

Original Article

Blackened Silver Production

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Abstract -The mechanical method of blackening of silver jewelry involves applying black patterns to silver manually using a special gruel of graphite with iron oxide and a small amount of turpentine, which is dried, and the remains are removed using a suede cloth previously soaked in alcohol. The chemical or electrochemical methods of blackening of silver jewelry result in oxidized silver, as a result of which the metal is covered with a coating (film), and the jewelry itself changes color. The chemical method of blackening of silver takes place in several stages: degreasing silver; preparing an aqueous solution of liver of sulfur (sulfur and potassium carbonate or soda ash), heated to **80-90°C**, applying it to the desired parts of the product and thoroughly washing the product under running water, gradually lowering its temperature, to fix the color, a well-dried product is polished. During the electrochemical blackening method, electrolysis of another type of solution is used, at a lower temperature (about **20°C**), which includes sulfuric acid, sodium sulfide and acetone, requiring much less time. After such treatment, the product is thoroughly washed in running water, dried, and then polished. This method is more preferable, since after such treatment, the product has a long-term change in the color of silver, and the polished edges shine brighter, and the decoration retains its original appearance for a long time. The article presents a new electrochemical method for stable and uniform blackening of silver jewelry, which uses a previously developed theoretical mechanism for the formation of electrolytic oxygen bubbles during water electrolysis for intensive uniform formation of microdispersed oxygen bubbles over the entire area of the anode from silver jewelry (oxidation) in a specially designed electrolyzer.

Keywords – Electrolyzer, Oxidation, Silver blackening, Electrolytic oxygen gas bubbles, Mechanical, Chemical and electrochemical blackening methods.

1. Introduction

Silver is one of the noble metals, which does not have a variety of colors, unlike gold, so several methods of processing silver were invented to give it a different color and texture. Pure silver has a white color with a silvery tint, and is too plastic; it is impossible to make filigree jewelry from it. Therefore, alloys of various metals are added to silver, and depending on the percentage of silver and alloy, the color of the product and its characteristics change.

There are several types of silver: matte, coin, filigree, and blackened [1].

- **Matte:** It is obtained in different ways: by etching a special emulsion, using a sandblasting machine or a vibrating engraver. The product has a fine-grained, rough surface without gloss. Matte silver items look very exquisite and unusual. Such items are often chosen as an exclusive decorative gift.
- **Coin:** Surprisingly, coins were not made from this type of silver, as it may seem mistakenly. Coin silver contains a large percentage of silver (**90%**) and only **10%** copper (less often nickel or zinc). This alloy composition ensures the strength and wear resistance of the products. And the name most likely comes from ancient times, when people brought silver coins to the master for remelting. Today, coin silver is **900** fineness silver.



- Filigree: This is silver with the highest 960 assay value; it consists of **96%** silver and **4%** alloys of other metals. A thin silver thread is forged from this silver, and then openwork patterns and complex ornaments are formed. Making jewelry from filigree silver is considered a very complex matter, which only true masters can do.
- Blackened: Blackened silver is silver of a black shade with a contrast of white and black colors, made using a special technology. Jewelry, made from blackened silver, looks authentic and elegant, and tableware adds luxury to any interior. The advantages of blackened silver are: it does not require careful maintenance, like ordinary silver; it retains a magnificent appearance longer and is highly durable; it has bactericidal properties of the metal, helping to destroy pathogenic bacteria and microbes on the surface of the skin.

Blackening methods are divided into mechanical, chemical and electrochemical [2].

- The mechanical method involves manually applying black patterns to silver, using a special gruel of graphite with iron oxide and a small amount of turpentine, which is dried, and then removing the remains using a suede cloth previously soaked in alcohol.
- The chemical or electrochemical methods oxidize silver, as a result of which the metal is covered with a coating (film), and the jewelry itself changes color. The chemical method of processing takes place in several stages: degreasing silver; preparing an aqueous solution of liver of sulfur (sulfur and potassium carbonate or soda ash), heated to **80-90°C**, applying it to the desired parts of the product and thoroughly washing the product under running water, gradually lowering its temperature, to fix the color, a well-dried product is polished.
- During the electrochemical blackening method, electrolysis of another type of solution is used, at a lower temperature (about **20°C**), which includes sulfuric acid, sodium sulfide and acetone, requiring much less time. After such treatment, the product is thoroughly washed in running water, dried, and then polished. This method is more preferable, since after such treatment, the product has a long-term change in the color of silver, and the polished edges shine brighter, and the decoration retains its original appearance for a long time.

