

# **Gold & Silver Coatings**

**By**

**A . T . Kakhia**

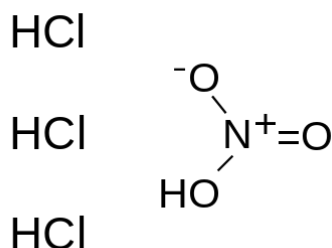




# **Part One**

## **General Knowledge**



## Aqua Regia ( Royal Acid )



	
<p><i>Freshly prepared aqua regia is colorless, but it turns orange within seconds. Here, fresh aqua regia has been added to these NMR tubes to remove all traces of organic material.</i></p>	<p><i>Freshly prepared aqua regia to remove metal salt deposits.</i></p>

### Contents

- 1 Introduction
- 2 Applications
- 3 Chemistry
  - 3.1 Dissolving gold
  - 3.2 Dissolving platinum
  - 3.3 Reaction with tin
  - 3.4 Decomposition of aqua regia
- 4 History

### 1 - Introduction

Aqua regia ( Latin and Ancient Italian , lit. "royal water"), *aqua regis* ( Latin, lit. "king's water") , or nitro – hydro chloric acid is a highly corrosive mixture of acids, a fuming yellow or red solution. The mixture is formed by freshly mixing concentrated nitric acid and hydro chloric acid , optimally in a volume ratio of 1:3. It was named

so because it can dissolve the so - called royal or noble metals, gold and platinum. However, titanium, iridium, ruthenium, tantalum, osmium, rhodium and a few other metals are capable of with standing its corrosive properties.

IUPAC name	
Nitric acid hydro chloride	
Other names	
aqua regia , Nitro hydrochloric acid	
Molecular formula	$\text{HNO}_3 + 3 \text{H Cl}$
Appearance	Red , yellow or gold fuming liquid
Density	1.01–1.21 g / cm <sup>3</sup>
Melting point	– 42 °C
Boiling point	108 °C
Solubility in water	miscible in water
Vapor pressure	21 mbar

## 2 – Applications

Aqua regia is primarily used to produce chloro auric acid, the electrolyte in the Wohl will process. This process is used for refining highest quality (99.999 %) gold.

Aqua regia is also used in etching and in specific analytic procedures. It is also used in some laboratories to clean glassware of organic compounds and metal particles. This method is preferred over the "traditional" chromic acid bath for cleaning NMR tubes, because no traces of paramagnetic chromium can remain to spoil spectra.<sup>[3]</sup> While chromic acid baths are discouraged because of the high toxicity of chromium and the potential for explosions, aqua regia is itself very corrosive and has been implicated in several explosions due to mishandling.

Due to the reaction between its components resulting in its decomposition , aqua regia quickly loses its effectiveness ( yet

remains a strong acid ) , so its components are usually only mixed immediately before use.

While local regulations may vary , aqua regia may be disposed of by careful neutralization , before being poured down the sink. If there is contamination by dissolved metals , the neutralized solution should be collected for disposal .

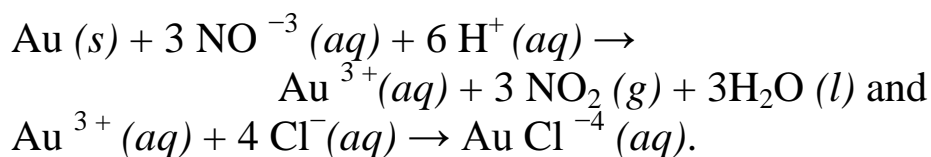
### 3 – Chemistry

#### 3 – 1 - Dissolving gold

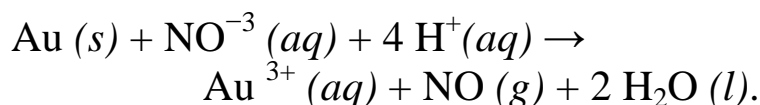


*Pure gold precipitate produced by the aqua regia chemical refining process*

Aqua regia dissolves gold, though neither constituent acid will do so alone, because, in combination, each acid performs a different task. Nitric acid is a powerful oxidizer, which will actually dissolve a virtually undetectable amount of gold, forming gold ions ( $\text{Au}^{3+}$ ). The hydrochloric acid provides a ready supply of chloride ions ( $\text{Cl}^-$ ), which react with the gold ions to produce tetra chloridoaurate (III) ion anions, also in solution. The reaction with hydro chloric acid is an equilibrium reaction which favors formation of chloro aurate anions ( $\text{AuCl}_4^-$ ). This results in a removal of gold ions from solution and allows further oxidation of gold to take place. The gold dissolves to become chloro auric acid. In addition, gold may be dissolved by the free chlorine present in aqua regia. Appropriate equations are:



The oxidation reaction can also be written with nitric oxide as the product rather than nitrogen dioxide :



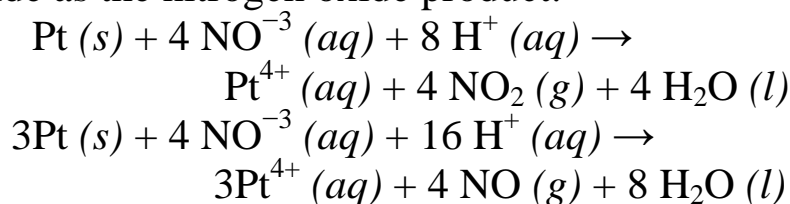
If the aqua regia solution only contains gold, solid tetra chloro auric acid may be prepared by boiling off excess aqua regia, and removing residual nitric acid by repeatedly heating with hydro chloric acid. That step reduces nitric acid . If elemental gold is desired, it may be selectively reduced with sulfur dioxide , hydrazine, oxalic acid, etc.

### 3 – 2 - Dissolving platinum

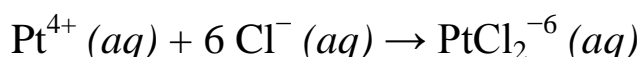


*Platinum being dissolved in aqua regia*

Similar equations can be written for platinum. As with gold, the oxidation reaction can be written with either nitric oxide or nitrogen dioxide as the nitrogen oxide product.

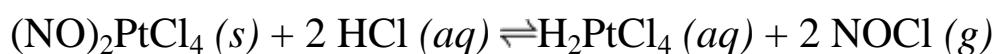
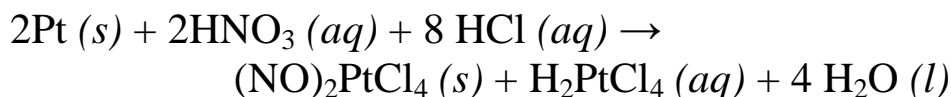


The oxidized platinum ion then reacts with chloride ions resulting in the chloro platinate ion.

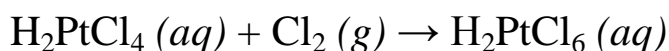




Experimental evidence reveals that the reaction of platinum with aqua regia is considerably more complex. The initial reactions produce a mixture of chloro platinous acid ( $\text{H}_2\text{PtCl}_4$ ) and nitroso platinic chloride ( $(\text{NO})_2\text{PtCl}_4$ ). The nitroso platinic chloride is a solid product. If full dissolution of the platinum is desired, repeated extractions of the residual solids with concentrated hydrochloric acid must be performed.

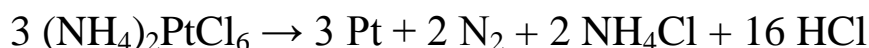


The chloro platinous acid can be oxidized to chloro platinic acid by saturating the solution with chlorine while heating.



Dissolving platinum solids in aqua regia was the mode of discovery for the most dense metals, iridium and osmium, both of which are found in platinum ore and will not be dissolved by the acid, instead collecting on the base of the vessel.

As a practical matter, when platinum group metals are purified through dissolution in aqua regia, gold (commonly associated with PGMs) is precipitated by treatment with iron (II) chloride. Platinum in the filtrate, as hexa chloro platinate (VI), is converted to ammonium hexa chloro platinate by the addition of ammonium chloride. This ammonium salt is extremely insoluble, and it can be filtered off. Ignition (strong heating) converts it to platinum metal :



Un precipitated hexa chloro platinate (IV) is reduced with elemental zinc, and a similar method is suitable for small scale recovery of platinum from laboratory residues.

### 3 – 3 - Reaction with tin

Aqua regia reacts with tin to form tin (IV) chloride, containing tin in its highest oxidation state:

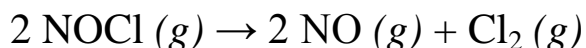


### 3 – 4 - Decomposition of aqua regia

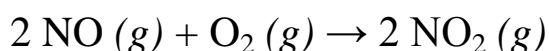
Upon mixing of concentrated hydrochloric acid and concentrated nitric acid, chemical reactions occur. These reactions result in the volatile products nitrosyl chloride and chlorine as evidenced by the fuming nature and characteristic yellow color of aqua regia. As the volatile products escape from solution, the aqua regia loses its potency.



Nitrosyl chloride can further decompose into nitric oxide and chlorine. This dissociation is equilibrium - limited. Therefore, in addition to nitrosyl chloride and chlorine, the fumes over aqua regia contain nitric oxide.



Because nitric oxide reacts readily with atmospheric oxygen, the gases produced also contain nitrogen dioxide,  $\text{NO}_2$ .



## 4 – History

Aqua regia first appeared in the work of medieval European alchemist Pseudo - Geber, dating from the 14th century. The third of Basil Valentine's keys shows a dragon in the foreground and a rooster eating a fox eating a rooster in the background. The rooster symbolizes gold (from its association with sunrise and the sun's association with gold), and the fox represents aqua regia. The repetitive dissolving, heating, and re dissolving ( the rooster eating the fox eating the rooster ) leads to the buildup of chlorine gas in the

flask. The gold then volatilizes in the form of gold chloride, whose red crystals were known as dragon's blood. The reaction was not reported in modern chemical literature until 1890.

Antoine Lavoisier called aqua regia nitro - muriatic acid in 1789. When Germany invaded Denmark in World War II, Hungarian chemist George de Hevesy dissolved the gold Nobel Prizes of German physicists Max von Laue (1914) and James Franck (1925) in aqua regia to prevent the Nazis from confiscating them. The German government had prohibited Germans from accepting or keeping any Nobel Prize after jailed peace activist Carl von Ossietzky had received the Nobel Peace Prize in 1935. De Hevesy placed the resulting solution on a shelf in his laboratory at the Niels Bohr Institute. It was subsequently ignored by the Nazis who thought the jar — one of perhaps hundreds on the shelving — contained common chemicals. After the war, de Hevesy returned to find the solution undisturbed and precipitated the gold out of the acid. The gold was returned to the Royal Swedish Academy of Sciences and the Nobel Foundation. They re - cast the medals and again presented them to Laue and Franck.

# Coating



*Coating on a roof*

## Contents

- 1 Introduction
- 2 Functions of coatings
- 3 Coating processes
  - 3.1 Vapor deposition
    - 3.1.1 Chemical vapor deposition
    - 3.1.2 Physical vapor deposition
  - 3.2 Chemical and electrochemical techniques
  - 3.3 Spraying
  - 3.4 Roll – to - roll coating processes
  - 3.5 Other

## 1 - Introduction

A coating is a covering that is applied to the surface of an object, usually referred to as the substrate. The purpose of applying the coating may be decorative, functional, or both. The coating itself may be an all-over coating, completely covering the substrate, or it may only cover parts of the substrate. An example of all of these types of coating is a product label on many drinks bottles- one side has an all-over functional coating (the adhesive) and the other side has one or more decorative coatings in an appropriate pattern (the printing) to form the words and images.

Paints and lacquers are coatings that mostly have dual uses of protecting the substrate and being decorative, although some artists paints are only for decoration, and the paint on large industrial pipes is presumably only for the function of preventing corrosion.

Functional coatings may be applied to change the surface properties of the substrate, such as adhesion, wettability, corrosion resistance, or wear resistance. In other cases, e.g. semiconductor device fabrication (where the substrate is a wafer), the coating adds a completely new property such as a magnetic response or electrical conductivity and forms an essential part of the finished product.

A major consideration for most coating processes is that the coating is to be applied at a controlled thickness, and a number of different processes are in use to achieve this control, ranging from a simple brush for painting a wall, to some very expensive machinery applying coatings in the electronics industry. A further consideration for 'non-all-over' coatings is that control is needed as to where the coating is to be applied. A number of these non-all-over coating processes are printing processes.

Many industrial coating processes involve the application of a thin film of functional material to a substrate, such as paper, fabric, film, foil, or sheet stock. If the substrate starts and ends the process wound up in a roll, the process may be termed "roll-to-roll" or "web-based" coating. A roll of substrate, when wound through the coating machine, is typically called a web.

Coatings may be applied as liquids, gases or solids.

## **2 - Functions of coatings**

***Adhesive – adhesive tape, pressure - sensitive labels , iron - on fabric***

Changing adhesion properties

Non-stick PTFE coated- cooking pans

Release coatings e.g. silicone-coated release liners for many self-adhesive products

primers encourage subsequent coatings to adhere well (also sometimes have anti-corrosive properties)

### ***Optical coatings***

Reflective coatings for mirrors

Anti - reflective coatings e.g. on spectacles

UV- absorbent coatings for protection of eyes or increasing the life of the substrate

Tinted as used in some coloured lighting, tinted glazing, or sunglasses

Catalytic e.g. some self-cleaning glass

Light - sensitive as previously used to make photographic film

Protective

Most paints are to some extent protecting the substrate

Hard anti-scratch coating on plastics and other materials e.g. of titanium nitride to reduce scratching, improve wear resistance, etc.

### ***Anti - corrosion***

Underbody sealant for cars

Many plating products

Waterproof fabric and water proof paper

antimicrobial surface

Magnetic properties such as for magnetic media like cassette tapes and floppy disks

Electrical or electronic properties

Conductive coatings e.g. to manufacture some types of resistors

Insulating coatings e.g. on magnet wires used in transformers

Scent properties such as scratch and sniff stickers and labels

## **3 - Coating processes**

Coating processes may be classified as follows:

### **3 – 1 - Vapor deposition**

#### **3 – 1 – 1 - Chemical vapor deposition**

Metal organic vapour phase epitaxy

Electrostatic spray assisted vapour deposition (ESAVD)

Sherardizing

Some forms of Epitaxy

Molecular beam epitaxy

#### **3 – 1 – 2 - Physical vapor deposition**

Cathodic arc deposition

Electron beam physical vapor deposition (EBPVD)

Ion plating

Ion beam assisted deposition (IBAD)  
Magnetron sputtering  
Pulsed laser deposition  
Sputter deposition  
Vacuum deposition  
Vacuum evaporation, evaporation (deposition)

### **3 – 2 - Chemical and electrochemical techniques**

Conversion coating  
Autophoretic coating  
Anodizing  
Chromate conversion coating  
Plasma electrolytic oxidation  
Phosphate (coating)  
Ion beam mixing  
Pickled and oiled, a type of plate steel coating  
Plating  
Electroless plating  
Electro plating

### **3 – 3 – Spraying**

Spray painting  
High velocity oxygen fuel (HVOF)  
Plasma spraying  
Thermal spraying  
Plasma transferred wire arc thermal spraying  
The common forms of Powder coating

### **3 – 4 - Roll – to - roll coating processes**

Common roll – to - roll coating processes include:  
Air knife coating  
Anilox coater  
Flexo coater  
Gap Coating  
Knife – over - roll coating  
Gravure coating

Hot Melt coating - when the necessary coating viscosity is achieved by temperature rather than solution of the polymers etc. This method commonly implies slot - die coating above room temperature, but it also is possible to have hot-melt roller coating; hot-melt metering - rod coating, etc.

Immersion (dip) coating

Kiss coating

Metering rod (Meyer bar) coating

Roller coating

Forward roller coating

Reverse roll coating

Silk Screen coater

Rotary screen

Slot Die coating

Extrusion coating - generally high pressure, often high temperature, and with the web travelling much faster than the speed of the extruded polymer.

Curtain coating - low viscosity, with the slot vertically above the web and a gap between slot die and web.

Slide coating - bead coating with an angled slide between the slotdie and the bead. Very successfully used for multilayer coating in the photographic industry.

Slot die bead coating- typically with the web backed by a roller and a very small gap between slot die and web.

Tensioned - web slot die coating- with no backing for the web.

Inkjet printing

Lithography

Flexography

Some dip coating processes

### **3 - 5 – Other**

Spin coating



## Coatings Category

- ▶ Ceramic glazes
- ▶ Glass coating and surface modification
- ▶ Metal plating
- ▶ Paints
- ▶ Thin film deposition
- ▶ Vitreous enamel

### Coatings Category :

#### A

Aircraft dope  
Alkaline Electroless Nickel Boron Coating  
Alkyd  
Anodizing  
Anti - climb paint  
Anti - graffiti coating

#### B

Biomimetic antifouling coating  
Black oxide  
Bluing (steel)  
Body Guardz  
Bresle method

#### C

Carbonyl metallurgy  
Cathodic arc deposition  
Chameleon coating  
Chemical vapor deposition  
Chromate conversion coating  
Coelan Marine Coatings  
Combustion chemical vapor deposition  
Conversion coating  
Curtain Coating

#### D

Diamond-like carbon  
Dip - coating

## **E**

Electrostatic spray-assisted vapour deposition

Enamel paint

Enteric coating

Environmental impact of paint

European Coatings Journal

European coil coating association

Extrusion coating

## **F**

Film coating

Food coating

Fusion bonded epoxy coating

## **G**

Gas dynamic cold spray

Gold plating

## **H**

Herbol

High - power impulse magnetron sputtering

Hot - dip galvanization

## **I**

Industrial coating

Industrial finishing

Industrial porcelain enamel

Ion Layer Gas Reaction

## **K**

Kinetic Monte Carlo surface growth method

## **L**

Lacquer

Light booth

Lunac (alloy and trans-ceramic coatings)

## **M**

Madapolam

Mechanical plating

Metallizing

## **O**

Optically active additive

## **P**

Paint adhesion testing  
Paint sealant  
Painter work  
Painting with Fire  
Parkerizing  
Pearlescent coating  
Persoz pendulum  
Phosphate conversion coating  
Physical vapor deposition  
Plasma transferred wire arc thermal spraying  
Plating  
Polyurethane  
Prepainted metal  
Protective finishing coat  
Pulsed Gas Dynamic Spray Process  
Pyrolytic chromium carbide coating

## **R**

Resputtering  
Rugosity  
Rust converter

## **S**

Salt spray test  
Silicate mineral paint  
Solution precursor plasma spray  
Spray-lining  
Sputtering  
Stone sealer

## **T**

Thermal spraying  
Tinning

## **V**

Vacuum coating  
Vernis Martin  
Vitreous enamel

## **W**

Water based pipe coating

Whitewash

**X**

Xylan (coating)

**Z**

Zircotec

## **Cyanides Category**

## **A**

Acetyl cyanide

Ammonium cyanide

## **B**

Barium cyanide

## **C**

Cadmium cyanide

Calcium cyanide

Cobalt(II) cyanide

Copper(I) cyanide

Cyano radical

Cyanogen

Cyanogen bromide

Cyanogen chloride

Cyanogen fluoride

Cyanogen halide

Cyanogen iodide

Cyano polyyne

Cyclo propyl cyanide

## **D**

Dicyano acetylene

Diethyl Aluminum cyanide

## **F**

Ferri cyanide

Ferro cyanide

## **H**

Hydrogen cyanide

## **I**

International Cyanide Management Code

## **K**

Krogmann's salt

## **L**

Lithium cyanide

## **M**

Mercury (II) cyanide

## **P**

Palladium (II) cyanide  
Platino cyanide  
Potassium argento cyanide  
Potassium cyanide  
Potassium ferri cyanide  
Potassium ferro cyanide  
Prussian blue

**S**

Silver cyanide  
Sodium cyanide  
Sodium ferro cyanide  
Sodium nitro prusside

**Z**

Zinc cyanide  
Zyklon B

## **Electro Plating**



*Copper electro plating machine for layering PCBs*

## **Contents**

### **1 Introduction**

### **2 Process**

#### **2.1 Strike**

#### **2.2 Pulse electro plating or Pulse Electro deposition (PED)**

#### **2.3 Brush electro plating**

#### **2.4 Electroless deposition**

#### **2.5 Cleanliness**

### **3 Effects**

### **4 History**

### **5 Uses**

### **6 Hull cell**

## **1 - Introduction**

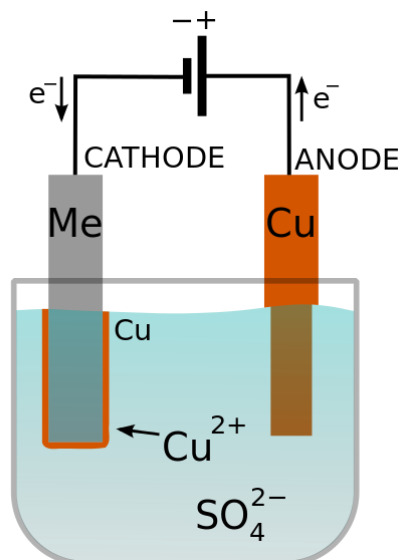
Electro plating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The term is also used for electrical oxidation of anions onto a solid substrate, as in the formation silver chloride on silver wire to make silver / silver - chloride electrodes. Electro plating is primarily used to change the surface properties of an object (e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.), but may also be used to build up thickness on undersized parts or to form objects by electroforming.

The process used in electro plating is called electro deposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is

made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.

Other electro plating processes may use a non - consumable anode such as lead or carbon. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution. The most common form of electro plating is used for creating coins such as pennies, which are small zinc plates covered in a layer of copper ,

## 2 - Process



*Electro plating of a metal (Me) with copper in a copper sulfate bath*

The cations associate with the anions in the solution. These cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at



the anode to  $\text{Cu}^{2+}$  by losing two electrons. The  $\text{Cu}^{2+}$  associates with the anion  $\text{SO}_4^{2-}$  in the solution to form copper sulfate. At the cathode, the  $\text{Cu}^{2+}$  is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder.

Many plating baths include cyanides of other metals (e.g., potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity. Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity.

When plating is not desired on certain areas of the substrate, stop - offs are applied to prevent the bath from coming in contact with the substrate. Typical stop - offs include tape, foil, lacquers, and waxes.

## **2 – 1 – Strike**

Initially, a special plating deposit called a "strike" or "flash" may be used to form a very thin ( typically less than 0.1 micrometer thick ) plating with high quality and good adherence to the substrate. This serves as a foundation for subsequent plating processes. A strike uses a high current density and a bath with a low ion concentration. The process is slow, so more efficient plating processes are used once the desired strike thickness is obtained.

The striking method is also used in combination with the plating of different metals. If it is desirable to plate one type of deposit onto a metal to improve corrosion resistance but this metal has inherently poor adhesion to the substrate, a strike can be first deposited that is compatible with both. One example of this situation is the poor

adhesion of electrolytic nickel on zinc alloys, in which case a copper strike is used, which has good adherence to both.

## **2 – 1 - Pulse electro plating or Pulse Electro deposition (PED )**

A simple modification in the electro plating process is the pulse electro plating. This process involves the swift alternating of the potential or current between two different values resulting in a series of pulses of equal amplitude, duration and polarity, separated by zero current. By changing the pulse amplitude and width , it is possible to change the deposited film's composition and thickness .

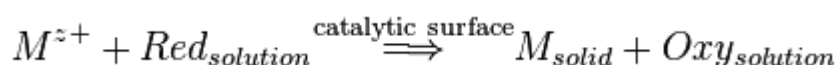
## **2 – 3 - Brush electro plating**

A closely related process is brush electro plating, in which localized areas or entire items are plated using a brush saturated with plating solution. The brush, typically a stainless steel body wrapped with a cloth material that both holds the plating solution and prevents direct contact with the item being plated, is connected to the positive side of a low voltage direct - current power source, and the item to be plated connected to the negative. The operator dips the brush in plating solution then applies it to the item, moving the brush continually to get an even distribution of the plating material. Brush electro plating has several advantages over tank plating, including portability, ability to plate items that for some reason cannot be tank plated (one application was the plating of portions of very large decorative support columns in a building restoration), low or no masking requirements, and comparatively low plating solution volume requirements. Disadvantages compared to tank plating can include greater operator involvement (tank plating can frequently be done with minimal attention), and inability to achieve as great a plate thickness.

## **2 – 4 - Electro less deposition**

Usually an electrolytic cell ( consisting of two electrodes, electrolyte, and external source of current ) is used for Electro deposition. In contrast, an electroless deposition process uses only one electrode and no external source of electric current. However, the

solution for the electroless process needs to contain a reducing agent so that the electrode reaction has the form:



In principle any water - based reducer can be used although the redox potential of the reducer half - cell must be high enough to overcome the energy barriers inherent in liquid chemistry. Electroless nickel plating uses hypophosphite as the reducer while plating of other metals like silver, gold and copper typically use low molecular weight aldehydes.

A major benefit of this approach over electro plating is that power sources and plating baths are not needed, reducing the cost of production. The technique can also plate diverse shapes and types of surface. The downside is that the plating process is usually slower and cannot create such thick plates of metal. As a consequence of these characteristics, electroless deposition is quite common in the decorative arts.

## 2 – 5 – Cleanliness

Cleanliness is essential to successful electro plating, since molecular layers of oil can prevent adhesion of the coating. ASTM B322 is a standard guide for cleaning metals prior to electro plating. Cleaning processes include solvent cleaning, hot alkaline detergent cleaning, electro-cleaning, and acid treatment etc. The most common industrial test for cleanliness is the waterbreak test, in which the surface is thoroughly rinsed and held vertical. Hydrophobic contaminants such as oils cause the water to bead and break up, allowing the water to drain rapidly. Perfectly clean metal surfaces are hydrophilic and will retain an unbroken sheet of water that does not bead up or drain off. ASTM F22 describes a version of this test. This test does not detect hydrophilic contaminants, but the electro plating process can displace these easily since the solutions are water-based. Surfactants such as soap reduce the sensitivity of the test and must be thoroughly rinsed off.

### **3 – Effects**

Electro plating changes the chemical, physical, and mechanical properties of the workpiece. An example of a chemical change is when nickel plating improves corrosion resistance. An example of a physical change is a change in the outward appearance. An example of a mechanical change is a change in tensile strength or surface hardness which is a required attribute in tooling industry.

### **4 – History**

Although it is not confirmed, the Parthian Battery may have been the first system used for electro plating.

Modern electrochemistry was invented by Italian chemist Luigi V. Brugnatelli in 1805. Brugnatelli used his colleague Alessandro Volta's invention of five years earlier, the voltaic pile, to facilitate the first Electro deposition. Brugnatelli 's inventions were suppressed by the French Academy of Sciences and did not become used in general industry for the following thirty years.

By 1839, scientists in Britain and Russia had independently devised metal deposition processes similar to Brugnatelli 's for the copper electro plating of printing press plates.

Boris Jacobi in Russia not only rediscovered galvano plastics, but developed electrotyping and galvano plastic sculpture. Galvano plastics quickly came into fashion in Russia, with such people as inventor Peter Bagration , scientist Heinrich Lenz and science fiction author Vladimir Odoyevsky all contributing to further development of the technology. Among the most notorious cases of electro plating usage in mid-19th century Russia were gigantic galvano plastic sculptures of St. Isaac's Cathedral in Saint Petersburg and gold-electroplated dome of the Cathedral of Christ the Saviour in Moscow, the tallest Orthodox church in the world .

Soon after, John Wright of Birmingham, England discovered that potassium cyanide was a suitable electrolyte for gold and silver electro plating. Wright's associates, George Elkington and Henry Elkington were awarded the first patents for electro plating in 1840.

These two then founded the electro plating industry in Birmingham from where it spread around the world.

The Nord deutsche Affinerie in Hamburg was the first modern electro plating plant starting its production in 1876.

As the science of electrochemistry grew, its relationship to the electro plating process became understood and other types of non-decorative metal electro plating processes were developed. Commercial electro plating of nickel, brass, tin, and zinc were developed by the 1850s. Electro plating baths and equipment based on the patents of the Elkingtons were scaled up to accommodate the plating of numerous large scale objects and for specific manufacturing and engineering applications.

The plating industry received a big boost with the advent of the development of electric generators in the late 19th century. With the higher currents available, metal machine components, hardware, and automotive parts requiring corrosion protection and enhanced wear properties, along with better appearance, could be processed in bulk.

The two World Wars and the growing aviation industry gave impetus to further developments and refinements including such processes as hard chromium plating, bronze alloy plating, sulfamate nickel plating, along with numerous other plating processes. Plating equipment evolved from manually operated tar-lined wooden tanks to automated equipment, capable of processing thousands of kilograms per hour of parts.

One of the American physicist Richard Feynman's first projects was to develop technology for electro plating metal onto plastic. Feynman developed the original idea of his friend into a successful invention, allowing his employer (and friend) to keep commercial promises he had made but could not have fulfilled otherwise.<sup>[9]</sup>

## 5 – Uses

Electro plating is a useful process. It is widely used in various industries for coating metal objects with a thin layer of a different metal. The layer of metal deposited has some desired property, which the metal of the object lacks. For example chromium plating is done on many objects such as car parts, bath taps, kitchen gas burners, wheel rims and many others for the fact that chromium is very corrosion resistant, and thus prolongs the life of the parts. Electro plating has wide usage in industries. It is also used in making unexpensive jewelry. Electro plating increases life of metal and prevents corrosion.

## 6 - Hull cell

The *Hull cell* is a type of test cell used to qualitatively check the condition of an electro plating bath. It allows for optimization for current density range, optimization of additive concentration, recognition of impurity effects and indication of macro-throwing power capability.<sup>[10]</sup> The Hull cell replicates the plating bath on a lab scale. It is filled with a sample of the plating solution, an appropriate anode which is connected to a rectifier. The "work" is replaced with a hull cell test panel that will be plated to show the "health" of the bath.

The Hull cell is a trapezoidal container that holds 267 ml of solution. This shape allows one to place the test panel on an angle to the anode. As a result, the deposit is plated at different current densities which can be measured with a hull cell ruler. The solution volume allows for a quantitative optimization of additive concentration: 1 gram addition to 267 mL is equivalent to 0.5 oz/gal in the plating tank.

# List of Alloys

## Contents

- 1 Alloys of Aluminum
- 2 Alloys of Bismuth
- 3 Alloys of Chromium
- 4 Alloys of Cobalt
- 5 Alloys of Copper
- 6 Alloys of Gallium
- 7 Alloys of Gold
- 8 Alloys of Indium
- 9 Alloys of Iron
- 10 Alloys of Lead
- 11 Alloys of Magnesium
- 12 Alloys of Mercury
- 13 Alloys of Nickel
- 14 Alloys of Potassium
- 15 Alloys of Plutonium
- 16 Alloys of Rare earth
- 17 Alloys of Rhodium
- 18 Alloys of Scandium
- 19 Alloys of Silver
- 20 Alloys of Sodium
- 21 Alloys of Titanium
- 22 Alloys of Tin
- 23 Alloys of Uranium
- 24 Alloys of Zinc
- 25 Alloys of Zirconium

## Introduction

This is a **list of named alloys** that are grouped alphabetically by base metal. Within these headings, the alloys are also grouped alphabetically. Some of the main alloying elements are optionally listed after the alloy names.

## 1 - Alloys of Aluminum

Aluminum also forms complex metallic alloys, like  $\beta$ -Al-Mg,  $\xi'$ -Al-Pd-Mn, T-Al<sub>3</sub>Mn

AA-8000 : used for electrical building wire in the U.S. per the National Electrical Code, replacing AA-1350.

Al–Li (lithium)

Alnico (nickel, cobalt): used for permanent magnets

Duralumin (copper)

Hiduminium or R.R. alloys (2% copper, iron, nickel): used in aircraft pistons

Kryon

Magnalium ( 5 % magnesium ) : used in airplane bodies , ladders , etc .

Nambe ( Aluminum plus seven other undisclosed metals), serveware, exclusively from the one manufacturer

Scandium– Aluminum (scandium)

Y alloy (4% copper, nickel, magnesium):

## **2 - Alloys of Bismuth**

Cerrosafe (lead, tin, cadmium)

Rose metal (lead, tin)

Wood's metal (lead, tin, cadmium)

## **3 - Alloys of Chromium**

Chromium hydride (hydrogen)

Nichrome (nickel)

## **4 - Alloys of Cobalt**

Megallium

Stellite (chromium, tungsten, carbon)

Talonite

Ultimet (chromium, nickel, molybdenum, iron, tungsten)

Vitallium

## **5 - Alloys of Copper**

Arsenical copper

Beryllium copper (beryllium)

Billon (silver)

Brass (zinc)

Calamine brass (zinc)



Chinese silver (zinc)  
Dutch metal (zinc)  
Gilding metal (zinc)  
Muntz metal (zinc)  
Pinchbeck (zinc)  
Prince's metal (zinc)  
Tombac (zinc)  
Bronze (tin, Aluminum or other element)  
Aluminum bronze (Aluminum)  
Arsenical bronze  
Bell metal (tin)  
Florentine bronze (Aluminum or tin)  
Guanín  
Gunmetal (tin, zinc)  
Glucydur  
Phosphor bronze (tin and phosphorus)  
Ormolu (Gilt Bronze) (zinc)  
Speculum metal (tin)  
Constantan (nickel)  
Copper hydride (hydrogen)  
Copper–tungsten (tungsten)  
Corinthian bronze (gold, silver)  
Cunife (nickel, iron)  
Cupronickel (nickel)  
Cymbal alloys (Bell metal) (tin)  
Devarda's alloy (Aluminum, zinc)  
Electrum (gold, silver)  
Hepatizon (gold, silver)  
Heusler alloy (manganese, tin)  
Manganin (manganese, nickel)  
Molybdochalkos (lead)  
Nickel silver (nickel)  
Nordic gold (Aluminum, zinc, tin)  
Shakudo (gold)  
Tumbaga (gold)

## **6 - Alloys of Gallium**

Galfenol (iron)

Galinstan (indium, tin)

## **7 - Alloys of Gold**

Colored gold (silver, copper)

Crown gold (silver, copper)

Electrum (silver, copper)

Rhodite (rhodium)

Rose gold (copper)

Tumbaga (copper)

White gold (nickel, palladium)

## **8 - Alloys of Indium**

Field's metal (bismuth, tin)

## **9 - Alloys of Iron**

Elinvar (nickel, chromium)

Fernico (nickel, cobalt)

Ferroalloys (Category:Ferroalloys)

Ferroboron

Ferrocerium

Ferrochrome

Ferromagnesium

Ferromanganese

Ferromolybdenum

Ferronickel

Ferrophosphorus

Ferrosilicon

Ferrotitanium

Ferrovandium

Invar (nickel)

Iron

Cast iron (carbon)

Pig iron (carbon)

Iron hydride (hydrogen)

Kovar (nickel, cobalt)

Spiegeleisen (manganese, carbon, silicon)  
Steel (carbon) (Category:Steels)  
Bulat steel  
Chromoly (chromium, molybdenum)  
Crucible steel  
Damascus steel  
High speed steel  
Mushet steel  
HSLA steel  
Maraging steel  
Reynolds 531  
Silicon steel (silicon)  
Spring steel  
Stainless steel (chromium, nickel)  
AL-6XN  
Alloy 20  
Celestrum  
Marine grade stainless  
Martensitic stainless steel  
Surgical stainless steel (chromium, molybdenum, nickel)  
Zeron 100 (chromium, nickel, molybdenum)  
Tool steel (tungsten or manganese)  
Silver steel (US:Drill rod) (manganese, chromium, silicon)  
Weathering steel ('Cor-ten') (silicon, manganese, chromium, copper, vanadium, nickel)  
Wootz steel

## **10 - Alloys of Lead**

Molybdochalkos (copper)

Solder (tin)

Terne (tin)

Type metal (tin, antimony)

## **Alloys of magnesium[edit]**

*Main article: Magnesium*

Elektron

Magnox ( Aluminum)

T-Mg-Al-Zn (Bergman phase) is a complex metallic alloy

## **11 - Alloys of Mercury**

Amalgam

## **12 - Alloys of Nickel**

Alnico ( Aluminum, cobalt; used in magnets)

Alumel (nickel, manganese, Aluminum, silicon)

Chromel (chromium)

Cupronickel (bronze, copper)

Ferronickel (iron)

German silver (copper, zinc)

Hastelloy (molybdenum, chromium, sometimes tungsten)

Inconel (chromium, iron)

Monel metal (copper, iron, manganese)

Nichrome (chromium)

Nickel-Carbon (Nickel, Carbon)

Nicrosil (chromium, silicon, magnesium)

Nisil (silicon)

Nitinol (titanium, shape memory alloy)

Magnetically "soft" alloys

Mu-metal (iron)

Permalloy (iron), (molybdenum)

Supermalloy (molybdenum)

## **13 - Alloys of potassium**

NaK (sodium)

KLi (lithium)

## **14 - Alloys of plutonium**

Plutonium– Aluminum

Plutonium–cerium

Plutonium–cerium–cobalt

Plutonium–gallium (gallium)

Plutonium–gallium–cobalt

Plutonium–zirconium

## **15 - Alloys of Rare Earth**

Mischmetal (various rare earth elements)

Terfenol-D (terbium, dysprosium, and iron), a highly magnetostrictive alloy used in portable speakers such as the SoundBug device

### **16 - Alloys of Rhodium**

Pseudo palladium (Rhodium–silver alloy)

### **17 - Alloys of Scandium**

Scandium hydride (hydrogen)

### **18 - Alloys of Silver**

Argentium sterling silver (copper , germanium)

Billon

Britannia silver (copper)

Doré bullion (gold)

Electrum (gold)

Goloid (copper, gold)

Platinum sterling (platinum)

Shibuichi (copper)

Sterling silver (copper)

Tibetan silver (copper)

### **19 - Alloys of Sodium**

NaK (potassium)

### **20 - Alloys of Titanium**

Beta C (vanadium, chromium, others)

6 al – 4v ( Aluminum, vanadium)

Titanium hydride (hydrogen)

### **21 - Alloys of Tin**

Babbitt (copper, antimony, lead; used for bearing surfaces)

Britannium (copper, antimony)[1]

Pewter (antimony, copper)

Solder (lead, antimony)

Terne (lead)

## **22 - Alloys of Uranium**

Staballoy (depleted uranium with other metals, usually titanium or molybdenum)

Uranium hydride (hydrogen)

## **23 - Alloys of Zinc**

Zamak (Aluminum, magnesium, copper)

Electroplated zinc alloys

## **24 - Alloys of zirconium**

*Main article: Zirconium*

Zircaloy (tin)

Zirconium hydride (hydrogen)

# Metal Clay



*Pendant made from metal clay with gold powder*

## Contents

- 1 Introduction
- 2 History
- 3 Silver metal clay
  - 3.1 Precious Metal Clay (PMC)
  - 3.2 Art Clay Silver (ACS)
- 4 Lump metal clays
- 5 Base metal clays

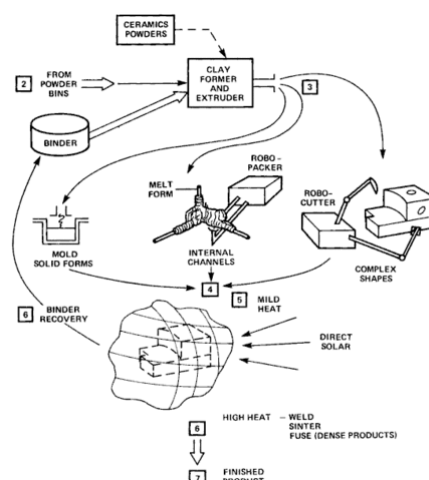
## 1 Introduction

Metal clay is a crafting medium consisting of very small particles of metal such as silver, gold, bronze, or copper mixed with an organic binder and water for use in making jewelry, beads and small sculptures. Originating in Japan in 1990, metal clay can be shaped just like any soft clay, by hand or using molds. After drying, the clay can be fired in a variety of ways such as in a kiln, with a handheld gas torch, or on a gas stove, depending on the type of clay and the metal in it. The binder burns away, leaving the pure sintered metal. Shrinkage of between 8 % and 30 % occurs (depending on the product used). Alloys such as bronze, sterling silver, and steel also are available.

## 2 – History

Metal clay first came out in Japan in 1990 to allow craft jewelry makers to make sophisticated looking jewelry without the years of study needed to make fine jewelry.

### 3 - Silver metal clay



#### *Metal clay and pottery manufacturing*

Fine silver metal clay results in objects containing 99.9% pure silver, which is suitable for enameling. Gold metal clay is more expensive and provides richer color. Lump metal clay is sold in sealed packets to keep it moist and workable. The silver versions are also available as a softer paste in a pre - filled syringe which can be used to produce extruded forms, in small jars of slip and as paper-like sheets, from which most of the moisture has been removed. Common brands of silver metal clay include Precious Metal Clay (PMC) and Art Clay Silver (ACS).

#### **3 – 1 - Precious Metal Clay ( PMC )**

PMC was developed in the early 1990s in Japan by metallurgist Masaki Morikawa . As a solid-phase sintered product of a precious metal powder used to form a precious metal article , the material consists of microscopic particles of pure silver or fine gold powder and a water - soluble, non - toxic, organic binder that burns off during firing. Success was first achieved with gold and later duplicated with silver. The PMC brand includes the following products:

The original formula of PMC, now called "standard": fired at 900 °C for 2 hours, shrinks by 30 % during firing.



