - 150	130
Brightener	Cm <sup>3</sup> /l	0 - 3	2
Wetting Agent	Cm <sup>3</sup> /l	0 - 3	2
PH		8.0 - 9.0	8.5
Solution Density	°Bé g/cm <sup>3</sup>	14 - 22 1.107 - 1.180	18 1.143
Temperature	°C	45 to 60	
Current Density	ASF A/dm <sup>-2</sup>	up to 800 up to 80	

**Table 3 Low Cyanide (Nitrate Type) Silver Chemistries.**

DESCRIPTION	UNIT	RANGE	OPTIMUM
Silver Concentration	g/l	50 - 80	65
pH (electrometric)		8.0 - 10.0	8.5
Temperature	°C	60 - 70	65
Current Density	A/dm <sup>2</sup> A/ft <sup>2</sup>	45 - 220 500 - 2500	as required as required
Specific Gravity	°Bé	1.12 - 1.16 16 - 20	1.14 18
Cathode Efficiency	%	85 - 95	-

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