The article presents a new electrochemical method for stable and uniform blackening of silver jewelry, which uses a previously developed theoretical mechanism of the formation of electrolytic oxygen bubbles during water electrolysis for intensive, uniform formation of microdispersed oxygen bubbles over the entire area of the anode from silver jewelry (oxidation) in a specially designed electrolyzer.

The novelty of the developed new electrochemical method for stable and uniform blackening of silver jewelry, unlike known methods, consists in the use of a previously developed theoretical mechanism of the formation of electrolytic oxygen bubbles during the electrolysis of water for the intensive uniform formation of microdispersed oxygen bubbles over the entire area of the anode from a silver jewelry (oxidation) in a specially designed electrolyzer.

2. Materials and Methods

An aqueous solution of sulfuric acid was used as a source for the electrochemical method of blackening the anode of silver jewelry. A physical mechanism was developed for the formation of negatively charged electrolytic microdispersed hydrogen bubbles on the cathode and positively charged electrolytic oxygen bubbles on the anode from a silver jewelry item during the process of water electrolysis for the intensive uniform formation of microdispersed hydrogen bubbles and oxygen bubbles comparable in microdispersion in an acidified environment over the entire area of the anode from a silver jewelry.

Water dissociates into ions:



During the electrolysis of water, two hydrogen cations $2H^+$ reach the cathode, taking two electrons from it (reducing), and four anions OH^- move to the anode made from silver jewelry, giving up (oxidizing) four electrons. Thus, neutral hydrogen atoms $2H$ are formed on the cathode, which, being unstable in a free state, combine into pairs of H_2 molecules, which are electrolytic bubbles of hydrogen. Two water molecules are formed on the anode, made from silver jewelry, and the resulting neutral oxygen atoms O_2 , being unstable in a free state, combine into pairs of diatomic oxygen molecules O_2 , which are electrolytic bubbles of oxygen.

As a result, electrolytic bubbles of hydrogen and electrolytic bubbles of oxygen, formed during the electrolysis of water, float to the free surface of the water:



The essence of the formation of negatively charged microdispersed electrolytic hydrogen bubbles on the cathode and positively charged oxygen bubbles on the anode from silver jewelry in the process of water electrolysis is as follows.

A hydrogen molecule in the form of a bubble, formed on the cathode, is immersed in a fog of positively charged hydrogen cations H^+ , which, when a direct current voltage is applied to it, are directed to the cathode, which leads to the forming the negative charge on the outer surface of the formed hydrogen bubble, while the inner surface of the hydrogen bubble becomes positively charged. The negative potential of the cathode shifts the negative charges of the outer surface of the hydrogen bubble to its upper "dome" and attracts the positive charges of the inner surface of the hydrogen bubble, collecting them in the near-cathode region (Figure 1, [3]). At the moment of detachment of the electrolytic hydrogen bubble, the positively charged part of the bubble in the near-cathode region remains on the cathode, and the detached hydrogen bubble with a negatively charged surface floats to the free surface of the water. The neutral oxygen molecule, formed on the anode from the silver jewelry in the form of an oxygen bubble is immersed in a fog of negatively charged hydroxyl anions OH^- , which, when a DC voltage is applied to the anode from the silver jewelry, induce a positive charge on the outer surface of the electrolytic oxygen bubble, while the inner surface of the electrolytic oxygen bubble is charged negatively. The positive potential of the anode from the silver jewelry, by means of the electrostatic repulsive force, will shift the positive charges on the outer surface of the bubble towards its "dome" and attract the negative charges on the inner surface of the bubble, collecting them in the near-anode region (Figure 2, [3]).