**PMC+** : fired at 900 °C for 10 minutes or 800 °C for 30 minutes; shrinks 15 %, due to a particle size reduction. PMC+ is also available in sheet form which can be worked like paper; for example, for origami.

**PMC3** : fired at 599 °C for 45 minutes or 699 °C for 10 minutes ; shrinks by 10 %. It can also be fired using a butane torch by heating it to orange heat for at least 2 minutes. It has a longer working life than the older formulations. It is also available in slip and paste forms which can be painted onto the surface of an object to be used as a mould.

**Aura 22** : a 22 k gilding material, a gold paste intended to be painted onto the surface of silver PMC pieces, or ready-made silver objects.

**PMC Pro** : a harder product which is only 0.900 silver, hence it cannot be hallmarked as sterling silver. It also requires kiln firing in a tub of activated carbon for 1 hour at 760 °C .

**PMC Sterling** : is fired at 815°C and shrinks by 10 – 15 %. Because of the copper content in this formula, firing is a two-step process; step one is an open - shelf firing and step two requires a firing pan with activated carbon media.

### **3 – 2 - Art Clay Silver (ACS)**

ACS was developed by AIDA Chemical Industries, also a Japanese company. ACS followed PMC Standard with their Art Clay Original clay (more like PMC+ than PMC Standard), which allows the user to fire with a handheld torch or on a gas hob. Owing to subtle differences in the binder and suggested firing times, this clay shrinks less than the PMC versions, approximately 8 – 10 % .

Further developments introduced the Art Clay Slow Dry, a clay with a longer working time. Art Clay 650 and Art Clay 650 Slow Dry soon followed ; both clays can be fired at 650 °C . allowing the user to combine the clay with glass and sterling silver , which are affected negatively by the higher temperatures needed to fire the first

generation clays. AIDA also manufacturers Oil Paste, a product used only on fired metal clay or milled fine silver, and Overlay Paste, which is designed for drawing designs on glass and porcelain.

In 2006 AIDA introduced the Art Clay Gold Paste, a more economical way to work with gold. The paste is painted onto the fired silver clay, then refired in a kiln, or with a torch or gas stove. When fired, it bonds with the silver, giving a 22ct gold accent. The same year also saw Art Clay Slow Tarnish introduced, a clay that tarnishes less rapidly than the other metal clays.

#### **4 - Lump metal clays**

Lump metal clay in bronze was introduced in 2008 by Metal Adventures Inc. and in 2009 by Prometheus. Lump metal clays in copper were introduced in 2009 by Metal Adventures Inc. and Aida. Because of the lower cost, the bronze and copper metal clays are used by artists more often than the gold and silver metal clays in the American market place. Due to Hallmarking requirements laid out in the UK Bronze and Copper are not regarded as highly. The actual creation time of a bronze or copper piece is also far greater than that of its PMC3 counterpart.

#### **5 - Base metal clays**

Base metal clays, such as bronze, copper, and steel metal clays are best fired in the absence of oxygen to eliminate the oxidation of copper by atmospheric oxygen . A simple means to accomplish this ( place the pieces in activated carbon inside a container ) was developed by Bill Struve.

## **Metal Plating Category**

### **A**

Acierage

Angel gilding

### **B**

Bethanization

### **C**

Chrome plating

Copper plating

### **D**

Diffusion barrier

### **E**

Electro galvanization

Electroless nickel

Electroless nickel immersion gold

Electroless nickel plating

Electro plating

### **G**

Galvanization

Galvannealed

Gilding

Gold plating

Goldgenie

### **H**

Hot - dip galvanization

### **K**

Keum - boo

### **M**

Mechanical plating

Nickel electro plating

### **O**

Ormolu

### **P**

Plated ware

### **S**

Sherardizing

Silver-gilt

**T**

Tinning

**V**

Vermeil

**Z**

Zinc alloy

Zincate

## **Metal Working Category**

- ▶ Abrasive blasting
- ▶ Artworks in metal
- ▶ Fabrication (metal)
- ▶ Metal forming
- ▶ Foundries
- ▶ Gilding
- ▶ Grinding and lapping
- ▶ Metal heat treatments
- ▶ Jewellery making
- ▶ Joining
- ▶ Machining
- ▶ Metal working occupations
- ▶ Plasma processing
- ▶ Metal plating
- ▶ Screws
- ▶ Shot peening
- ▶ Silver smithing
- ▶ Surface finishing
- ▶ Metalworking terminology
- ▶ Metalworking tools
- ▶ Metal trade unions
- ▶ Metalworking stubs (114 P)

### **Metal Working Category :**

#### **A**

Abrasive  
Abrasive flow machining  
Accumulative roll bonding  
Air carbon arc cutting  
Aluminum foil  
American Machinists' Handbook  
Architectural ironmongery  
Architectural metals

Autofrettage

## **B**

Ball (bearing)

Birmingham toy industry

Blowpipe (tool)

Bronze and brass ornamental work

Brushed metal

## **C**

Capacitor discharge sintering

Cast iron

Centerless grinding

Ceramsite sand

Chemical milling

Chip formation

Cladding (metalworking)

Copper plating

Copper slag

Cupola furnace

Cutting fluid

## **D**

Damascus steel

Decambering

Differential screw

Direct metal laser sintering

## **E**

Electro polishing

Electrostatic spray-assisted vapour deposition

Engraving

Equal channel angular extrusion

## **F**

Faggoting (metalworking)

Ferdinando Marinelli Artistic Foundry

Filing (metalworking)

Fillet weld

Finery forge

Flame cleaning

Foil (metal)

Forge

Forming (metalworking)

Foundry

**G**

Gilding

Goldsmith

**H**

High Frequency Impact Treatment

Hot iso static pressing

Hot pressing

Hot working

**I**

Indo - MIM

Industrial finishing

International Deep Drawing Research Group

Ironwork

**J**

Junker test

**K**

Knife making

**L**

Laser peening

Lock – N - Stitch

Low plasticity burnishing

**M**

Machinery's Handbook

Mass finishing

Metal clay

Metal fume fever

Metal injection molding

Mill finish

Milling (machining)

Miter joint

Model engineering

Mokume - gane

Moving crack (metalworking)

## **P**

Parkerizing  
Parts cleaning  
Patina  
Peening  
Pickling (metal)  
Pig iron  
Pin brazing  
Planing ( shaping )  
Polishing ( metal working )  
Powder metallurgy  
Primer (paint)

## **R**

Reeding  
Rivet  
Rotten stone  
Rust converter

## **S**

Scissel  
Screw  
Selective laser sintering  
Semi-solid metal casting  
Shock hardening  
Shot tower  
Silca S.p.A.  
Silent butler  
Sintering  
Skiving machine  
Slitting mill  
Slotted angle  
Smooth clean surface  
Soldering  
Solvent degreasing  
Spark plasma sintering  
Spark testing  
Spray forming  
Steel wool



Super forming

Sword making

## **T**

Tension control bolt

Tin ware

Tool steel

Tool wear

Tool room

Tumble finishing

## **U**

Ultrasonic impact treatment

## **V**

V - block

Vapor degreasing

Vibratory finishing

## **W**

Work hardening

Wrought iron

## Metallizing

Metallizing is the general name for the technique of coating metal on the surface of non - metallic objects.

Techniques for metallization started as early as mirror making. In 1835, Justus von Liebig discovered the process of coating a glass surface with metallic silver, making the glass mirror one of the earliest items being metallized. Plating other non - metallic objects grew rapidly with introduction of ABS plastic. Because a non-metallic object tends to be a poor electrical conductor, the object's surface must be made conductive before plating can be performed. The plastic part is first etched chemically by a suitable process, such as dipping in a hot chromic acid - sulfuric acid mixture. The etched surface is sensitized and activated by first dipping in tin (II) chloride solution, then palladium chloride solution. The processed surface is then coated with electroless copper or nickel before further plating. This process gives useful ( about 1 to 6 kgf / cm or 10 to 60 N / cm or 5 to 35 lbf / in ) adhesion force, but is much weaker than actual metal-to-metal adhesion strength.

Vacuum metallizing involves heating the coating metal to its boiling point in a vacuum chamber, then letting condensation deposit the metal on the substrate's surface. Resistance heating, electron beam, or plasma heating is used to vaporize the coating metal. Vacuum metallizing was used to deposit aluminum on the large glass mirrors of reflecting telescopes, such as with the Hale telescope.

Thermal spray processes are often referred to as metallizing.

Cold spray able metal – Vero Metal® is a metallizing process that seamlessly applies cold sprayable or putty able metal to almost any surface. The composite metal consists of two (water based binder) or three different ingredients: metal powder, binder and hardener. The mixture of the ingredients is cast or sprayed on the substrate at room temperature. The desired effect and the necessary final treatment define the thickness of the layer, which normally varies between 80

and 150  $\mu\text{m}$ . After the spraying process the work piece should rest for approximately 60 minutes. Then the work piece is dried for 6-12 hours at a temperature of 20 - 60  $^{\circ}\text{C}$ . Afterwards the surface is ready for the next treatment steps.

# Potassium Cyanide

## Contents



- 1 Introduction
- 2 Production
  - 2.1 Modern Production
  - 2.2 Historical Production
- 3 Structure
- 4 Applications
  - 4.1 Potassium gold cyanide
- 5 Toxicity

## 1 - Introduction

Potassium cyanide is a compound with the formula KCN. This colorless crystalline salt, similar in appearance to sugar, is highly soluble in water. Most KCN is used in gold mining , organic synthesis, and electro plating. Smaller applications include jewelry for chemical gilding and buffing.

KCN is highly toxic. The moist solid emits small amounts of hydrogen cyanide due to hydrolysis, which tastes like bitter almonds . Not every one, however, can taste this: the ability to do so is a genetic trait.

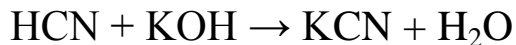
IUPAC name : Potassium cyanide	
Molecular formula	K CN
Molar mass	65 g / mol
Appearance	White crystalline solid deliquescent
Odor	Faint , almond - like
Density	1.52 g / cm <sup>3</sup>
Melting point	634.5 °C
Boiling point	1,625 °C
Solubility in water	71.6 g / 100 ml ( 25 °C )
	100 g / 100 mL ( 100 °C )
Solubility in methanol	4.91 g/100 mL ( 20 °C )

Solubility in glycerol	soluble
Solubility in formamide	14.6 g / 100 mL
Solubility in ethanol	0.57 g / 100mL
Solubility in hydroxylamine	41 g/100 mL
Refractive index ( $n_D$ )	1.410
EU classification	 T +  N
Flash point	Non - flammable
LD <sub>50</sub>	5–10 mg / kg (oral in rats, mice, rabbits)

## 2 - Production

### 2 – 1 - Modern Production

KCN is produced by treating hydrogen cyanide with a 50 % aqueous solution of potassium hydroxide , followed by evaporation of the solution in a vacuum :



or by treating formamide with potassium hydroxide:



Approximately 50,000 tons of potassium cyanide are produced yearly.

### 2 – 2 - Historical Production

Prior to 1900 AD, before the invention of the Castner process, potassium cyanide was the most important source of alkali metal cyanides . In this historical process potassium cyanide was produced by decomposing potassium ferro cyanide :



### 3 – Structure

In aqueous solution, KCN is dissociated into hydrated potassium ( $K^+$ ) ions and cyanide ( $CN^-$ ) ions. The common form of solid KCN, stable at ambient pressure and temperature, has the same cubic crystal structure as sodium chloride, with each potassium ion surrounded by six cyanide ions, and vice versa. Despite the cyanide ions being diatomic, and thus less symmetric than chloride, they rotate so rapidly that their time averaged shape is spherical. At low temperature and high pressure this free rotation is hindered, resulting in a less symmetric crystal structure with the cyanide ions arranged in sheets.

### 4 – Applications

KCN and its close relative sodium cyanide ( $NaCN$ ) are widely used in organic synthesis for the preparation of nitriles and carboxylic acids, particularly in the von Richter reaction. It also finds use for the synthesis of hydantoins, which can be useful synthetic intermediates, when reacted with a carbonyl compound such as an aldehyde or ketone in the presence of ammonium carbonate.

#### 4 – 1 - Potassium gold cyanide

In gold mining, KCN forms the water-soluble salt potassium gold cyanide (or gold potassium cyanide) and potassium hydroxide from gold metal in the presence of oxygen (usually from the surrounding air) and water :

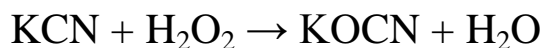


A similar process uses sodium cyanide ( $NaCN$ , a close relative of potassium cyanide) to produce sodium gold cyanide ( $NaAu(CN)_2$ ).

Very few other methods exist for this extraction process.

### 5 – Toxicity

KCN can be detoxified most efficiently with hydrogen peroxide or with a solution of sodium hypochlorite. Such solutions should be kept basic when ever possible so as to eliminate the possibility of generation of hydrogen cyanide :



Cyanide is a potent inhibitor of cellular respiration, acting on mitochondrial cytochrome c oxidase and hence blocking oxidative phosphorylation. This prevents the body from oxidizing food to produce useful energy. Lactic acidosis then occurs as a consequence of anaerobic metabolism. Initially, acute cyanide poisoning causes a red or ruddy complexion in the victim because the tissues are not able to use the oxygen in the blood. The effects of potassium and sodium cyanide are identical. The person loses consciousness, and death eventually follows over a period of time. During this period, convulsions may occur. Death occurs not by cardiac arrest, but by hypoxia of neural tissue.

The lethal dose for potassium cyanide is 200–300 mg.<sup>[8]</sup> The toxicity of potassium cyanide when ingested depends on the acidity of the stomach, because it must react with an acid to become hydrogen cyanide, the deadly form of cyanide. Grigori Rasputin may have survived a potassium cyanide poisoning because his stomach acidity was unusually low .

A number of prominent persons were killed or committed suicide using potassium cyanide, including members of the Young Bosnia and members of the Nazi Party, such as Hermann Göring and Heinrich Himmler, World War II era British agents (using purpose-made suicide pills), computer scientist Alan Turing, and various religious cult suicides such as by the Peoples Temple and Heaven's Gate. Danish writer Gustav Wied and members of the LTTE involved in the assassination of Indian prime minister Rajiv Gandhi also committed suicide using potassium cyanide.

It is used by professional entomologists as a killing agent in collecting jars, as insects succumb within seconds to the HCN fumes it emits, thereby minimizing damage to even highly fragile specimens.

# Thin Film

## Contents

- 1 Introduction
- 2 Deposition
  - 2.1 Chemical deposition
  - 2.2 Physical deposition
- 3 Thin - film photovoltaic cells
- 4 Thin - film batteries

## 1 - Introduction

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin-film construction.

A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors. A very-thin-film coating (less than about 50 nanometers thick) is used to produce two-way mirrors.

The performance of optical coatings (e.g., anti reflective, or AR, coatings) are typically enhanced when the thin-film coating consists of multiple layers having varying thicknesses and refractive indices. Similarly, a periodic structure of alternating thin films of different materials may collectively form a so-called superlattice which exploits the phenomenon of quantum confinement by restricting electronic phenomena to two - dimensions.

Work is being done with ferromagnetic and ferroelectric<sup>[1]</sup> thin films for use as computer memory. It is also being applied to pharmaceuticals, via thin-film drug delivery. Thin-films are used to produce thin - film batteries. Thin films are also used in dye-sensitized solar cells.

Ceramic thin films are in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of



interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude.

Research is being done on a new class of thin-film inorganic oxide materials, called amorphous heavy - metal cation multi component oxides , which could be used to make transparent transistors that are inexpensive, stable, and environmentally benign.

## **2 - Deposition**

The act of applying a thin film to a surface is *thin-film deposition* – any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometers. Molecular beam epitaxy allows a single layer of atoms to be deposited at a time.

It is useful in the manufacture of optics (for reflective, anti-reflective coatings or self-cleaning glass, for instance), electronics (layers of insulators, semiconductors, and conductors form integrated circuits), packaging (i.e., Aluminum - coated PET film), and in contemporary art . Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electro plating, and the deposition of silicon and enriched uranium by a CVD - like process after gas-phase processing.

Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical .

### **2 – 1 - Chemical deposition**

Here , a fluid precursor under goes a chemical change at a solid surface, leaving a solid layer. An every day example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, deposition happens on every surface, with little regard to direction; thin films from chemical deposition techniques tend to be *conformal*, rather than *directional*.

Chemical deposition is further categorized by the phase of the precursor:

Plating relies on liquid precursors, often a solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution (usually for noble metals), but by far the most commercially important process is electro plating. It was not commonly used in semiconductor processing for many years, but has seen a resurgence with more widespread use of chemical-mechanical polishing techniques.

Chemical solution deposition (CSD) or Chemical bath deposition (CBD) uses a liquid precursor, usually a solution of organo metallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin film process that is able to produce stoichiometric ally accurate crystalline phases. This technique is also known as the sol-gel method because the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system.

Spin coating or spin casting, uses a liquid precursor, or sol-gel precursor deposited onto a smooth, flat substrate which is subsequently spun at a high velocity to centrifugally spread the solution over the substrate. The speed at which the solution is spun and the viscosity of the sol determine the ultimate thickness of the deposited film. Repeated depositions can be carried out to increase the thickness of films as desired. Thermal treatment is often carried out in order to crystallize the amorphous spin coated film. Such crystalline films can exhibit certain preferred orientations after crystallization on single crystal substrates.

Chemical vapor deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas.

Plasma enhanced CVD (PECVD) uses an ionized vapor, or plasma, as a precursor. Unlike the soot example above, commercial

PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical reaction, to produce a plasma.

Atomic layer deposition (ALD) uses gaseous precursor to deposit conformal thin films one layer at a time. The process is split up into two half reactions, run in sequence and repeated for each layer, in order to ensure total layer saturation before beginning the next layer. Therefore, one reactant is deposited first, and then the second reactant is deposited, during which a chemical reaction occurs on the substrate, forming the desired composition. As a result of the stepwise, the process is slower than CVD, however it can be run at low temperatures, unlike CVD.

## **2 – 2 - Physical deposition**

Physical deposition uses mechanical, electromechanical or thermo dynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low- pressure vapor environment to function properly; most can be classified as physical vapor deposition (PVD).

The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly *directional*, rather than *conformal*.

### ***Examples of physical deposition include :***

A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum, both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the

residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a particularly sophisticated form of thermal evaporation.

An electron beam evaporator fires a high - energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapor pressure materials can be deposited. The beam is usually bent through an angle of  $270^\circ$  in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nanometres per second.

In molecular beam epitaxy (MBE), slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as gallium arsenide are usually deposited by repeatedly applying a layer of one element (i.e., gallium), then a layer of the other (i.e., arsenic), so that the process is chemical, as well as physical. The beam of material can be generated by either physical means ( that is, by a furnace) or by a chemical reaction (chemical beam epitaxy ) .

Sputtering relies on a plasma (usually a noble gas, such as argon) to knock material from a "target" a few atoms at a time. The target can be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where different components would otherwise tend to evaporate at different rates. Note, sputtering's step coverage is more or less conformal. It is also widely used in the optical media. The manufacturing of all formats of CD, DVD, and BD are done with the help of this technique. It is a fast technique and also it provides a good thickness control. Presently, nitrogen and oxygen gases are also being used in sputtering .

Pulsed laser deposition systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material

and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.

Cathodic arc deposition (arc-PVD) which is a kind of ion beam deposition where an electrical arc is created that literally blasts ions from the cathode. The arc has an extremely high power density resulting in a high level of ionization (30–100%), multiply charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.

Electro hydrodynamic deposition (electrospray deposition) is a relatively new process of thin film deposition. The liquid to be deposited, either in the form of nano-particle solution or simply a solution, is fed to a small capillary nozzle (usually metallic) which is connected to a high voltage. The substrate on which the film has to be deposited is connected to ground. Through the influence of electric field, the liquid coming out of the nozzle takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets under the influence of Rayleigh charge limit. The droplets keep getting smaller and smaller and ultimately get deposited on the substrate as a uniform thin layer.

### **3 – Thin - film photovoltaic cells**

Thin - film technologies are also being developed as a means of substantially reducing the cost of photovoltaic (PV) systems. The rationale for this is that thin-film modules are cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. This is especially represented in the use of printed electronics (roll-to-roll) processes.

Thin films belong to the second and third photovoltaic cell generations.

#### **4 – Thin - film batteries**

Thin - film printing technology is being used to apply solid-state lithium polymers to a variety of substrates to create unique batteries for specialized applications. Thin - film batteries can be deposited directly onto chips or chip packages in any shape or size. Flexible batteries can be made by printing onto plastic, thin metal foil, or paper.

# **Part Two**

## **Gold**





# Gold

Ag



**Au**



Rg

## Contents

Introduction

1 Etymology

2 Characteristics

2.1 Color

2.2 Isotopes

3 Applications

3.1 Monetary exchange

3.2 Investment

3.3 Jewelry

3.4 Medicine

3.5 Food and drink

3.6 Industry

3.7 Electronics

3.8 Commercial chemistry

4 Cultural history

5 Occurrence

5.1 Seawater

5.2 Specimens of crystalline native gold

6 Production

7 Mining

7.1 Prospecting

8 Bioremediation

9 Extraction

9.1 Refining

10 Synthesis from other elements

11 Consumption

12 Pollution

13 Chemistry

13.1 Less common oxidation states

13.2 Mixed valence compounds

14 Toxicity

15 Price

15.1 History

16 Symbolism

## Introduction

**Gold** is a chemical element with the symbol **Au** and atomic number 79 . It is a dense, soft, malleable and ductile metal with a bright yellow color and luster, the properties of which remain without tarnishing when exposed to air or water. Chemically, gold is a transition metal and a group 11 element. It is one of the least reactive chemical elements, and is solid under standard conditions. The metal therefore occurs often in free elemental (native) form, as nuggets or grains, in rocks, in veins and in alluvial deposits. Less commonly, it occurs in minerals as gold compounds, such as with tellurium as calaverite , sylvanite , or krennerite.

As the metallic native element mineral, gold structurally belongs to the isometric copper group. It also forms a solid solution series with the native element silver (Ag) to which it is often naturally alloyed (electrum). Other common natural gold alloys are with copper and palladium (Pd).

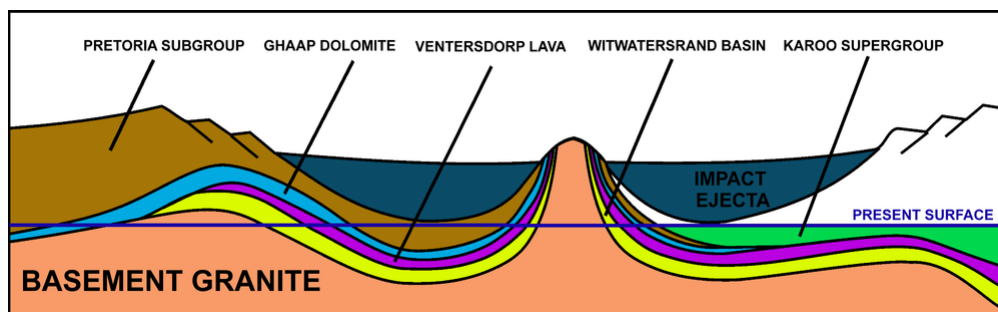
Gold resists attacks by individual acids, but it can be dissolved by aqua regia ( nitro - hydrochloric acid ) , so named because it dissolves gold. Gold also dissolves in alkaline solutions of cyanide, which have been used in mining. It dissolves in mercury, forming amalgam alloys; it is insoluble in nitric acid, which dissolves silver and base metals, a property that has long been used to confirm the presence of gold in items, giving rise to the term *acid test*.

This metal has been a valuable and highly sought - after precious metal for coinage, jewelry, and other arts since long before the beginning of recorded history. In the past, the Gold standard has been implemented as a monetary policy, but it was widely supplanted by fiat currency starting in the 1930s. The last gold certificate and

gold coin currencies were issued in the U.S. in 1932. In Europe, most countries left the gold standard with the start of World War I in 1914 and, with huge war debts, did not return to gold as a medium of exchange. The value of gold is rooted in its medium rarity, easily handling, easy smelting, non - corrosiveness, distinct colour and non-reactiveness to other elements; qualities most other metals lack.

A total of 174,100 tones of gold have been mined in human history, according to GFMS as of 2012. This is roughly equivalent to 5.6 billion troy ounces or, in terms of volume, about 9261 m<sup>3</sup>, or a cube 21.0 m on a side. The world consumption of new gold produced is about 50 % in jewelry, 40% in investments, and 10 % in industry.<sup>[3]</sup>

Besides its widespread monetary and symbolic functions, gold has many practical uses in dentistry, electronics, and other fields. Its high malleability, ductility, resistance to corrosion and most other chemical reactions, and conductivity of electricity have led to many uses, including electric wiring, colored - glass production, and gold leafing.



*A schematic diagram of a NE (left) to SW (right) cross-section through the 2.020 billion year old Vredefort impact crater in South Africa and how it distorted the contemporary geological structures. The present erosion level is shown. Johannesburg is located where the Witwatersrand Basin (the yellow layer) is exposed at the "present surface" line, just inside the crater rim, on the left. Not to scale.*

Most of the Earth's gold probably lies at its core, the metal's high density having made it sink there in the planet's youth. Virtually

all discovered gold is considered to have been deposited later by meteorites that contained the element.

The asteroid that formed Vredefort crater 2.020 billion years ago is often credited with seeding the Witwatersrand basin in South Africa with the richest gold deposits on earth.<sup>[9][10][11][12]</sup> However, the gold bearing Wit water sand rocks were laid down between 700 and 950 million years before the Vredefort impact. These gold bearing rocks had furthermore been covered by a thick layer of Ventersdorp lavas, and the Transvaal Super group of rocks before the meteor struck. What the Vredefort impact achieved, however, was to distort the Witwatersrand basin in such a way that the gold bearing rocks were brought to the present erosion surface in Johannesburg, on the Witwatersrand, just inside the rim of the original 300 km diameter crater caused by the meteor strike. This brought their rich gold deposits to the notice of humans in 1886, and launched the Witwatersrand Gold Rush. Nearly 50 % of all the gold ever mined on earth has been extracted from these Witwatersrand rocks.

Name , symbol , number	Gold , Au , 79
Element category	transition metal
Group, period, block	11 , 6 , d
Standard atomic weight	197
Phase	solid
Density (near r.t.)	19.30 g·cm <sup>-3</sup>
Liquid density at m.p.	17.31 g·cm <sup>-3</sup>
Melting point	1064 °C,
Boiling point	2970 °C
Heat of fusion	12.55 kJ·mol <sup>-1</sup>
Heat of vaporization	342 kJ·mol <sup>-1</sup>
Molar heat capacity	25.418 J·mol <sup>-1</sup> ·K <sup>-1</sup>
Oxidation states	5, 4, 3, 2, 1, -1 (amphoteric oxide)

Electro negativity	2.54 (Pauling scale)
Ionization energies	1st: 890.1 kJ·mol <sup>-1</sup>
	2nd: 1980 kJ·mol <sup>-1</sup>
Atomic radius	144 pm
Covalent radius	136±6 pm
Van der Waals radius	166 pm
Electrical resistivity	( 20 °C ) 22.14 n Ω · m
Thermal conductivity	318 W·m <sup>-1</sup> ·K <sup>-1</sup>
Thermal expansion	(25 °C) 14.2 μm·m <sup>-1</sup> ·K <sup>-1</sup>
Speed of sound (thin rod)	(r.t.) 2030 m·s <sup>-1</sup>
Tensile strength	120 MPa
Poisson ratio	0.44
Mohs hardness	2.5
Vickers hardness	216 MPa
Naming	<i>aurum</i> in Latin , meaning glow of sunrise
Discovery	Middle Easterns ( before 6000 BC )

## 1 - Etymology

"Gold" is cognate with similar words in many Germanic languages, deriving via Proto - Germanic *\*gulþą* from Proto-Indo-European *\*ǵ<sup>h</sup>el-* ( "yellow / green" ) .

The symbol **Au** is from the Latin: *aurum*, the Latin word for "gold". The Proto - Indo - European root was *\*h<sub>2</sub>é-h<sub>2</sub>us-o-*, meaning "glow", also the ancestor the Latin word *Aurora*, "dawn". This etymological relationship is presumably behind the frequent claim in scientific publications that *aurum* meant "shining dawn".

## 2 - Characteristics

Gold is the most malleable of all metals; a single gram can be beaten into a sheet of 1 square meter, or an ounce into 300 square

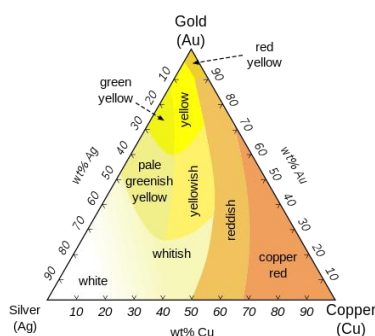
feet. Gold leaf can be beaten thin enough to become transparent. The transmitted light appears greenish blue, because gold strongly reflects yellow and red. Such semi - transparent sheets also strongly reflect infrared light, making them useful as infrared ( radiant heat ) shields in visors of heat - resistant suits, and in sun-visors for spacesuits.

Gold readily dissolves in mercury at room temperature to form an amalgam, and forms alloys with many other metals at higher temperatures. These alloys can be produced to modify the hardness and other metallurgical properties, to control melting point or to create exotic colors. Gold is a good conductor of heat and electricity and reflects infrared radiation strongly. Chemically, it is unaffected by air, moisture and most corrosive reagents, and is therefore well suited for use in coins and jewelry and as a protective coating on other, more reactive metals. However, it is not chemically inert. Gold is almost insoluble, but can be dissolved in aqua regia or solutions of sodium or potassium cyanide, for example.

Common oxidation states of gold include +1 ( gold (I) or aurous compounds) and +3 ( gold (III) or auric compounds ). Gold ions in solution are readily reduced and precipitated as metal by adding any other metal as the reducing agent. The added metal is oxidized and dissolves, allowing the gold to be displaced from solution and be recovered as a solid precipitate.

In addition, gold is very dense, a cubic meter weighing 19300 kg. By comparison, the density of lead is  $11,340 \text{ kg} / \text{m}^3$ , and that of the densest element, osmium, is  $22,588 \pm 15 \text{ kg/m}^3$ .

## 2 – 1 – Color



*Different colors of Ag-Au-Cu alloys*

Where as most other pure metals are gray or silvery white, gold is yellow. This color is determined by the density of loosely bound (valence) electrons; those electrons oscillate as a collective "plasma" medium described in terms of a quasi particle called plasmon. The frequency of these oscillations lies in the ultraviolet range for most metals, but it falls into the visible range for gold due to subtle relativistic effects that affect the orbitals around gold atoms.<sup>[25][26]</sup> Similar effects impart a golden hue to metallic caesium.

Common colored gold alloys such as rose gold can be created by the addition of various amounts of copper and silver, as indicated in the triangular diagram to the left. Alloys containing palladium or nickel are also important in commercial jewelry as these produce white gold alloys. Less commonly, addition of manganese, Aluminum, iron, indium and other elements can produce more unusual colors of gold for various applications.

## 2 – 2 - Isotopes

Gold has only one stable isotope,  $^{197}\text{Au}$ , which is also its only naturally occurring isotope . Thirty - six radioisotopes have been synthesized ranging in atomic mass from 169 to 205. The most stable of these is  $^{195}\text{Au}$  with a half - life of 186.1 days. The least stable is  $^{171}\text{Au}$ , which decays by proton emission with a half-life of 30  $\mu\text{s}$ . Most of gold's radioisotopes with atomic masses below 197 decay by some combination of proton emission,  $\alpha$  decay, and  $\beta^+$  decay. The exceptions are  $^{195}\text{Au}$ , which decays by electron capture, and  $^{196}\text{Au}$ , which decays most often by electron capture ( 93 % ) with a minor  $\beta^-$  decay path ( 7 % ). All of gold's radioisotopes with atomic masses above 197 decay by  $\beta^-$  decay.

At least 32 nuclear isomers have also been characterized, ranging in atomic mass from 170 to 200. Within that range, only  $^{178}\text{Au}$ ,  $^{180}\text{Au}$ ,  $^{181}\text{Au}$ ,  $^{182}\text{Au}$ , and  $^{188}\text{Au}$  do not have isomers. Gold's most stable isomer is  $^{198\text{m}2}\text{Au}$  with a half-life of 2.27 days. Gold's least stable isomer is  $^{177\text{m}2}\text{Au}$  with a half-life of only 7 ns.  $^{184\text{m}1}\text{Au}$  has three decay paths:  $\beta^+$  decay, isomeric transition, and alpha decay. No other isomer or isotope of gold has three decay paths.

### 3 - Applications

#### 3 – 1 - Monetary exchange

	
<p><i>Two golden 20 kr coins from the Scandinavian Monetary Union, which was based on a gold standard. The coin to the left is Swedish and the right one is Danish.</i></p>	<p><i>Gold is commonly formed into bars for use in monetary exchange.</i></p>

Gold has been widely used throughout the world as money, for efficient indirect exchange (versus barter), and to store wealth in hoards. For exchange purposes, mints produce standardized gold bullion coins, bars and other units of fixed weight and purity.

The first coins containing gold were struck in Lydia, Asia Minor, around 600 BC.<sup>[29]</sup> The *talent* coin of gold in use during the periods of Grecian history both before and during the time of the life of Homer weighed between 8.42 and 8.75 grams.<sup>[30]</sup> From an earlier preference in using silver, European economies re-established the minting of gold as coinage during the thirteenth and fourteenth centuries.

Bills ( that mature into gold coin ) and gold certificates (convertible into gold coin at the issuing bank ) added to the circulating stock of gold standard money in most 19th century industrial economies. In preparation for World War I the warring nations moved to fractional gold standards, inflating their currencies to finance the war effort. Post-war, the victorious countries, most notably Britain, gradually restored gold - convertibility, but international flows of gold via bills of exchange remained embargoed; international shipments were made exclusively for bilateral trades or to pay war reparations.



After World War II gold was replaced by a system of nominally convertible currencies related by fixed exchange rates following the Bretton Woods system. Gold standards and the direct convertibility of currencies to gold have been abandoned by world governments, led in 1971 by the United States' refusal to redeem its dollars in gold. Fiat currency now fills most monetary roles. Switzerland was the last country to tie its currency to gold; it backed 40 % of its value until the Swiss joined the International Monetary Fund in 1999.

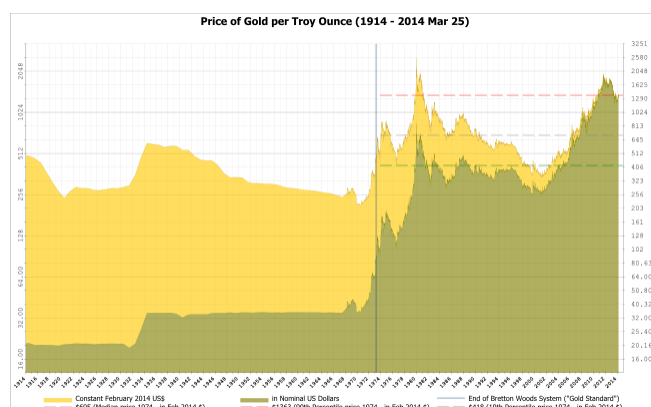
Central banks continue to keep a portion of their liquid reserves as gold in some form, and metals exchanges such as the London Bullion Market Association still clear transactions denominated in gold, including future delivery contracts. Today, gold mining output is declining . With the sharp growth of economies in the 20th century, and increasing foreign exchange, the world's gold reserves and their trading market have become a small fraction of all markets and fixed exchange rates of currencies to gold have been replaced by floating prices for gold and gold future contract. Though the gold stock grows by only 1 or 2 % per year, very little metal is irretrievably consumed. Inventory above ground would satisfy many decades of industrial and even artisan uses at current prices.

The gold content of alloys is measured in carats (k). Pure gold is designated as 24k. English gold coins intended for circulation from 1526 into the 1930s were typically a standard 22k alloy called crown gold,<sup>[34]</sup> for hardness ( American gold coins for circulation after 1837 contained the slightly lower amount of 0.900 fine gold, or 21.6 kt ).

Although the prices of some platinum group metals can be much higher, gold has long been considered the most desirable of precious metals, and its value has been used as the standard for many currencies. Gold has been used as a symbol for purity, value, royalty, and particularly roles that combine these properties. Gold as a sign of wealth and prestige was ridiculed by Thomas More in his treatise *Utopia*. On that imaginary island, gold is so abundant that it is used to make chains for slaves, tableware, and lavatory seats. When ambassadors from other countries arrive, dressed in ostentatious gold

jewels and badges, the Utopians mistake them for menial servants, paying homage instead to the most modestly dressed of their party.

### 3 – 2 – Investment



*Gold prices ( US \$ per troy ounce ) ,  
in nominal US \$ and inflation adjusted US \$.*

Many holders of gold store it in form of bullion coins or bars as a hedge against inflation or other economic disruptions. However, economist Martin Feldstein does not believe gold serves as a hedge against inflation or currency depreciation.

The ISO 4217 currency code of gold is XAU.

Modern bullion coins for investment or collector purposes do not require good mechanical wear properties; they are typically fine gold at 24k, although the American Gold Eagle and the British gold sovereign continue to be minted in 22k metal in historical tradition, and the South African Krugrand, first released in 1967, is also 22k . The *special issue* Canadian Gold Maple Leaf coin contains the highest purity gold of any bullion coin, at 99.999 % or 0.99999 , while the *popular issue* Canadian Gold Maple Leaf coin has a purity of 99.99 %.

Several other 99.99 % pure gold coins are available. In 2006, the United States Mint began producing the American Buffalo gold bullion coin with a purity of 99.99 %. The Australian Gold Kangaroos were first coined in 1986 as the Australian Gold Nugget but changed

the reverse design in 1989. Other modern coins include the Austrian Vienna Philharmonic bullion coin and the Chinese Gold Panda.

### 3 – 3 - Jewelry



*Moche gold necklace depicting feline heads.  
Larco Museum Collection. Lima - Peru*

Because of the softness of pure (24k) gold, it is usually alloyed with base metals for use in jewelry, altering its hardness and ductility, melting point, color and other properties. Alloys with lower carat rating, typically 22 k, 18 k, 14 k or 10 k, contain higher percentages of copper or other base metals or silver or palladium in the alloy. Copper is the most commonly used base metal, yielding a redder color.

Eighteen - carat gold containing 25% copper is found in antique and Russian jewelry and has a distinct, though not dominant, copper cast, creating rose gold. Fourteen - carat gold - copper alloy is nearly identical in color to certain bronze alloys, and both may be used to produce police and other badges. Blue gold can be made by alloying with iron and purple gold can be made by alloying with Aluminum, although rarely done except in specialized jewelry. Blue gold is more brittle and therefore more difficult to work with when making jewelry.

Fourteen- and eighteen - carat gold alloys with silver alone appear greenish-yellow and are referred to as green gold. White gold alloys can be made with palladium or nickel. White 18-carat gold containing 17.3 % nickel, 5.5 % zinc and 2.2 % copper is silvery in appearance. Nickel is toxic, however, and its release from nickel white gold is controlled by legislation in Europe.

Alternative white gold alloys are available based on palladium, silver and other white metals , but the palladium alloys are more expensive than those using nickel. High-carat white gold alloys are far more resistant to corrosion than are either pure silver or sterling silver. The Japanese craft of Mokume - gane exploits the color contrasts between laminated colored gold alloys to produce decorative wood-grain effects.

### **3 – 4 - Medicine**

Gold is perhaps the most anciently administered medicine ( apparently by shamanic practitioners ) and known to Dioscorides, apparent paradoxes of the actual toxicology of the substance nevertheless suggests the possibility still of serious gaps in understanding of action on physiology.

In medieval times, gold was often seen as beneficial for the health, in the belief that something so rare and beautiful could not be anything but healthy. Even some modern esotericists and forms of alternative medicine assign metallic gold a healing power.<sup>[43]</sup> Some gold salts do have anti - inflammatory properties and are used as pharmaceuticals in the treatment of arthritis and other similar conditions. Gold based injections have been explored as a means to help to reduce the pain and swelling of rheumatoid arthritis and tuberculosis . However, only salts and radioisotopes of gold are of pharmacological value, as elemental ( metallic ) gold is inert to all chemicals it encounters inside the body.

Gold alloys are used in restorative dentistry, especially in tooth restorations, such as crowns and permanent bridges. The gold alloys' slight malleability facilitates the creation of a superior molar mating surface with other teeth and produces results that are generally more satisfactory than those produced by the creation of porcelain crowns. The use of gold crowns in more prominent teeth such as incisors is favored in some cultures and discouraged in others.

Colloidal gold preparations (suspensions of gold nanoparticles) in water are intensely red - colored, and can be made with tightly controlled particle sizes up to a few tens of nanometers across by

reduction of gold chloride with citrate or ascorbate ions. Colloidal gold is used in research applications in medicine, biology and materials science. The technique of immunogold labeling exploits the ability of the gold particles to adsorb protein molecules onto their surfaces. Colloidal gold particles coated with specific antibodies can be used as probes for the presence and position of antigens on the surfaces of cells . In ultrathin sections of tissues viewed by electron microscopy, the immune gold labels appear as extremely dense round spots at the position of the antigen.

Gold, or alloys of gold and palladium, are applied as conductive coating to biological specimens and other non-conducting materials such as plastics and glass to be viewed in a scanning electron microscope. The coating, which is usually applied by sputtering with an argon plasma, has a triple role in this application. Gold's very high electrical conductivity drains electrical charge to earth, and its very high density provides stopping power for electrons in the electron beam, helping to limit the depth to which the electron beam penetrates the specimen. This improves definition of the position and topography of the specimen surface and increases the spatial resolution of the image. Gold also produces a high output of secondary electrons when irradiated by an electron beam, and these low-energy electrons are the most commonly used signal source used in the scanning electron microscope.

The isotope gold - 198 ( half - life 2.7 days ) is used, in nuclear medicine, in some cancer treatments and for treating other diseases.



### **3 – 5 - Food and drink**

Gold can be used in food and has the E number 175.

Gold leaf, flake or dust is used on and in some gourmet foods, notably sweets and drinks as decorative ingredient . Gold flake was used by the nobility in medieval Europe as a decoration in food and drinks, in the form of leaf, flakes or dust, either to demonstrate the host's wealth or in the belief that something that valuable and rare must be beneficial for one's health.

Danziger Gold wasser ( German: Gold water of Danzig ) or Gold wasser ( English: Gold water ) is a traditional German herbal liqueur produced in what is today Gdańsk, Poland, and Schwabach, Germany, and contains flakes of gold leaf. There are also some expensive ( ~ \$ 1000 ) cocktails which contain flakes of gold leaf.<sup>[53]</sup> However, since metallic gold is inert to all body chemistry, it has no taste, it provides no nutrition, and it leaves the body unaltered.

### 3 – 6 – Industry

	
<p><i>The world's largest gold bar has a mass of 250 kg. Toi museum, Japan.</i></p>	<p><i>Mirror for the future James Webb Space Telescope coated in gold to reflect infrared light</i></p>

Gold solder is used for joining the components of gold jewelry by high-temperature hard soldering or brazing. If the work is to be of hallmarking quality, gold solder must match the carat weight of the work, and alloy formulas are manufactured in most industry-standard carat weights to color match yellow and white gold. Gold solder is usually made in at least three melting-point ranges referred to as Easy, Medium and Hard. By using the hard, high-melting point solder first, followed by solders with progressively lower melting points, goldsmiths can assemble complex items with several separate soldered joints.

Gold can be made into thread and used in embroidery.

Gold produces a deep, intense red color when used as a coloring agent in cranberry glass.

In photography, gold toners are used to shift the color of silver bromide black – and - white prints towards brown or blue tones, or to increase their stability. Used on sepia-toned prints, gold toners produce red tones. Kodak published formulas for several types of gold toners, which use gold as the chloride.

Gold is a good reflector of electromagnetic radiation such as infrared and visible light as well as radio waves. It is used for the protective coatings on many artificial satellites, in infrared protective faceplates in thermal protection suits and astronauts' helmets and in electronic warfare planes like the EA - 6B Prowler.

Gold is used as the reflective layer on some high-end CDs.

Automobiles may use gold for heat shielding. McLaren uses gold foil in the engine compartment of its F1 model.

Gold can be manufactured so thin that it appears transparent. It is used in some aircraft cockpit windows for de-icing or anti-icing by passing electricity through it. The heat produced by the resistance of the gold is enough to deter ice from forming.

### **3 – 7 - Electronics**

The concentration of free electrons in gold metal is  $5.90 \times 10^{22} \text{ cm}^{-3}$ . Gold is highly conductive to electricity, and has been used for electrical wiring in some high - energy applications (only silver and copper are more conductive per volume, but gold has the advantage of corrosion resistance). For example, gold electrical wires were used during some of the Manhattan Project's atomic experiments, but large high current silver wires were used in the calutron isotope separator magnets in the project.

Though gold is attacked by free chlorine, its good conductivity and general resistance to oxidation and corrosion in other environments ( including resistance to non - chlorinated acids ) has led to its widespread industrial use in the electronic era as a thin layer coating electrical connectors, thereby ensuring good connection. For

example, gold is used in the connectors of the more expensive electronics cables, such as audio, video and USB cables. The benefit of using gold over other connector metals such as tin in these applications has been debated; gold connectors are often criticized by audio - visual experts as unnecessary for most consumers and seen as simply a marketing ploy. However, the use of gold in other applications in electronic sliding contacts in highly humid or corrosive atmospheres, and in use for contacts with a very high failure cost (certain computers, communications equipment, spacecraft, jet aircraft engines) remains very common.

Besides sliding electrical contacts, gold is also used in electrical contacts because of its resistance to corrosion, electrical conductivity, ductility and lack of toxicity.<sup>[59]</sup> Switch contacts are generally subjected to more intense corrosion stress than are sliding contacts. Fine gold wires are used to connect semiconductor devices to their packages through a process known as wire bonding.

### **3 – 8 - Commercial chemistry**

Gold is attacked by and dissolves in alkaline solutions of potassium or sodium cyanide, to form the salt gold cyanide — a technique that has been used in extracting metallic gold from ores in the cyanide process. Gold cyanide is the electrolyte used in commercial electro plating of gold onto base metals and electro forming.

Gold chloride ( chloro auric acid ) solutions are used to make colloidal gold by reduction with citrate or ascorbate ions. Gold chloride and gold oxide are used to make cranberry or red - colored glass, which, like colloidal gold suspensions, contains evenly sized spherical gold nanoparticles.

### **4 - Cultural history**

Gold artifacts found at the Nahal Kana cave cemetery dated during the 1980s, showed these to be from within the Chalcolithic, and considered the earliest find from the Levant ( Gopher *et al.* 1990 ) Gold artifacts in the Balkans also appear from the 4th millennium BC,



such as those found in the Varna Necropolis near Lake Varna in Bulgaria, thought by one source (La Niece 2009) to be the earliest "well-dated" find of gold artifacts . Gold artifacts such as the golden hats and the Nebra disk appeared in Central Europe from the 2nd millennium BC Bronze Age.

	
<p><i>Jason returns with the golden fleece on an Apulian red-figure calyx krater, ca. 340–330 BC.</i></p>	<p><i>Funerary mask of Tutankhamun</i></p>
	
<p><i>Ancient Greek golden decorated crown, funerary or marriage material, 370–360 BC. From a grave in Armento, Campania</i></p>	

Egyptian hieroglyphs from as early as 2600 BC describe gold, which king Tushratta of the Mitanni claimed was "more plentiful than

dirt" in Egypt. Egypt and especially Nubia had the resources to make them major gold - producing areas for much of history. The earliest known map is known as the Turin Papyrus Map and shows the plan of a gold mine in Nubia together with indications of the local geology. The primitive working methods are described by both Strabo and Diodorus Siculus, and included fire - setting. Large mines were also present across the Red Sea in what is now Saudi Arabia.

The legend of the golden fleece may refer to the use of fleeces to trap gold dust from placer deposits in the ancient world. Gold is mentioned frequently in the Old Testament, starting with Genesis 2:11 (at Havilah), the story of The Golden Calf and many parts of the temple including the Menorah and the golden altar. In the New Testament, it is included with the gifts of the magi in the first chapters of Matthew. The Book of Revelation 21:21 describes the city of New Jerusalem as having streets "made of pure gold, clear as crystal". Exploitation of gold in the south - east corner of the Black Sea is said to date from the time of Midas, and this gold was important in the establishment of what is probably the world's earliest coinage in Lydia around 610 BC . From the 6th or 5th century BC, the Chu (state) circulated the Ying Yuan, one kind of square gold coin.

The Portuguese over seas expansion started in 1415 with the taking of Ceuta, to control the gold trade coming across the desert. Although the caravan trade routes were then diverted, the Portuguese continued expanding southwards along the coast and eventually buying the gold directly (or less indirectly) from the Africans in the Gulf of Guinea .

The European exploration of the Americas was fueled in no small part by reports of the gold ornaments displayed in great profusion by Native American peoples, especially in Central America, Peru, Ecuador and Colombia. The Aztecs regarded gold as literally the product of the gods, calling it "god excrement" (*teocuitlatl* in Nahuatl), and after Montezuma was killed, most of this gold was shipped to Spain . However, for the indigenous peoples of North America gold was considered useless and they saw much greater

value in other minerals which were directly related to their utility, such as obsidian, flint, and slate.

Gold played a role in western culture, as a cause for desire and of corruption, as told in children's fables like Rumpelstiltskin, where the peasant's daughter turns hay into gold, in return for giving up her child when she becomes a princess, and stealing the hen that lays golden eggs in Jack and the beanstalk.

The top prize at the Olympic games is the gold medal.

There is an age - old tradition of biting gold to test its authenticity. Although this is certainly not a professional way of examining gold, the *bite test* was not to check if the coin was gold (90% gold coins are fairly strong) but to see if the coin was gold plated lead. A lead coin would be very soft and thus teeth marks would result. Fake gold coins were a common problem before 1932 so weighing a coin and also sliding a coin through a "counterfeit detector" slot was common (making a lead coin thicker would add weight thus why slide it through a measured slot). Most establishments ( especially US Western saloons ) would never accept a gold ( or silver ) coin of high value before weighing such an item.

75 % of all gold ever produced has been extracted since 1910. It has been estimated that all gold ever refined would form a single cube 20 m (66 ft) on a side (equivalent to 8,000 m<sup>3</sup>).<sup>[69]</sup>

One main goal of the alchemists was to produce gold from other substances, such as lead — presumably by the interaction with a mythical substance called the philosopher's stone. Although they never succeeded in this attempt, the alchemists promoted an interest in what can be done with substances, and this laid a foundation for today's chemistry. Their symbol for gold was the circle with a point at its center (☉), which was also the astrological symbol and the ancient Chinese character for the Sun.

Golden treasures have been rumored to be found at various locations, following tragedies such as the Jewish temple treasures in

the Vatican, following the temple's destruction in 70 AD, a gold stash on the Titanic, the Nazi gold train – following World War II.

The Dome of the Rock on the Jerusalem temple site is covered with an ultra-thin golden glasure.<sup>[clarification needed]</sup> The Sikh Golden temple, the Harmandir Sahib, is a building covered with gold. Similarly the Wat Phra Kaew emerald Budha temple in Thailand has ornamental gold statues walls and roofs. Some European king and queen's crowns were made of gold, and gold was used for the bridal crown since antiquity. An ancient Talmudic text circa 100 AD describes Rachel, Rabbi Akiba's wife asking for a "Jerusalem of Gold" (crown). A Greek burial crown made of gold was found in a grave circa 370 BC.

## 5 - Occurrence



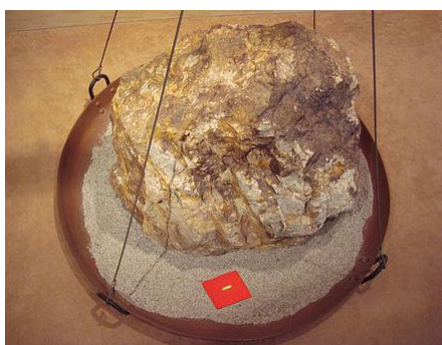
*This 156 - troy - ounce ( 4.9 kg ) nugget, known as the Mojave Nugget, was found by an individual prospector in the Southern California Desert using a metal detector.*

Gold's atomic number of 79 makes it one of the higher atomic number elements that occur naturally. Although gold has been thought to have formed by supernova nucleo synthesis, a new theory suggests that gold and other elements heavier than iron are made by the collision of neutron stars instead . Either way, satellites should be able to detect the resulting gold, "but we have no spectroscopic evidence that [such] elements have truly been produced."<sup>[73]</sup> These theories hold that the resulting explosions scattered metal-containing dusts (including heavy elements like gold) into the region of space in which they later condensed into our solar system and the Earth.

Because the Earth was molten when it was just formed, almost all of the gold present on Earth sank into the core. Most of the gold that is present today in the Earth's crust and mantle was delivered to Earth by asteroid impacts during the late heavy bombardment.

On Earth, gold is found in ores in rock formed from the Precambrian time onward.<sup>[62]</sup> It most often occurs as a native metal, typically in a metal solid solution with silver ( i.e. as a gold silver alloy ) . Such alloys usually have a silver content of 8 – 10 %. Electrum is elemental gold with more than 20 % silver. Electrum's color runs from golden-silvery to silvery, dependent upon the silver content. The more silver, the lower the specific gravity.

Native gold occurs as very small to microscopic particles embedded in rock, often together with quartz or sulfide minerals such as "Fool's Gold", which is a pyrite.<sup>[76]</sup> These are called lode deposits. The metal in a native state is also found in the form of free flakes, grains or larger nuggets that have been eroded from rocks and end up in alluvial deposits called placer deposits. Such free gold is always richer at the surface of gold - bearing veins owing to the oxidation of accompanying minerals followed by weathering, and washing of the dust into streams and rivers, where it collects and can be welded by water action to form nuggets.



*Relative sizes of an 860 kg block of gold ore, and the 30 g of gold that can be extracted from it. Toi gold mine, Japan.*

Gold some times occurs combined with tellurium as the minerals calaverite , krennerite , nagyagite , petzite and sylvanite , and as the rare bismuthide maldonite (  $\text{Au}_2 \text{Bi}$  ) and antimonide aurostibite (  $\text{Au Sb}_2$  ) . Gold also occurs in rare alloys with copper,

lead, and mercury: the minerals auricupride (  $\text{Cu}_3 \text{Au}$  ) , novodneprite (  $\text{Au Pb}_3$  ) and weishanite [ (  $\text{Au , Ag}$  )  $_3 \text{Hg}_2$  ].

Recent research suggests that microbes can sometimes play an important role in forming gold deposits, transporting and precipitating gold to form grains and nuggets that collect in alluvial deposits.

Another recent study has claimed water in faults vaporizes during an earthquake, depositing gold. When an earthquake strikes, it moves along a fault. Water often lubricates faults, filling in fractures and jogs. About 6 miles (10 kilometers) below the surface, under incredible temperatures and pressures, the water carries high concentrations of carbon dioxide, silica, and gold. During an earthquake, the fault jog suddenly opens wider. The water inside the void instantly vaporizes, flashing to steam and forcing silica, which forms the mineral quartz, and gold out of the fluids and onto nearby surfaces.

### **5 – 1 - Seawater**

The world's oceans contain gold. Measured concentrations of gold in the Atlantic and Northeast Pacific are 50 – 150 fmol / L or 10 – 30 parts per 1,000,000,000,000,000 quadrillion ( about 10 – 30 g /  $\text{km}^3$  ) . In general , gold concentrations for south Atlantic and central Pacific samples are the same ( ~50 fmol / L ) but less certain. Mediterranean deep waters contain slightly higher concentrations of gold ( 100 – 150 fmol / L ) attributed to wind - blown dust and/or rivers. At 10 parts per quadrillion the Earth's oceans would hold 15,000 tonnes of gold. These figures are three orders of magnitude less than reported in the literature prior to 1988, indicating contamination problems with the earlier data.

A number of people have claimed to be able to economically recover gold from sea water, but so far they have all been either mistaken or acted in an intentional deception. Prescott Jernegan ran a gold-from-seawater swindle in the United States in the 1890s. A British fraudster ran the same scam in England in the early 1900s.<sup>[80]</sup> Fritz Haber (the German inventor of the Haber process) did research on the extraction of gold from sea water in an effort to help pay



Germany's reparations following World War I.<sup>[81]</sup> Based on the published values of 2 to 64 ppb of gold in seawater a commercially successful extraction seemed possible. After analysis of 4,000 water samples yielding an average of 0.004 ppb it became clear that the extraction would not be possible and he stopped the project.<sup>[82]</sup> No commercially viable mechanism for performing gold extraction from sea water has yet been identified. Gold synthesis is not economically viable and is unlikely to become so in the foreseeable future.

## 5 – 2 - Specimens of crystalline native gold

	
<i>"Rope gold" from Lena River, Sakha Republic, Russia.</i>	<i>Native gold nuggets</i>

## 6 - Production



*Pure gold precipitate produced by the aqua regia refining process*



*Time trend of gold production*

At the end of 2009, it was estimated that all the gold ever mined totaled 165,000 tones. This can be represented by a cube with an edge length of about 20.28 meters. At \$ 1,600 per troy ounce, 165,000 metric tones of gold would have a value of \$ 8.5 trillion.

World production for 2011 was at 2,700 tones, compared to 2,260 tones for 2008.

Since the 1880s, South Africa has been the source for a large proportion of the world's gold supply, with about 50% of all gold ever produced having come from South Africa. Production in 1970 accounted for 79 % of the world supply, producing about 1,480 tones. In 2007 China (with 276 tones ) overtook South Africa as the world's largest gold producer, the first time since 1905 that South Africa has not been the largest.

## **7 - Mining**

The city of Johannesburg located in South Africa was founded as a result of the Witwatersrand Gold Rush which resulted in the discovery of some of the largest gold deposits the world has ever seen. The gold fields are confined to the northern and north-western edges of the Wit water srand basin, which is a 5 – 7 km thick layer of archean rocks located, in most places, deep under the Free State, Gauteng and surrounding provinces . These Witwatersrand rocks are exposed at the surface on the Witwatersrand, in and around Johannesburg, but also in isolated patches to the south-east and south-west of Johannesburg, as well as in an arc around the Vredefort Dome which lies close to the center of the Wit water srand basin . From these surface exposures the basin dips extensively, requiring some of the mining to occur at depths of nearly 4000 m, making them, especially the Savuka and TauTona mines to the south-west of Johannesburg, the deepest mines on earth. The gold is found only in six areas where archean rivers from the north and north - west formed extensive pebbly braided river deltas before draining into the "Wit water srand sea" where the rest of the Witwatersrand sediments were deposited.



The Second Boer War of 1899 – 1901 between the British Empire and the Afrikaner Boers was at least partly over the rights of miners and possession of the gold wealth in South Africa.

Other major producers are the United States, Australia, Russia, and Peru, as well as, Ghana, Burkina Faso, Mali, Indonesia and Uzbekistan. Mines in South Dakota and Nevada supply two-thirds of gold used in the United States. In South America, the controversial project Pascua Lama aims at exploitation of rich fields in the high mountains of Atacama Desert, at the border between Chile and Argentina. Today about one - quarter of the world gold output is estimated to originate from artisanal or small scale mining.<sup>[85]</sup>

### **7 – 1 - Prospecting**

During the 19th century, gold rushes occurred whenever large gold deposits were discovered. The first documented discovery of gold in the United States was at the Reed Gold Mine near George ville, North Carolina in 1803 . The first major gold strike in the United States occurred in a small north Georgia town called Dahlonega.<sup>[87]</sup> Further gold rushes occurred in California, Colorado, the Black Hills, Otago in New Zealand, Australia, Witwatersrand in South Africa, and the Klondike in Canada.

### **8 - Bioremediation**

A sample of the fungus *Aspergillus niger* was found growing from gold mining solution; and was found to contain cyano metal complexes; such as gold, silver, copper iron and zinc. The fungus also plays a role in the solubilization of heavy metal sulfides.<sup>[88]</sup>

### **9 - Extraction**

Gold extraction is most economical in large, easily mined deposits. Ore grades as little as 0.5 mg / kg ( 0.5 parts per million, ppm ) can be economical. Typical ore grades in open-pit mines are 1– 5 mg / kg ( 1 – 5 ppm ) ; ore grades in underground or hard rock mines are usually at least 3 mg / kg ( 3 ppm ). Because ore grades of 30 mg /kg ( 30 ppm ) are usually needed before gold is visible to the naked eye, in most gold mines the gold is invisible.

The average gold mining and extraction costs were about US \$ 317 / oz in 2007, but these can vary widely depending on mining type and ore quality; global mine production amounted to 2,471.1 tones.

### **9 – 1 - Refining**

After initial production, gold is often subsequently refined industrially by the Wohlwill process which is based on electrolysis or by the Miller process, that is chlorination in the melt. The Wohlwill process results in higher purity, but is more complex and is only applied in small-scale installations.<sup>[90][91]</sup> Other methods of assaying and purifying smaller amounts of gold include parting and inquartation as well as cupellation, or refining methods based on the dissolution of gold in aqua regia.

### **10 - Synthesis from other elements**

Gold was synthesized from mercury by neutron bombardment in 1941, but the isotopes of gold produced were all radioactive . In 1924, a Japanese physicist , Hantaro Nagaoka, accomplished the same feat.

Gold can currently be manufactured in a nuclear reactor by irradiation either of platinum or mercury.

Only the mercury isotope  $^{196}\text{Hg}$ , which occurs with a frequency of 0.15 % in natural mercury, can be converted to gold by neutron capture, and following electron capture-decay into  $^{197}\text{Au}$  with slow neutrons. Other mercury isotopes are converted when irradiated with slow neutrons into one another, or formed mercury isotopes which beta decay into thallium.

Using fast neutrons, the mercury isotope  $^{198}\text{Hg}$ , which composes 9.97 % of natural mercury, can be converted by splitting off a neutron and becoming  $^{197}\text{Hg}$ , which then disintegrates to stable gold. This reaction, however , possesses a smaller activation cross-section and is feasible only with un - moderated reactors.

It is also possible to eject several neutrons with very high energy into the other mercury isotopes in order to form  $^{197}\text{Hg}$ . However such high-energy neutrons can be produced only by particle accelerators .

## 11 - Consumption

The consumption of gold produced in the world is about 50% in jewelry, 40 % in investments, and 10 % in industry.

India is the world's largest single consumer of gold, as Indians buy about 25 % of the world's gold,<sup>[95]</sup> purchasing approximately 800 tonnes of gold every year, mostly for jewelry. India is also the largest importer of gold; in 2008, India imported around 400 tonnes of gold.<sup>[96]</sup> Indian households hold 18,000 tonnes of gold which represents 11% of the global stock and worth more than \$950 billion.

### *Gold jewelry consumption by country in tones .*

<b>Country</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>	<b>2012</b>	<b>2013</b>
India	442.37	745.70	986.3	864	974
Greater China	376.96	428.00	921.5	817.5	1120.1
United States	150.28	128.61	199.5	161	190
Turkey	75.16	74.07	143	118	175.2
Saudi Arabia	77.75	72.95	69.1	58.5	72.2
Russia	60.12	67.50	76.7	81.9	73.3
United Arab Emirates	67.60	63.37	60.9	58.1	77.1
Egypt	56.68	53.43	36	47.8	57.3
Indonesia	41.00	32.75	55	52.3	68
United Kingdom	31.75	27.35	22.6	21.1	23.4
Japan	21.85	18.50	-30.1	7.6	21.3
South Korea	18.83	15.87	15.5	12.1	17.5
Vietnam	15.08	14.36	100.8	77	92.2
Thailand	7.33	6.28	107.4	80.9	140.1
<b>Total</b>	<b>1508.70</b>	<b>1805.60</b>			
<i>Other Countries</i>	<i>251.6</i>	<i>254.0</i>	<i>390.4</i>	<i>393.5</i>	<i>450.7</i>
<b>World Total</b>	<b>1760.3</b>	<b>2059.6</b>	<b>3487.5</b>	<b>3163.6</b>	<b>3863.5</b>

## 12 - Pollution

Gold production is associated with contribution to hazardous pollution . The ore, generally containing less than one ppm gold

metal, is ground and mixed with sodium cyanide or mercury to react with gold in the ore for gold separation. Cyanide is a highly poisonous chemical, which can kill living creatures when exposed in minute quantities. Many cyanide spills<sup>[103]</sup> from gold mines have occurred in both developed and developing countries which killed marine life in long stretches of affected rivers. Environmentalists consider these events major environmental disasters. When mercury is used in gold production, minute quantity of mercury compounds reach water bodies, causing heavy metal contamination. Mercury can then enter into the human food chain in the form of methylmercury. Mercury poisoning in humans causes incurable brain function damage and severe retardation.

Thirty tones of used ore is dumped as waste for producing one 1 ounce ( 28 g ) of gold. Gold ore dumps are the source of many heavy elements such as cadmium, lead, zinc, copper, arsenic, selenium and mercury. When sulfide bearing minerals in these ore dumps are exposed to air and water, the sulfide transforms into sulfuric acid which in turn dissolves these heavy metals facilitating their passage into surface water and ground water. This process is called acid mine drainage. These gold ore dumps are long term, highly hazardous wastes second only to nuclear waste dumps.

Gold extraction is also a highly energy intensive industry, extracting ore from deep mines and grinding the large quantity of ore for further chemical extraction requires with 25 kW·h of electricity required per gram of gold produced.

### 13 – Chemistry

*Gold (III) chloride solution in water*



Although gold is the most noble of the noble metals, it still forms many diverse compounds. The oxidation state of gold in its compounds ranges from  $-1$  to  $+5$ , but Au (I) and Au (III) dominate its chemistry. Au (I), referred to as the aurous ion, is the most common oxidation state with soft ligands such as thioethers, thiolates, and tertiary phosphines. Au (I) compounds are typically linear. A good example is  $\text{Au}(\text{CN})_2^-$ , which is the soluble form of gold encountered in mining. Curiously, aurous complexes of water are rare. The binary gold halides, such as Au Cl, form zigzag polymeric chains, again featuring linear coordination at Au. Most drugs based on gold are Au (I) derivatives.

Au (III) (auric) is a common oxidation state, and is illustrated by gold (III) chloride,  $\text{Au}_2\text{Cl}_6$ . The gold atom centers in Au (III) complexes, like other  $d^8$  compounds, are typically square planar, with chemical bonds that have both covalent and ionic character.

Aqua regia, a 1 : 3 mixture of nitric acid and hydrochloric acid, dissolves gold. Nitric acid oxidizes the metal to  $+3$  ions, but only in minute amounts, typically undetectable in the pure acid because of the chemical equilibrium of the reaction. However, the ions are removed from the equilibrium by hydrochloric acid, forming  $\text{AuCl}_4^-$  ions, or chloro auric acid, thereby enabling further oxidation.

Some free halogens react with gold. Gold also reacts in alkaline solutions of potassium cyanide. With mercury, it forms an amalgam.

### 13 – 1 - Less common oxidation states

Less common oxidation states of gold include  $-1$ ,  $+2$ , and  $+5$ .

The  $-1$  oxidation state occurs in compounds containing the  $\text{Au}^-$  anion, called aurides. Caesium auride ( $\text{Cs Au}$ ), for example, crystallizes in the caesium chloride motif. Other aurides include those of  $\text{Rb}^+$ ,  $\text{K}^+$ , and tetra methyl ammonium ( $(\text{CH}_3)_4\text{N}^+$ ). Gold has the highest Pauling electro negativity of any metal, with a value of 2.54, making the auride anion relatively stable.

Gold (II) compounds are usually diamagnetic with Au – Au bonds such as  $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2$ . The evaporation of a solution of  $\text{Au}(\text{OH})_3$  in concentrated  $\text{H}_2\text{SO}_4$  produces red crystals of gold (II) sulfate,  $\text{Au}_2(\text{SO}_4)_2$ . Originally thought to be a mixed-valence compound, it has been shown to contain  $\text{Au}^{4+2}$  ions. A noteworthy, legitimate gold (II) complex is the tetra xenon gold (II) cation, which contains xenon as a ligand, found in  $[\text{AuXe}_4](\text{Sb}_2\text{F}_{11})_2$ .

Gold penta fluoride, along with its derivative anion,  $\text{AuF}_6^-$ , and its difluorine complex, gold hepta fluoride, is the sole example of gold (V), the highest verified oxidation state.

Some gold compounds exhibit *aurophilic bonding*, which describes the tendency of gold ions to interact at distances that are too long to be a conventional Au – Au bond but shorter than van der Waals bonding. The interaction is estimated to be comparable in strength to that of a hydrogen bond.

### 13 – 2 - Mixed valence compounds

Well-defined cluster compounds are numerous. In such cases, gold has a fractional oxidation state. A representative example is the octahedral species  $\{\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)\}_6^{2+}$ . Gold chalcogenides, such as gold sulfide, feature equal amounts of Au (I) and Au (III).

### 14 - Toxicity

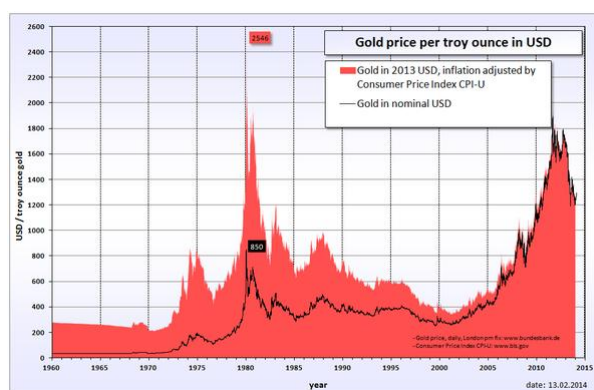
Pure metallic (elemental) gold is non-toxic and non-irritating when ingested and is sometimes used as a food decoration in the form of gold leaf. Metallic gold is also a component of the alcoholic drinks Goldschläger, Gold Strike, and Goldwasser. Metallic gold is approved as a food additive in the EU (E175 in the Codex Alimentarius). Although the gold ion is toxic, the acceptance of metallic gold as a food additive is due to its relative chemical inertness, and resistance to being corroded or transformed into soluble salts (gold compounds) by any known chemical process which would be encountered in the human body.

Soluble compounds (gold salts) such as gold chloride are toxic to the liver and kidneys. Common cyanide salts of gold such as

potassium gold cyanide, used in gold electro plating, are toxic by virtue of both their cyanide and gold content. There are rare cases of lethal gold poisoning from potassium gold cyanide . Gold toxicity can be ameliorated with chelation therapy with an agent such as dimercaprol.

Gold metal was voted Allergen of the Year in 2001 by the American Contact Dermatitis Society. Gold contact allergies affect mostly women . Despite this, gold is a relatively non - potent contact allergen, in comparison with metals like nickel.

## 15 - Price



*Gold price history in 1960–2011*

*old is currently valued at around US \$ 62,000 per kilogram.*

Like other precious metals, gold is measured by troy weight and by grams. When it is alloyed with other metals the term *carat* or *karat* is used to indicate the purity of gold present, with 24 carats being pure gold and lower ratings proportionally less. The purity of a gold bar or coin can also be expressed as a decimal figure ranging from 0 to 1, known as the millesimal fineness, such as 0.995 being very pure.

### 15 – 1 - History

The price of gold is determined through trading in the gold and derivatives markets, but a procedure known as the Gold Fixing in London, originating in September 1919, provides a daily benchmark price to the industry. The afternoon fixing was introduced in 1968 to provide a price when US markets are open.

Historically gold coinage was widely used as currency; when paper money was introduced, it typically was a receipt redeemable for gold coin or bullion. In a monetary system known as the gold standard, a certain weight of gold was given the name of a unit of currency. For a long period, the United States government set the value of the US dollar so that one troy ounce was equal to \$ 20.67 ( \$ 664.56 / kg ), but in 1934 the dollar was devalued to \$ 35.00 per troy ounce ( \$ 1125.27 / kg ). By 1961, it was becoming hard to maintain this price, and a pool of US and European banks agreed to manipulate the market to prevent further currency devaluation against increased gold demand.

On 17 March 1968, economic circumstances caused the collapse of the gold pool, and a two - tiered pricing scheme was established whereby gold was still used to settle international accounts at the old \$ 35.00 per troy ounce ( \$ 1.13 / g ) but the price of gold on the private market was allowed to fluctuate; this two-tiered pricing system was abandoned in 1975 when the price of gold was left to find its free-market level. Central banks still hold historical gold reserves as a store of value although the level has generally been declining. The largest gold depository in the world is that of the U.S. Federal Reserve Bank in New York, which holds about 3%<sup>[125]</sup> of the gold ever mined, as does the similarly laden U.S. Bullion Depository at Fort Knox. In 2005 the World Gold Council estimated total global gold supply to be 3,859 tones and demand to be 3,754 tones, giving a surplus of 105 tones.

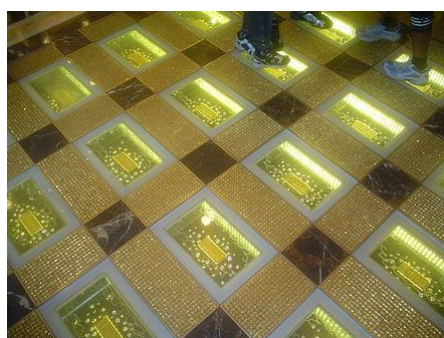
Some time around 1970 the price began in trend to greatly increase , and since 1968 the price of gold has ranged widely, from a high of \$ 850 /oz ( \$ 27,300 / kg ) on 21 January 1980 , to a low of \$ 252.90 /oz ( \$ 8,131 / kg ) on 21 June 1999 ( London Gold Fixing ) . The period from 1999 to 2001 marked the "Brown Bottom" after a 20 - year bear market . Prices increased rapidly from 2001, but the 1980 high was not exceeded until 3 January 2008 when a new maximum of \$ 865.35 per troy ounce was set. Another record price was set on 17 March 2008 at \$ 1023.50 / oz ( \$ 32,900 / kg ) .



In late 2009, gold markets experienced renewed momentum upwards due to increased demand and a weakening US dollar. On 2 December 2009, Gold reached a new high closing at \$ 1,217.23. Gold further rallied hitting new highs in May 2010 after the European Union debt crisis prompted further purchase of gold as a safe asset . On 1 March 2011, gold hit a new all-time high of \$ 1432.57, based on investor concerns regarding ongoing unrest in North Africa as well as in the Middle East.

Since April 2001 the gold price has more than quintupled in value against the US dollar, hitting a new all - time high of \$ 1,913.50 on 23 August 2011, prompting speculation that this long secular bear market has ended and a bull market has returned.

## 16 – Symbolism



*Gold bars at the Emperor Casino in Macau*

Great human achievements are frequently rewarded with gold, in the form of gold medals, golden trophies and other decorations. Winners of athletic events and other graded competitions are usually awarded a gold medal. Many awards such as the Nobel Prize are made from gold as well. Other award statues and prizes are depicted in gold or are gold plated .

Aristotle in his ethics used gold symbolism when referring to what is now commonly known as the golden mean. Similarly, gold is associated with perfect or divine principles, such as in the case of the golden ratio and the golden rule.

Gold is further associated with the wisdom of aging and fruition. The fiftieth wedding anniversary is golden. Our most valued or most successful latter years are sometimes considered "golden years". The height of a civilization is referred to as a "golden age".

In some forms of Christianity and Judaism, gold has been associated both with holiness and evil. In the Book of Exodus, the Golden Calf is a symbol of idolatry, while in the Book of Genesis, Abraham was said to be rich in gold and silver, and Moses was instructed to cover the Mercy Seat of the Ark of the Covenant with pure gold. In Byzantine iconography the halos of Christ, Mary and the Christian saints are often golden.

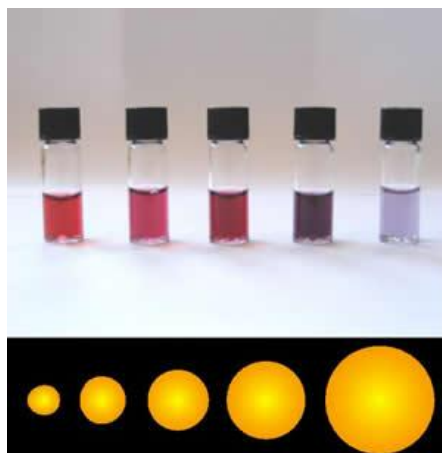
Medieval kings were inaugurated under the signs of sacred oil and a golden crown, the latter symbolizing the eternal shining light of heaven and thus a Christian king's divinely inspired authority

According to Christopher Columbus, those who had something of gold were in possession of something of great value on Earth and a substance to even help souls to paradise.

Wedding rings have long been made of gold. It is long lasting and unaffected by the passage of time and may aid in the ring symbolism of eternal vows before God and/or the sun and moon and the perfection the marriage signifies. In Orthodox Christian wedding ceremonies, the wedded couple is adorned with a golden crown (though some opt for wreaths, instead) during the ceremony, an amalgamation of symbolic rites.

In popular culture gold has many connotations but is most generally connected to terms such as good or great, such as in the phrases: "has a heart of gold", "that's golden!", "golden moment", "then you're golden!" and "golden boy". It remains a cultural symbol of wealth and through that, in many societies, success.

# Colloidal Gold



*Solutions of gold nanoparticles of various sizes.  
The size difference causes the difference in colors.*

## Contents

### Introduction

#### 1 History

#### 2 Synthesis

##### 2.1 Turkevich method

##### 2.2 Brust method

##### 2.3 Perrault Method

##### 2.4 Navarro method

##### 2.5 Sonolysis

##### 2.6 Block Copolymer-mediated Method

#### 3 Electron Microscopy

#### 4 Medical research

##### 4.1 Drug carrier

##### 4.2 Tumor detection

##### 4.3 Gene therapy

##### 4.4 Photo thermal agents

##### 4.5 Radiotherapy dose enhancer

##### 4.6 Detection of toxic gas

## - Introduction

**Colloidal gold** is a suspension (or colloid) of sub micro meter-size particles of gold in a fluid, usually water. The liquid is usually either an intense red colour ( for particles less than 100 nm ) or blue /

purple ( for larger particles ) . Due to the unique optical, electronic, and molecular - recognition properties of gold nanoparticles, they are the subject of substantial research, with applications in a wide variety of areas, including electron microscopy, electronics, nanotechnology, and materials science.

Properties and applications of colloidal gold nanoparticles strongly depend upon their size and shape. For example, rod like particles have both transverse and longitudinal absorption peak, and anisotropy of the shape affects their self-assembly.

## 1 – History



*This cranberry glass bowl was made by adding a gold salt (probably gold chloride) to molten glass.*

Known, or at least used ( perhaps proceeding by accident without much understanding of the process ) since ancient times, the synthesis of colloidal gold was crucial to the 4<sup>th</sup> - century Lycurgus Cup, which changes colour depending on the direction of the light. Later it was used as a method of staining glass.

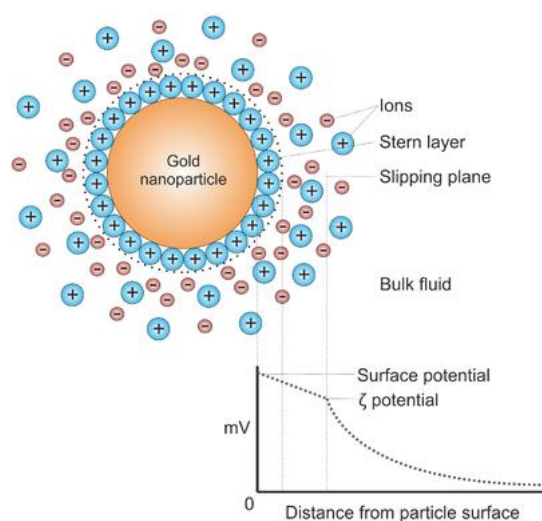
A so - called Elixir of Life , a potion made from gold, was discussed, if not actually manufactured, in ancient times. In the 16th century, the alchemist Paracelsus claimed to have created a potion called *Aurum Potabile* (Latin: potable gold). In *The newe iewell of health*, 1576, translator George Baker promoted the use and preparation of potable gold, along with other "most excellent secretes of phisicke and philosophie".

In the 17th century, the glass - colouring process was refined by Andreus Cassius and Johann Kunckel, allowing them to produce a striking deep-ruby colored form of glass. In 1842, John Herschel invented a photographic process called chrysotype ( from the Greek χρῦσός meaning "gold") that used colloidal gold to record images on paper.

Modern scientific evaluation of colloidal gold did not begin until Michael Faraday's work of the 1850s. Paracelsus' work is known to have inspired Faraday to prepare the first pure sample of colloidal gold, which he called 'activated gold', in 1857. He used phosphorus to reduce a solution of gold chloride.

For a long time, the composition of the Cassius ruby-gold was unclear. Several chemists suspected it to be a gold tin compound, due to its preparation . Faraday was the first to recognize that the color was actually due to the minute size of the gold particles . In 1898, Richard Adolf Zsigmondy prepared the first colloidal gold in diluted solution.<sup>[12]</sup> Apart from Zsigmondy, Theodor Svedberg, who invented ultracentrifugation, and Gustav Mie, who provided the theory for scattering and absorption by spherical particles, were also interested in understanding synthesis and properties of colloidal gold.

## 2 – Synthesis



*Potential difference as a function of distance from particle surface.*

Generally, gold nano particles are produced in a liquid ("liquid chemical methods") by reduction of chloro auric acid (  $\text{H} [\text{AuCl}_4]$  ). After dissolving  $\text{H} [\text{AuCl}_4]$  , the solution is rapidly stirred while a reducing agent is added. This causes  $\text{Au}^{3+}$  ions to be reduced to neutral gold atoms. As more and more of these gold atoms form, the solution becomes super saturated, and gold gradually starts to precipitate in the form of sub - nanometer particles. The rest of the gold atoms that form stick to the existing particles, and, if the solution is stirred vigorously enough, the particles will be fairly uniform in size.