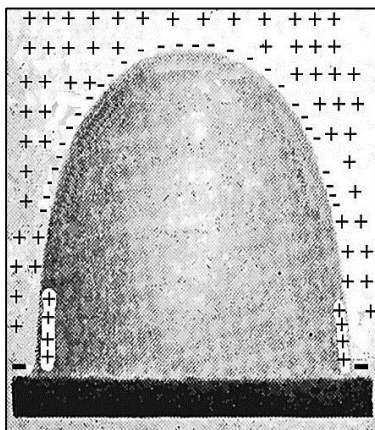


Fig. 1 Photo of the electrolytic bubble of hydrogen with the angle of contact of $\theta=97^\circ$ on the cathode (increase in $\times 7.5$), [3].
 "+" – is the cations of hydrogen H^+ , the positive charges of the inside of the surface of the electrolytic bubble of hydrogen on the cathode;
 "-" – is the negative charge of the cathode, negative charges of the external surface of the electrolytic bubble of hydrogen.

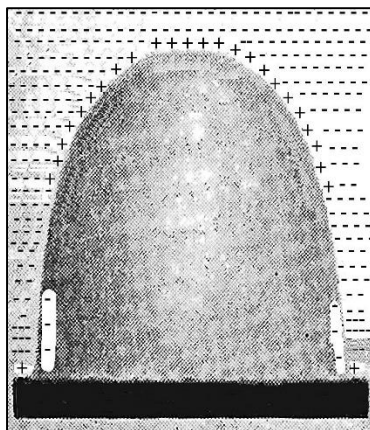


Fig. 2 Photo of the electrolytic bubble of oxygen with the angle of contact of $\theta=97^\circ$ on the (increase in $\times 7.5$), [3].

“+” – is the positive charge of silver jewelry anode and of the external surface of the bubble of oxygen;

“-” – is the negative charges of OH^- around the bubble of oxygen and of the internal surface of the bubble of oxygen near the silver jewelry anode.

Thus, during the process of electrolysis, a negatively charged electrolytic bubble of hydrogen breaks away from the negatively charged cathode and floats, and a positively charged electrolytic bubble of oxygen breaks away from the positively charged anode and floats, that is, the sign of the charge of the gas bubble corresponds to the sign of the charge of the electrode on which it was formed.

The following forces act on an electrolytic bubble of hydrogen or oxygen, fixed to the horizontal surface of the cathode or anode, made from silver jewelry, causing the electrolytic bubbles of hydrogen and oxygen to detach from the electrodes:

- The surface tension force of the gas bubble F_σ , holding the gas bubble on the electrode surface, acting along the perimeter of the contact of the gas bubble with the electrode surface and equal to the product of the value of this perimeter πa and the value of the vertical component of the surface tension σ , that is, $F_\sigma = \pi a \sigma \sin(\theta)$, where a is the diameter of the circle, along which the bubble is attached to the electrode surface; θ is the contact angle at the metal + water + gas phase boundary; σ is the surface tension at the water + gas phase boundary.
- The buoyant force of a bubble rising in water according to Archimedes' law is $F_A = \rho g V$, where V is the volume of the bubble; ρ is the density of water; g is the acceleration of gravity directed upwards towards the free surface of the water.
- Two electrostatic forces F_E of repulsion of the corresponding gas bubble from the corresponding electrode, and attraction F_{E1} of the potential of the corresponding ion fog to the corresponding outer surface of the gas bubble.

Then the resulting force, acting on the gas bubble at the points of its contact with the electrode surface, can be represented as $F_\sigma = F_A + F_E + F_{E1}$. For small bubbles, when $F_\sigma > F_A$, the contribution of F_E and F_{E1} to the detachment of the gas bubble from the electrode is significant. With increasing bubble size, F_A grows faster than F_σ , since F_A is proportional to the third power of the linear dimensions of the gas bubble, and F_σ is proportional to the first power. It follows that in this case, the F_A detaches the gas bubble from the electrode surface.

Consequently, the higher the electric potential of the electrode and the ion fog around the gas bubble, the smaller the size of the gas bubble, since the higher the electric potential of the electrode and the ion fog around of the gas bubble, the greater the force of electrostatic repulsion, acting between the electrode and the similarly charged electrolytic bubble, formed on it and, consequently, the greater the force of detachment of the gas bubble from the electrode surface and the less time is required for the gas bubble to detach.

On the other hand, the faster the electrolytic bubble of hydrogen or oxygen breaks away from the electrode surface, the faster its place is taken by the next electrolytic bubble, which leads to an intensification of the formation of electrolysis bubbles. Thus, by increasing the electrical potential of the electrode, it is possible to control the size of the electrolytic bubble formed on it and make it as small as required by the technological process, as well as control the intensification of the formation of electrolysis bubbles, that is, the intensification of the technological process.