To prevent the particles from aggregating, some sort of stabilizing agent that sticks to the nanoparticle surface is usually added. Also, gold colloids can be synthesized without stabilizers by laser ablation in liquids.

They can be functionalized with various organic ligands to create organic - inorganic hybrids with advanced functionality.

## **2 – 1 - Turkevich method**

The method pioneered by J. Turkevich et al. in 1951 and refined by G. Frens in 1970s , is the simplest one available. In general, it is used to produce modestly mono disperse spherical gold nano particles suspended in water of around 10 – 20 nm in diameter. Larger particles can be produced, but this comes at the cost of mono dispersity and shape. It involves the reaction of small amounts of hot chloro auric acid with small amounts of sodium citrate solution. The colloidal gold will form because the citrate ions act as both a reducing agent and a capping agent.

Recently, the evolution of the spherical gold nano particles in the Turkevich reaction has been elucidated. It is interesting to note that extensive net works of gold nano wires are formed as a transient intermediate. These gold nanowires are responsible for the dark appearance of the reaction solution before it turns ruby – red .

To produce larger particles, less sodium citrate should be added (possibly down to 0.05 % , after which there simply would not be enough to reduce all the gold). The reduction in the amount of sodium citrate will reduce the amount of the citrate ions available for stabilizing the particles, and this will cause the small particles to aggregate into bigger ones ( until the total surface area of all particles becomes small enough to be covered by the existing citrate ions ).

## **2 – 2 - Brust method**

This method was discovered by Brust and Schiffrin in early 1990s , and can be used to produce gold nano particles in organic liquids that are normally not miscible with water ( like toluene ) . It involves the reaction of a chlor auric acid solution with tetra octyl ammonium bromide ( TOAB ) solution in toluene and sodium boro hydride as an anti - coagulant and a reducing agent, respectively.

Here, the gold nano particles will be around 5 – 6 nm .  $\text{NaBH}_4$  is the reducing agent, and TOAB is both the phase transfer catalyst and the stabilizing agent.

It is important to note that TOAB does not bind to the gold nanoparticles particularly strongly, so the solution will aggregate gradually over the course of approximately two weeks. To prevent this, one can add a stronger binding agent, like a thiol (in particular, alkan ethiols ), which will bind to gold, producing a near-permanent solution. Alkan ethiol protected gold nanoparticles can be precipitated and then redissolved. Some of the phase transfer agent may remain bound to the purified nanoparticles, this may affect physical properties such as solubility. In order to remove as much of this agent as possible the nanoparticles must be further purified by soxhlet extraction.

## **2 – 3 - Perrault Method**

This approach, discovered by Perrault and Chan in 2009 , uses hydro quinone to reduce  $\text{H Au Cl}_4$  in an aqueous solution that contains gold nano particle seeds. This seed - based method of synthesis is similar to that used in photographic film development, in

which silver grains within the film grow through addition of reduced silver onto their surface. Likewise, gold nano particles can act in conjunction with hydroquinone to catalyze reduction of ionic gold onto their surface. The presence of a stabilizer such as citrate results in controlled particle growth. Typically, the nanoparticle seeds are produced using the citrate method. The hydroquinone method complements that of Frens, as it extends the range of mono dispersed spherical particle sizes that can be produced. Whereas the Frens method is ideal for particles of 12 - 20 nm, the hydroquinone method can produce particles of at least 30 – 250 nm.

## **2 – 4 - Navarro method**

As pointed out before, the precise size control with a low poly dispersity of spherical gold nanoparticles remains difficult for particles larger than 30 nm. In order to provide maximum control on the NP structure along with synthetic straightforwardness, Navarro and co-workers used a ‘one - pot’ protocol, relying on a modified Turkevitch - Frens procedure. The method consist in the addition of sodium acetyl acetate [  $\text{Na}(\text{acac})$  ] allowing the complexation and reduction of  $\text{Au III}$  to  $\text{Au I}$  immediately followed by the addition of sodium citrate (reduction of  $\text{Au I}$  to  $\text{Au 0}$ ). For this experiment, sodium acetyl acetate purity is really important. The concentration of sodium acetyl acetate directly impacts the nuclei numbers inducing a size evolution of the gold core up to 90 nm with a narrow size distribution. Practically, the tetra chloro aurate and sodium citrate concentration are fixed to 0.30 m M and 0.255 m M ( ratio sodium citrate to gold: 0.85 ). In these conditions, and without sodium acetyl acetate, the obtained nanoparticles precipitate immediately. The concentration of sodium acetyl acetate can be tuned from 0.33 m M to 1.0 m M. The addition of the  $\text{Na}(\text{acac})$  and sodium citrate to the yellow boiling gold ions solution results in a colorless one indicating the complexation and reduction of  $\text{Au III}$  to  $\text{Au I}$ . Within a few minutes, the solution turns light blue-purple, featuring the formation of the gold nuclei. The small crystalline structures will then diffuse over the solution allowing the growth of the final spherical particles.



## **2 – 5 – Sonolysis**

Another method for the experimental generation of gold particles is by sonolysis. In one such process based on ultra sound, the reaction of an aqueous solution of  $\text{H Au Cl}_4$  with glucose , the reducing agents are hydroxyl radicals and sugar pyrolysis radicals ( forming at the interfacial region between the collapsing cavities and the bulk water ) and the morphology obtained is that of nano ribbons with width 30 – 50 nm and length of several micrometers. These ribbons are very flexible and can bend with angles larger than  $90^\circ$ . When glucose is replaced by cyclo dextrin (a glucose oligomer), only spherical gold particles are obtained, suggesting that glucose is essential in directing the morphology toward a ribbon.

## **2 – 6 - Block Copolymer-mediated Method**

An economical, environmentally benign and fast synthesis methodology for gold nano particles using block copolymer has been developed . In this synthesis methodology, block copolymer plays the dual role of a reducing agent as well as a stabilizing agent. The formation of gold nanoparticles comprises three main steps: reduction of gold salt ion by block copolymers in the solution and formation of gold clusters, adsorption of block copolymers on gold clusters and further reduction of gold salt ions on the surfaces of these gold clusters for the growth of gold particles in steps, and finally its stabilization by block copolymers. But this method usually has a limited-yield (nanoparticle concentration), which does not increase with the increase in the gold salt concentration. Recently, Ray et al. demonstrated that the presence of an additional reductant ( tri sodium citrate ) in 1 : 1 molar ratio with gold salt enhances the yield by many fold.

## **3 - Electron Microscopy**

Colloidal gold and various derivatives have long been among the most widely used labels for antigens in biological electron microscopy . Colloidal gold particles can be attached to many traditional biological probes such as antibodies , lectins , super antigens, glycans , nucleic acids , and receptors. Particles of different

sizes are easily distinguishable in electron micrographs, allowing simultaneous multiple-labelling experiments.

## **4 - Medical research**

### **4 – 1 - Drug carrier**

Gold nanoparticles can be used to optimize the biodistribution of drugs to diseased organs, tissues or cells, in order to improve and target drug delivery. It is important to realize that the nanoparticle-mediated drug delivery is feasible only if the drug distribution is otherwise inadequate. These cases include drug targeting of difficult, unstable molecules ( proteins , si RNA , DNA ), delivery to the difficult sites ( brain , retina, tumors , intracellular organelles ) and drugs with serious side effects ( e.g. anti - cancer agents ) . The performance of the nano particles depends on the size and surface functionalities in the particles. Also, the drug release and particle disintegration can vary depending on the system ( eg. biodegradable polymers sensitive to pH ) . An optimal nano drug delivery system ensures that the active drug is available at the site of action for the correct time and duration, and their concentration should be above the minimal effective concentration (MEC) and below the minimal toxic concentration (MTC).

Gold nanoparticles are being investigated as carriers for drugs such as Paclitaxel. The administration of hydrophobic drugs require molecular encapsulation and it is found that nano sized particles are particularly efficient in evading the reticuloendothelial system.

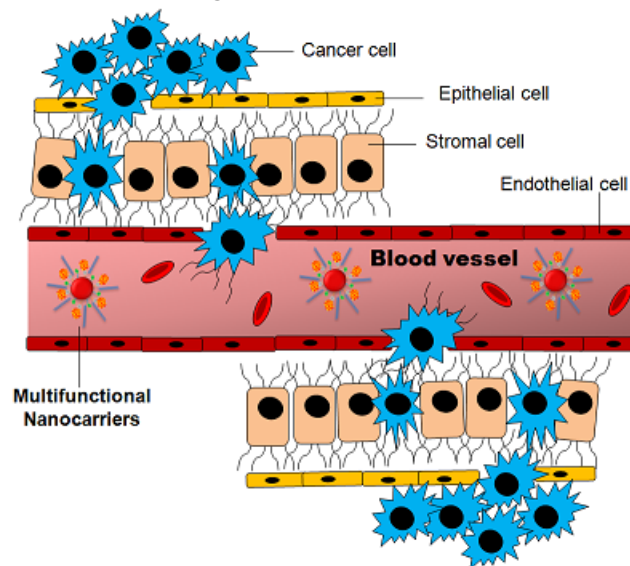
Gold nanoparticles are also used to circumvent multidrug resistance ( MDR ) mechanisms. Mechanisms of MDR include decreased uptake of drugs, reduced intracellular drug concentration by activation of the efflux transporters, modifications in cellular pathways by altering cell cycle checkpoints, increased metabolism of drugs, induced emergency response genes to impair apoptotic pathways and altered DNA repair mechanisms.

### **4 – 2 - Tumor detection**

In cancer research, colloidal gold can be used to target tumors and provide detection using SERS ( Surface Enhanced Raman Spectro

scopy ) *in vivo*. These gold nano particles are surrounded with Raman reporters, which provide light emission that is over 200 times brighter than quantum dots. It was found that the Raman reporters were stabilized when the nanoparticles were encapsulated with a thiol-modified polyethylene glycol coat. This allows for compatibility and circulation *in vivo*. To specifically target tumor cells, the pegylated gold particles are conjugated with an antibody (or an antibody fragment such as scFv), against, e.g. Epidermal growth factor receptor, which is sometimes overexpressed in cells of certain cancer types. Using SERS, these pegylated gold nanoparticles can then detect the location of the tumor.

Gold nanoparticles accumulate in tumors, due to the leakiness of tumor vasculature, and can be used as contrast agents for enhanced imaging in a time-resolved optical tomography system using short-pulse lasers for skin cancer detection in mouse model. It is found that intravenously administrated spherical gold nanoparticles broadened the temporal profile of reflected optical signals and enhanced the contrast between surrounding normal tissue and tumors.

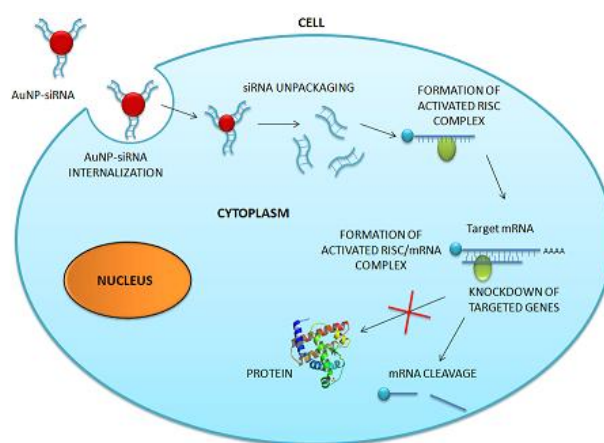


Tumor targeting via multifunctional nanocarriers. Cancer cells reduce adhesion to neighboring cells and migrate into the vasculature-rich stroma. Once at the vasculature, cells can freely enter the blood stream. Once the tumor is directly connected to the main blood circulation system, multifunctional nano carriers can interact directly with cancer cells and effectively target tumors.

There fore, gold nano particles have the potential to join numerous therapeutic functions into a single platform, by targeting specific tumor cells, tissues and organs. Actually, Conde et al reported the evaluation of the inflammatory response and therapeutic si RNA silencing via RGD - nano particles in a lung cancer mouse model. This study reported the use of si RNA / RGD gold nanoparticles capable of targeting tumor cells in two lung cancer xenograft mouse models, resulting in successful and significant *c-Myc* oncogene down regulation followed by tumor growth inhibition and prolonged survival of the animals. This delivery system can achieve translocation of si RNA duplexes directly into the tumour cell cytoplasm and accomplish successful silencing of an oncogene expression. Actually, RGD / si RNA- Au NPs can target preferentially and be taken up by tumor cells via integrin  $\alpha\beta 3$ -receptor-mediated endocytosis with no cytotoxicity, showing that can accumulate in tumor tissues overexpressing  $\alpha\beta 3$  integrins and selectively delivered *c- Myc* si RNA to suppress tumor growth and angiogenesis.

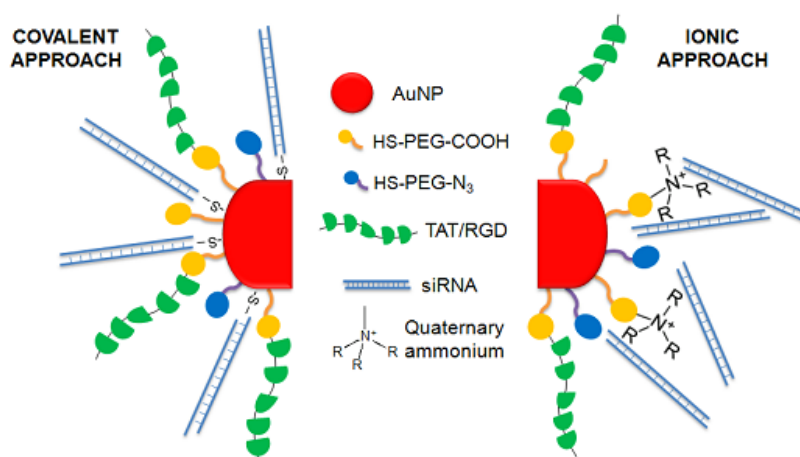
#### 4 – 3 - Gene therapy

Gene therapy is receiving increasing attention and, in particular, small - interference RNA ( si RNA ) shows importance in novel molecular approaches in the knockdown of specific gene expression in cancerous cells. The major obstacle to clinical application is the uncertainty about how to deliver therapeutic si RNAs with maximal therapeutic impact. Gold nanoparticles have shown potential as intracellular delivery vehicles for si RNA oligonucleotides with maximal therapeutic impact.



Regulation of gene expression via si RNA - gold nanoparticles. Engineered nanoparticles modified with si RNA can represent a delivery system of si RNA and a useful tool to block gene function and for sequence-specific post - transcriptional gene silencing. siRNA-modified nano carriers can enter cells and subsequently unwound si RNA strands and assembled into an effector complex, RNA Induced Silencing Complex (RISC), which can direct RNA cleavage, mediate translational repression or induce chromatin modification. The antisense strand then binds to its complementary / target m RNA ( activated RISC / mRNA complex ) . The catalytic RISC recognizes mRNAs containing perfect or near-perfect complementary sequence to the guide si RNA and cleaves the mRNAs at a site precisely 10 nucleotides from the 5'-end of the guide strand. Finally, mRNA degradation is achieved by endo - and exo nucleases, resulting in knockdown of the expression of the corresponding genes.

Recently, Conde et al. provided evidence of *in vitro* and *in vivo* RNAi triggering via the synthesis of a library of novel multifunctional gold nanoparticles, using a hierarchical approach including three biological systems of increasing complexity: *in vitro* cultured human cells, *in vivo* freshwater polyp ( *Hydra vulgaris* ) , and *in vivo* mice models. The authors developed effective conjugation strategies to combine, in a highly controlled way, specific biomolecules to the surface of gold nanoparticles such as: (a) biofunctional spacers: Poly(ethylene glycol) ( PEG ) spacers used to increase solubility and biocompatibility; ( b ) cell penetrating peptides such as TAT and RGD peptides: A novel class of membrane trans locating agents named cell penetrating peptides ( CPPs ) that exploit more than one mechanism of endocytosis to overcome the lipophilic barrier of the cellular membranes and deliver large molecules and even small particles inside the cell for their biological actions; and (c) siRNA complementary to a master regulator gene, the proto oncogene c-myc, were bond covalently ( thiol – si RNA) and ionically ( naked / unmodified si RNA ) to gold nano particles.



Multi functional si RNA - gold nano particles with several biomolecules: PEG, cell penetration and cell adhesion peptides and siRNA. Two different approaches were employed to conjugate the siRNA to the gold nano particle: (1) **Covalent approach:** use of thiolated siRNA for gold - thiol binding to the nanoparticle; (2) **Ionic approach:** interaction of the negatively charged si RNA to the modified surface of the Au NP through ionic interactions.

Gold nanoparticles have also shown potential as intracellular delivery vehicles for antisense oligonucleotides ( ssDNA , dsDNA ) by providing protection against intracellular nucleases and ease of functionalization for selective targeting . Recently, Conde et al developed a new theranostic system capable of intersecting all RNA pathways: from gene specific down regulation to silencing the silencers, i.e. si RNA and miRNA pathways. The authors reported the development gold nanoparticles functionalized with a fluoro phore labeled hairpin-DNA, i.e. gold nano beacons, capable of efficiently silencing single gene expression, exogenous siRNA and endogenous miRNAs while yielding a quantifiable fluorescence signal directly proportional to the level of silencing . This method describes a gold nano particle - based nano beacon as an innovative theranostic approach for detection and inhibition of sequence - specific DNA and RNA for *in vitro* and *ex vivo* applications. Under hairpin configuration, proximity to gold nanoparticles leads to fluorescence quenching; hybridization to a complementary target restores fluorescence emission due to the gold nano beacons' conformational reorganization that causes the fluorophore and the gold nanoparticle

to part from each other . This concept can easily be extended and adapted to assist the in vitro evaluation of silencing potential of a given sequence to be later used for *ex vivo* gene silencing and RNAi approaches, with the ability to monitor real-time gene delivery action.

#### **4 – 4 – Photo thermal agents**

Gold nano rods are being investigated as photo thermal agents for in - vivo applications. Gold nano rods are rod - shaped gold nanoparticles whose aspect ratios tune the surface plasmon resonance (SPR) band from the visible to near-infrared wavelength. The total extinction of light at the SPR is made up of both absorption and scattering. For the smaller axial diameter nano rods (~10 nm), absorption dominates, whereas for the larger axial diameter nano rods (>35 nm) scattering can dominate. As a consequence, for in - vivo applications, small diameter gold nano rods are being used as photo thermal converters of near - infrared light due to their high absorption cross - sections . Since near - infrared light transmits readily through human skin and tissue, these nano rods can be used as ablation components for cancer, and other targets. When coated with polymers, gold nano rods have been known to circulate in - vivo for greater than 15 hours half - life . Apart from rod - like gold nanoparticles, also spherical colloidal gold nanoparticles are recently used as markers in combination with photo thermal single particle microscopy.

#### **4 – 5 - Radiotherapy dose enhancer**

Following work by Hainfield et al . there has been considerable interest in the use of gold and other heavy-atom containing nanoparticles to enhance the dose delivered to tumors. Since the gold nanoparticles are taken up by the tumors more than the nearby healthy tissue, the dose is selectively enhanced. The biological effectiveness of this type of therapy seems to be due to the local deposition of the radiation dose near the nanoparticles . This mechanism is the same as occurs in heavy ion therapy.

#### **4 – 6 - Detection of toxic gas**

Researchers have developed simple inexpensive methods for on-site detection of hydrogen sulfide  $\text{H}_2\text{S}$  present in air based on the anti aggregation of gold nanoparticles ( Au NPs ). Dissolving  $\text{H}_2\text{S}$  into a weak alkaline buff solution leads to the formation of  $\text{HS}^-$ , which can stabilize AuNPs and ensure they maintain their red color allowing for visual detection of toxic levels of  $\text{H}_2\text{S}$ .



# Electrum

	
<p><i>Electrum coin of the Byzantine Emperor Alexius I Comnenus.</i></p>	<p><i>Early 6th century BC Lydian electrum coin (one-third stater denomination)</i></p>

## Contents

- 1 Introduction
- 2 Composition
- 3 Appearance
- 4 History

## 1 - Introduction

**Electrum** is a naturally occurring alloy of gold and silver, with trace amounts of copper and other metals. It has also been produced artificially, and is often known as **green gold**. The ancient Greeks called it 'gold' or 'white gold', as opposed to 'refined gold'. Its colour ranges from pale to bright yellow, depending on the proportions of gold and silver.

The gold content of naturally occurring electrum in modern Western Anatolia ranges from 70 % to 90 %, in contrast to the 45 –55 % of electrum used in ancient Lydian coinage of the same geographical area. This suggests that one reason for the invention of coinage in that area was to increase the profits from seignior age by issuing currency with a lower gold content than the commonly circulating metal.

Electrum was used for the earliest metal coins, and as early as the third millennium BC in Old Kingdom Egypt, sometimes as an exterior coating to the pyramidions atop ancient Egyptian pyramids

and obelisks. Electrum was also used in the making of ancient drinking vessels. For several decades the medals awarded with the Nobel Prize have been made of gold-plated green gold.

The name electrum was also used to denote German silver, mainly for its use in making technical instruments.

## **2 – Composition**

Electrum consists primarily of gold and silver but is sometimes found with traces of platinum, copper, and other metals. It is mostly applied informally to compositions between about 20 – 80 % gold and 20-80% silver atoms, but is strictly called gold or silver depending on the dominant element. Analysis of the composition of electrum in ancient Greek coinage dating from about 600 BC shows that the gold composition was about 55.5 % in the coinage issued by Phocaea. In the early classical period, the gold content of electrum ranged from 46 % in Phocaia to 43 % in Mytilene. In later coinage from these areas, dating to 326 BC, the gold content averaged 40 % to 41 %. In the Hellenistic period, electrum coins with a regularly decreasing proportion of gold were issued by the Carthaginians. In the later Eastern Roman Empire controlled from Constantinople, the purity of the gold coinage was reduced, and an alloy that can be called electrum began to be used.

## **3 – Appearance**

The colour of electrum is pale yellow or yellowish-white and the name is a Latinized form of the Greek word ἤλεκτρον (*èlektron*), mentioned in the *Odyssey* referring to a metallic substance consisting of gold alloyed with silver. The same word was also used for the substance amber, likely because of the pale yellow colour of certain varieties, and it is from amber's electrostatic properties that the modern English words "electron" and "electricity" are derived. Electrum was often referred to as white gold in ancient times, but could be more accurately described as "pale gold". The modern use of the term white gold usually concerns gold alloyed with any one or a combination of nickel, silver, platinum and palladium to produce a silver - coloured gold.

## 4 – History

Electrum is mentioned in an account of an expedition sent by Pharaoh Sahure of the Fifth dynasty of Egypt . It is also discussed by Pliny the Elder in his *Naturalis Historia*.

Electrum is believed to have been used in coins circa 600 BC in Lydia under the reign of Alyattes II.

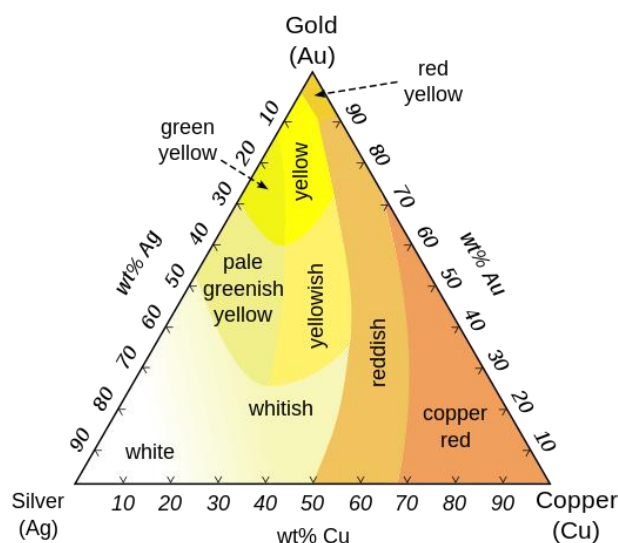
Electrum was much better for coinage than gold, mostly because it was harder and more durable, but also because techniques for refining gold were not widespread at the time. The discrepancy between gold content of electrum from modern Western Anatolia (70–90%) and ancient Lydian coinage ( 45 – 55 % ) suggests that the Lydians had already solved the refining technology for silver and were adding refined silver to the local native electrum some decades before introducing the pure silver coins cited below.

In Lydia, electrum was minted into 4.7 - gram coins, each valued at  $1 / 3$  *stater* (meaning "standard" ) . Three of these coins (with a weight of about 14.1 grams, almost half an ounce ) totaled one stater, about one month's pay for a soldier. To complement the stater, fractions were made: the *trite* ( third ), the *hekte* (sixth), and so forth, including  $1/24$  of a stater, and even down to  $1 / 48$ th and  $1/96$ th of a stater. The  $1 / 96$  stater was only about 0.14 to 0.15 grams. Larger denominations, such as a one stater coin, were minted as well.

Because of variation in the composition of electrum, it was difficult to determine the exact worth of each coin. Widespread trading was hampered by this problem, as cautious foreign merchants offered poor rates on local electrum coin .

These difficulties were eliminated in 570 BC when pure silver coins were introduced. However, electrum currency remained common until approximately 350 BC. The simplest reason for this was that, because of the gold content, one 14.1 gram stater was worth as much as ten 14.1 gram silver pieces.

# Colored Gold



*Ternary plot of different colors of Ag - Au - Cu alloys  
Pure gold is yellow in color, but **colored gold** in various other colors  
can be produced.*

## Contents

### 1 Introduction

### 2 Alloys

#### 2.1 White gold

#### 2.2 Rose, red, and pink gold

#### 2.3 Rose gold

#### 2.4 Span gold

#### 2.5 Green gold

#### 2.6 Grey gold

### 3 Intermetallic

#### 3.1 Purple

#### 3.2 Blue gold

### 4 Surface treatments

#### 4.1 Black gold

#### 4.2 Blue gold

## 1 Introduction

Colored golds can be classified to three groups :

Alloys with silver and copper in various proportions, producing white, yellow, green and red golds ; typically malleable alloys

Intermetallic compounds, producing blue and purple golds, as well as other colors. These are typically brittle but can be used as gems and inlays

Surface treatments such as oxide layers

Pure 100 % gold is 24 karat by definition, so all colored golds are less than this, with the common being 18 K ( 75 % ), 14 K (58 %), and 9K ( 38 % ) .

## **2 – Alloys**

### **2 – 1 - White gold**



*Rhodium - plated white gold wedding ring*

**White gold** is an alloy of gold and at least one white metal, usually nickel, manganese or palladium. Like yellow gold, the purity of white gold is given in karats.

White gold's properties vary depending on the metals and proportions used. As a result, white gold alloys can be used for many different purposes; while a nickel alloy is hard and strong and therefore good for rings and pins, gold-palladium alloys are soft, pliable and good for white gold gemstone settings, sometimes with other metals like copper, silver, and platinum for weight and durability, although this often requires specialized goldsmiths. The term white gold is used very loosely in the industry to describe karat gold alloys with a whitish hue. Many believe that the color of the rhodium plating, which is seen on many commercial pieces, is actually the color of white gold. The term "white" covers a large spectrum of colors that borders or overlaps pale yellow, tinted brown,

and even very pale rose. The jewelry industry often improves these off - white colors by rhodium plating.

A common white gold formulation consists of 90 wt.% gold and 10 wt.% nickel. Copper can be added to increase malleability.

The strength of gold – nickel - copper alloys is caused by formation of two phases, a gold - rich Au - Cu, and a nickel - rich Ni – Cu , and the resulting hardening of the material.

The alloys used in jewelry industry are gold - palladium-silver and gold - nickel - copper - zinc. Palladium and nickel act as primary bleaching agents for gold; zinc acts as a secondary bleaching agent to attenuate the color of copper.

**Contact allergy** The nickel used in some white gold alloys can cause an allergic reaction when worn over long periods ( also notably on some wrist-watch casings ). This reaction, typically a minor skin rash, occurs in about one out of eight people and because of this, many countries do not use nickel in their white gold formulations.

## **2 – 2 – Rose , red , and pink gold**

**Rose gold** is a gold and copper alloy widely used for specialized jewelry. Rose gold, also known as **pink gold** and **red gold**, was popular in Russia at the beginning of the nineteenth century, and was also known as **Russian gold**, although this term is now obsolete. Rose gold jewelry is becoming more popular in the 21st century and is commonly used for wedding rings, bracelets, and other jewelry.

Although the names are often used interchangeably, the difference between red, rose, and pink gold is the copper content – the higher the copper content, the stronger the red coloration. Pink gold uses the least amount of copper content, followed by rose gold, and red gold has the highest copper content. Examples of the common alloys for 18K rose gold, 18K red gold, and 18K pink gold:

18K Red gold : 75 % gold, 25 % copper

18K Rose gold : 75 % gold, 22.25 % copper, 2.75 % silver

18K Pink gold : 75 % gold, 20 % copper, 5 % silver

12K Red gold: 50 % gold and 50% copper .

Up to 15 % zinc can be added to copper - rich alloys to change their color to reddish yellow or dark yellow.

During ancient times, due to impurities in the smelting process, gold frequently turned a reddish color. This is why many Greco-Roman texts, and even many texts from the Middle Ages, describe gold as "red".

## **2 - 2 - Rose gold**

The highest karat version of rose gold is also known as crown gold, which is 22 karat. Eighteen karat red gold may be made of 25 % copper and 75 % gold. For 18 karat rose gold, typically about 4 % silver is added to 75 % gold and 21 % copper to give a rose color. 14 karat *red gold* is often found in the Middle East and contains 41.67 % copper.

High -end flutes are very commonly made of solid rose gold, the most common alloy being 14K .

## **2 - 3 - Span gold**

Some gold copper - aluminum alloys form a fine surface texture at heat treatment, yielding an interesting spangling effect. At cooling, they undergo a quasi-martensitic transformation from body-centered cubic to body-centered tetragonal phase; the transformation does not depend on the cooling rate. A polished object is heated in hot oil to 150 - 200°C for 10 minutes then cooled below 20°C, forming a sparkly surface covered with tiny facets.

The alloy of 76 % gold, 19 % copper, and 5 % aluminum yields a yellow color, the alloy of 76 % gold , 18 % copper and 6 % aluminum is pink.

## **2 - 4 - Green gold**

Green gold was known to Lydians as long ago as 860 BC under the name electrum, a naturally-occurring alloy of silver and gold . It actually appears as a greenish-yellow rather than green. Eighteen

karat green gold would therefore contain a mix of 75% gold and 25% silver ( or 73 % gold and 27 % silver ) . Fired enamels adhere better to these alloys.

Cadmium can also be added to gold alloys but there are health concerns regarding its use. The alloy of 75 % gold, 23 % copper , and 2 % cadmium yields light - green 18 - karat gold. The alloy of 75 % gold , 15 % silver, 6 % copper, and 4 % cadmium yields a dark -green alloy,

## **2 - 4 - Grey gold**

**Grey gold** alloys are made by adding silver, manganese and copper in specific ratios to the gold.<sup>[6]</sup>

## **3 – Intermetallic**

All the  $AuX_2$  inter metallics have crystal structure of  $CaF_2$  and therefore are brittle . Deviation from the stoichiometry results in loss of color. Slightly nonstoichiometric compositions are however used, to achieve a fine - grained two- or three - phase microstructure with reduced brittleness. A small amount of palladium, copper or silver can be added to achieve a less brittle microstructure .

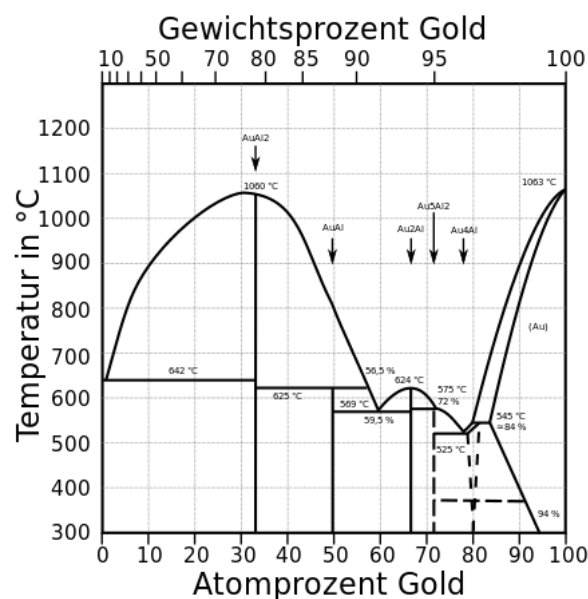
The intermetallic compounds tend to have poor corrosion resistance. The less noble elements are leached to the environment, and a gold - rich surface layer is formed. Direct contact of blue and purple gold elements with skin should be avoided as exposure to sweat may result in metal leaching and discoloration of the metal surface.

## **3 - 1 – Purple**

**Purple gold** (also called amethyst gold and violet gold) is an alloy of gold and aluminum rich in gold - aluminum intermetallic ( $AuAl_2$ ). Gold content in  $AuAl_2$  is around 79 % and can therefore be referred to as 18 karat gold. Purple gold is more brittle than other gold alloys, (a serious fault when it forms in electronics ), as it is an intermetallic compound instead of a malleable alloy, and a sharp blow may cause it to shatter. It is therefore usually machined and faceted to be used as a "gem" in conventional jewelry rather than by itself. At a



lower content of gold, the material is composed of the intermetallic and an aluminum-rich solid solution phase. At a higher content of gold, the gold - richer intermetallic Au Al forms; the purple color is preserved to about 15 % of aluminum. At 88 % of gold the material is composed of Au Al and changes color . ( The actual composition of Au Al<sub>2</sub> is closer to Al<sub>11</sub> Au<sub>6</sub> as the sub lattice is incompletely occupied ) .



*Gold-aluminium phase diagram*

### 3 - 2 - Blue gold

Blue gold is an alloy of gold and indium.<sup>[9]</sup> It contains 46 % gold (about 12 karat ) and 54 % indium , forming an intermetallic compound AuIn<sub>2</sub>. While several sources remark this intermetallic to have "a clear blue color", in fact the effect is slight: AuIn<sub>2</sub> has CIE LAB color coordinates of 79 , - 3.7 , - 4.2 which appears roughly as a greyish color. With gallium, gold forms an intermetallic AuGa<sub>2</sub> (58.5% Au, 14ct) which has slighter bluish hue. The melting point of AuIn<sub>2</sub> is 541 °C, for AuGa<sub>2</sub> it is 492 °C. AuIn<sub>2</sub> is less brittle than AuGa<sub>2</sub>, which itself is less brittle than AuAl<sub>2</sub>.

A surface plating of blue gold on karat gold or sterling silver can be achieved by a gold plating of the surface, followed by indium plating, with layer thickness matching the 1 : 2 atomic ratio. A heat

treatment then causes inter diffusion of the metals and formation of the required intermetallic compound.

#### **4 - Surface treatments**

##### **4 – 1 - Black gold**

**Black gold** is a type of gold used in jewelry . Black-colored gold can be produced by various methods :

Electroplating, using black rhodium or ruthenium . Solutions that contain ruthenium give a slightly harder black coating than those that contain rhodium .

Patination by applying sulfur - and oxygen - containing compounds.

Plasma - assisted chemical-vapor deposition process involving amorphous carbon

Controlled oxidation of gold containing chromium or cobalt ( e.g. 75 % gold, 25 % cobalt ) .

A range of colors from brown to black can be achieved on copper-rich alloys by treatment with potassium sulfide.

Cobalt - containing alloys, e.g. 75 % gold with 25 % cobalt, form a black oxide layer with heat treatment at 700 - 950 °C. Copper, iron and titanium can be also used for such effect. Gold-cobalt-chromium alloy ( 75 % gold , 15 % cobalt, 10 % chromium ) yields a surface oxide that's olive-tinted because of the chromium (III) oxide content, is about five times thinner than Au - Co and has significantly better wear resistance. The gold-cobalt alloy consists of gold-rich (about 94 % Au ) and cobalt - rich ( about 90 % Co) phases; the cobalt-rich phase grains are capable of oxide-layer formation on their surface.

More recently , black gold can be formed by creating nanostructures on the surface. A femtosecond laser pulse deforms the

surface of the metal, creating an immensely increased surface area which absorbs virtually all the light that falls on it, thus rendering it deep black , but this method is used in high technology applications rather than for appearance in jewelry.

#### **4 – 2 - Blue gold**

Oxide layers can also be used to obtain blue gold from an alloy of 75 % gold, 24.4 % iron , and 0.6% nickel; the layer forms on heat treatment in air between 450 – 600 °C.

A rich sapphire blue colored gold of 20 - 23K can also be obtained by alloying with ruthenium, rhodium and three other elements and heat-treating at 1800 °C, to form the 3 – 6 micrometers thick colored surface oxide layer.

## Gold Compounds Category

Auranofin

Aurothioglucose

Aurotioprol

Bromo ( tetra hydro thiophene ) gold (I)

Caesium Auride

Chloro ( dimethyl sulfide ) gold (I)

Chloro (tetra hydro thiophene ) gold (I)

Chloro Auric Acid

Disodium aurothiomalate

Gold Chalcogenides

Gold Cluster

Gold Halide

Gold Hepta Fluoride

Gold Mono Iodide

Gold Penta Fluoride

Gold Tri Iodide

Gold (I) Bromide

Gold (I) Chloride

Gold (I) Fluoride

Gold(I) Sulfide

Gold (I,III) Chloride

Gold (III) Bromide

Gold (III) Chloride

Gold (III) Fluoride

Gold (III) Hydroxide

Gold (III) Oxide

Sodium Auro Thio Malate

Sodium Auro Thio Sulfate

Tetra Bromo Auric Acid

Tetra Xenono Gold (II)

(2,4,6 -Tri Methyl Phenyl ) Gold

# Gold cyanidation

## Contents

- 1 Introduction
- 2 History
- 3 Chemical reactions
- 4 Application
  - 4.1 Effect of dissolved oxygen
  - 4.2 Pre-aeration and ore washing
- 5 Recovery of gold from cyanide solutions
- 6 Cyanide remediation processes
- 7 Effects on the environment
- 8 Alternatives to cyanide

## 1 - Introduction

**Gold cyanidation** ( also known as the **cyanide process** or the **MacArthur - Forrest process** ) is a metallurgical technique for extracting gold from low - grade ore by converting the gold to a water soluble coordination complex. It is the most commonly used process for gold extraction . Production of reagents for mineral processing to recover gold, copper, zinc and silver represents approximately 13 % of cyanide consumption globally, with the remaining 87 % of cyanide used in other industrial processes such as plastics, adhesives, and pesticides. Due to the highly poisonous nature of cyanide, the process is controversial and its usage is banned in a number of countries and territories.

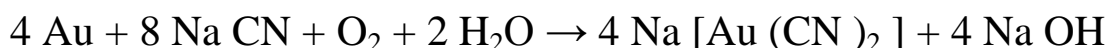
## 2 – History

In 1783, Carl Wilhelm Scheele discovered that gold dissolved in aqueous solutions of cyanide. He had earlier discovered cyanide salts . Through the work of Bagration ( 1844 ) , Elsner ( 1846 ) , and Faraday ( 1847 ) , it was determined that each atom of gold requires two cyanide, i.e. the stoichiometry of the soluble compound. Cyanide was not applied to extraction of gold ores until 1887, when the MacArthur - Forrest Process was developed in Glasgow, Scotland by John Stewart MacArthur, funded by the brothers Dr Robert and Dr William Forrest. In 1896, Bodländer confirmed that oxygen was

necessary, something that was doubted by MacArthur, and discovered that hydrogen peroxide was formed as an intermediate.

### 3 - Chemical reactions

The chemical reaction for the dissolution of gold, the "Elsner Equation", follows :



In this redox process, oxygen removes, via a two step reaction, one electron from each gold atom to form the complex  $\text{Au(CN)}_2^-$  ion.

### 4 – Application

The ore is comminuted using grinding machinery. Depending on the ore, it is sometimes further concentrated by froth flotation or by centrifugal ( gravity ) concentration. Water is added to produce a slurry or *pulp*. The alkaline ore slurry can be combined with a solution of sodium cyanide or potassium cyanide, however many operations utilize calcium cyanide, which is more cost effective.

To prevent the creation of toxic hydrogen cyanide during processing, lime ( calcium hydroxide ) or soda ( sodium hydroxide ) is added to the extracting solution to ensure that the acidity during cyanidation is maintained over pH 10.5 - strongly alkaline. Lead nitrate can improve gold leaching speed and quantity recovered, particularly in processing partially oxidized ores.

#### 4 – 1 - Effect of dissolved oxygen

Oxygen is one of the reagents consumed during cyanidation, and a deficiency in dissolved oxygen slows leaching rate. Air or pure oxygen gas can be purged through the pulp to maximize the dissolved oxygen concentration. Intimate oxygen - pulp contactors are used to increase the partial pressure of the oxygen in contact with the solution, thus raising the dissolved oxygen concentration much higher than the saturation level at atmospheric pressure. Oxygen can also be added by dosing the pulp with hydrogen peroxide solution.

## 4 – 2 – Pre - aeration and ore washing

In some ores , particularly those that are partially sulfidized , aeration ( prior to the introduction of cyanide ) of the ore in water at high pH can render elements such as iron and sulfur less reactive to cyanide, and therefore the gold cyanidation process more efficient. Specifically, the oxidation of iron to iron (III) oxide and subsequent precipitation as iron hydroxide minimizes loss of cyanide from the formation of ferrous cyanide complexes. The oxidation of sulfur compounds to sulfate ions avoids the consumption of cyanide to thio cyanate (  $\text{SCN}^-$  ) byproduct.

## 5 - Recovery of gold from cyanide solutions

In order of decreasing economic efficiency, the common processes for recovery of the solubilized gold from solution are (certain processes may be precluded from use by technical factors) :

- Carbon in pulp
- Electro winning
- Merrill - Crowe process

## 6 - Cyanide remediation processes

The various species of cyanide that remain in tails streams from gold plants are potentially toxic, and on some operations the waste streams are processed through a detoxification process prior to tails deposition. This reduces the concentrations of these cyanide compounds, but does not completely eliminate them from the stream. The two major processes utilized are the INCO - licenced process or the Caro's acid process. Both processes utilize oxidants to oxidize cyanide to cyanate , which is not as toxic as the cyanide ion, and which can then react to form carbonates and ammonia:



The Inco process can typically reduce cyanide concentrations to below 50 mg / L , while the Caro's acid process can reduce cyanide levels to between 10 and 50 mg / L , with the lower concentrations achievable in solution streams rather than slurries. Hydrogen peroxide

and alkaline chlorination can also be used, although these are typically less common.

One of the alternative oxidants for the degradation of cyanides that has been attracting industrial interest is Caro's acid – per oxo mono sulphuric acid (  $\text{H}_2\text{SO}_5$  ). Caro's acid converts cyanide to cyanate. Cyanate then hydrolyses in the water to ammonium and carbonate ions. The Caro's acid process is able to achieve discharge levels of WAD below 50 mg / L , which is generally suitable for discharge to tailings. Generally, the best application of this process is with tailings slurries containing low to moderate initial levels of cyanide and when treated cyanide levels of less than about 10 to 50 mg/L are required .

Over 90 mines worldwide now use an Inco  $\text{SO}_2$ /air detoxification circuit to convert cyanide to the much less toxic cyanate before waste is discharged to a tailings pond. Typically, this process blows compressed air through the tailings while adding sodium meta bisulfite which releases  $\text{SO}_2$ , lime to maintain the pH at around 8.5, and copper sulfate as a catalyst if there is insufficient copper in the ore extract. This procedure can reduce concentrations of "Weak Acid Dissociable" ( WAD ) cyanide to below the 10 ppm mandated by the EU's Mining Waste Directive. This level compares to the 66-81 ppm free cyanide and 500 - 1000 ppm total cyanide in the pond at Baia Mare. Remaining free cyanide degrades in the pond, while cyanate ions hydrolyze to ammonium. Recent studies show that residual cyanide trapped in the gold - mine tailings causes persistent release of toxic metals (e.g. mercury ) into the groundwater and surface water systems.

## **7 - Effects on the environment**

Despite being used in 90 % of gold production , gold cyanidation is controversial due to the toxic nature of cyanide. Although aqueous solutions of cyanide degrade rapidly in sunlight, the less-toxic products , such as cyanates and thio cyanates , may persist for some years. The famous disasters have killed few people — humans can be warned not to drink or go near polluted water — but cyanide spills can have a devastating effect on rivers, sometimes



killing everything for several miles downstream. However, the cyanide is soon washed out of river systems and, as long as organisms can migrate from unpolluted areas upstream, affected areas can soon be repopulated. According to Romanian authorities, in the Someş river below Baia Mare, the plankton returned to 60% of normal within 16 days of the spill, however the numbers were not confirmed by Hungary or Yugoslavia . Famous cyanide spills include :

Year	Mine	Country	Incident
1985-91	Summitville	US	Leakage from leach pad
1980s-present	Ok Tedi	Papua New Guinea	Unrestrained waste discharge
1995	Omai	Guyana	Collapse of tailings dam
1998	Kumtor	Kyrgyzstan	Truck drove over bridge
2000	Baia Mare	Romania	Collapse of containment dam
2000	Tolukuma	Papua New Guinea	Helicopter dropped crate into rainforest

Such spills have prompted fierce protests at new mines that involve use of cyanide, such as Roşia Montană in Romania, Lake Cowal in Australia, Pascua Lama in Chile, and Bukit Koman in Malaysia.

## 8 - Alternatives to cyanide

Although cyanide is cheap, effective, and biodegradable, its high toxicity has led to new methods for extracting gold using less toxic reagents. Other extractants have been examined including thiosulfate ( $S_2O_3^{2-}$ ), thio urea ( $SC(NH_2)_2$ ), iodine / iodide, ammonia, and alpha - cyclo dextrin. Challenges include reagent cost and the efficiency of gold recovery. Thio urea has been implemented commercially for ores containing stibnite.

# Gold Extraction

## Contents

- 1 Introduction
- 2 History
- 3 Types of ore
- 4 Concentration
- 5 Leaching
- 6 Refractory gold processes
- 7 Gold smelting
  - 7.1 History of smelting
  - 7.2 Mercury removal
  - 7.3 Iron removal
- 8 Gold refining and parting

## 1 - Introduction

**Gold extraction** or recovery from its ores may require a combination of comminution , mineral processing , hydro metallurgical , and pyro metallurgical processes to be performed on the ore .

Gold mining from alluvium ores was once achieved by techniques associated with placer mining such as simple gold panning and sluicing, resulting in direct recovery of small gold nuggets and flakes. Placer mining techniques since the mid to late 20th century have generally only been the practice of artisan miners. Hydraulic mining was used widely in the Californian gold rush, and involved breaking down alluvial deposits with high - pressure jets of water. Hard rock ores have formed the basis of the majority of commercial gold recovery operations since the middle of the 20th century where open pit and or sub - surface mining techniques are used.

Once the ore is mined it can be treated as a whole ore using a dump leaching or heap leaching processes. This is typical of low-grade, oxide deposits. Normally, the ore is crushed and agglomerated prior to heap leaching. High grade ores and ores resistant to cyanide leaching at coarse particle sizes, require further processing in order to recover the gold values. The processing techniques can include

grinding, concentration, roasting, and pressure oxidation prior to cyanidation.

## **2 – History**

According to de Lecerda and Salomons ( 1997 ) mercury was first in use for extraction at about 1000 BC., according to Meech and others ( 1998 ) , mercury was used in obtaining gold until the latter period of the first millennia . A technique known to Pliny the Elder was extraction by way of crushing, washing, and then applying heat, with the resultant material powdered .

The solubility of gold in a water and cyanide solution was known by 1783 (Scheele), by Bagration in 1843 and Elsner in 1846 who recognized the necessity of oxygen in the process, (a method of extraction by chlorination (Plattner) considered during 1848 proved uneconomical) this prior to the discovery of an economical method of treatment with potassium cyanide by J.S. MacArthur (with R. and, or, W. Forrest). Development of understanding from 1887 led to the discovery dated to 1888 (and elsewhere 1890) that is known as the *MacArthur-Forrest process*.

The method heap leaching was first proposed during 1969 by the United States of Americas' Bureau of Mines,<sup>[16]</sup> in use by the 1970s.

## **3 - Types of ore**

Gold occurs principally as a native metal, usually alloyed to a greater or lesser extent with silver ( as electrum ) , or sometimes with mercury ( as an amalgam ) . Native gold can occur as sizeable nuggets, as fine grains or flakes in alluvial deposits, or as grains or microscopic particles embedded in other rocks.

Ores in which gold occurs in chemical composition with other elements are comparatively rare. They include calaverite, sylvanite, nagyagite , petzite and krennerite.

## **4 – Concentration**

Gravity concentration has been historically the most important way of extracting the native metal using pans or washing tables. Amalgamation with mercury was used to enhance recovery, often by adding it directly to the riffle tables, and mercury is still widely used in small diggings across the world. However, froth flotation processes may also be used to concentrate the gold. In some cases, particularly when the gold is present in the ore as discrete coarse particles, a gravity concentrate can be directly smelted to form gold bars. In other cases, particularly when the gold is present in the ore as fine particles or is not sufficiently liberated from the host rock, the concentrates are treated with cyanide salts, a process known as cyanidation leaching, followed by recovery from the leach solution. Recovery from solution typically involves adsorption on activated carbon followed by solution concentration or stripping and or electro winning.

Froth flotation is usually applied when the gold present in an ore is closely associated with sulfide minerals such as pyrite or arsenopyrite, and when such sulfides are present in large quantities in the ore. In this case, concentration of the sulfides results in concentration of gold values. Generally, recovery of the gold from the sulfide concentrates requires further processing, usually by roasting or wet pressure oxidation. These pyro metallurgical or hydrometallurgical treatments are themselves usually followed by cyanidation and carbon adsorption techniques for final recovery of the gold.

Sometimes gold is present as a minor constituent in a base metal (e.g. copper) concentrate, and is recovered as a by-product during production of the base metal. For example, it can be recovered in the anode slime during the electro refining process.

## **5 – Leaching**

If the gold can not be concentrated for smelting , then it is leached by an aqueous solution :

The cyanide process is the industry standard.

Thio sulfate leaching has been proven to be effective on ores with high soluble copper values or ores which experience *preg-robbing*: the absorption by carbonaceous components which preferentially absorbs gold and gold-cyanide complexes.

Leaching, Bulk leach extractable gold or BLEG, is also a process that is used to test an area for gold concentrations where gold may not be immediately visible.

## **6 - Refractory gold processes**

A "refractory" gold ore is an ore that is naturally resistant to recovery by standard cyanidation and carbon adsorption processes. These refractory ores require pre - treatment in order for cyanidation to be effective in recovery of the gold. A refractory ore generally contains sulfide minerals, organic carbon, or both. Sulfide minerals often trap or occlude gold particles, making it difficult for the leach solution to complex with the gold. Organic carbon present in gold ore may adsorb dissolved gold - cyanide complexes in much the same way as activated carbon. This so - called "preg - robbing" carbon is washed away because it is significantly finer than the carbon recovery screens typically used to recover activated carbon.

Pre - treatment options for refractory ores include :

Roasting

Bio - oxidation

Pressure oxidation

Ultrafine grinding

The refractory ore treatment processes may be preceded by concentration ( usually sulfide flotation ) . Roasting is used to oxidize both the sulfur and organic carbon at high temperatures using air and/or oxygen. Bio - oxidation involves the use of bacteria that promote oxidation reactions in an aqueous environment. Pressure oxidation is an aqueous process for sulfur removal carried out in a continuous autoclave, operating at high pressures and somewhat elevated temperatures. Ultra fine grinding may be used when

liberation of gold particles from the surrounding mineral matrix is the primary refractory characteristic of the ore.

## **7 - Gold smelting**

### **7 – 1 - History of smelting**

The smelting of gold began sometime around 6000 - 3000 BC. According to one source the technique began to be in use in Mesopotamia or Syria.

In ancient Greece, Heraclitus wrote on the subject.<sup>[22]</sup>

### **7 – 2 - Mercury removal**

Mercury is a health hazard, especially when in gas form. To remove this hazard, before smelting, gold precipitates from electro winning or Merrill - Crowe processes are usually heated in a retort to recover any mercury present, that would otherwise cause health and environmental problems due to its release ( volatilization ) during smelting. The mercury present is not usually from the mercury amalgamation process that is no longer used by formal gold mining companies, but from mercury in the ore that has followed gold through the leaching and precipitation processes.

In the event that there are high levels of copper or silver present, leaching of the precipitate using nitric or sulfuric acids may be required.

### **7 – 3 - Iron removal**

Nitric acid or forced air oven oxidation can also be used to dissolve iron from the electro winning cathodes before smelting. Gravity concentrates can often contain high grinding steel contents, and so their removal using shaking tables or magnets is used before smelting. During smelting iron can be oxidized using niter . Excessive use of niter will corrode the smelting pot, increasing both maintenance costs and the risk of catastrophic leaks (known as *run-aways*, or holes in the pot through which the molten charge is lost).

## **8 - Gold refining and parting**

Gold parting is primarily the removing of silver from gold and therefore increasing the purity of gold. The parting of gold from silver has been done since ancient times starting in Lydia in the 6th century BC. Various techniques have been practiced; salt cementation from ancient times, parting using distilled mineral acids from medieval times, and in modern times using chlorination using the Miller process and electrolysis using the Wohlwill process.

## Gold - Filled Jewelry



**Gold-filled jewelry**, also known as "rolled gold" or "rolled gold plate" is composed of a solid layer of gold bonded with heat and pressure to a base metal such as brass. Some high quality gold-filled pieces have the same appearance as 14 karat ( 58 % ) gold. In the USA the quality of gold filled is defined by the Federal Trade Commission. If the gold layer is 10 kt fineness the minimum layer of karat gold in an item stamped GF must equal at least 1/10 the weight of the total item. If the gold layer is 12 kt or higher the minimum layer of karat gold in an item stamped GF must equal at least 1/20 the weight of the total item. The most common stamps found on gold-filled jewelry are 1 / 20 12 kt GF and 1 / 20 14kt GF. Also common is 1/10 10kt. Some products are made using sterling silver as the base, although this more expensive version is not common today.

"Double clad" gold - filled sheet is produced with 1 / 2 the thickness of gold on each side. 1 / 20 14 Kt double clad gold - filled has a layer on each side of 1 / 40 th 14 Kt making the total content of gold 1 / 20 . The thinner layer on each side does not wear as well as single clad gold - filled.



The Federal Trade Commission allows the use of "Rolled Gold Plate" or "R.G.P". on items with lower thicknesses of gold than are required for "gold - filled." A 12 kt gold layer that is 1 / 60 the weight of the total item is designated as 1 / 60 12 kt RGP. This lower quality does not wear as well as gold - filled items.

Gold - filled items, even with daily wear, can last five to 30 years but will eventually wear through. The gold layer on gold-plated jewelry varies greatly depending on manufacturer, so there is no single, simple comparison. Gold-filled items are 50 to 100,000 times thicker than regular gold plating, and 17 to 25,000 times thicker than heavy gold electroplate (sometimes stamped HGE or HGP — usually found on cubic zirconia "cocktail rings").

## Gold Glass

	
<p><i>Gold sandwich glass was also used for the gold tesserae used in Late Antique, Byzantine and medieval mosaics, as here in Hagia Sophia</i></p>	<p><i>Rather roughly trimmed Christian piece with Jonah and the Whale, 10.5 cm across, 4th century</i></p>

### Contents

- 1 Introduction
- 2 Technique
- 3 Grave-markers
- 4 Hellenistic period
- 5 Roman period
- 6 Iconography of the vessel bottoms

### 1 - Introduction

**Gold glass** or **gold sandwich glass** is a luxury form of glass where a decorative design in gold leaf is fused between two layers of glass. First found in Hellenistic Greece, it is especially characteristic of the Roman glass of the Late Empire in the 3rd and 4th century AD, where the gold decorated roundels of cups and other vessels were often cut out of the piece they had originally decorated and cemented to the walls of the catacombs of Rome as grave markers for the small recesses where bodies were buried. About 500 pieces of gold glass used in this way have been recovered.<sup>[2]</sup> Complete vessels are far rarer. Many show religious imagery from Christianity, traditional Greco-Roman religion and its various cultic developments, and in a few examples Judaism. Others show portraits of their owners, and the finest are "among the most vivid portraits to survive from Early Christian times. They stare out at us with an extraordinary stern and

melancholy intensity". From the 1st century AD the technique was also used for the gold colour in mosaics.

Various different techniques may sometimes also be described as "gold glass". Zwischen gold glass is very similar but the two layers of glass are cemented, not fused. It mostly comes from Germany and Bohemia from the 18th and 19th centuries. Verre églomisé properly covers a single layer of glass which is gilded ( or coated with other types of metal leaf ) on the back, as used in 19th century shop signs and the like. One process was revived by Jean - Baptise Glomy (1711–1786), hence the name. Both of these processes were also used in ancient times, and the German and French languages often use their native terms for what is called "gold glass" in English. Gold ruby glass or "cranberry glass" is actually red, coloured by the addition of gold oxide. **Gold - band glass** is another ancient technique covered below.

## 2 – Technique

The manufacturing process for gold glass was difficult and required great skill. For a Late Roman glass, first a small round flat disc, typically about three to five inches across, was cut away from a blown sphere with a flattened bottom, either made of coloured or plain glass. A piece of gold leaf was then glued to this with gum Arabic . The design was created by scraping away gold leaf. The main vessel, a cup or bowl, was formed by blowing and cutting, with a flat bottom the same size as the first disc. This was then heated again and carefully lowered onto the disc with the design, superimposing the flat bottom with the disc with the design so that they fused together. The complete vessel was then heated a final time to complete the fusing. Different accounts of different periods vary somewhat as to the precise sequence of stages and other details, but the process is essentially the same.

The larger Hellenistic glass bowls are thought to have been formed using moulds rather than blown, as the whole bowl is doubled and the inner and outer vessels must fit together exactly . Some of the finer later medallions seem to have been made as such from the

start, and some contain pigments other than the gold.<sup>[7]</sup> These smoother - edged medallions exploited the medium of glass as a matrix for portrait miniatures, and it has proved to be a very effective one, outlasting all alternatives except for precious metal and engraved gems. They were probably initially made to be hung for display, or set in jewellery in smaller examples like that of Gennadios, but were also used for funerary purposes, and often use a base of blue glass. They are a few Roman examples of vessels from Cologne of a different style where several of what have been called "sidewall blobs", small gold glass medallions about 2 – 3 cm across, with images, are fused into the walls of a vessel

Apart from roundels with figurative images the fused sandwich technique was used to create the tesserae for gold in mosaics, and for beads and the like. Gold glass tesserae, at least by Byzantine times, had a very thin top layer of glass, which was probably poured onto the lower glass with the gold leaf glued to it. Tesserae were made in blocks or "cakes" and then cut into cubes, which are relatively large in the case of gold back grounds. Gold backgrounds were laid over earth red or yellow ochre backgrounds which enhanced their visual effect. Most colours of tesserae seem to have been made locally to the mosaic, but there is some discussion as to whether this was true for gold glass ones. In the 11th century the relatively new Christian center of Kiev seems to have used gold tesserae made in Constantinople.

Roman gold glass beads were made by using an inner tube or rod to which the gold leaf was stuck. A larger tube was slid over that and the beads crimped off. Easily transported and very attractive, Roman gold glass beads have been found as far outside the Empire as the Wari - Bateshwar ruins in Bangladesh, and sites in China, Korea, Thailand and Malaysia.

**Gold - band glass** is a related Hellenistic and Roman technique, where strips of gold leaf, sandwiched between colour less glass, are used as part of the marbling effect in onyx glass. It is mostly found in small perfume bottles and the like.

### 3 – Grave – markers

	
<p><i>4th century married couple, inscribed "ΠΙΕ ΖΕΣΕΣ" ("Drink, may you live")</i></p>	<p><i>Dougga banquet scene, 3rd century</i></p>

The most common form of vessel in late Roman examples was a bowl or drinking cup, which are thought to have been originally family gifts for weddings, anniversaries, New Year, the various religious festivals and the like, in some cases perhaps presented at birth or Christian baptism. None of the type of gold glass vessels cut down as grave - markers has survived complete, though about 500 of the cut-off bottoms are known, but since so many have inscriptions encouraging the owner to drink, they are usually referred to as "cups" or "glasses". However Roman drinking cups and glasses were often very wide and shallow, though tall straight-sided or slightly flared shapes like modern tumblers are also found. A mosaic in the North African ruins of Dougga shows two hefty slaves pouring wine from *amphorae* into two shallow bowls held by slaves waiting on the banquet. The two *amphorae* are inscribed with "ΠΙΕ" and "ΣΗΧΗ" the Greek originals of the toasting formulae "pie zeses" ("Drink, may you live", discussed below) so common on Roman glasses, and it has been suggested that the mosaic shows the shape a complete cup would have had.

At what was probably a much later date, perhaps after decades of use, on the death of the owner the main vessel of undecorated glass was cut away and trimmed to leave only the gold glass roundel, which

was then used in the catacombs as a grave marker. Presumably in many cases the cup had already broken in the normal course of use, and the thick bottom with the decoration had been preserved for later use in this way. Bodies were buried in the catacombs in small recesses called *loculi*, stacked one above another mostly along narrow corridors hollowed out from the soft rock, and no doubt some form of marker was necessary for visitors to locate the right spot. They may also have functioned as a seal on the grave, as they were pressed into the mortar or stucco forming the final surface of the wall of the *loculus*; other classes of small decorative objects were also used in the same way. They may also have been regarded as capable of warding off evil spirits, especially in the later part of the period, when portraits of saints become most common. The very untidy trimming of many examples may be explained by this; an example in the Metropolitan Museum of Art is still attached to a chunk of mortar round much of its edge, showing that the mortar overlapped the edge of the glass. Rough edges would mostly have been hidden by the mortar and also provided a firmer key for the mortar to hold the glass in place (as it happens the edges of the New York piece are unusually neatly trimmed).

Many pieces of gold glass had portraits of private individuals, mostly married couples, who may have included the deceased, while others had portraits of religious figures such as saints, or religious symbols. This custom was followed by Christian, Jewish (13 identifiably Jewish examples are known) and pagan Romans. The different sets of imagery, apart from the increased number of private portraits, are typical of the paintings also found in the catacombs and other Early Christian art and its Jewish equivalent from the period. As Christian art developed in the late 4th and 5th centuries, its changes are reflected in the subjects and their treatment in gold glass, before the catacombs ceased to be used and the supply of examples ends.

#### **4 - Hellenistic period**

The technique was used in Hellenistic times, and Hellenistic examples are generally both more technically ambitious than Roman ones, with wide bowls or drinking cups decorated all round their

curved sides in gold glass, and executed with more artistry. The British Museum has a virtually complete bowl (broken but repaired) 19.3 cm wide and 11.4 cm high, one of two from a tomb in Canosa in Apulia dating to around 270 -160 BC. It has most of the interior very finely decorated with lotus and acanthus motifs, which are more typical of gold glass in this period than designs with human figures. There are a handful of other near complete examples, and rather more fragments. These pieces are usually assigned to Alexandria in Egypt, which is often seen as the originating centre for luxury Hellenistic glass, and is mentioned as the source of over-elaborate glass by the 1st century satirist Martial and other sources; one seems to show a Nilotic landscape, though this was a popular subject elsewhere. However fragments have been found when excavating a glass factory on Rhodes.<sup>[20]</sup> A description perhaps dating from the 270s BC (surviving in the works of the later writer Athenaeus) mentions two vessels that are *diachysa* ("with gold in it") and very likely made by this technique.

### **Roman period[edit]**

Gold glass mosaic tesserae begin to be used in domestic mosaics in the 1st century AD, with Rome apparently the first location. They continued to be used throughout the ancient and medieval periods into the modern day. By around 400 gold began to be used as the background colour for Christian religious mosaics, as it was throughout the Byzantine period.

The decorated late Roman pieces are usually assumed to have been made in and around Rome, especially in the case of portraits of residents there, but also in the Rhineland around Cologne and Augusta Treverorum , modern Trier, which was a center for other luxury glass products like cage cups. Alexandria is still thought to have been a major center, and from linguistic analysis of the inscriptions it has been suggested that the technique, and perhaps the actual artists and craftsmen, reached Rome and Germany from there. Yet it may just be a coincidence of survival that the other large body of "middle - class" portraiture from the period is the Fayum mummy portraits from Egypt . Apart from the Rhineland finds discussed



below, small numbers of cut - off vessel bases have been found in northern Italy and modern Hungary and Croatia.

The Gennadios medallion in New York, illustrated above, is a fine example of an Alexandrian portrait on blue glass, using a rather more complex technique and naturalistic style than most Roman examples, including painting onto the gold to create shading, and with the Greek inscription showing local dialect features. He had perhaps been given or commissioned the piece to celebrate victory in a musical competition . One of the most famous Alexandrian-style portrait medallions, with an inscription in Egyptian Greek, was later mounted in an Early Medieval *crux gemmata* in Brescia, in the mistaken belief that it showed the pious empress and Gothic queen Galla Placida (died 450) and her children ; in fact the knot in the central figure's dress may mark a devotee of Isis . This is one of a group of 14 pieces dating to the 3rd century AD, all individualized secular portraits of high quality. It is thought that the tiny detail of pieces such as these can only have been achieved using lenses.<sup>[29]</sup> Where the refined "Alexandrian" medallions, wherever they were actually produced, mostly have a simple thin gold line framing the subject, the Roman examples have a variety of heavier frames, often using two round borders, the style of which forms part of efforts to group them by workshop. The level of portraiture is rudimentary, with features, hairstyles and clothes all following stereotypical styles.

An "Alexander plate with hunting scene" in the Cleveland Museum of Art is, if genuine , a very rare example of a complete vessel decorated with gold glass, and comes from the upper elite of Roman society. It is a shallow bowl or plate 25.7 cm (10 1/8 inches) in diameter and 4.5 cm high. The decorated flat roundel in the centre takes about two thirds of the whole diameter. It shows a mounted huntsman with a spear pursuing two elk, while beneath his horse a huntsman on foot with a hound on a leash confronts a wild boar. The Latin inscription "ALEXANDER HOMO FELIX PIE ZESES CUM TUIS" means "Alexander fortunate man, drink, may you live, together with yours". The identity of "Alexander" has been the subject of discussion, but he is on the whole thought to be an unknown aristocrat



rather than Alexander the Great or the Emperor Alexander Severus (reigned 232-235). The dish is perhaps slightly later than his reign and at least during his reign he could never be addressed as merely a "man" . The Greek drinking toast ZHCAIC given in Latin letters as ZESES, meaning "live!" or "may you live", is a very common part of inscriptions on gold glass , and sometimes the only inscription.<sup>[35]</sup> It is more common than the Latin equivalent VIVAS, probably because it was considered more refined, somewhat like the modern "bon appétit" used in English. Two glasses including images of Jesus "misspell" "ZESES" as "ZESUS", managing to achieve wordplay between a drinking toast and the name of the Christian saviour.<sup>[36]</sup>

Such secular "blessings" are typical, and on roundels made from cups they often urge the owner to drink, even when the iconography is religious. One Jewish example has the usual array of symbols and the inscription "Drink, [so] you may live, Elares". The Wedding at Cana is a popular Christian subject, with one example inscribed "Worthy of your friends, may you live in the peace of God, drink".<sup>[37]</sup> Another popular phrase is DIGNITAS AMICORUM or "[you are] the honour of your friends" . The majority of inscriptions are made up of either names or such conventional expressions, or the two combined. An example inscribed "DIGNITAS AMICORVM PIE ZESES VIVAS" typifies the tendency to pile together the common phrases.

One round bottom from a larger bowl found in the catacombs is 10.8 cm across, and now in the Ashmolean Museum in Oxford. It has five abbreviated scenes from the Old and New Testaments surrounding a married couple in a roundel, with the feet of the outer figures to the center . A large and complex bowl from Cologne was decorated all over with Christian scenes and Imperial portraits, but presumably because of its size ( height 8.6, diameter 11.4 cm ) no second layer of glass was fused on, so the gold has now all been lost, though the shapes of the design can be seen. The portraits of the sons of Constantine I allow an unusually precise probable dating to 326, his *vicennalia*, or the 25th anniversary of his reign . Another complete piece is a paten from the Basilica of St. Severin, Cologne, founded in the 4th century. This is decorated with roundels containing

Old Testament scenes and floral motifs. According to the *Liber Pontificalis*, Pope Zephyrinus, in office from 199-217, had approved the use of glass patens, and ones in other glass techniques survive. A variant technique is only known from vessels from Cologne with what have been called "sidewall blobs", where small gold glass medallions with images are fused into the walls of a vessel; one of the few examples was found in the cemetery of St Severin.

## 6 - Iconography of the vessel bottoms

Almost all the Roman vessel bottoms have imagery of some sort, and around 240 have legible inscriptions as well. Of these, about half of the total number of gold glasses known, portraits are most common, but there are small narrative scenes, mainly Christian but a few pagan. Portraits of Christian sacred figures are on about half the full corpus. There are a small number of depictions of sports, animals, wreaths and the like, and a single example with a central image of a plant. No Imperial portraits are recorded, nor military scenes; unlike so much Roman public art the glasses concentrate on the private interests of individuals. Apart from a single near-naked Venus and some figures of erotes, sexual themes are another notable absence compared to much Roman art. Most glasses feature a single image occupying most of the round space within the border, but some have a number of small scenes, usually arranged in small circular frames around a central image. Most portraits are between bust and half-length. The small number of glasses with Jewish iconography are covered separately below.

Either portraits or inscriptions naming private individuals are very common, though other examples have no personalizing aspect and were perhaps just bought from a dealer's stock.<sup>[48]</sup> Portraits of married couples are at first most the common, but saints were more numerous towards the end of the period; the two are also often combined.<sup>[49]</sup> It is not always possible to distinguish the two confidently, despite *tituli* inscriptions and a convention of using contemporary dress for owners and a conventional out of date costume for sacred figures, even recent male ones such as Pope Damasus I (r. 366 – 384). Damasus, exceptionally for a

contemporary cleric, appears on at least four glasses, or at least it is thought he is who "DAMAS" refers to.

Saints Peter and Paul together are very common, usually facing each other in profile, but sometimes with other figures. Both were martyred in Rome, and especially popular there ; other local martyrs such as Agnes are depicted several times , and according to Lucy Grig "the *Roman - ness* of the saints portrayed on the Roman glasses is striking", and five popes from the 3rd and 4th centuries are probably depicted . Christ is shown in a number of examples, usually as clean-shaven and youthful, as well as figures such as the Good Shepherd which may symbolize him, or in some cases Orpheus or general bucolic imagery. A small Christ may stand between the heads of a married couple, blessing them . Orants perhaps representing the soul of an owner when not identified as a saint, and as in the catacombs always shown as female, appear a number of times, and female saints and the Virgin are always shown in the orant pose.

Narrative scenes from the Old Testament are more common than miracles of Christ, as in the catacomb paintings, and the same "abbreviated representations" of scenes of deliverance feature: the story of Jonah, Daniel in the lions' den, the three youths in the Fiery Furnace.<sup>[56]</sup> The most common scenes in later Christian art, centred around the liturgical calendar, are very rare. There are really only two non-Christian narrative scenes: one labour of Hercules ( two more are shown in "sidewall blobs" ) , and one of Achilles, but a number of "portrait" figures, as with Christian sacred figures often combined with owners.

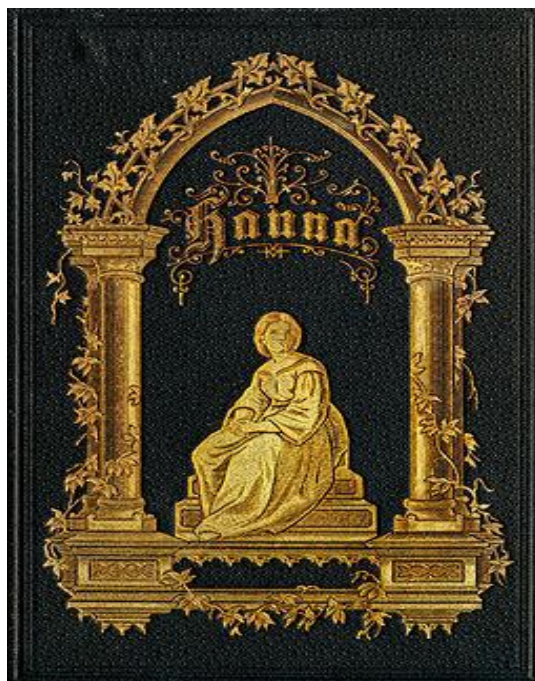
There are a small number of "agonistic" or sporting scenes, with wrestlers, boxers, one gladiator, and several racing chariot teams. Several of these, like others seeming to represent victory in a musical or dramatic context, feature palms and crowns and may well have been presented to celebrate victory in these fields in some amateur or professional setting, like the Alexandrian Gennadios portrait. Two identical glasses featuring two boxers with a trainer, all named, suggest that the glasses may sometimes have been ordered in sets; one may speculate that this may have been common.<sup>[58]</sup> Single examples

show Athena presiding over shipbuilders, a pair of personifications of Rome and Constantinople, and female figures representing the *monetae* or mints, which are often shown on coins. A number have animals that may carry symbolic meaning, or objects such as scrolls or wreaths.

The short inscriptions tend to be similar regardless of the content of the image, with names and the "convivial formulae" described above together or separately predominating. A religious implication (as may be intended in *vivas* or *zeses* for example) is relatively rarely explicitly stated. The names are in the single *cognomen* form which is hard to relate to such records as survive, but three glasses can possibly be related to known individuals who were potential owners, and one to a family ( that of the poet Ausonius ).

These persons are rather grand, and one might think belonged to the classes buried in sarcophagi rather than *loculi*; the glasses perhaps belonged to "*amici*", clients or dependents, or had passed as gifts or legacies by the subjects. One glass in the British Museum is unusual in a number of respects: between a named couple is a smaller figure of Hercules, and the inscription: "ORFITVS ET CONSTANTIA IN NOMINE HERCVLIS ACERENTINO FELICES BIBATIS" or "Orfitus and Constantia, may you live/drink in happiness in the name of Hercules of Acerentia". This may well represent Memmius Vitruvius Orfitus, prefect of Rome, and his wife. Acerentia in southern Italy had a local cult of Hercules.<sup>[64]</sup> For some historians Orfitus was "notorious as the propaganda mastermind of the 'pagan revival'" of his day.

# Gold Leaf



*Early 20th century leather book cover, with gold leaf ornamentation.*

## Contents

- 1 Introduction
- 2 In art
- 3 Culinary uses

## 1 - Introduction

**Gold leaf** is gold that has been hammered into extremely thin sheets by goldbeating and is often used for gilding. Gold leaf is available in a wide variety of karats and shades. The most commonly used gold is 22 - karat yellow gold.

Gold leaf is sometimes confused with metal leaf but they are different products. The term *metal leaf* is normally used for thin sheets of metal of any color that do not contain any real gold. Pure gold is 24 karats. Real yellow gold leaf is about 91 % pure gold. Silver colored white gold is approximately 50 % pure gold.

Layering gold leaf over a surface is called **gold leafing** or gilding. Traditional water gilding is the most difficult and highly

regarded form of gold leafing. It has remained virtually unchanged for hundreds of years and is still done by hand.

## 2 - In art



*22k gold leaf applied with an ox hair brush  
during the process of gilding*

Gold leaf is sometimes used in art in a "raw" state, without a gilding process. In cultures including the European Bronze Age it was used to wrap objects such as bullae simply by folding it tightly over, and the Classical group of gold lunulae are so thin, especially in the center, that they might be classed as gold leaf. It has been used in jewellery in various periods, often as small pieces hanging freely.

Gold leaf has traditionally been most popular and most common in its use as gilding material for decoration of art (including statues and Eastern Christian icons) or the picture frames that are often used to hold or decorate paintings, mixed media, small objects (including jewelry) and paper art. Gold glass is gold leaf held between two pieces of glass, and was used for decorated Ancient Roman vessels, where some of the gold was scraped off to form an image, as well as tesserae gold mosaics. "Gold - ground" paintings, where the back ground of the figures was all in gold, was introduced in mosaics in later Early Christian art, and then used in icons and Western panel paintings until the late Middle Ages; all techniques use gold leaf. Gold leaf is also used in Buddhist art to decorate statues and symbols. Gold leafing can also be seen on domes in religious and public architecture. "Gold" frames made without leafing are also available for a considerably lower price, but traditionally some form of gold or

metal leaf was preferred when possible and gold leafed (or silver leafed) moulding is still commonly available from many of the companies that produce commercially - available moulding for use as picture frames.

### 3 - Culinary uses

Gold leaf ( as well as other Metal leaf such as Vark ) is sometimes used to decorate food or drink, typically to promote a perception of luxury and high value; however, it is flavorless.<sup>[1]</sup> It is occasionally found in desserts and confectionery, including chocolates and *mithai*. In India it may be used effectively as a garnish, with thin sheets placed on a main dish, especially on festive occasions. When used as an additive to food, gold has the E-number E175.





*Austrian Liquor with gold leaves*

In Continental Europe liquors with tiny floating pieces of gold leaf are known of since the late 16th century; originally the practice was regarded as medicinal. Well-known examples are Danziger Goldwasser, originally from Gdańsk, Poland, which has been produced since at least 1598, Gold strike from Amsterdam, and the Swiss Gold schläger, which is perhaps the best known in the United States.



# Gold Mining

	
<i>Gold-bearing quartz veins in Alaska</i>	<i>The Super Pit gold mine in Australia</i>

## Contents

- 1 Introduction
- 2 History
- 3 Methods
  - 3.1 Placer mining
    - 3.1.1 Panning
    - 3.1.2 Sluicing
    - 3.1.3 Dredging
    - 3.1.4 Rocker box
  - 3.2 Hard rock mining
  - 3.3 By product gold mining
- 4 Gold ore processing
  - 4.1 Cyanide process
- 5 Business
  - 5.1 Small operations
  - 5.2 Large companies

## 1 - Introduction

Gold mining is the process of mining of gold or gold ores from the ground. There are several techniques and processes by which gold may be extracted from the earth.



## 2 – History



*Annual world production of mined gold, 1940 - 2012*

It is impossible to know the exact date that humans first began to mine gold, but some of the oldest known gold artifacts were found in the Varna Necropolis in Bulgaria. The graves of the necropolis were built between 4700 and 4200 BC, indicating that gold mining could be at least 7000 years old . A group of German and Georgian archaeologists claim the Sakdrisi site in southern Georgia, dating to the 3rd or 4th millennium BC, may be the world's oldest known gold mine.

Bronze age gold objects are plentiful, especially in Ireland and Spain, and there are several well known possible sources. Romans used hydraulic mining methods , such as hushing and ground sluicing on a large scale to extract gold from extensive alluvial deposits, such as those at Las Medulas. Mining was under the control of the state but the mines may have been leased to civilian contractors some time later. The gold served as the primary medium of exchange within the empire, and was an important motive in the Roman invasion of Britain by Claudius in the first century AD, although there is only one known Roman gold mine at Dolaucothi in west Wales. Gold was a prime motivation for the campaign in Dacia when the Romans invaded Transylvania in what is now modern Romania in the second century AD. The legions were led by the emperor Trajan, and their exploits are shown on Trajan's Column in Rome and the several reproductions of the column elsewhere ( such as the Victoria and Albert Museum in London ) . Under the Eastern Roman Empire

Emperor Justinian's rule, gold was mined in the Balkans, Anatolia, Armenia, Egypt, and Nubia.

In the area of the Kolar Gold Fields in Bangarpet Taluk, Kolar District of Karnataka state, India, gold was first mined prior to the 2nd and 3rd century AD by digging small pits. (Golden objects found in Harappa and Mohenjo - daro have been traced to Kolar through the analysis of impurities — the impurities include 11% silver concentration, found only in KGF ore ) , The Champion reef at the Kolar gold fields was mined to a depth of 50 meters during the Gupta period in the fifth century AD. During the Chola period in the 9th and 10th century AD, the scale of the operation grew . The metal continued to be mined by the eleventh century kings of South India, the Vijayanagara Empire from 1336 to 1560, and later by Tipu Sultan, the king of Mysore state and the British. It is estimated that the total gold production in Karnataka to date is 1000 tons .

The mining of the Slovak deposit primarily around Kremnica was the largest of the Medieval period in Europe.

During the 19th century, numerous gold rushes in remote regions around the globe caused large migrations of miners, such as the California Gold Rush of 1849, the Victorian Gold Rush, and the Klondike Gold Rush. The discovery of gold in the Witwatersrand led to the Second Boer War and ultimately the founding of South Africa.

The Carlin Trend of Nevada, U.S., was discovered in 1961. Official estimates indicate that total world gold production since the beginning of civilization has been 4,970,000,000 troy ounces (155,000 t) and total Nevada production is three percent of that, which ranks Nevada as one of the Earth's primary gold producing regions.

### **3 – Methods**

#### **3 – 1 - Placer mining**

Placer mining is the technique by which gold that has accumulated in a placer deposit is extracted. Placer deposits are composed of relatively loose material that makes tunneling difficult,

and so most means of extracting it involve the use of water or dredging.

### **3 – 1 – 1 – Panning**



*Gold in a pan—Alaska*

Gold panning is mostly a manual technique of separating gold from other materials. Wide, shallow pans are filled with sand and gravel that may contain gold. The pan is submerged in water and shaken, sorting the gold from the gravel and other material. As gold is much denser than rock, it quickly settles to the bottom of the pan. The panning material is usually removed from stream beds, often at the inside turn in the stream, or from the bedrock shelf of the stream, where the density of gold allows it to concentrate, a type called placer deposits.

Gold panning is the easiest and quickest technique for searching for gold, but is not commercially viable for extracting gold from large deposits, except where labor costs are very low or gold traces are substantial. Panning is often marketed as a tourist attraction on former gold fields. Before large production methods are used, a new source must be identified and panning is useful to identify placer gold deposits to be evaluated for commercial viability.

### **3 – 1 – 2 – Sluicing**

Using a sluice box to extract gold from placer deposits has long been a very common practice in prospecting and small - scale mining.

A sluice box is essentially a man made channel with riffles set in the bottom. The riffles are designed to create dead zones in the current to allow gold to drop out of suspension. The box is placed in the stream to channel water flow. Gold - bearing material is placed at the top of the box. The material is carried by the current through the volt where gold and other dense material settles out behind the riffles. Less dense material flows out of the box as tailings.