Another factor affecting the size of the electrolytic bubble is the concentration of alkalinity (electrolytic bubbles of hydrogen) or acidity (electrolytic bubbles of oxygen) of the aqueous medium. The higher the concentration of alkalinity or acidity, the higher the electric potential of the corresponding ionic fog (hydrogen cations in the case of an alkaline aqueous medium and hydroxyl anions in the case of an acidic aqueous medium) and, consequently, the force of electrostatic attraction, acting between the corresponding ionic fog and the outer layer of the corresponding electrolytic bubble, the greater the force of detachment of the electrolytic bubble from the electrode surface and the faster it detaches.

Consequently, electrolytic hydrogen bubbles in alkaline aqueous solutions are many times smaller than electrolytic oxygen bubbles (almost 16 times), and electrolytic oxygen bubbles in acidic aqueous solutions are significantly smaller in size during water electrolysis. For blackening silver, the described mechanism for controlling the size and intensity of electrolytic oxygen bubbles on the anode from silver jewelry in an acidic aqueous medium (oxidation) during electrolysis was used. As an acidic medium, it was used a small solution of sulfuric acid H_2SO_4 , was used; the dissociation of the molecule of which has the following form:



During electrolysis, the following reactions occur on the electrodes:

$2H^+ + 2e^- = H_2\uparrow$ (hydrogen is released in the form of bubbles) on the cathode, $SO_4^{-2} - 2e^- = SO_4$ (a neutral group SO_4 is formed) on the silver jewelry anode. The neutral group SO_4 is chemically very active and enters into a secondary reaction. Since the silver jewelry anode is a silver jewelry, SO_4 reacts only with water:



Anions SO_4^{-2} , running to the silver jewelry anode, strengthen the fog of negatively charged hydroxyl anions OH^- , which leads to small sizes of the resulting electrolytic bubbles and their intensive formation, which leads to uniform and intense saturation (oxidation) of the anode from silver jewelry and the formation of a thin and durable black film on it.

The above-described control of the size and intensity of the formation of electrolytic oxygen bubbles formed the basis for the design of an electrolyzer for blackening silver, shown in Figure 3.

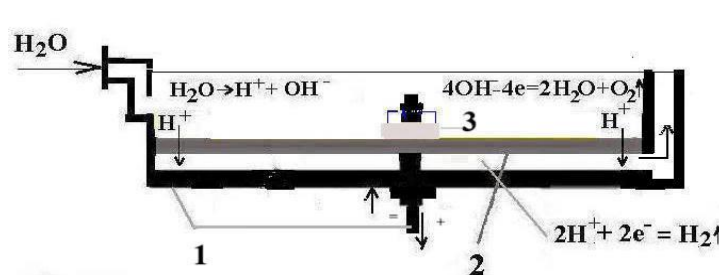


Fig. 3 Electrolyzer for blackening silver

The electrolyzer includes an electrolysis base (1), consisting of a steel cathode and an anode (3), made from silver jewelry; electric current is supplied to the electrolysis base, using a special plug, which is a combined tube: an outer tube connected to the cathode, located at the bottom of the electrolyzer, having an inner tube with insulation from the outer tube and a thread at the top, where special inserts, made from steel with insulation with open ends connected to the anode, made from silver jewelry are fixed.

Special inserts at both ends fix the anode, made from silver jewelry, to the membrane by tightening the nut at the top of the inner tube with insulation and supply an electric voltage to the anode made from silver jewelry. There is a whole set of such inserts suitable for any silver jewelry. The membrane (2) serves to pass hydrogen cations H^+ and water to the cathode and prevents the penetration of hydroxyl anions OH^- and SO_4^{2-} to the cathode, holding them in the near-anode space. The gap between the cathode and the silver jewelry anode, located on the membrane, is adjusted, using a set of plastic frames of different thicknesses, in which one side is passed through to allow the passage of hydrogen bubbles and water from the electrolyzer chamber. This plastic frame is located on the cathode.

The electrolyzer operates as follows.