*Taking gold out of a sluice box, western North America, 1900s*

Larger commercial placer mining operations employ screening plants , or trommels , to remove the larger alluvial materials such as boulders and gravel, before concentrating the remainder in a sluice box or jig plant. These operations typically include diesel powered, earth moving equipment, including excavators, bulldozers, wheel loaders, and rock trucks.

### **3 – 1 – 3 – Dredging**

Although this method has largely been replaced by modern methods, some dredging is done by small-scale miners using suction dredges. These are small machines that float on the water and are usually operated by one or two people. A suction dredge consists of a sluice box supported by pontoons, attached to a suction hose which is controlled by a miner working beneath the water.

State dredging permits in many of the United States gold dredging areas specify a seasonal time period and area closures to avoid conflicts between dredgers and the spawning time of fish

populations. Some states, such as Montana, require an extensive permitting procedure, including permits from the U.S. Corps of Engineers, the Montana Department of Environmental Quality, and the local county water quality boards.

Some large suction dredges ( 100 horse power ( 75 kW ) & 250 mm ) are used in commercial production throughout the world. Small suction dredges are much more efficient at extracting smaller gold than the old *bucket line*. This has improved the chances of finding gold. Smaller dredges with 50 – to – 100 - millimeter suction tubes are used to sample areas behind boulders and along potential pay streaks, until "color" ( gold ) appears.

Other larger scale dredging operations take place on exposed river gravel bars at seasonal low water. These operations typically use a land based excavator to feed a gravel screening plant and sluice box floating in a temporary pond. The pond is excavated in the gravel bar and filled from the natural water table. "Pay" gravel is excavated from the front face of the pond and processed through the floating plant, with the gold trapped in the onboard sluice box and tailings stacked behind the plant, steadily filling in the back of the pond as the operation moves forward. This type of gold mining is characterized by its low cost, as each rock is moved only once. It also has low environmental impact, as no stripping of vegetation or overburden is necessary, and all process water is fully recycled. Such operations are typical on New Zealand's South Island and in the Klondike region of Canada.

### **3 – 1 – 4 – Rocker box**

The rocker box, also called a cradle, uses a riffles located in a high-walled box to trap gold in a similar manner to the sluice box. A rocker box uses less water than a sluice box and is thus well suited for areas where water is limited. A rocking motion provides the water movement needed for the gravity separation of gold in placer material.

### **3 – 2 – Hard rock mining**



*Hard rock mining at the Associated Gold Mine,  
Kalgoorlie , Australia, 1951*

Hard rock gold mining extracts gold encased in rock, rather than fragments in loose sediment, and produces most of the world's gold. Sometimes open-pit mining is used, such as at the Fort Knox Mine in central Alaska. Barrick Gold Corporation has one of the largest open-pit gold mines in North America located on its Gold strike mine property in northeastern Nevada. Other gold mines use underground mining, where the ore is extracted through tunnels or shafts. South Africa has the world's deepest hard rock gold mine up to 3,900 meters under ground. At such depths, the heat is unbearable for humans, and air conditioning is required for the safety of the workers. The first such mine to receive air conditioning was Robinson Deep, at that time the deepest mine in the world for any mineral.

### **3 – 3 – By product gold mining**

Gold is also produced by mining in which it is not the principal product. Large copper mines, such as the Bingham Canyon mine in Utah, often recover considerable amounts of gold and other metals along with copper. Some sand and gravel pits, such as those around Denver, Colorado, may recover small amounts of gold in their washing operations. The largest producing gold mine in the world, the Grasberg mine in Papua, Indonesia, is primarily a copper mine.

## **4 - Gold ore processing**

In placer mines, the gold is recovered by gravity separation. For hard rock mining, other methods are usually used.<sup>[citation needed]</sup>

### **4 – 1 - Cyanide process**

Cyanide extraction of gold may be used in areas where fine gold-bearing rocks are found. Sodium cyanide solution is mixed with finely ground rock that is proven to contain gold or silver, and is then separated from the ground rock as gold cyanide or silver cyanide solution. Zinc is added to precipitate out residual zinc as well as the silver and gold metals. The zinc is removed with sulfuric acid, leaving a silver or gold sludge that is generally smelted into an ingot then shipped to a metals refinery for final processing into 99.9999% pure metals.

Advancements in the 1970s have seen activated carbon used in extracting gold from the leach solution. The gold is absorbed into the porous matrix of the carbon. Activated carbon has so much internal surface area , that fifteen grams ( half an ounce ) has the equivalent surface area of the Melbourne Cricket Ground (18,100 square meters ) The gold can be removed from the carbon by using a strong solution of caustic soda and cyanide, a process known as elution. Gold is then plated out onto steel wool through electro winning. Gold specific resins can also be used in place of activated carbon, or where selective separation of gold from copper or other dissolved metals is required.

The technique using dissolution with alkaline cyanide has been highly developed over recent years. It is particularly appropriate for low grade gold and silver ore processing ( e.g. less than 5 ppm gold) but its use is not restricted to such ores. There are many environmental hazards associated with this extraction method, largely due to the high acute toxicity of the cyanide compounds involved. A major example of this hazard was demonstrated in the 2000 Baia Mare cyanide spill, when a break in holding pond dam at a mine waste reprocessing facility near Baia Mare in northern Romania released approximately 100,000 cubic meters of waste water contaminated with heavy metal sludge and up to 120 tons of cyanide

into the Tisza River.<sup>[9]</sup> As a consequence, most countries now have strict regulations for cyanide in plant discharges, and plants today include a specific cyanide - destruction step before discharging their tailings to a storage facility.

## **5 – Business**

### **5 – 1 - Small operations**



*Woman panning for gold in Guinea*

While most of the gold is produced by major corporations, tens of thousands of people work independently in smaller, artisan operations, in some cases illegally. In Ghana, for instance, the *galamseys* are estimated to number 20,000 to 50,000 . In neighboring francophone countries, such workers are called *orpailleurs*. In Brazil, such workers are called *garimpeiros*.

The high risk of such ventures was seen in the collapse of an illegal mine at Dompase, Ashanti Region, Ghana, on 12 November 2009, when 18 workers were killed, including 13 women. Many women work at such mines as porters. It was the worst mining disaster in Ghanaian history.

In order to maximize gold extraction, mercury is often used to amalgamate with the metal. The gold is produced by boiling away the mercury from the amalgam, a hazardous process due to toxicity of mercury vapour. Mercury is effective in extracting very small gold particles, but should be reclaimed, instead, in an effective and safe process.





## **5 – 2 - Large companies**

Barrick Gold , Gold corp , Newmont Mining Corporation, Newcrest Mining, and AngloGold Ashanti are the world's five largest gold mining companies by market capitalization in 2008.

\

\

# Gold Plating

	
<p><i>Gold - plated electrical connectors</i></p>	<p><i>A gold plated desktop Stirling engine</i></p>

## Contents

- 1 Introduction
- 2 Gold plating types
- 3 Gold plating chemistry
- 4 Jewellery
- 5 Electronics
- 6 Soldering issues

## 1 - Introduction

**Gold Plating** is a method of depositing a thin layer of gold onto the surface of another metal, most often copper or silver (to make silver-gilt), by chemical or electrochemical plating. This article covers plating methods used in the modern electronics industry; for more traditional methods, often used for much larger objects, see gilding .

## 2 - Gold plating types

There are several types of gold plating used in the electronics industry :

**Soft , pure gold plating** is used in the semiconductor industry. The gold layer is easily soldered and wire bonded. Its Knoop hardness ranges between 60 - 85. The plating baths have to be kept free of contamination.

**Bright hard gold on contacts**, with Knoop hardness between 120-300 and purity of 99.7 - 99.9 % gold. Often contains a small amount of nickel and/or cobalt; these elements interfere with die bonding, therefore the plating baths cannot be used for semi conductors.

**Bright hard gold on printed circuit board tabs** is deposited using lower concentration of gold in the baths. Usually contains nickel and/or cobalt as well. Edge connectors are often made by controlled-depth immersion of only the edge of the boards.

**Soft , pure gold** is deposited from special electrolytes. Entire printed circuit boards can be plated. This technology can be used for depositing layers suitable for wire bonding.

### **3 - Gold plating chemistry**

There are five recognized classes of gold plating chemistry:

Alkaline gold cyanide, for gold and gold alloy plating

Neutral gold cyanide, for high - purity plating

Acid gold plating for bright hard gold and gold alloy plating

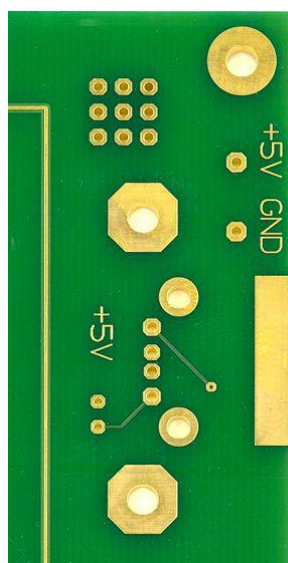
Non - cyanide, generally sulfite or chloride-based for gold and gold alloy plating

Miscellaneous

### **4 – Jewellery**

Gold plating of silver is used in the manufacture of jewellery. Like copper, silver atoms diffuse into the gold layer, causing slow gradual fading of its colour and eventually causing tarnishing of the surface. This process may take months and even years, depending on the thickness of the gold layer. A barrier metal layer is used to counter this effect. Copper, which also migrates into gold, does so more slowly than silver. The copper is usually further plated with nickel. A gold-plated silver article is usually a silver substrate with layers of copper, nickel, and gold deposited on top of it.

## 5 - Electronics



*Gold - plated printed circuit board*

Gold plating is often used in electronics, to provide a corrosion-resistant electrically conductive layer on copper, typically in electrical connectors and printed circuit boards.

With direct gold - on - copper plating, the copper atoms tend to diffuse through the gold layer, causing tarnishing of its surface and formation of an oxide and/or sulfide layer.

A layer of a suitable barrier metal, usually nickel, is often deposited on the copper substrate before the gold plating. The layer of nickel provides mechanical backing for the gold layer, improving its wear resistance. It also reduces the impact of pores present in the gold layer.

Both the nickel and gold layers can be plated by electrolytic or electroless processes. There are many factors to consider in selection of either electrolytic or electroless plating methods. These include what the deposit will be used for, configuration of the part, materials compatibility and cost of processing. In different applications, electrolytic or electroless plating can have cost advantages.

At higher frequencies, the skin effect may cause higher losses due to higher electrical resistance of nickel ; a nickel - plated trace can

have its useful length shortened three times in the 1 GHz band in comparison with the non - plated one. Selective plating is used, depositing the nickel and gold layers only on areas where it is required and does not cause the detrimental side effects.

Gold plating may lead to formation of gold whiskers.

Wire bonding between gold plated contacts and Aluminum wires or between Aluminum contacts and gold wires under certain conditions develops a brittle layer of gold - Aluminum inter metallica, known as purple plague.

## **6 - Soldering issues**

Soldering gold - plated parts can be problematic as gold is soluble in solder. Solder which contains more than 4 - 5 % gold can become brittle. The joint surface is dull - looking.

Gold reacts with both tin and lead in their liquid state, forming brittle inter metallica. When eutectic 63 % tin – 37 % lead solder is used, no lead - gold compounds are formed, because gold preferentially reacts with tin, forming the  $\text{Au Sn}_4$  compound. Particles of  $\text{AuSn}_4$  disperse in the solder matrix, forming preferential cleavage planes, significantly lowering the mechanical strength and therefore reliability of the resulting solder joints.

If the gold layer does not completely dissolve into the solder, then slow intermetallic reactions can proceed in the solid state as the tin and gold atoms cross - migrate. Inter metallica have poor electrical conductivity and low strength. The ongoing inter metallic reactions also cause Kirkendall effect, leading to mechanical failure of the joint, similar to the degradation of gold- Aluminum bonds known as purple plague.

A 2 - 3  $\mu\text{m}$  layer of gold dissolves completely within one second during typical wave soldering conditions . Layers of gold thinner than 0.5  $\mu\text{m}$  ( 0.02 thou ) also dissolve completely into the solder, exposing the underlying metal ( usually nickel ) to the solder. Impurities in the nickel layer can prevent the solder from bonding to

it. Electro less nickel plating contains phosphorus. Nickel with more than 8 % phosphorus is not solder able . Electrodeposited nickel may contain nickel hydroxide. An acid bath is required to remove the passivation layer before applying the gold layer; improper cleaning leads to a nickel surface difficult to solder. A stronger flux can help, as it aids dissolving the oxide deposits. Carbon is another nickel contaminant that hinders solder ability.

## Goloid

**Goloid** is an alloy of silver, gold and copper patented by Dr. William Wheeler Hubbell on May 22, 1877 ( U.S. patent #191,146 ). The patent specifies 1 part gold ( about 3.6% ), 24 parts silver (about 87.3 % ) , and 2.5 parts copper ( about 9.1% , all by weight ) ; however, the patent also states that "The proportions may be slightly varied" and goes on to specify that the silver portion can range from 20 times to 30 times that of the gold, and the copper could range from one - eighth to one - twelfth ( from 12.5 % to 8.33 %) of the total mixture. The patent specifies that the metals be separately melted, then mixed, along with "sulfate of sodium or sulfate of potassium" in the amount of one part sulfate to one thousand parts metal. The alloy, in varying proportions ( some times slightly out of these specifications ) , was used by the United States Mint to strike pattern dollars, sometimes called "metric dollars" (some were marked with "metric" in the coin design, while all had metal proportions and total coin weight as design features ) from 1878 to 1880. Patterns of the same design were struck in other metals, including aluminum, copper, normal coin silver, lead, and white metal.

In the end, goloid was rejected as a coinage metal because it could not be distinguished from the normal U.S. 90 % silver coin alloy without chemical analysis, thus inviting counterfeiters to use silver - copper alloys alone to make lower - value copies.

## Metal Leaf

**Metal leaf**, also called **composition leaf** or **schlag metal** , is a thin foil used for decoration. Metal leaf can come in many different shades. Some metal leaf may look like gold leaf but not contain any real gold. This metal leaf is often referred to as **imitation leaf**.

Metal leaf is usually made of gold (including many alloys), silver, copper, aluminum, brass ( some times called " Dutch metal" typically 85 % Copper and 15 % zinc ) or palladium , some times also platinum.

**Vark** is a type of silver leaf used for decoration in Indian cuisine.

Gold beating, the technique of producing metal leaf, has been known for more than 5,000 years.



## Miller Process

The **Miller process** is an industrial - scale chemical procedure used to refine gold to a high degree of purity ( 99.95 % ) . It was invented by Francis Bowyer Miller. This chemical process involves blowing a stream of pure chlorine gas over and through a crucible filled with molten, but impure , gold. This process purifies the gold because nearly all other elements will form chlorides before gold does, and they can then be removed as salts that are insoluble in the molten metal.

When all impurities have been removed from the gold (observable by a change in flame color) the gold is removed and processed in the manner required for sale or use. The resulting gold is 99.95% pure, but of lower purity than gold produced by the other common refining method, the Wohlwill process, which produces gold to 99.999 % purity.

The Miller process is commonly used for producing high-purity gold, such as in electronics work and the manufacture of some silicates, where exacting standards of purity are not required. When highest purity gold is not required, refiners often utilize the Miller process due to its relative ease, quicker turnaround times, and because it does not tie up the large amount of gold in the form of chloroauric acid which the Wohlwill process permanently requires for the electrolyte.

## Mosaic Gold



*The Angel of Life by Giovanni Segantini. This work uses bronze powder, along with other media on paper.*

**Mosaic gold** or **bronze powder** refers to tin (IV) sulfide as used as a pigment in bronzing and gilding wood and metal work. It is obtained as a yellow scaly crystalline powder. The alchemists referred to it as aurum musivum , or aurum mosaicum . The term mosaic gold has also been used to refer to ormolu and to cut shapes of gold leaf, some darkened for contrast, arranged as a mosaic. The term bronze powder may also refer to powdered bronze alloy.

Alchemists prepared this by combining mercury, tin, sal ammoniac, and sublimated sulfur ( fleur de soufre ) , grinding, mixing, then setting them for three hours in a sand heat. The dirty sublimate being taken off, aurum mosaicum was found at the bottom of the matrass. It was recommended in most chronic and nervous cases, and particularly convulsions of children ; however, it is no longer recommended for any medical uses.

# Tumbaga



*A pectoral of tumbaga, of the Quimbaya culture; 300 – 1600 AD.*

## Contents

- 1 Introduction
- 2 Composition and properties
- 3 Use and function
- 4 The "Tumbaga" Wreck

### 1 - Introduction

**Tumbaga** was the name given by Spaniards to a non-specific alloy of gold and copper which they found in wide spread use in pre - Columbian Mesoamerica and South America.

### 2 - Composition and properties

Tumbaga is an alloy composed mostly of gold and copper. It has a significantly lower melting point than gold or copper alone. It is harder than copper, but maintains malleability after being pounded.

Tumbaga can be treated with a simple acid, like citric acid, to dissolve copper off the surface. What remains is a shiny layer of nearly pure gold on top of a harder, more durable copper - gold alloy sheet. This process is referred to as depletion gilding.

### 3 - Use and function

Tumbaga was widely used by the pre - Columbian cultures of Central America to make religious objects. Like most gold alloys,

tumbaga was versatile and could be cast, drawn, hammered, gilded, soldered, welded, plated, hardened, annealed, polished, engraved, embossed, and inlaid.

The proportion of gold to copper in artifacts varies widely; items have been found with as much as 97 % gold while others instead contain 97 % copper. Some tumbaga has also been found to be composed of metals besides gold and copper, up to 18% of the total mass of the tumbaga.

Tumbaga objects were often made using the lost wax technique and the alloy used was a mixture of copper (80 % ) , silver ( 15 % ) , and gold ( 5 % ) . The indicated concentrations varied from object to object. Once the object was taken out of the cast, it was burned and as a consequence, copper from the surface of the object was oxidized to copper oxide and was then removed mechanically. The object was then placed in an oxidizing solution containing, it is believed, sodium chloride (salt), and ferric sulfate. This process removed through oxidation the silver from the surface of the object leaving only gold. When looking through a microscope, one may clearly see the empty spots from where the original elements copper and silver were removed .

#### **4 - The " Tumbaga " Wreck**

In 1992, approximately 200 silver "tumbaga" bars were recovered in wreckage off Grand Bahama Island. They were composed of mainly silver, copper, and gold plundered by the Spaniards during the conquests of Cortés and hastily melted into bars of tumbaga for transport across the Atlantic. Because all the metals that reached Europe were melted back into their constituent metals in Spain, the bars found in the shipwreck are the only known bars of this type that remain.

# **Part Three :**

# **Silver**



# Silver ( Ag )

Cu

↑

Ag

↓

Au

## Contents

- 1 Introduction
- 2 Characteristics
- 3 Isotopes
- 4 Compounds
- 5 Applications
  - 5.1 Currency
  - 5.2 Jewelry and silverware
  - 5.3 Dentistry
  - 5.4 Photography and electronics
  - 5.5 Mirrors and optics
  - 5.6 Other industrial and commercial applications
  - 5.7 Biology
  - 5.8 Medicine
  - 5.9 Investing
  - 5.10 Clothing
- 6 History
  - 6.1 World War II
- 7 Occurrence and extraction
- 8 Price
- 9 Human exposure and consumption
  - 9.1 Monitoring exposure
  - 9.2 Use in food

## 1 - Introduction

Silver is a chemical element with the chemical symbol Ag (Greek : *árgyros*, Latin: *argentum*, both from the Indo - European root \* *arg* - for " grey " or " shining " ) and atomic number 47. A soft,

white, lustrous transition metal, it possesses the highest electrical conductivity of any element and the highest thermal conductivity of any metal. The metal occurs naturally in its pure, free form ( native silver ) , as an alloy with gold and other metals, and in minerals such as argentite and chlor argyrite . Most silver is produced as a byproduct of copper, gold, lead, and zinc refining.

Silver has long been valued as a precious metal, used in currency coins, to make ornaments, jewelry, high-value tableware and utensils ( hence the term silverware ) and as an investment in the forms of coins and bullion. Silver metal is used industrially in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions. Its compounds are used in photographic film and dilute silver nitrate solutions and other silver compounds are used as disinfectants and micro biocides ( oligo dynamic effect ) . While many medical antimicrobial uses of silver have been supplanted by antibiotics , further research into clinical potential continues.

Name, symbol, number	silver, Ag, 47
Element category	transition metal
Group, period, block	11, 5, d
Standard atomic weight	107.8682
Electron configuration	2 , 8 , 18 , 18 , 1
Phase	solid
Density (near r.t.)	10.49 g·cm <sup>-3</sup>
Liquid density at m.p.	9.320 g·cm <sup>-3</sup>
Melting point	961.78 °C,
Boiling point	2162 °C
Heat of fusion	11.28 kJ·mol <sup>-1</sup>
Heat of vaporization	254 kJ·mol <sup>-1</sup>
Molar heat capacity	25.350 J·mol <sup>-1</sup> ·K <sup>-1</sup>
Oxidation states	1, 2, 3 (amphoteric oxide)



Electro negativity	1.93 (Pauling scale)
Ionization energies	1 <sup>st</sup> : 731.0 kJ·mol <sup>-1</sup>
	2 <sup>nd</sup> : 2070 kJ·mol <sup>-1</sup>
	3 <sup>rd</sup> : 3361 kJ·mol <sup>-1</sup>
Electrical resistivity	(20 °C ) 15.87 n Ω·m
Thermal conductivity	429 W·m <sup>-1</sup> ·K <sup>-1</sup>
Thermal diffusivity	(300 K) 174 mm <sup>2</sup> /s
Thermal expansion	(25 °C) 18.9 μm·m <sup>-1</sup> ·K <sup>-1</sup>
Speed of sound (thin rod)	(r.t.) 2680 m·s <sup>-1</sup>
Mohs hardness	2.5
Discovery	before 5000 BC

## 2 – Characteristics

Silver is produced from lighter elements in the Universe through the r-process, a form of nuclear fusion believed to take place during certain types of supernova explosions. This produces many elements heavier than iron, of which silver is one.

Silver is a very ductile, malleable ( slightly harder than gold ) , monovalent coinage metal, with a brilliant white metallic luster that can take a high degree of polish. It has the highest electrical conductivity of all metals, even higher than copper, but its greater cost has prevented it from being widely used in place of copper for electrical purposes. An exception to this is in radio-frequency engineering, particularly at VHF and higher frequencies, where silver plating to improve electrical conductivity of parts, including wires, is widely employed. During World War II in the US, 13,540 tons were used in the electromagnets used for enriching uranium, mainly because of the wartime shortage of copper.

Among metals, pure silver has the highest thermal conductivity (the nonmetal carbon in the form of diamond and superfluid helium II are higher) and one of the highest optical reflectivities . ( Aluminum slightly outdoes silver in parts of the visible spectrum, and silver is a

poor reflector of ultraviolet). Silver is the best conductor of heat and electricity of any metal on the periodic table. Silver also has the lowest contact resistance of any metal. Silver halides are photosensitive and are remarkable for their ability to record a latent image that can later be developed chemically. Silver is stable in pure air and water, but tarnishes when it is exposed to air or water containing ozone or hydrogen sulfide, the latter forming a black layer of silver sulfide which can be cleaned off with dilute hydrochloric acid.<sup>[7]</sup> The most common oxidation state of silver is +1 (for example, silver nitrate,  $\text{AgNO}_3$ ); the less common +2 compounds (for example, silver (II) fluoride,  $\text{AgF}_2$ ), and the even less common +3 (for example, potassium tetra fluoro argentate (III),  $\text{KAgF}_4$ ) and even +4 compounds (for example, potassium hexa fluoro argentate (IV),  $\text{K}_2\text{AgF}_6$ ) are also known.

### 3 – Isotopes

Naturally occurring silver is composed of two stable isotopes,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , with  $^{107}\text{Ag}$  being slightly more abundant (51.839 % natural abundance). Silver's isotopes are almost equal in abundance, something which is rare in the periodic table. Silver's atomic weight is 107.8682 g N/ mol.

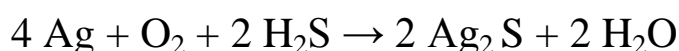
Twenty - eight radioisotopes have been characterized, the most stable being  $^{105}\text{Ag}$  with a half-life of 41.29 days,  $^{111}\text{Ag}$  with a half-life of 7.45 days, and  $^{112}\text{Ag}$  with a half-life of 3.13 hours. This element has numerous meta states, the most stable being  $^{108\text{m}}\text{Ag}$  ( $t_{1/2} = 418$  years),  $^{110\text{m}}\text{Ag}$  ( $t_{1/2} = 249.79$  days) and  $^{106\text{m}}\text{Ag}$  ( $t_{1/2} = 8.28$  days). All of the remaining radioactive isotopes have half-lives of less than an hour, and the majority of these have half-lives of less than three minutes.

Isotopes of silver range in relative atomic mass from 93.943 ( $^{94}\text{Ag}$ ) to 126.936 ( $^{127}\text{Ag}$ ); the primary decay mode before the most abundant stable isotope,  $^{107}\text{Ag}$ , is electron capture and the primary mode after is beta decay. The primary decay products before  $^{107}\text{Ag}$  are palladium (element 46) isotopes, and the primary products after are cadmium (element 48) isotopes.

The palladium isotope  $^{107}\text{Pd}$  decays by beta emission to  $^{107}\text{Ag}$  with a half-life of 6.5 million years. Iron meteorites are the only objects with a high-enough palladium – to – silver ratio to yield measurable variations in  $^{107}\text{Ag}$  abundance. Radiogenic  $^{107}\text{Ag}$  was first discovered in the Santa Clara meteorite in 1978. The discoverers suggest the coalescence and differentiation of iron – cored small planets may have occurred 10 million years after a nucleosynthetic event.  $^{107}\text{Pd} - ^{107}\text{Ag}$  correlations observed in bodies that have clearly been melted since the accretion of the solar system must reflect the presence of unstable nuclides in the early solar system.

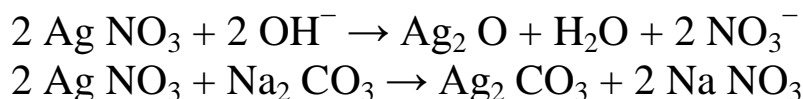
#### 4 – Compounds

Silver metal dissolves readily in nitric acid ( $\text{HNO}_3$ ) to produce silver nitrate ( $\text{AgNO}_3$ ), a transparent crystalline solid that is photosensitive and readily soluble in water. Silver nitrate is used as the starting point for the synthesis of many other silver compounds, as an antiseptic, and as a yellow stain for glass in stained glass. Silver metal does not react with sulfuric acid, which is used in jewelry-making to clean and remove copper oxide fire scale from silver articles after silver soldering or annealing. Silver reacts readily with sulfur or hydrogen sulfide  $\text{H}_2\text{S}$  to produce silver sulfide, a dark-colored compound familiar as the tarnish on silver coins and other objects. Silver sulfide  $\text{Ag}_2\text{S}$  also forms silver whiskers when silver electrical contacts are used in an atmosphere rich in hydrogen sulfide.



Silver chloride (  $\text{AgCl}$  ) is precipitated from solutions of silver nitrate in the presence of chloride ions, and the other silver halides used in the manufacture of photographic emulsions are made in the same way, using bromide or iodide salts. Silver chloride is used in glass electrodes for pH testing and potentiometric measurement, and as a transparent cement for glass. Silver iodide has been used in attempts to seed clouds to produce rain.<sup>[7]</sup> Silver halides are highly insoluble in aqueous solutions and are used in gravimetric analytical methods.

Silver oxide ( Ag O ) , produced when silver nitrate solutions are treated with a base, is used as a positive electrode (anode) in watch batteries. Silver carbonate ( $\text{Ag}_2\text{CO}_3$ ) is precipitated when silver nitrate is treated with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).



Silver fulminate ( Ag O N C ) , a powerful, touch - sensitive explosive used in percussion caps, is made by reaction of silver metal with nitric acid in the presence of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ). Other dangerously explosive silver compounds are silver azide ( $\text{AgN}_3$ ), formed by reaction of silver nitrate with sodium azide ( $\text{NaN}_3$ ) , and silver acetylide, formed when silver reacts with acetylene gas.

Latent images formed in silver halide crystals are developed by treatment with alkaline solutions of reducing agents such as hydro quinone, metol (4- (methyl amino)phenol sulfate) or ascorbate , which reduce the exposed halide to silver metal. Alkaline solutions of silver nitrate can be reduced to silver metal by reducing sugars such as glucose, and this reaction is used to silver glass mirrors and the interior of glass Christmas ornaments. Silver halides are soluble in solutions of sodium thiosulfate (  $\text{Na}_2 \text{ S}_2 \text{ O}_3$  ) which is used as a photographic fixer, to remove excess silver halide from photographic emulsions after image development.

Silver metal is attacked by strong oxidizers such as potassium permanganate (  $\text{K Mn O}_4$  ) and potassium dichromate (  $\text{K}_2 \text{ Cr}_2 \text{ O}_7$  ), and in the presence of potassium bromide (K Br); these compounds are used in photography to bleach silver images, converting them to silver halides that can either be fixed with thiosulfate or redeveloped to intensify the original image. Silver forms cyanide complexes (silver cyanide) that are soluble in water in the presence of an excess of cyanide ions. Silver cyanide solutions are used in electro plating of silver.

Although silver normally has oxidation state +1 in compounds, other oxidation states are known , such as +3 in  $\text{Ag F}_3$ , produced by

the reaction of elemental silver or silver fluoride with krypton di fluoride.

Silver artifacts primarily under go three forms of deterioration. Silver sulfide is the most common form of silver degradation. Silver chloride is purple to silvery - yellow colored, and projects slightly from the surface of the artifact or coin. The precipitation of copper in ancient silver can be used to date artifacts.

## **5 – Applications**

Many well - known uses of silver involve its precious metal properties, including currency, decorative items, and mirrors. The contrast between its bright white color and other media makes it very useful to the visual arts. It has also long been used to confer high monetary value as objects ( such as silver coins and investment bars ) or make objects symbolic of high social or political rank. Silver salts have been used since the Middle Ages to produce a yellow or orange colors to stained glass, and more complex decorative color reactions can be produced by incorporating silver metal in blown, kilnformed or torchworked glass.

### **5 – 1 – Currency**

Silver, in the form of electrum ( a gold – silver alloy ), was coined to produce money around 700 BC by the Lydians. Later, silver was refined and coined in its pure form. Many nations used silver as the basic unit of monetary value. In the modern world, silver bullion has the ISO currency code XAG. The name of the pound sterling (£) reflects the fact it originally represented the value of one pound Tower weight of sterling silver; other historical currencies, such as the French livre, have similar etymologies. During the 19th century, the bimetallism that prevailed in most countries was undermined by the discovery of large deposits of silver in the Americas; fearing a sharp decrease in the value of silver and thus the currency, most states switched to a gold standard by 1900. In some languages, such as Sanskrit, Spanish, French, and Hebrew, the same word means both silver and money.

The 20 th century saw a gradual movement to fiat currency, with most of the world monetary system losing its link to precious metals after Richard Nixon took the United States dollar off the gold standard in 1971; the last currency backed by gold was the Swiss franc, which became a pure fiat currency on 1 May 2000. During this same period, silver gradually ceased to be used in circulating coins. In 1964, the United States stopped minting their silver dime and quarter. They minted their last circulating silver coin in 1970 in its 40% half-dollar.

In 1968, Canada minted their last circulating silver coins which were the 50% dime and the 50 % quarter. The Royal Canadian Mint still makes many collectible silver coins with various dollar denominations. In addition to Canada, the United States and many other countries continue to mint silver coins that are collected for their bullion and numismatic value. The U.S. coin is known as the "Eagle".

Silver is used as a currency by many individuals, and is legal tender in the US state of Utah . Silver coins and bullion are also used as an investment to guard against inflation and devaluation.

## **5 – 2 - Jewelry and silver ware**



*Silver plate with goddess Minerva from the Hildesheim Treasure,  
1st century BC*

Jewelry and silverware are traditionally made from sterling silver (standard silver), an alloy of 92.5 % silver with 7.5 % copper. In the US, only an alloy consisting of at least 90.0 % fine silver can be marketed as "silver" (thus frequently stamped 900 ) . Sterling silver (stamped 925) is harder than pure silver, and has a lower melting

point ( 893°C ) than either pure silver or pure copper . Britannia silver is an alternative, hallmark - quality standard containing 95.8 % silver, often used to make silver tableware and wrought plate. With the addition of germanium, the patented modified alloy Argentium Sterling silver is formed, with improved properties, including resistance to fire scale.

Sterling silver jewelry is often plated with a thin coat of .999 fine silver to give the item a shiny finish. This process is called "flashing". Silver jewelry can also be plated with rhodium (for a bright, shiny look) or gold ( to produce silver gilt ) .

Silver is a constituent of almost all colored carat gold alloys and carat gold solders, giving the alloys paler color and greater hardness. White 9 carat gold contains 62.5 % silver and 37.5 % gold, while 22 carat gold contains a minimum of 91.7 % gold and 8.3% silver or copper or other metals.

Historically, the training and guild organization of goldsmiths included silversmiths, as well, and the two crafts remain largely overlapping. Unlike blacksmiths, silversmiths do not shape the metal while it is red - hot, but instead, work it at room temperature with gentle and carefully placed hammer blows. The essence of silversmithing is to take a flat piece of metal and to transform it into a useful object using different hammers, stakes and other simple tools.

While silversmiths specialize in, and principally work silver, they also work with other metals, such as gold, copper, steel, and brass. They make jewelry, silverware, armor, vases, and other artistic items. Because silver is such a malleable metal, silversmiths have a large range of choices with how they prefer to work the metal. Historically, silversmiths are mostly referred to as goldsmiths, which was usually the same guild. In the western Canadian silversmith tradition, guilds do not exist; however, mentoring through colleagues becomes a method of professional learning within a community of crafts people.

Traditionally, silversmiths mostly made "silverware" ( cutlery, tableware, bowls, candlesticks and such ) . Only in more recent times has silver smithing become mainly work in jewelry, as much less solid silver tableware is now handmade.

### **5 – 3 – Dentistry**

Silver can be alloyed with mercury at room temperature to make amalgams that are widely used for dental fillings. To make dental amalgam, a mixture of powdered silver and other metals such as tin and gold is mixed with mercury to make a stiff paste that can be adapted to the shape of a cavity. The dental amalgam achieves initial hardness within minutes, and sets hard in a few hours.

### **5 – 4 - Photography and electronics**

Photography used 30.98 % of the silver consumed in 1998 in the form of silver nitrate and silver halides. In 2001, 23.47 % was used for photography, while 20.03 % was used in jewelry, 38.51 % for industrial uses, and only 3.5 % for coins and medals. The use of silver in photography has rapidly declined, due to the lower demand for consumer color film from the advent of digital technology; since 2007, of the 907 million ounces of silver in supply, just 117.6 million ounces ( 13 % ) were consumed by the photographic sector, about 50 % of the amount used in photography in 1998. By 2010, the supply had increased by about 10 % to 1056.8 million ounces, of which 72.7 million ounces were used in the photographic sector, a decline of 38% compared with 2007.

Some electrical and electronic products use silver for its superior conductivity, even when tarnished. The primary example of this is in high quality RF connectors. The increase in conductivity is also taken advantage of in RF engineering at VHF and higher frequencies, where conductors often cannot be scaled by 6 %, due to tuning requirements, e.g. cavity filters. As an additional example, printed circuits and RFID antennas can be made using silver paints , and computer keyboards use silver electrical contacts. Silver cadmium oxide is used in high-voltage contacts because it can withstand arcing.



Some manufacturers produce audio connector cables, speaker wires, and power cables using silver conductors, which have a 6% higher conductivity than ordinary copper ones of identical dimensions, but cost much more. Though debatable, many hi-fi enthusiasts believe silver wires improve sound quality .

Small devices, such as hearing aids and watches, commonly use silver oxide batteries due to their long life and high energy-to-weight ratio. Another usage is high - capacity silver-zinc and silver-cadmium batteries.

### **5 – 5 - Mirrors and optics**

Mirrors which need superior reflectivity for visible light are commonly made with silver as the reflecting material in a process called silvering, though common mirrors are backed with Aluminum. Using a process called sputtering, silver, along with other optically transparent layers, is applied to glass, creating low emissivity coatings used in high - performance insulated glazing. The amount of silver used per window is small because the silver layer is only 10–15 nanometers thick . However, the amount of silver - coated glass worldwide is hundreds of millions of square meters per year, leading to silver consumption on the order of 10 cubic meters or 100 metric tons/year. Silver color seen in architectural glass and tinted windows on vehicles is produced by sputtered chrome, stainless steel or other alloys. Silver is seldom used as the reflector in telescope mirrors, where aluminum is generally preferred because it is cheaper and less susceptible to tarnishing and corrosion . Silver is the reflective coating of choice for solar reflectors.

### **5 – 6 - Other industrial and commercial applications**

Silver and silver alloys are used in the construction of high-quality musical wind instruments of many types. Flutes , in particular, are commonly constructed of silver alloy or silver plated, both for appearance and for the frictional surface properties of silver.

Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions, for example, the production of formaldehyde

from methanol and air by means of silver screens or crystallites containing a minimum 99.95 weight - percent silver. Silver ( upon some suitable support ) is probably the only catalyst available today to convert ethylene to ethylene oxide ( later hydrolyzed to ethylene glycol, used for making polyesters ) — an important industrial reaction. It is also used in the Oddy test to detect reduced sulfur compounds and carbonyl sulfides.

Because silver readily absorbs free neutrons, it is commonly used to make control rods to regulate the fission chain reaction in pressurized water nuclear reactors, generally in the form of an alloy containing 80 % silver, 15 % indium, and 5 % cadmium.

Silver is used to make solder and brazing alloys, and as a thin layer on bearing surfaces can provide a significant increase in galling resistance and reduce wear under heavy load, particularly against steel.

### **5 – 7 – Biology**

Silver stains are used in biology to increase the contrast and visibility of cells and organelles in microscopy. Camillo Golgi used silver stains to study cells of the nervous system and the Golgi apparatus.<sup>[31]</sup> Silver stains are used to stain proteins in gel electrophoresis and polyacrylamide gels, either as primary stains or to enhance the visibility and contrast of colloidal gold stain.<sup>[32]</sup> Different yeasts from Brazilian gold mines, bio accumulate free and complexed silver ions. A sample of the fungus *Aspergillus niger* was found growing from gold mining solution; and was found to contain cyano metal complexes; such as gold, silver, copper iron and zinc. The fungus also plays a role in the solubilization of heavy metal sulfides.

### **5 – 8 – Medicine**

The medical uses of silver include its incorporation into wound dressings, and its use as an antibiotic coating in medical devices. Wound dressings containing silver sulfadiazine or silver nano materials may be used to treat external infections. Silver is also used in some medical applications, such as urinary catheters and

endotracheal breathing tubes, where there is tentative evidence that it is effective in reducing catheter-related urinary tract infections and ventilator - associated pneumonia respectively . The silver ion (  $\text{Ag}^+$  ) is bioactive and in sufficient concentration readily kills bacteria *in vitro*. Silver and silver nanoparticles are used as an antimicrobial in a variety of industrial, healthcare and domestic applications.

### **5 – 9 - Investing[edit]**

Silver coins and bullion are used for investing. Mints sell a wide variety of silver products for investors and collectors. Various institutions provide safe storage for large physical silver investments, and various types of silver investments can be made on the stock markets, including mining stocks. Silver bullion bars are sold in a wide range of ounces, provided by various mints and mines around the world. Silver coins and bullion bars are generally 99.9 % pure, and labeled with ".999".

### **5 – 10 – Clothing**

Silver inhibits the growth of bacteria and fungi on clothing, such as socks, so is some times added to reduce odors and the risk of bacterial and fungal infections. It is incorporated into clothing or shoes either by integrating silver nanoparticles into the polymer from which yarns are made or by coating yarns with silver . The loss of silver during washing varies between textile technologies , and the resultant effect on the environment is not yet fully known.

## **6 – History**



*The crescent moon  
has been used since ancient times to represent silver.*

Silver has been used for thousands of years for ornaments and utensils, trade, and as the basis for many monetary systems. Its value as a precious metal was long considered second only to gold. The

word "silver" appears in Anglo - Saxon in various spellings, such as *seolfor* and *siolfor*. A similar form is seen throughout the Germanic languages ( compare Old High German *silabar* and *silbir* ). The chemical symbol Ag is from the Latin word for "silver", *argentum* (compare Greek *árgyros* ) , from the Indo - European root *\*arg-*, meaning "white" or "shining". Silver has been known since ancient times. Mentioned in the Book of Genesis, slag heaps found in Asia Minor and on the islands of the Aegean Sea indicate silver was being separated from lead as early as the 4th millennium BC using surface mining.

The stability of the Roman currency relied to a high degree on the supply of silver bullion, which Roman miners produced on a scale unparalleled before the discovery of the New World. Reaching a peak production of 200 t per year, an estimated silver stock of 10,000 t circulated in the Roman economy in the middle of the second century AD, five to ten times larger than the combined amount of silver available to medieval Europe and the Caliphate around 800 AD.<sup>[42][43]</sup> Financial officials of the Roman Empire worried about the loss of silver to pay for highly demanded silk from Sinica (China).

In the Gospels, Jesus' disciple Judas Iscariot is infamous for having taken a bribe of 30 coins of silver from religious leaders in Jerusalem to turn Jesus of Nazareth over to soldiers of the High Priest Caiaphas.

The Chinese Empire during most of its history primarily used silver as a means of exchange. In the 19th century, the threat to the balance of payments of the United Kingdom from Chinese merchants demanding payment in silver in exchange for tea, silk, and porcelain led to the Opium War because Britain had to find a way to address the imbalance in payments, and they decided to do so by selling opium produced in their colony of British India to China.

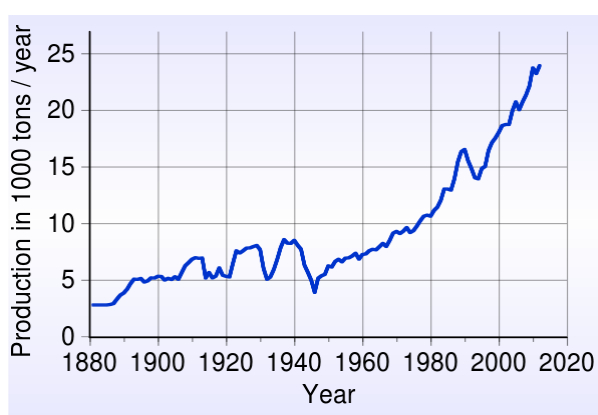
In certain circumstances, Islam permits Muslim men to wear silver jewelry. Muhammad himself wore a silver signet ring.

In the Americas, high temperature silver - lead cupellation technology was developed by pre - Inca civilizations as early as AD 60 – 120.

### 6 – 1 - World War II

During World War II, the short supply of copper led to the substitution of silver in many industrial applications. The United States government loaned out silver from its massive reserve located in the West Point vaults to a wide range of industrial users. One very important use was for bus bars for new aluminum plants needed to make aircraft. During the war, many electrical connectors and switches were silver plated. Another use was aircraft master rod bearings and other types of bearings. Since silver can replace tin in solder at a lower volume, a large amount of tin was freed up for other uses by substituting government silver. Silver was also used as the reflector in searchlights and other types of lights. One high-tech use of silver was for conductors at Oak Ridge National Laboratory used in calutrons to isolate uranium as part of the Manhattan project. (After the war ended, the silver was returned to the vaults.)<sup>[49]</sup> Silver was used in nickels during the war to save that metal for use in steel alloys.

## 7 - Occurrence and extraction



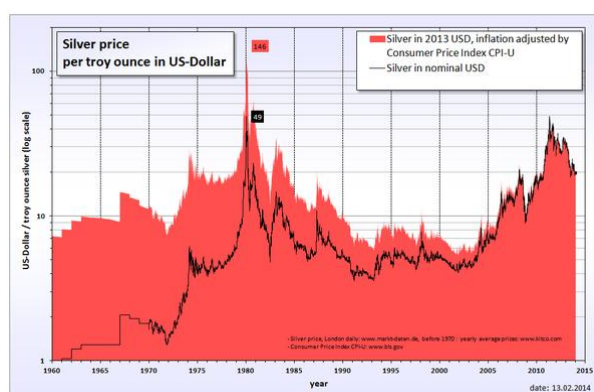
*Time trend of silver production*

Silver is found in native form, as an alloy with gold (electrum), and in ores containing sulfur, arsenic, antimony or chlorine. Ores include argentite (  $\text{Ag}_2\text{S}$  ), chlor argyrite (  $\text{AgCl}$  ) which includes

horn silver, and pyrargyrite (  $\text{Ag}_3\text{SbS}_3$  ) . The principal sources of silver are the ores of copper, copper - nickel, lead, and lead-zinc obtained from Peru, Bolivia, Mexico, China, Australia, Chile, Poland and Serbia.<sup>[7]</sup> Peru, Bolivia and Mexico have been mining silver since 1546, and are still major world producers. Top silver-producing mines are Cannington (Australia), Fresnillo (Mexico), San Cristobal (Bolivia), Antamina (Peru), Rudna (Poland), and Penasquito (Mexico) . Top near-term mine development projects through 2015 are Pascua Lama (Chile), Navidad (Argentina), Jaunicipio (Mexico), Malku Khota (Bolivia) , and Hackett River (Canada). In Central Asia, Tajikistan is known to have some of the largest silver deposits in the world.

The metal is primarily produced as a byproduct of electrolytic copper refining, gold, nickel, and zinc refining, and by application of the Parkes process on lead metal obtained from lead ores that contain small amounts of silver. Commercial - grade fine silver is at least 99.9% pure, and purities greater than 99.999 % are available. In 2011, Mexico was the top producer of silver ( 4,500 tones or 19 % of the world's total ), closely followed by Peru (4,000 t) and China (4,000 t).

## 8 – Price



*Silver price history in 1960 – 2011*

As of 26 August 2013, the price of silver is US \$ 773 per kilogram ( US \$ 24.04 per troy ounce ) . This equates to approximately 1 / 58 the price of gold. The ratio has varied from 1 / 15 to 1 / 100 in the past 100 years . Physical silver bullion prices are

higher than the paper prices, with premiums increasing when demand is high and local shortages occur.

In 1980, the silver price rose to a peak for modern times of US \$ 49.45 per troy ounce (ozt) due to market manipulation of Nelson Bunker Hunt and Herbert Hunt. Inflation-adjusted to 2012, this is approximately US \$ 138 per troy ounce. Some time after Silver Thursday, the price was back to \$ 10 / ozt. From 2001 to 2010, the price moved from \$ 4.37 to \$ 20.19 (average London US\$/oz).<sup>[58]</sup> According to the Silver Institute, silver's recent gains have greatly stemmed from a rise in investor interest and an increase in fabrication demand. In late April 2011, silver reached an all - time high of \$ 49.76 / ozt.

In earlier times, silver has commanded much higher prices. In the early 15th century, the price of silver is estimated to have surpassed \$1,200 per ounce, based on 2011 dollars . The discovery of massive silver deposits in the New World during the succeeding centuries has been stated as a cause for its price to have diminished greatly.

The price of silver is important in Judaic law. The lowest fiscal amount a Jewish court, or Beth Din, can convene to adjudicate a case over is a *shova pruta* (value of a Babylonian *pruta* coin) . This is fixed at .025 grams ( 0.00088 oz ) of pure, unrefined silver, at market price. In a Jewish tradition, still continuing today, on the first birthday of a first - born son , the parents pay the price of five pure-silver coins to a *Kohen* (priest). Today, the Israel mint fixes the coins at 117 grams (4.1 oz) of silver. The *Kohen* will often give those silver coins back as a gift for the child to inherit.

## **9 - Human exposure and consumption**

Silver plays no known natural biological role in humans, and possible health effects of silver are a disputed subject. Silver itself is not toxic to humans, but most silver salts are. In large doses, silver and compounds containing it can be absorbed into the circulatory system and become deposited in various body tissues, leading to

argyria, which results in a blue - grayish pigmentation of the skin, eyes, and mucous membranes. Argyria is rare, and although, so far as known, this condition does not otherwise harm a person's health, it is disfiguring and usually permanent. Mild forms of Argyria are sometimes mistaken for cyanosis.

### **9 – 1 - Monitoring exposure**

Over exposure to silver can occur in workers in the metallurgical industry, persons taking silver - containing dietary supplements , patients who have received silver sulfadiazine treatment , and individuals who accidentally or intentionally ingest silver salts. Silver concentrations in whole blood, plasma, serum, or urine may be measured to monitor for safety in exposed workers, to confirm the diagnosis in potential poisoning victims, or to assist in the forensic investigation in a case of fatal over dosage.

### **9 – 2 - Use in food**

Silver is used in food coloring; it has the E174 designation and is approved in the European Union.

The safety of silver for use in food is disputed . Traditional Indian dishes sometimes include the use of decorative silver foil known as *vark* , and in various cultures, silver *dragée* are used to decorate cakes, cookies, and other dessert items . The use of silver as a food additive is not approved in the United States.



## Category : Silver

Argent

Argentium sterling silver

Argyria

Billon (alloy)

BIS hallmark

Britannia silver

Chinese Gold and Silver Exchange Society

Coconut cup

Coinage Act of 1873

Consulado de mercaderes

Cornish hurling

Alastair Dickenson

Doré bullion

Electrum

Francis 1st

Free silver

Ginza (agency)

Goloid

Good Delivery

Grande Baroque

Hallmark

Household silver

Isotopes of silver

London Silver Vaults

Martelé (silver)  
Medical uses of silver  
Mercury silvering  
Metallurgical assay  
Millesimal fineness

Nickel silver  
Niello

Parkes process  
Pattison's Process  
Platinum sterling  
Potin

Sheffield plate  
Shibuichi S cont.  
Sibplaz  
Silver (color)  
Silver as an investment  
Silver certificate (United States)  
Silver Nano  
Silver Party  
List of countries by silver production  
Silver Republican Party  
Silver standard  
Silver standards  
Silver Thursday  
Silvering  
Silverite  
Sterling silver

Vark  
Vermeil

Weighted sterling

Zinc matrix battery

## Silver Compounds Category

Argyrol

Fulminating silver

Organo silver chemistry

Potassium argento cyanide

Rubidium silver iodide

Silver acetate

Silver acetylide

Silver arsenate

Silver azide

Silver behenate

Silver bromate

Silver bromide

Silver carbonate

Silver chlorate

Silver chloride

Silver chromate

Silver cyanate .

Silver cyanide

Silver dichromate

Silver fulminate

Silver halide

Silver hexa fluoro phosphate

Silver iodate

Silver iodide

Silver molybdate

Silver nitrate

Silver nitride

Silver nitrite

Silver oxalate

Silver oxide

Silver perchlorate  
Silver permanganate  
Silver per rhenate  
Silver phosphate  
Silver proteinate  
Silver selenite  
Silver sub fluoride  
Silver sulfadiazine  
Silver sulfate  
Silver sulfide  
Silver telluride  
Silver tetra fluoro borate  
Silver thio cyanate  
Silver tri fluoro methane sulfonate  
Silver (I) fluoride  
Silver (I) selenide  
Silver (I,III) oxide  
Silver (II) fluoride  
Tetrakis(pyridine)silver(II) peroxydisulfate  
Tollens' reagent  
  
Walden reductor  
  
Zinag  
Zinagizado

# Silver Cyanide

## Contents

- 1 Introduction
- 2 Structure
- 3 Reactions
- 4 Uses

## 1 - Introduction

Silver cyanide is the chemical compound with the formula  $\text{Ag CN}$ . This white solid forms upon treatment of solutions containing  $\text{Ag}^+$  with cyanide. This precipitation step is used in some schemes to recover silver from solution. Silver cyanide is used in silver - plating.

IUPAC name :	Silver cyanide
Other names :	Argentous cyanide
Molecular formula	$\text{Ag C N}$
Molar mass	133.88 g / mol
Appearance	colorless, gray (impure) crystals
Odor	odorless
Density	3.943 g / $\text{cm}^3$
Melting point	335 °C (decomposes)
Solubility in water	0.000023 g / 100 mL ( 20 °C )
Solubility	soluble in concentrated ammonia, boiling nitric acid, ammonium hydroxide, KCN insoluble in alcohol, dilute acid
Refractive index ( $n_D$ )	1 / 685
Crystal structure	hexagonal
Main hazards	toxic
Flash point	320 °C
LD <sub>50</sub>	123 mg / kg ( oral , rat )

## 2 – Structure

Its structure consist of - [ Ag – C N ] - chains in which the linear two-coordinate  $\text{Ag}^+$  ions , typical of silver (I) and other  $d^{10}$  ions are bridge by the cyanide ions. ( This is the same binding mode as seen in the more famous case of Prussian blue ) .These chains then pack hexagonally with adjacent chains of set by  $+ / - 1 / 3$  of the "c" lattice parameter. This is the same as the structure adopted by the high temperature polymorph of copper (I) cyanide. The silver to carbon and silver to nitrogen bond lengths in Ag CN are both  $\sim 2.09 \text{ \AA}$  and the cyanide groups show head – to - tail disorder .

## 3 – Reactions

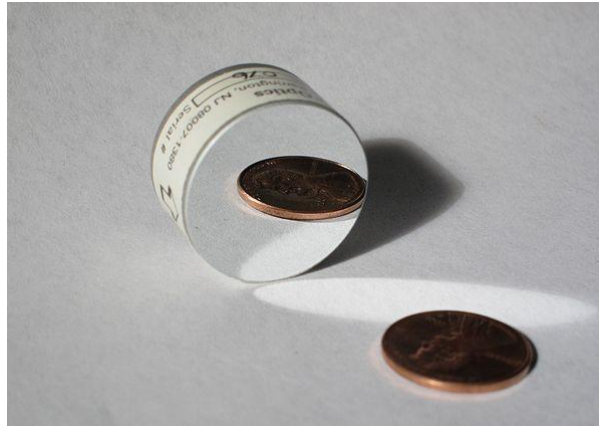
Ag CN precipitates upon the addition of sodium cyanide to a solution containing  $\text{Ag}^+$ . The precipitate dissolves upon the addition of further amounts of cyanide to form linear  $[\text{Ag} (\text{CN})_2]^-_{(\text{aq})}$  and  $[\text{Ag} (\text{CN})_3]^{2-}_{(\text{aq})}$  on the addition of further cyanide. Silver cyanide is also soluble in solutions containing other ligands such as ammonia or tertiary phosphines.

Silver cyanides form structurally complex materials upon reaction with other anions.<sup>[4]</sup> Some silver cyanides are luminescent.

## 4 – Uses

Both Ag CN and K Ag (CN)<sub>2</sub> have been used in silver-plating solutions since at least 1840 when the Elkington brothers patented their recipe for a silver-plating solution. A typical, traditional silver-plating solution would contain K Ag (CN)<sub>2</sub> 15 - 40 gL<sup>-1</sup> , KCN 12 - 120 gL<sup>-1</sup> and K<sub>2</sub> CO<sub>3</sub> g L<sup>-1</sup>.

# Silver Mirror



*A first surface mirror coated with aluminum and enhanced with dielectric coatings. The mirror was constructed from an optical flat with a flatness of  $\lambda / 20$ , which equates to a surface deviation less than 31.6 nanometers.*

## Contents

- 1 Introduction
- 2 History
- 3 Manufacturing
- 4 Types of glass mirrors
- 5 Effects
  - 5.1 Shape of a mirror's surface
  - 5.2 Mirror image
- 6 Applications
  - 6.1 Safety and easier viewing
  - 6.2 One - way mirrors and windows
  - 6.3 Signalling
  - 6.4 Technology
    - 6.4.1 Televisions and projectors
    - 6.4.2 Solar power
    - 6.4.3 Instruments
      - 6.4.3.1 Face – to - face mirrors
    - 6.4.4 Military applications
    - 6.4.5 Seasonal lighting
  - 6.5 Arts & design
    - 6.5.1 Architecture
    - 6.5.2 Fine art

6.5.2.1 Paintings

6.5.2.2 Other artistic mediums

6.5.3 Decoration

6.5.4 Entertainment

6.5.5 Film and television

6.5.6 Literature

7 Mirrors and animals

8 Unusual kinds of mirrors

## **1 - Introduction**

A mirror is an object that reflects light in a way that preserves much of its original quality subsequent to its contact with the mirror.

Some mirrors also filter out some wavelengths, while preserving other wavelengths in the reflection. This is different from other light-reflecting objects that do not preserve much of the original wave signal other than color and diffuse reflected light. The most familiar type of mirror is the plane mirror, which has a flat surface. Curved mirrors are also used, to produce magnified or diminished images or focus light or simply distort the reflected image.

Mirrors are commonly used for personal grooming or admiring oneself (in which case the archaic term looking-glass is sometimes still used), decoration, and architecture. Mirrors are also used in scientific apparatus such as telescopes and lasers, cameras, and industrial machinery. Most mirrors are designed for visible light; however, mirrors designed for other types of waves or other wavelengths of electromagnetic radiation are also used, especially in non - optical instruments.

## **2 – History**

The first mirrors used by people were most likely pools of dark, still water, or water collected in a primitive vessel of some sort. The earliest manufactured mirrors were pieces of polished stone such as obsidian, a naturally occurring volcanic glass. Examples of obsidian mirrors found in Anatolia ( modern - day Turkey ) have been dated to around 6000 BC. Polished stone mirrors from Central and South



America date from around 2000 BC onwards.<sup>[1]</sup> Mirrors of polished copper were crafted in Mesopotamia from 4000 BC,<sup>[1]</sup> and in ancient Egypt from around 3000 BC.<sup>[2]</sup> In China, bronze mirrors were manufactured from around 2000 BC, some of the earliest bronze and copper examples being produced by the Qijia culture. Mirrors made of other metal mixtures (alloys) such as copper and tin speculum metal may have also been produced in China and India.<sup>[4]</sup> Mirrors of speculum metal or any precious metal were hard to produce and were only owned by the wealthy.

Metal - coated glass mirrors are said to have been invented in Sidon (modern - day Lebanon) in the first century AD, and glass mirrors backed with gold leaf are mentioned by the Roman author Pliny in his *Natural History*, written in about 77 AD.<sup>[7]</sup> The Romans also developed a technique for creating crude mirrors by coating blown glass with molten lead.

Parabolic mirrors were described and studied in classical antiquity by the mathematician Diocles in his work *On Burning Mirrors*.<sup>[9]</sup> Ptolemy conducted a number of experiments with curved polished iron mirrors , and discussed plane, convex spherical, and concave spherical mirrors in his *Optics* . Parabolic mirrors were also described by the physicist Ibn Sahl in the 10th century and Ibn al-Haytham discussed concave and convex mirrors in both cylindrical and spherical geometries , carried out a number of experiments with mirrors, and solved the problem of finding the point on a convex mirror at which a ray coming from one point is reflected to another point.<sup>[14]</sup> By the 11th century, clear glass mirrors were being produced in Moorish Spain.

In China, people began making mirrors with the use of silver-mercury amalgams as early as 500 AD. Some time during the early Renaissance, European manufacturers perfected a superior method of coating glass with a tin-mercury amalgam. The exact date and location of the discovery is unknown, but in the 16th century, Venice, a city famed for its glass - making expertise, became a center of mirror production using this new technique. Glass mirrors from this

period were extremely expensive luxuries. The Saint - Gobain factory, founded by royal initiative in France, was an important manufacturer, and Bohemian and German glass, often rather cheaper, was also important.

The invention of the silvered - glass mirror is credited to German chemist Justus von Liebig in 1835. His process involved the deposition of a thin layer of metallic silver onto glass through the chemical reduction of silver nitrate. This silvering process was adapted for mass manufacturing and led to the greater availability of affordable mirrors. Nowadays, mirrors are often produced by the wet deposition of silver (or sometimes aluminum via vacuum deposition ) directly onto the glass substrate.

### **3 – Manufacturing**

Mirrors are manufactured by applying a reflective coating to a suitable substrate. The most common substrate is glass, due to its transparency, ease of fabrication, rigidity, hardness, and ability to take a smooth finish. The reflective coating is typically applied to the back surface of the glass, so that the reflecting side of the coating is protected from corrosion and accidental damage by the glass on one side and the coating itself and optional paint for further protection on the other.

In classical antiquity, mirrors were made of solid metal (bronze, later silver) and were too expensive for widespread use by common people; they were also prone to corrosion. Due to the low reflectivity of polished metal, these mirrors also gave a darker image than modern ones, making them unsuitable for indoor use with the artificial lighting of the time ( candles or lanterns ) .

The method of making mirrors out of plate glass was invented by 16th-century Venetian glassmakers on the island of Murano, who covered the back of the glass with mercury, obtaining near - perfect and undistorted reflection. For over one hundred years, Venetian mirrors installed in richly decorated frames served as luxury decorations for palaces throughout Europe, but the secret of the

mercury process eventually arrived in London and Paris during the 17th century, due to industrial espionage. French workshops succeeded in large scale industrialization of the process, eventually making mirrors affordable to the masses, although mercury's toxicity remained a problem.

In modern times, the mirror substrate is shaped, polished and cleaned, and is then coated. Glass mirrors are most often coated with non toxic silver or Aluminum, implemented by a series of coatings :

- Tin (II) chloride
- Silver
- Chemical activator
- Copper
- Paint

The tin (II) chloride is applied because silver will not bond with the glass. The activator causes the tin / silver to harden. Copper is added for long - term durability. The paint protects the coating on the back of the mirror from scratches and other accidental damage .

]

In some applications, generally those that are cost-sensitive or that require great durability, mirrors are made from a single, bulk material such as polished metal . For technical applications such as laser mirrors, the reflective coating is typically applied by vacuum deposition on the *front* surface of the substrate. This eliminates refraction and double reflections (a weak reflection from the surface of the glass, and a stronger one from the reflecting metal) and reduces absorption of light by the mirror. Technical mirrors may use a silver, Aluminum, or gold coating (the latter typically for infrared mirrors), and achieve reflectivities of 90 – 95 % when new. A protective transparent overcoat may be applied to prevent oxidation of the reflective layer. Applications requiring higher reflectivity or greater durability, where wide bandwidth is not essential, use dielectric coatings, which can achieve reflectivities as high as 99.999 % over a narrow range of wavelengths.

#### **4 - Types of glass mirrors**

There are many types of glass mirrors, each representing a different manufacturing process and reflection type.

An Aluminum glass mirror is made of a float glass manufactured using vacuum coating, i.e. Aluminum powder is evaporated (or "sputtered") onto the exposed surface of the glass in a vacuum chamber and then coated with two or more layers of water proof protective paint.

A low Aluminum glass mirror is manufactured by coating silver and two layers of protective paint on the back surface of glass. A low Aluminum glass mirror is very clear, light trans missive, smooth, and reflects accurate natural colors. This type of glass is widely used for framing presentations and exhibitions in which a precise color representation of the artwork is truly essential or when the background color of the frame is predominantly white.

A safety glass mirror is made by adhering a special protective film to the back surface of a silver glass mirror, which prevents injuries in case the mirror is broken. This kind of mirror is used for furniture, doors, glass walls, commercial shelves, or public areas.

A silk screen printed glass mirror is produced using inorganic color ink that prints patterns through a special screen onto glass. Various colors, patterns, and glass shapes are available. Such a glass mirror is durable and more moisture resistant than ordinary printed glass and can serve for over 20 years. This type of glass is widely used for decorative purposes (e.g., on mirrors, table tops, doors, windows, kitchen chop boards, etc.).

A silver glass mirror is an ordinary mirror, coated on its back surface with silver, which produces images by reflection. This kind of glass mirror is produced by coating a silver, copper film and two or more layers of waterproof paint on the back surface of float glass, which perfectly resists acid and moisture. A silver glass mirror

provides clear and actual images, is quite durable, and is widely used for furniture, bathroom and other decorative purposes.

Decorative glass mirrors are usually handcrafted. A variety of shades, shapes and glass thickness are often available.

## **5 – Effects**

### **5 – 1 - Shape of a mirror's surface**

A beam of light reflects off a mirror at an angle of reflection equal to its angle of incidence ( if the size of a mirror is much larger than the wavelength of light ). That is, if the beam of light is shining on a mirror's surface at a  $\theta^\circ$  angle vertically, then it reflects from the point of incidence at a  $\theta^\circ$  angle from vertically in the opposite direction. This law mathematically follows from the interference of a plane wave on a flat boundary (of much larger size than the wave length).

In a plane mirror, a parallel beam of light changes its direction as a whole, while still remaining parallel; the images formed by a plane mirror are virtual images, of the same size as the original object.

In a concave mirror, parallel beams of light become a convergent beam, whose rays intersect in the focus of the mirror. Also known as converging mirror

In a convex mirror, parallel beams become divergent, with the rays appearing to diverge from a common point of intersection "behind" the mirror.

Spherical concave and convex mirrors do not focus parallel rays to a single point due to spherical aberration. However, the ideal of focusing to a point is a commonly-used approximation. Parabolic reflectors resolve this, allowing incoming parallel rays (for example, light from a distant star) to be focused to a small spot; almost an ideal point. Parabolic reflectors are not suitable for imaging nearby objects because the light rays are not parallel.

## **5 – 2 - Mirror image**

*Mail* If one looks in a mirror, one's image reverses (e.g., if one raises one's right hand, one's left hand will appear to go up in the mirror). However, a mirror does not "swap" left and right, any more than it swaps top and bottom. A mirror reverses the forward/backward axis, and we define left and right relative to front and back. Flipping front/back and left / right is equivalent to a rotation of 180 degrees about the vertical axis (in the same way that text which is back – to – front *and* upside – down simply looks like it has been rotated 180 degrees on the page). There fore, looking at an image of oneself with the front/back axis flipped is the same as looking at an image with the left/right axis flipped and the whole figure rotated 180 degrees about the vertical axis, which is exactly what one sees when standing in front of a mirror.

## **6 – Applications**

### **6 – 1 - Safety and easier viewing**

#### ***Convex mirrors***

Convex mirrors provide a wider field of view than flat mirrors, and are often used on vehicles, especially large trucks, to minimize blind spots. They are sometimes placed at road junctions, and corners of sites such as parking lots to allow people to see around corners to avoid crashing into other vehicles or shopping carts. They are also sometimes used as part of security systems, so that a single video camera can show more than one angle at a time. <sup>[citation needed]</sup>

#### ***Mouth mirrors or "dental mirrors"***

Mouth mirrors or "dental mirrors" are used by dentists to allow indirect vision and lighting within the mouth. Their reflective surfaces may be either flat or curved. Mouth mirrors are also commonly used by mechanics to allow vision in tight spaces and around corners in equipment.

#### ***Rear - view mirrors***

Rear - view mirrors are widely used in and on vehicles ( such as auto mobiles, or bicycles ), to allow drivers to see other vehicles coming up behind them. Some motorcycle helmets have a built-in so-called MROS (Multiple Reflective Optic System): a set of reflective

surfaces inside the helmet that together function as a rear-view mirror. On rear-view sunglasses, the left end of the left glass and the right end of the right glass work as mirrors.

## **6 – 2 – One - way mirrors and windows[edit]**

### ***One - way mirrors***

One - way mirrors ( also called two - way mirrors ) work by overwhelming dim transmitted light with bright reflected light. A true one - way mirror that actually allows light to be transmitted in one direction only without requiring external energy is not possible as it violates the second law of thermodynamics: if one placed a cold object on the transmitting side and a hot one on the blocked side, radiant energy would be transferred from the cold to the hot object. Thus, though a one-way mirror can be made to appear to work in only one direction at a time, it is actually reflective from either side.

### ***One - way windows***

One - way windows can be made to work with polarized light in the laboratory without violating the second law. This is an apparent paradox that stumped some great physicists, although it does not allow a practical one-way mirror for use in the real world.<sup>[23][24]</sup> Optical isolators are one-way devices that are commonly used with lasers.

## **6 – 3 – Signalling**

With the sun as light source, a mirror can be used to signal by variations in the orientation of the mirror. The signal can be used over long distances, possibly up to 60 kilometers on a clear day. This technique was used by Native American tribes and numerous militaries to transmit information between distant outposts.

Mirrors can also be used for search to attract the attention of search and rescue helicopters. Specialized signalling mirrors are available and are often included in military survival kits.

## **6 – 4 – Technology**

### **6 – 4 – 1 - Televisions and projectors**

Microscopic mirrors are a core element of many of the largest high-definition televisions and video projectors. A common technology of this type is Texas Instruments' DLP. A DLP chip is a postage stamp-sized microchip whose surface is an array of millions of microscopic mirrors. The picture is created as the individual mirrors move to either reflect light toward the projection surface (pixel on), or toward a light absorbing surface (pixel off).

Other projection technologies involving mirrors include LCoS. Like a DLP chip, LCoS is a microchip of similar size, but rather than millions of individual mirrors, there is a single mirror that is actively shielded by a liquid crystal matrix with up to millions of pixels. The picture, formed as light, is either reflected toward the projection surface (pixel on), or absorbed by the activated LCD pixels (pixel off). LCoS-based televisions and projectors often use 3 chips, one for each primary color.



*Parabolic trough at Harper Lake in California*

Large mirrors are used in rear projection televisions. Light (for example from a DLP as mentioned above) is "folded" by one or more mirrors so that the television set is compact.

### **6 – 4 – 2 - Solar power**

Mirrors are integral parts of a solar power plant. The one shown in the picture to the right uses concentrated solar power from an array of parabolic troughs.



### 6 – 4 – 3 – Instruments

Telescopes and other precision instruments use *front silvered* or first surface mirrors, where the reflecting surface is placed on the front (or first) surface of the glass ( this eliminates reflection from glass surface ordinary back mirrors have ) . Some of them use silver, but most are Aluminum, which is more reflective at short wave lengths than silver. All of these coatings are easily damaged and require special handling. They reflect 90 % to 95 % of the incident light when new. The coatings are typically applied by vacuum deposition. A protective overcoat is usually applied before the mirror is removed from the vacuum, because the coating otherwise begins to corrode as soon as it is exposed to oxygen and humidity in the air. *Front silvered* mirrors have to be resurfaced occasionally to keep their quality. There are optical mirrors such as mangin mirrors that are *second surface mirrors* (reflective coating on the rear surface) as part of their optical designs, usually to correct optical aberrations.

The reflectivity of the mirror coating can be measured using a reflect meter and for a particular metal it will be different for different wavelengths of light. This is exploited in some optical work to make cold mirrors and hot mirrors. A cold mirror is made by using a transparent substrate and choosing a coating material that is more reflective to visible light and more transmissive to infrared light.

A hot mirror is the opposite, the coating preferentially reflects infrared. Mirror surfaces are sometimes given thin film overcoatings both to retard degradation of the surface and to increase their reflectivity in parts of the spectrum where they will be used. For instance, aluminum mirrors are commonly coated with silicon dioxide or magnesium fluoride. The reflectivity as a function of wavelength depends on both the thickness of the coating and on how it is applied.

For scientific optical work, dielectric mirrors are often used. These are glass (or some times other material) substrates on which one or more layers of dielectric material are deposited, to form an optical coating. By careful choice of the type and thickness of the dielectric layers, the range of wavelengths and amount of light

reflected from the mirror can be specified. The best mirrors of this type can reflect  $> 99.999\%$  of the light (in a narrow range of wave lengths) which is incident on the mirror. Such mirrors are often used in lasers.

In astronomy, adaptive optics is a technique to measure variable image distortions and adapt a deformable mirror accordingly on a timescale of milliseconds, to compensate for the distortions.

Although most mirrors are designed to reflect visible light, surfaces reflecting other forms of electromagnetic radiation are also called "mirrors". The mirrors for other ranges of electromagnetic waves are used in optics and astronomy. Mirrors for radio waves (sometimes known as reflectors) are important elements of radio telescopes.

#### **6 – 4 – 3 - 1 – Face - to - face mirrors**

Two or more mirrors placed exactly face to face can give an infinite regress of reflections. Some devices use this to generate multiple reflections :

Fabry – Pérot interferometer

Laser (which contains an optical cavity)

3D Kaleidoscope to concentrate light

Momentum - enhanced solar sail

#### **6 – 4 – 4 - Military applications**

It has been said that Archimedes used a large array of mirrors to burn Roman ships during an attack on Syracuse. This has never been proven or disproved; however, it has been put to the test. Recently, on a popular Discovery Channel show, *MythBusters*, a team from MIT tried to recreate the famous "Archimedes Death Ray". They were unsuccessful at starting a fire on the ship; however, previous attempts to light the boat on fire using only the bronze mirrors available in Archimedes' time were unsuccessful, and the time taken to ignite the craft would have made its use impractical, resulting in the Myth Busters team deeming the myth "busted". It was however found that the mirrors made it very difficult for the passengers of the targeted

boat to see, likely helping to cause their defeat, which may have been the origin of the myth.

### **6 – 4 – 5 - Seasonal lighting**

Due to its location in a steep - sided valley, the Italian town of Viganella gets no direct sunlight for seven weeks each winter. In 2006 a € 100,000 computer - controlled mirror, 8×5 m, was installed to reflect sunlight into the town's piazza. In early 2007 the similarly situated village of Bondo, Switzerland, was considering applying this solution as well . In 2013, mirrors were installed to reflect sunlight into the town square in the Norwegian town of Rjukan. Mirrors can be used to produce enhanced lighting effects in greenhouses or conservatories.

### **6 – 5 – Arts & design**

#### **6 – 5 – 1 – Architecture**

Mirrors are a popular design theme in architecture, particularly with late modern and post-modernist high - rise buildings in major cities. Early examples include the Campbell Center in Dallas, which opened in 1972 , and the John Hancock Tower in Boston.

More recently, two skyscrapers designed by architect Rafael Viñoly, the Vdara in Las Vegas and 20 Fenchurch Street in London, have experienced unusual problems due to their concave curved glass exteriors acting as respectively cylindrical and spherical reflectors for sunlight. In 2010, the Las Vegas Review Journal reported that sunlight reflected off the Vdara's south-facing tower could singe swimmers in the hotel pool, as well as melting plastic cups and shopping bags; employees of the hotel referred to the phenomenon as the "Vdara death ray". In 2013, sunlight reflecting off 20 Fenchurch Street melted parts of a Jaguar car parked nearby and scorching the carpet of a nearby barber shop.

### **6 – 5 – 2 - Fine art**

#### **6 – 5 – 2 – 1 - Paintings**

Painters depicting someone gazing into a mirror often also show the person's reflection. This is a kind of abstraction—in most cases

the angle of view is such that the person's reflection should not be visible. Similarly, in movies and still photography an actor or actress is often shown ostensibly looking at him- or herself in the mirror, and yet the reflection faces the camera. In reality, the actor or actress sees only the camera and its operator in this case, not their own reflection.

The mirror is the central device in some of the greatest of European paintings :

Édouard Manet's *A Bar at the Folies-Bergère*

Titian's *Venus with a Mirror*

Jan van Eyck's *Arnolfini Portrait*

Pablo Picasso's *Girl before a Mirror* (1932)

Diego Velázquez's *Las Meninas*, wherein the viewer is both the watcher (of a self-portrait in progress) and the watched, and the many adaptations of that painting in various media

Veronese's *Venus with a Mirror*

Mirrors have been used by artists to create works and hone their craft:

Filippo Brunelleschi discovered linear perspective with the help of the mirror .

Leonardo da Vinci called the mirror the "master of painters". He recommended, "When you wish to see whether your whole picture accords with what you have portrayed from nature take a mirror and reflect the actual object in it. Compare what is reflected with your painting and carefully consider whether both likenesses of the subject correspond, particularly in regard to the mirror " .

Many self-portraits are made possible through the use of mirrors:

Without a mirror, the great self-portraits by Dürer , Frida Kahlo, Rembrandt, and Van Gogh could not have been painted.

M. C. Escher used special shapes of mirrors in order to achieve a much more complete view of his surroundings than by direct

observation in *Hand with Reflecting Sphere* (also known as *Self-Portrait in Spherical Mirror*).

Mirrors are sometimes necessary to fully appreciate art work:

István Orosz's anamorphic works are images distorted such that they only become clearly visible when reflected in a suitably shaped and positioned mirror.

### **6 – 5 – 2 – 2 - Other artistic mediums**

Some other contemporary artists use mirrors as the material of art :

A Chinese magic mirror is an art in which the face of the bronze mirror projects the same image that was cast on its back. This is due to minute curvatures on its front.

Specular holography uses a large number of curved mirrors embedded in a surface to produce three - dimensional imagery.

Paintings on mirror surfaces ( such as silkscreen printed glass mirrors )

Sculptures comprised entirely or in part of mirrors

*Infinity Also Hurts* is a mirror, glass and silicone sculpture by artist, Seth Wulsin

*Sky Mirror* is a public sculpture by artist, Anish Kapoor

Special mirror installations

*Follow Me* mirror labyrinth by artist, Jeppe Hein (see also, Entertainment: Mirror mazes, below)

*Mirror Neon Cube* by artist, Jeppee Hein

### **6 – 5**

Mirrors, typically large and unframed, are frequently used in interior decoration to create an illusion of space and amplify the apparent size of a room . They come also framed in a variety of forms, such as the pier glass and the over mantle mirror.

Mirrors are used also in some schools of feng shui, an ancient Chinese practice of placement and arrangement of space, to achieve harmony with the environment.

The softness of old mirrors is sometimes replicated by contemporary artisans for use in interior design. These reproduction antiqued mirrors are works of art and can bring color and texture to an other wise hard, cold reflective surface. It is an artistic process that has been attempted by many and perfected by few.

A decorative reflecting sphere of thin metal-coated glass, working as a reducing wide - angle mirror, is sold as a Christmas ornament called a *bauble*.

#### **6 – 5 – 4 – Entertainment**

Illuminated rotating disco balls covered with small mirrors are used to cast moving spots of light around a dance floor.

The hall of mirrors, commonly found in amusement parks, is an attraction in which a number of distorting mirrors are used to produce unusual reflections of the visitor.

Mirrors are employed in kaleidoscopes, personal entertainment devices invented in Scotland by Sir David Brewster.

Mirrors are often used in magic to create an illusion. One effect is called Pepper's ghost.

Mirror mazes, often found in amusement parks as well, contain large numbers of mirrors and sheets of glass. The idea is to navigate the disorientating array without bumping into the walls. Mirrors in attractions like this are often made of Plexiglas as to assure that they do not break.

#### **6 – 5 – 5 – Film and television**

*Candyman* is a horror movie about mirrors.

*Mirrors* is a horror movie about mirrors.

*Poltergeist III* features mirrors as a major theme.

*The 10th Kingdom* miniseries requires the use of a magic mirror for the characters to change setting between modern day New York City (the 10th Kingdom), and the Nine Kingdoms of fairy tale, primarily the 4th Kingdom from Snow White.

## 6 – 5 – 6 – Literature

Mirrors play a powerful role in cultural literature.

Christian Bible passage, 1 Corinthians 13:12 ("Through a Glass Darkly"), references a dim mirror image or poor mirror reflection.

*Narcissus* of Greek mythology wastes away while gazing, self-admiringly, at his reflection in water.

In the European fairy tale, "Snow White" (collected by Brothers Grimm in 1812), the evil queen asks, "Mirror, mirror, on the wall... who's the fairest of them all?"

In Alfred, Lord Tennyson's famous poem "The Lady of Shalott" (1833, revised in 1842), the titular character possesses a mirror that enables her to look out on the people of Camelot, as she is under a curse that prevents her from seeing Camelot directly.

Lewis Carroll's *Through the Looking-Glass and What Alice Found there* (1871) is one of the best-loved uses of mirrors in literature. The text itself utilizes a narrative that mirrors that of its predecessor, *Alice's Adventures in Wonderland*.

In Oscar Wilde's novel, *The Picture of Dorian Gray* (1890), a portrait serves as a magical mirror that reflects the true visage of the perpetually youthful protagonist, as well as the effect on his soul of each sinful act.

The short story *Tlön, Uqbar, Orbis Tertius* of Jorge Luis Borges begins with the phrase "I owe the discovery of Uqbar to the conjunction of a mirror and an encyclopedia" and contains other references to mirrors.

The magical objects in the *Harry Potter* series (1997-2011) include the Mirror of Erised and two-way mirrors.

Under "Appendix: Variant Planes & Cosmologies" of the *Dungeons & Dragons Manual Of The Planes* (2000), is The Plane of Mirrors (page 204). It describes the Plane of Mirrors as a space existing behind reflective surfaces, and experienced by visitors as a

long corridor. The greatest danger to visitors upon entering the plane is the instant creation of a mirror-self with the opposite alignment of the original visitor.

## 7 - Mirrors and animals



*4.5-metre high acoustic mirror near Kilnsea Grange,  
East Yorkshire, UK*

Only a few animal species have been shown to have the ability to recognize themselves in a mirror, most of them mammals. Experiments have found that the following animals can pass the mirror test:

### ***All great apes:***

Humans. Humans tend to fail the mirror test until they are about 18 months old, or what psychoanalysts call the "mirror stage".<sup>[38][39][40]</sup>

Bonobos

Chimpanzees

Orangutans

Gorillas. Initially, it was thought that gorillas did not pass the test, but there are now several well-documented reports of gorillas (such as Koko ) passing the test.

Bottlenose dolphins

Orcas

Elephants

European Magpies

## 8 - Unusual kinds of mirrors

Other types of reflecting device are also called "mirrors".



Acoustic mirrors are passive devices used to reflect and perhaps to focus sound waves. Acoustic mirrors were used for selective detection of sound waves, especially during World War II. They were used for detection of enemy aircraft prior to the development of radar. Acoustic mirrors are used for remote probing of the atmosphere; they can be used to form a narrow diffraction - limited beam . They can also be used for underwater imaging.

Active mirrors are mirrors that amplify the light they reflect. They are used to make disk lasers . The amplification is typically over a narrow range of wavelengths, and requires an external source of power.

Atomic mirrors are devices which reflect matter waves. Usually, atomic mirrors work at grazing incidence. Such mirrors can be used for atomic interferometry and atomic holography. It has been proposed that they can be used for non-destructive imaging systems with nanometer resolution.