- When voltage is applied to the cathode and the silver jewelry anode, the process of electrolysis of acidified water occurs.
- As a result, hydrogen cations H^+ rush to the cathode through the membrane and, having reached it, take away an electron from it, turning into a neutral hydrogen atom H , which, in a free state, being unstable, combines with an adjacent hydrogen atom into a pair, forming a hydrogen molecule H_2 .
- Four hydroxyl anions ($4OH^-$) and the SO_4^{2-} anion rush to the silver jewelry anode and are concentrated in the near-anode space due to the membranes.
- Four hydroxyl anions, giving up four electrons to the silver jewelry anode, form two water molecules and release an oxygen molecule (O_2) in the form of an electrolytic oxygen bubble, which floats to the free surface of the acidified water; the SO_4^{2-} anion gives up two electrons to the silver jewelry anode, becoming neutral SO_4 .
- SO_4 , interacting with two water molecules in the near-anode space, forms two molecules of sulfuric acid and releases an oxygen molecule in the form of an oxygen bubble, which floats to the free surface of the acidified water.

As described earlier, over the entire area of the silver jewelry anode, there is an intensive and uniform formation of electrolytic oxygen bubbles, which uniformly saturate the silver jewelry anode (oxidation), forming a thin, durable, indelible black film.

3. Results and Discussions

Practical use of the developed electrolyzer showed multiple advantages in terms of energy consumption compared to the existing means of electrochemical blackening of silver.

The horizontal placement of the cathode and silver jewelry anode above it allows changing the electric voltage on the electrodes from 10 V to 100 V at a maximum current of one ampere, i.e. energy consumption of 100 W. A maximum concentration of sulfuric acid solution of 5% for maximum saturation of the silver jewelry anode by electrolytic oxygen bubbles (oxidation), whereas in known devices for electrochemical blackening of silver, a solution of 70% sulfuric acid is used to achieve a positive effect. In comparison, at a maximum permissible voltage of 30 V, the electric current reaches at least 100 amperes, i.e. energy consumption is 3 kW.

The use of a membrane in the developed electrolyzer permitted to form a concentrated fog of hydroxyl anions (OH^-) and SO_4^{2-} anions in the near-anode space, isolating the silver jewelry anode from hydrogen cations (H^+), which contributed to the intensive formation of electrolytic oxygen bubbles and saturation of the silver product with them during the electrolysis process.

The developed electrolyzer allows blackening of silver jewelry with a thin, durable and indelible black film, which does not require careful maintenance, like ordinary silver, retains its magnificent appearance longer and is distinguished by high strength, bactericidal properties of the metal, which help destroy pathogenic bacteria and microbes on the surface of the skin. Figure 4 shows examples of blackened 925 silver jewelry.



Fig. 4 Examples of blackened 925 silver jewelry

4. Conclusion

Thus, the developed theoretical mechanism of formation of electrolytic oxygen bubbles during electrolysis for intensive formation of microdispersed oxygen bubbles on the silver jewelry anode (oxidation) allowed developing a new electrochemical method of silver blackening.

The developed mechanism became the basis of the developed electrolyzer, which, in practice, implemented a new electrochemical method of silver blackening.

A specially developed electrolyzer, using a horizontal arrangement of electrodes, in contrast to known devices for electrochemical blackening, allowed to use a voltage on the electrodes from 10 V to 100 V at a maximum current of one ampere, i.e. power consumption of 100 W, and a maximum concentration of 5% sulfuric acid solution for maximum saturation of the silver jewelry anode of silver jewelry with electrolytic oxygen bubbles (oxidation), while in known devices for electrochemical blackening of silver, a 70% sulfuric acid solution is used to achieve a positive effect, and at a maximum permissible voltage of 30 V, the electric current reaches at least 100 amperes, i.e. power consumption is 3 kW. The hydroxyl anions (OH^-) and SO_4^{2-} anions in the near-anode space, isolating the silver jewelry anode from hydrogen cations (H^+), which contributed to the intensive formation of electrolytic oxygen bubbles and saturation of the silver product with them during electrolysis.

The developed electrolyzer permits blackening silver jewelry with a thin, durable and indelible black film, which does not require careful maintenance, like regular silver, retains its magnificent appearance longer and is distinguished by its high strength, bactericidal properties of the metal, which help destroy pathogenic bacteria and microbes on the surface of the skin.

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