Cold mirrors are dielectric mirrors that reflect the entire visible light spectrum, while efficiently transmitting infrared wave lengths. These are the converse of hot mirrors.

Corner reflectors use three flat mirrors to reflect light back towards its source, they may also be implemented with prisms that reflect using total internal reflection that have no mirror surfaces. They are used for emergency location, and even laser ranging to the Moon.

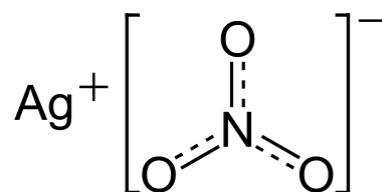
Hot mirrors reflect infrared light while allowing visible light to pass. These can be used to separate useful light from unneeded infrared to reduce heating of components in an optical device. They can also be used as dichroic beamsplitters. (Hot mirrors are the converse of cold mirrors ) .

Metallic reflectors are used to reflect infra red light (such as in space heaters or micro waves).

Non-reversing mirrors are mirrors that provide a non-reversed image of their subjects.

X - ray mirrors produce specular reflection of X - rays . All known types work only at angles near grazing incidence, and only a small fraction of the rays are reflected.

# Silver Nitrate



## Contents

- 1 Introduction
- 2 Discovery
- 3 Synthesis
- 4 Reactions
- 5 Uses
  - 5.1 Precursor to other silver compounds
  - 5.2 Halide abstraction
  - 5.3 Organic synthesis
  - 5.4 Biology
- 6 Medicine
  - 6.1 Disinfection
  - 6.2 Against warts
- 7 Safety

## 1 - Introduction

Silver nitrate is an inorganic compound with chemical formula  $\text{AgNO}_3$ . This compound is a versatile precursor to many other silver compounds, such as those used in photography. It is far less sensitive to light than the halides. It was once called *lunar caustic* because silver was called *luna* by the ancient alchemists, who believed that silver was associated with the moon.

In solid silver nitrate, the silver ions are three-coordinated in a trigonal planar arrangement.

## 2 – Discovery

Albertus Magnus, in the 13th century, documented the ability of nitric acid to separate gold and silver by dissolving the silver.<sup>[4]</sup>

Magnus noted that the resulting solution of silver nitrate could blacken skin. Its common name at the time was nitric acid silver.

### 3 – Synthesis

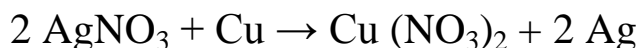
Silver nitrate can be prepared by reacting silver, such as a silver bullion or silver foil, with nitric acid, resulting in silver nitrate, water, and oxides of nitrogen. Reaction byproducts depend upon the concentration of nitric acid used.



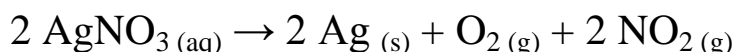
This is performed under a fume hood because of toxic nitrogen oxide (s) evolved during the reaction.

### 4 – Reactions

A typical reaction with silver nitrate is to suspend a rod of copper in a solution of silver nitrate and leave it for a few hours. The silver nitrate reacts with copper to form hair like crystals of silver metal and a blue solution of copper nitrate :



Aqueous silver nitrate also decomposes when heated:



Most metal nitrates thermally decompose to the respective oxides, but silver oxide decomposes at a lower temperature than silver nitrate, so the decomposition of silver nitrate yields elemental silver instead.

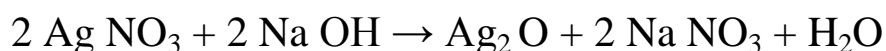
### 5 – Uses

#### 5 – 1 - Precursor to other silver compounds

Silver nitrate is the least expensive salt of silver; it offers several other advantages as well. It is non - hygroscopic, in contrast to silver fluoro borate and silver per chlorate. It is relatively stable to light.

Finally, it dissolves in numerous solvents, including water. The nitrate can be easily replaced by other ligands, rendering  $\text{AgNO}_3$  versatile. Treatment with solutions of halide ions gives a precipitate of  $\text{Ag X}$  (  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  ) . When making photographic film, silver nitrate is treated with halide salts of sodium or potassium to form insoluble silver halide in situ in photographic gelatin, which is then applied to strips of tri-acetate or polyester. Similarly, silver nitrate is used to prepare some silver-based explosives, such as the fulminate, azide, or acetylide, through a precipitation reaction.

Treatment of silver nitrate with base gives dark grey silver oxide :



### 5 – 12 - Halide abstraction

The silver cation,  $\text{Ag}^+$  , reacts quickly with halide sources to produce the insoluble silver halide, which is a cream precipitate if  $\text{Br}^-$  is used, a white precipitate if  $\text{Cl}^-$  is used and a yellow precipitate if  $\text{I}^-$  is used. This reaction is commonly used in inorganic chemistry to abstract halides :



Other silver salts with non - coordinating anions, namely silver tetra fluoro borate and silver hexa fluoro phosphate are used for more demanding applications.

Similarly, this reaction is used in analytical chemistry to confirm the presence of chloride, bromide, or iodide ions can be tested by adding silver nitrate solution. Samples are typically acidified with dilute nitric acid to remove interfering ions, e.g. carbonate ions and sulfide ions. This step avoids confusion of silver sulfide or silver carbonate precipitates with that of silver halides. The color of precipitate varies with the halide: white (silver chloride), pale yellow/cream (silver bromide), yellow (silver iodide).  $\text{AgBr}$  and especially  $\text{AgI}$  photo - decompose to the metal, as evidence by a grayish color on exposed samples.

### **5 – 3 - Organic synthesis**

Silver nitrate is used in many ways in organic synthesis, e.g. for deprotection and oxidations.  $\text{Ag}^+$  binds alkenes reversibly, and silver nitrate has been used to separate mixtures of alkenes by selective absorption. The resulting adduct can be decomposed with ammonia to release the free alkene.

### **5 – 4 – Biology**

In histology, silver nitrate is used for silver staining, for demonstrating reticular fibers, proteins and nucleic acids. For this reason it is also used to demonstrate proteins in PAGE gels. It can be used as a stain in scanning electron microscopy.

### **6 – Medicine**

Silver salts have antiseptic properties. Until the development and widespread adoption of antibiotics, dilute solutions of  $\text{AgNO}_3$  used to be dropped into new born babies' eyes at birth to prevent contraction of gonorrhea from the mother. Eye infections and blindness of newborns was reduced by this method; incorrect dosage, however, could cause blindness in extreme cases. This protection was first used by Credé in 1881. Fused silver nitrate, shaped into sticks, was traditionally called "lunar caustic". It is used as a cauterizing agent, for example to remove granulation tissue around a stoma. General Sir James Abbott noted in his journals that in India in 1827 it was infused by a British surgeon into wounds in his arm resulting from the bite of a mad dog to cauterize the wounds and prevent the onset of rabies . Dentists some times use silver nitrate infused swabs to heal oral ulcers. Silver nitrate is also used by some podiatrists to kill cells located in the nail bed. Silver nitrate is also used to cauterize superficial blood vessels in the nose to help prevent nose bleeds.

The Canadian physician C. A. Douglas Ringrose researched the use of silver nitrate for sterilization procedures on women. A specialist in obstetrics and gynaecology , Ringrose believed that the corrosive properties of silver nitrate could be used to block and corrode the fallopian tubes, in a process that he called "office tubal sterilization".<sup>[13]</sup> The technique was ineffective; in fact at least two

women underwent abortions. Ringrose was sued for malpractice, although these suits were unsuccessful.

### **6 – 1 – Disinfection**

Much research has been done in evaluating the ability of the silver ion at inactivating *Escherichia coli*, a microorganism commonly used as an indicator for fecal contamination and as a surrogate for pathogens in drinking water treatment. Concentrations of silver nitrate evaluated in inactivation experiments range from 10–200 micrograms per liter as  $\text{Ag}^+$ . Silver's antimicrobial activity saw many applications prior to the discovery of modern antibiotics, when it fell into near disuse. Its association with argyria made consumers wary and led them to turn away from it when given an alternative.

### **6 – 2 - Against warts**

Repeated daily application of silver nitrate can induce adequate destruction of cutaneous warts, but occasionally pigmented scars may develop. In a placebo-controlled study of 70 patients, silver nitrate given over nine days resulted in clearance of all warts in 43 % and improvement in warts in 26 % one month after treatment compared to 11 % and 14 %, respectively, in the placebo group.



*Skin on hand stained by silver nitrate*

### **7 – Safety**

As an oxidant, silver nitrate should be properly stored away from organic compounds. Despite its common usage in extremely low concentrations to prevent gonorrhea and control nose bleeds, silver nitrate is still very much toxic and corrosive.<sup>[16]</sup> Brief exposure will not produce any immediate side effects other than the purple, brown or black stains on the skin, but upon constant exposure to high

concentrations, side effects will be noticeable, which include burns. Long-term exposure may cause eye damage. Silver nitrate is known to be a skin and eye irritant.

Silver nitrate is currently unregulated in water sources by the Environmental Protection Agency. However, if more than 1 gram of silver is accumulated in the body, a condition called argyria may develop. Argyria is a permanent cosmetic condition in which the skin and internal organs turn a blue-gray color. The United States Environmental Protection Agency used to have a maximum contaminant limit for silver in water until 1990, when it was determined that argyria did not impact the function of any affected organs.<sup>[17]</sup> Argyria is more often associated with the consumption of colloidal silver solutions rather than with silver nitrate, since it is only used at extremely low concentrations to disinfect the water. However, it is still important to be wary before ingesting any sort of silver-ion solution.



## Silver Potassium Cyanide

Potassium argento cyanide	
Molecular formula	$\text{K Ag (CN)}_2$
Molar mass	199 g / mol
Appearance	white crystals
Density	2.36 g / cm <sup>3</sup>
Solubility in water	Soluble
Solubility	insoluble in acids
Refractive index ( $n_D$ )	1.625

Potassium argento cyanide is a white solid used in silver plating, as a bactericide, and in the manufacture of antiseptics.

It is manufactured by adding silver chloride to a solution of potassium cyanide.

# Silvering

## Contents

- 1 Introduction
- 2 History
- 3 Modern silvering process

## 1 - Introduction

Silvering is the chemical process of coating glass with a reflective substance. When glass mirrors first gained wide spread usage in Europe during the 16th century, most were silvered with an amalgam of tin and mercury, but by the 19th century mirrors were commonly made through a process by which silver was coated onto a glass surface. Today, sputtering Aluminum or other compounds are more often used for this purpose, although the process may either maintain the name "silvering" or be referred to as aluminising.

## 2 – History

The earliest mirrors were made from polished obsidian during the Stone Age, but by the Bronze Age most cultures had adopted mirrors made from polished discs of bronze, copper or other metals.<sup>[2]</sup> Such metal mirrors remained the norm through to Greco - Roman Antiquity and throughout the Middle Ages in Europe.<sup>[3]</sup> It was not until the 1st century CE that glass mirrors began to show up, now believed to have originated in Sidon, in what is modern - day Lebanon.<sup>[4]</sup> In Ptolemaic Egypt small glass mirrors were made backed by lead, tin, or antimony. In the early 10th century, the Muslim scientist al - Razi described ways of silvering and gilding in a book on alchemy, but this was not done for the purpose of making mirrors.

In 1835 German chemist Justus von Liebig developed a process for depositing silvering on the rear surface of a piece of glass that gained wide acceptance after improvement by Liebig in 1856 . The process was further refined and made easier by French chemist Petitjean (1857). This reaction is a variation of the Tollens' reagent for aldehydes. A di ammine silver (I) solution is mixed with a sugar and sprayed onto the glass surface. The sugar is oxidized by silver (I),

which is itself reduced to silver (0) , i.e. elemental silver, and deposited onto the glass.

In 1856 - 57 Karl August von Steinheil and Léon Foucault introduced the process of depositing an ultra thin layer of silver on front surface of a piece of glass, making the first optical quality first surface glass mirrors, replacing the use of speculum metal mirrors in reflecting telescopes. These techniques soon became standard for technical equipment.

An aluminum vacuum - deposition process invented in 1930 by Caltech physicist and astronomer John Strong, led to most reflecting telescopes shifting to aluminum.<sup>[8]</sup> Nevertheless, some modern telescopes use silver, such as the Kepler space observatory.<sup>[9][10]</sup> The *Kepler* mirror's silver was deposited using ion assisted evaporation.

### **3 - Modern silvering process**

In modern aluminum silvering, a sheet of glass is placed in a vacuum chamber with electrically heated nichrome coils that can evaporate aluminum. In a vacuum, the hot aluminum atoms travel in straight lines. When they hit the surface of the mirror, they cool and stick. Some mirror makers evaporate a layer of quartz on the mirror; others expose it to pure oxygen or air in an oven so that it will form a tough, clear layer of aluminum oxide.

Mirrors made by this method are classified as either *back-silvered*, with the silvered layer viewed through the glass; or *front-silvered*, ( called a first surface mirror ) with the reflective layer on the surface towards the incoming light or image. Most common household mirrors are back - silvered, since this protects the fragile reflective layer from corrosion, scratches, and other damage. However, precision optical surfaces normally need the reflective material on the front surface of the glass to avoid introducing optical aberrations. First surface mirrors use the substrate to keep form. There are optical mirrors such as mangin mirrors that are *back-silvered* (reflective coating on the rear surface) as part of their optical design.

Although the silvering on a second surface mirror such as a household mirror is often actual silver the "silvering" on precision optical instruments such as telescopes is usually aluminum. Even though silver has the best initial front-surface reflectivity in the visible spectrum it is unsuitable for optical mirrors because it quickly oxidizes and absorbs atmospheric sulfur to create a dark, low-reflectivity tarnish. Although aluminum also oxidizes quickly, the thin aluminum oxide ( sapphire ) layer is transparent, and so the high-reflectivity underlying aluminum stays visible.

The "silvering" on infrared instruments is usually gold. It has the best reflectivity in the infrared spectrum, and has high resistance to oxidation and corrosion.

# Sterling Silver

## Contents

- 1 Introduction
- 2 Etymology
- 3 History
- 4 Hallmarks
- 5 Uses
- 6 Tarnish and corrosion

## 1 - Introduction

**Sterling silver** is an alloy of silver containing 92.5 % by mass of silver and 7.5 % by mass of other metals, usually copper. The sterling silver standard has a minimum millesimal fineness of 925.

*Fine silver*, for example 99.9 % pure silver, is generally too soft for producing functional objects; there fore, the silver is usually alloyed with copper to give it strength while preserving the ductility and beauty of the precious metal. Other metals can replace the copper, usually with the intention of improving various properties of the basic sterling alloy such as reducing casting porosity, eliminating fire scale, and increasing resistance to tarnish . These replacement metals include germanium, zinc and platinum, as well as a variety of other additives, including silicon and boron . Alloys such as Argentium sterling silver have appeared in recent decades.

## 2 – Etymology

One of the earliest attestations of the term is in Old French form *esterlin*, in a charter of the abbey of Les Pr aux, dating to either 1085 or 1104. The English chronicler Orderic Vitalis (1075 – c. 1142) uses the Latin forms *libr  sterilensium* and *libr  sterilensis monet *. The word in origin refers to the newly introduced Norman silver penny.

According to the Oxford English Dictionary, the most plausible etymology is derivation from a late Old English *steorling* (with (or like) a "little star"), as some early Norman pennies were imprinted with a small star. There are a number of obsolete hypotheses. One suggests a connection with starling, because four birds (in fact

martlets) were depicted on a penny of Edward I, and another, a supposed connection with *easterling*, a term for natives of the Baltic, or the Hanse, towns of eastern Germany. This etymology is itself medieval, suggested by Walter de Pinchebek (ca. 1300) with the explanation that the coin was originally made by moneyers from that region.

The British numismatist Philip Grierson points out that the stars appeared on Norman pennies only for the single three-year issue from 1077 - 1080 (the Normans changed coin designs every three years), and that the star - theory thus fails on linguistic grounds: extensive research has been done on how coins acquire names, including nicknames. Grierson's proposed alternative involves an analogy with the Byzantine solidus, originally known as the *solidus aureus* meaning "solid gold" or "reliable gold". Even though English silver pennies were known for their consistent weight and purity in the days of Offa, King of Mercia, by the time of the Conquest English coinage had seriously degenerated. One of the first acts of the Normans was to restore the coinage to what it had been in the days of Offa, and to maintain it consistently. Grierson thus proposes that "sterling" derives from "ster" meaning "strong" or "stout".<sup>[2]</sup>

### 3 – History

The sterling alloy originated in continental Europe and was being used for commerce as early as the 12th century in the area that is now northern Germany.

In England the composition of sterling silver was subject to official assay at some date before 1158, during the reign of Henry II, but its purity was probably regulated from centuries earlier, in Saxon times. A piece of sterling silver dating from Henry II's reign was used as a standard in the Trial of the Pyx until it was deposited at the Royal Mint in 1843. It bears the royal stamp *ENRI. REX* ("King Henry") but this was added later, in the reign of Henry III. The first legal definition of sterling silver appeared in 1275, when a statute of Edward I specified that 12 ounces of silver for coinage should contain

11 ounces 2 ¼ pennyweights of silver and 17 ¾ pennyweights of alloy, with 20 penny weights to the Troy ounce.

In Colonial America, sterling silver was used for currency and general goods as well. Between 1634 and 1776, some 500 silversmiths created items in the “New World” ranging from simple buckles to ornate Rococo coffee pots. Although silversmiths of this era were typically familiar with all precious metals, they primarily worked in sterling silver. The colonies lacked an assay office during this time (the first would be established in 1814 ) , so American silversmiths adhered to the standard set by the London Goldsmiths Company: sterling silver consisted of 91.5 - 92.5 % by weight silver and 8.5 - 7.5 wt % copper.<sup>[4]</sup> Stamping each of their pieces with their personal maker's mark, colonial silversmiths relied upon their own status to guarantee the quality and composition of their products.<sup>[4]</sup>

Colonial silversmiths used many of the techniques developed by those in Europe. Casting was frequently the first step in manufacturing silver pieces, as silver workers would melt down sterling silver into easily manageable ingots. Occasionally, they would create small components (e.g. teapot legs) by casting silver into iron or graphite molds, but it was rare for an entire piece to be fabricated via casting.<sup>[5]</sup> Next, silversmiths would forge the ingots into the shapes they desired, often hammering the thinned silver against specially shaped dies to "mass produce" simple shapes like the oval end of a spoon. This process occurred at room temperature, and thus is called “cold-working” . The repeated strikes of the hammer work hardened (sterling) silver, causing it to become brittle and difficult to manipulate.<sup>[5]</sup> To combat work-hardening, silversmiths would anneal their pieces—heat it to a dull red and then quench it in water--to relieve the stresses in the material and return it to a more ductile state. Hammering required more time than all other silver manufacturing processes, and therefore accounted for the majority of labor costs.<sup>[5]</sup> Silversmiths would then seam parts together to create incredibly complex and artistic items, sealing the gaps with a solder of 80 wt % silver and 20 wt % bronze. Finally, they would file and polish their work to remove all seams, finishing off with engraving and a maker's mark.

The American revolutionary Paul Revere was regarded as one of the best silversmiths from this “Golden Age of American Silver.” Following the Revolutionary War, Revere acquired and made use of a silver rolling mill from England. Not only did the rolling mill increase his rate of production — hammering and flattening silver took most of a silversmith’s time — he was able to roll and sell silver of appropriate, uniform thickness to other silversmiths.<sup>[10]</sup> He retired a wealthy artisan, his success partly due to this strategic investment: although he is celebrated for his beautiful hollowware, Revere made his fortune primarily on low - end goods produced by the mill, such as flatware. With the onset of the first Industrial Revolution, many smiths followed suit and silver smithing as an artistic occupation eventually dwindled.

From about 1840 to 1940 in the United States and Europe, sterling silver cutlery US flatware became *de rigueur* when setting a proper table. There was a marked increase in the number of silver companies that emerged during that period. The height of the silver craze was during the 50-year period from 1870 to 1920. Flatware lines during this period sometimes included up to 100 different types of pieces.

A number of factors converged to make sterling fall out of favor around the time of World War II . The cost of labor rose (sterling pieces were all still mostly handmade, with only the basics being done by machine). Only the wealthy could afford the large number of servants required for fancy dining with ten courses. And changes in aesthetics resulted in people desiring simpler dinnerware that was easier to clean.

#### **4 – Hallmarks**

Some countries developed systems of hallmarking silver:

To indicate the purity of the silver alloy used in the manufacture or hand - crafting of the piece.

To identify the silversmith or company that made the piece.

To note the date and/or location of the manufacture or tradesman.



## 5 – Uses



*Pair of sterling silver forks*

Individual eating implements often included :  
forks (dinner fork, place fork, salad fork, pastry fork, shrimp or cocktail fork)  
spoons (teaspoon, coffee spoon, demitasse spoon, bouillon spoon, gumbo soup spoon, iced tea spoon) and  
knives (dinner knife, place knife, butter spreader, fruit knife, cheese knife).

This was especially true during the Victorian period, when etiquette dictated nothing should be touched with one's fingers.

Serving pieces were often elaborately decorated and pierced and embellished with ivory, and could include any or all of the following : carving knife and fork, salad knife and fork, cold meat fork, punch ladle, soup ladle, gravy ladle, casserole - serving spoon, berry spoon, lasagna server, macaroni server, asparagus server, cucumber server,

tomato server, olive spoon , cheese scoop, fish knife and fork, pastry server, *petit four* server, cake knife, bon bon spoon, salt spoon, sugar sifter or caster and crumb remover with brush.

Cutlery sets were often accompanied by tea sets, hot water pots, chocolate pots, trays and salvers, goblets, demitasse cups and saucers, liqueur cups, bouillon cups, egg cups, plates, napkin rings, water and wine pitchers and coasters, candelabra and even elaborate centerpieces.

The interest in sterling extended to business (sterling paper clips, mechanical pencils, letter openers, calling card boxes, cigarette cases), to the boudoir (sterling dresser trays, mirrors, hair and suit brushes, pill bottles, manicure sets, shoehorns, perfume bottles, powder bottles, hair clips) and even to children (cups, cutlery, rattles, christening sets).

***Other uses of sterling include :***

Evidence of silver and/or silver-alloy surgical and medical instruments has been found in civilizations as early as Ur, Hellenistic-era Egypt and Rome, and their use continued until largely replaced in Western countries in the mid to late 20th century by cheaper, disposable plastic items. Its natural malleability is an obvious physical advantage, but it also exhibits medically specific utility, including the fact that it is naturally aseptic, and, in respect of modern medical practices, it is resistant to antiseptics, heat sterilisation and body fluids.

Due to sterling silver having a special sound character, some brasswind instrument manufacturers use 92.5% sterling silver as the material for making their instruments, including the flute and saxophone. For example, some leading saxophone manufacturers such as Selmer and Yanagisawa have crafted some of their saxophones from sterling silver, which they believe will make the instruments more resonant and colorful in timbre.

## 6 - Tarnish and corrosion

Chemically, silver is not very reactive — it does not react with oxygen or water at ordinary temperatures, so does not easily form a silver oxide. However, it is attacked by common components of atmospheric pollution: silver sulfide slowly appears as a black tarnish during exposure to airborne compounds of sulfur (byproducts of the burning of fossil fuels and some industrial processes), and low level ozone reacts to form silver oxide.<sup>[12]</sup> As the purity of the silver decreases, the problem of corrosion or tarnishing increases because other metals in the alloy, usually copper, may react with oxygen in the air.

The black silver sulfide (  $\text{Ag}_2\text{S}$  ) is among the most insoluble salts in aqueous solution, a property that is exploited for separating silver ions from other positive ions.

Sodium chloride (  $\text{NaCl}$  ) or common table salt is known to corrode silver - copper alloy, typically seen in silver salt shakers where corrosion appears around the holes in the top.

Several products have been developed for the purpose of polishing silver that serve to remove sulfur from the metal without damaging or warping it. Because harsh polishing and buffing can permanently damage and devalue a piece of antique silver, valuable items are typically hand - polished to preserve the unique patinas of older pieces. Techniques such as wheel polishing, which are typically performed by professional jewelers or silver repair companies, are reserved for extreme tarnish or corrosion.

# Gold and Silver Plating Basics

## Contents

- 1 Introduction
- 2 Gold Plating
  - 2.1 Cyanide - Based Gold - Plating Systems
  - 2.2 Alkaline Color - Flash Golds
  - 2.3 Silver - Brightened Golds
  - 2.4 Neutral Golds
  - 2.5 Acid Hard Golds
  - 2.6 Mono valent Gold Strikes
  - 2.7 Trivalent Golds
  - 2.8 Non cyanide Gold Plating
- 3 Silver Plating
  - 3.1 Cyanide Silver Solutions
  - 3.2 Non cyanide Silver Plating

## 1 - Introduction

Gold and silver share a number of chemical and physical properties. Both are soft, malleable and ductile materials, with melting points of 1,065°C and 961°C, respectively. Both crystallize in face-centered cubic configurations and form stable alloys with each other in all proportions. Both resist most common acids, although silver is readily attacked by nitric acid, and gold by aqua regia. Both form complexes with alkali cyanides.

Silver and gold are widely employed as coinage metals. Because of this and their relative rarity, both have been sought since ancient times. Much of recorded history involves them, and they continue to be valued for decorative, monetary and usage-driven applications.

## 2 - Gold Plating

Early applications of gold plating and its predecessors, fire gilding and leafing, were almost exclusively decorative. The rise of the electrical and electronics industries in the latter half of the 19th and throughout the 20th centuries created applications for gold based on its chemical inertness, low and stable contact resistance, conductivity, and resistance to arcing.

Because of its price, it has always been important to deposit gold only in those areas and at such thickness as the application actually required. Thus, selective techniques for gold deposition were developed quite early, and continue to be improved.

## **2 – 1 - Cyanide - Based Gold - Plating Systems**

Most plating of gold and its alloys is carried out from solutions containing gold as a soluble cyanide complex . Gold reacts with alkali cyanides to form either monovalent  $\{M Au (CN)_2\}$  or trivalent  $\{M Au (CN)_4\}$  complexes, wherein M is an alkali metal or, in some cases, ammonium ion. Gold plating solutions as originally configured contained some excess of free alkali cyanide, which served as a portion of the electrolyte. This automatically established the solution pH in the range of about 10 – 12 ; and since cyanide is highly surface active and difficult to rinse, occasioned staining problems as well.

Around 1950, it was recognized that monovalent alkali gold cyanides were stable in water at pH values as low as 3.2. Trivalent alkali gold cyanides are stable almost to pH zero. This realization allowed the development of purpose - designed gold plating electrolytes, free of excess cyanide and operating over a wide range of pH; containing, as necessary, various additives for brightening, hardening, grain refinement, depolarization and/or range extension.

Over time, a number of general solution classes have evolved, some of which may be listed in order of decreasing pH, as found in Table I.

## **2 – 2 - Alkaline Color - Flash Golds**

Color - flash golds are formulated to produce thin coatings of a definite color as a final finish to work that has previously been prepared. Color - flash solutions typically contain quite small amounts 0.5 – 1.5 g / L) of gold. Potassium gold cyanide,  $K Au (CN)_2$  , together with dipotassium or disodium phosphate, is the normal electrolyte containing a small amount ( 0 – 7.5 g / L ) of free KCN, and additives such as  $K Ag (CN)_2$  ,  $K Cu (CN)_2$  , and/or  $K_2 Ni (CN)_4$  in amounts sufficient to produce the desired color. The solutions are

operated at temperatures of 50 – 70°C and plating is usually done at 4 – 6 V for 10 –12 seconds.

Color - flash golds typically contain no brighteners, and since the deposits are very thin ( 0.025 – 0.075  $\mu\text{m}$  ) and highly alloyed, they are not abrasion - resistant. Good practice requires applying a layer of abrasion-resistant hard gold prior to the final color flash.

### **2 – 3 - Silver - Brightened Golds**

Silver was the first commercially successful brightening agent for gold. Early formulations of this system, as well as of similar formulations employing antimony or tin, made use of large concentrations of free cyanide ( 90 – 120 g / L ), which caused staining problems and attacked printed circuit board laminates then in use. These solutions have been reformulated with electrolytes similar to those of the color-flash baths, based on phosphate and with the free cyanide reduced to 0–7.5 g/L. Deposits with silver content in the range of about 4–9 weight percent are particularly durable in sliding friction, and are still used for slide wire and rotary-switch applications.

### **2 – 4 - Neutral Golds**

Neutral golds comprise a very large class of electrolytes aimed at deposition of very pure, soft deposits for electrical and electronic applications. There is no free cyanide. Electrolytes are based on phosphates, phosphonates or the salts of various organic acids. Most neutral gold solutions operate in the pH range of about 6–7, although it is common to raise pH somewhat so as to minimize immersion deposition, or to reduce it somewhat so as to avoid dissolution of photoresists. Similarly, quantities of the various components may be maximized to obtain higher overall conductivity for barrel applications or minimized to obtain greater fluidity for efficient pumping.

Deposits from neutral gold solutions are usually required to have excellent solder ability and wire bonding capability, both of which are usually associated with softness and high purity. There are

certain classes of brightening agents referred to as grain refiners that allow the maintenance of deposit hardnesses below 90 Knoop and purities above 99.9 percent while improving the overall reflectivity of the deposits and expanding the working range of current densities over which they may be obtained.

Thallium, lead and arsenic are examples of metallic grain refiners, often used in concentrations of about 1–3 ppm. Organic grain refiners include various polyamines and polyfunctional compounds. Thallium in solution concentrations greater than about 10 ppm have been implicated in embrittling wirebonds. Arsenic at concentrations above 30 ppm produces mirror-bright deposits with hardnesses above 140 Knoop from neutral solutions, but valence instability renders arsenic very difficult to control.

## **2 – 5 - Acid Hard Golds**

Acid hard-gold systems were the immediate beneficiaries of the realization that alkali - gold cyanides such as  $\text{KAu}(\text{CN})_2$  were stable in solutions without free cyanide at pH values as low as 3.2. By operating in the pH range of 4–5, it is possible to incorporate transition metals such as cobalt, nickel and iron into alloyed gold deposits that are hard (130–200 Knoop), bright, ductile and, with suitable fluxing, solderable. Deposit compositions are 99.7 weight percent gold or higher, and both composition and physical properties can be maintained even when plating in ranges of current density. The acid hard golds rapidly became the finish of choice for separable electrical connectors.

Acid hard - gold plating systems have been intensively developed for operation at very high current densities, also for uniform deposit distribution and for compatibility with various types of selective plating apparatus. Most current electrolytes are based on mixtures of weak organic acids and their salts. Depending on the choice of electrolyte, the metallic brighteners may be added in simple, complexed or chelated form, together with surfactants, range extenders and depolarizing agents, as needed.

## 2 – 6 - Mono Valent Gold Strikes

A strike solution is one in which the ratio of crystallite nucleation to grain growth is enhanced by operating at higher than normal current densities from a solution containing only a small amount of metal. The danger of dendritic growth, or burning, is minimized by keeping the current efficiency low and the deposition time short. The result is a fine-grained, thin deposit of highly uniform distribution and excellent adhesion. Strike coatings are often used prior to heavy deposition from a conventional plating solution.

Because of stability considerations, monovalent gold-strike solutions are limited to a minimum pH of about 3.5, which is sufficient to obtain adhesion to nickel and alloys such as Kovar, but not to most stainless steels. The maximum pH is ordinarily about 4.5. As with the acid hard golds, electrolytes tend to be based on phosphates, weak organic acids, or mixtures thereof. Brightener systems are sometimes employed to allow heavier deposits, but this is unusual in strike solutions.

## 2 – 7 - Trivalent Golds

The reaction of chloro auric acid,  $\text{H Au (Cl)}_4$ , with an alkali cyanide yields the alkali gold (III) cyanide  $\text{M Au (CN)}_4$ , where M is sodium or potassium. As mentioned previously, these species are stable at pH values down to almost zero. This allows the formulation of gold - strike solutions capable of activating and adhering to stainless steels. Somewhat similar solutions have been prepared using chloro auric acid itself. In practice, the cyanide - containing solution yields finer-grained deposits and is less subject to immersion deposition.

Trivalent gold - cyanide solutions also have been used in jewelry plating to deposit very bright, adherent layers up to about 5 microns thickness. Electrolytes for these processes operate typically over a pH range from about 2.5 – 3.0. Below pH 2.5, most organic acids are only weakly ionized, requiring additions of inorganic sulfates or chlorides to provide conductivity. Above pH 3.0, trivalent gold tends to revert to monovalent, particularly if organics are



allowed to accumulate in the solution. This condition can be alleviated by destroying the organics with peroxide, but the peroxide has to be removed completely in order to restore current efficiency.

## **2 – 8 – Non cyanide Gold Plating**

Gold can be deposited from the chloro aurate. Various other forms, such as the iodide, thiosulfate, thio cyanate and thio malate also have been proposed, but have not been commercialized. The preparation of sodium gold sulfite,  $\text{Na}_3\text{Au}(\text{SO}_3)_2$ , was reported in 1845, but commercialization of processes based on sulfite began only in the early 1960s. Since that time, sulfite-based processes have come into fairly wide use, particularly for semiconductor applications. More recently, there has been renewed interest in thiosulfate systems as well.

A sulfite gold-plating solution consists of the alkali gold sulfite, a conducting electrolyte and at least some excess of free alkali sulfite. The stability constants for sulfite complexes are lower than those for cyanides, and the excess is required to stabilize the gold complex. Sulfites are stable at alkaline pH. Addition of acid to sulfite ion releases hydrogen sulfite ion, and then sulfur dioxide. Since the anode reaction removes hydroxyl ions and thus tends to acidify the solution, it is common to operate sulfite golds at alkaline pH, usually 9.0 or above.

Brightening agents for sulfite gold systems have included arsenic, antimony and thallium. Recently a newer, stabilized series of sulfite golds have made it possible to operate at pH values below neutral. This has made it possible to employ cobalt, nickel, or organic polymers as brightening agents, or to operate without brighteners entirely.

## **3 - Silver Plating**

Whereas the complex cyanides of gold are stable at pH values low enough to allow the use of electrolytes without free cyanide, the complex cyanide of silver (only the monovalent species is formed) is unstable below neutrality, hydrolyzing to release insoluble  $\text{AgCN}$ .

This imposes a requirement to maintain at least some free cyanide in the system, and sets a minimum operating pH for cyanide silver plating solutions of at least 8.0–8.5. Within the general class of cyanide silvers there are numerous variations; optimized, variously, toward anode corrosion, deposit brightness, and plating speed.

### **3 – 1 - Cyanide Silver Solutions**

Typical general - purpose cyanide silver-plating solutions consist simply of about 90 – 120 g of free alkali cyanide per liter, together with about 25 – 40 g metallic silver per liter, added in the form of the corresponding alkali silver cyanide, or as Ag CN.

At one time, the use of sodium cyanide was the norm, but this was largely superseded by potassium cyanide because of the higher solubility of most potassium salts. As a result of hydrolysis, carbonate gradually forms in alkaline cyanide systems, and at concentrations greater than about 90 g / L , sometimes less, impedes dissolution of the anode and causes deposit roughness. Excess carbonate can be “frozen out” from sodium cyanide-based solutions by chilling the solution to 3°C or so and filtering. This is not possible in potassium-based solutions, which require treatment with calcium cyanide or barium cyanide. Some brightener systems, particularly selenium or sulfur-based, are more effective in sodium - based solutions.

Free cyanide in a silver bath performs several functions. It solubilizes the silver, functions as the electrolyte and corrodes the anodes. As noted previously for gold, cyanide ion is highly surface-active and requires thorough rinsing after plating.

Carbonate is sometimes added at makeup to increase conductivity and to allow the free cyanide to be reduced somewhat; but since carbonate forms as the solution is worked, this is often dispensed with. Nitrate and alkali hydroxide have both been used to increase the corrosion rate of the anodes and, in the case of hydroxide, to retard decomposition of the cyanide as well. In any event, the anode efficiency of cyanide silver processes almost never actually achieves 100 percent, and it is periodically necessary to replenish a

portion of the plated - out silver with alkali silver cyanide or with Ag CN.

Brightening agents for silver include various compounds containing antimony, bismuth, selenium and sulfur. Most are proprietary. The sulfur-bearing materials in particular are often complex, being reaction products of various organic compounds with carbon disulfide, sodium thiosulfate or similar reagents. For this reason, they are often referred to as “organic” brightening agents, but in almost all cases the active functionality derives from the sulfur.

Brightener systems for cyanide silver solutions almost always include both the primary brightener and a surface - active agent, the functionality of which is not completely understood. One possible mechanism would be for the surfactant to allow the primary brightener to adsorb in one particular orientation onto the crystallite surface.

Another would be to control the viscosity of the diffusion layer so as to regulate the access of the primary brightener to the surface. In any event, various surfactants appear to be optimal for specific primary brighteners, and in general the effects of the added surfactants are most easily discernable at lower current densities.

Brightened silver deposits of all types are significantly harder in the as-plated condition than annealed, wrought silver. In most cases, the hardness of un annealed silver deposits decreases slowly over time after plating, presumably owing to recrystallization and grain growth. Antimony-brightened deposits, however, relax quite slowly over time, and are considered to be permanently hardened.

Electrolytes for high-speed plating of cyanide silver are of two general types: 1) solutions containing appreciable amounts of free cyanide, in which replenishment of the silver is accomplished at least partially by anodic dissolution, and 2) solutions designed for use with insoluble anodes and containing only as much free cyanide as necessary to prevent precipitation of Ag CN at the anodes.

Solutions of the first type are commonly used for plating wire and for overall or controlled-depth plating of electronic components. Solutions of the second type are used in applications requiring solution impingement or very high solution velocity, as in spot or stripe plating.

Silver is electrochemically noble with respect to most other metals — even to gold in the cyanide system. It thus is highly prone to immersion deposit onto less noble surfaces, a condition which can be somewhat mitigated by maintaining a relatively high level of free cyanide.

Solutions of the high - velocity, low-free-cyanide type are very immersion-prone, particularly because they are commonly operated at high metal content and at elevated temperature. It is common practice to employ a pretreatment to partially passivate the substrate surface prior to entering these solutions.

An overall silver strike, if permissible, is a useful alternative. Some solutions of the low - free - cyanide type also contain components designed to minimize immersion deposition. Cyanide silver strike solutions for general applications typically contain 2 – 2.5 g silver metal / L , together with about 90 – 105 g / L of free alkali cyanide. They are operated at ambient temperature and at relatively low tank voltage. For passive - prone metals, particularly for carbon steels, you may want to employ a mixed silver-copper strike solution followed by a pure silver strike prior to silver plating. A sulfamate nickel strike without chloride or bromide is an alternative to mixed silver-copper strike.

### **3 – 2 - Non cyanide Silver Plating**

Of the various soluble non cyanide forms of silver, only two have achieved commercial success in electro plating applications. These include organosilver complexes, of which the complex with succinimide is best known; and the alkaline thiosulfate, to which succinimide is added as an anode activator.

The design of electrolytes for noncyanide silver plating is constrained by the requirement to maintain the anodes in an active and film - free condition as a source of silver for replenishment. Nitrate, lactate and sulfamate are suitable for this purpose, and various combinations have been employed. A further consideration is that succinimide hydrolyzes slowly at the operating pH ( generally from about 7.5 – 9 ) and has to be periodically replenished, regardless of whether or not the plating solution is actually being used. Since the hydrolysis process consumes hydroxyl ions, the solution pH falls slowly as well, and must be periodically adjusted.

For all these considerations, however, deposits from the succinimide solutions are semi bright , with good conductivity and above-average resistance to wear. In the as - plated condition they are harder (120 – 130 Knoop ) and more stressed than corresponding deposits from cyanide solution; but as with cyanide deposits, they show relaxation with time at ambient conditions, and can be annealed by post-baking. In the as-plated condition they are more easily subject to tarnishing than are deposits from cyanide, but this can be largely overcome by chemical treatment and stress relief, even by immersion in hot water.

More recently, a series of silver complexes with hydantoin and substituted hydantoins have been prepared and are coming into use. These promise improved pH stability and solution control, as well as higher brightness and greater resistance to tarnishing.

<b>Contents</b>	<b>Page</b>
<b>Part One : General Knowledge</b>	
Aqua Regia ( Royal Acid )	5
Coating	12
Coatings Category	17
Cyanides Category	21
Electro Plating	23
List of Alloys	31
Metal Clay	39
Metal Plating Category	43
Metal Working Category	45
Metallizing	50
Potassium Cyanide	52
Thin Film	56
<b>Part Two : Gold</b>	63
Gold	65
Colloidal Gold	99
Electrum	113
Gold Colored	116
Gold Compounds Category	124
Gold Cyanidation	126
Gold Extraction	130
Gold Filled Jewelry	136
Gold Glass	138
Gold Leaf	149
Gold Mining	152
Gold Plating	162
Goloid	167
Metal Leaf	168
Miller Process	169
Mosaic Gold	170
Tumbaga	171
<b>Part Three : Silver</b>	173
Silver	175

Silver Category	193
Silver Compounds Category	195
Silver Cyanide	197
Silver Mirror	199
Silver Nitrate	219
Silver Potassium Cyanide	225
Silvering	226
Sterling Silver	229
Gold and Silver Plating Basics	236
<b>Contents</b>	<b>246</b>