European Journal of Science and Theology, March 2005, Vol.1, No.1, 77-83

ON THE ULTRASOUND CLEANING OF SILVER ICON WORKS

Nicoleta Melniciuc Puică*

University "Al. I. Cuza", Faculty of Theology, Department of Conservation- Restoration, 9 Closca, 700065 Iasi, Romania

(Received 7 February 2005)

Abstract

The paper deals with the silver corrosion of religious art objects and their non-destructive restoration treatment. One of the non-destructive methods used for the metal objects restoration and conservation is the ultrasound cleaning. The analysis of some as processed silver icons, by means of Scanning Electronic Microscopy, proved that the ultrasound treatment could be recommended for the cleaning of silver tarnish.

Keywords: ultrasound, cleaning, silver, corrosion

1. Introduction

The dialogue between Theology and Science was always desired and has preoccupied the humanity in the course of time. During the history of humanity there have been periods when either Theology or Science dominated the reasoning preoccupations in dialogue with Mystery.

There is a strong link between the God glorification through art and the processing of precious metals by their changing into beautiful religious pieces. Exquisite works of art (like icons, vessels, etc.) are usually used in cult and their preservation always presented interest for both the priest and the handicraftsman.

Even the King David′s words from Ps. 12,6 confirm a technique of working silver by cleaning, necessary for honouring the Creator: "The words of the LORD are pure words: as silver tried in a furnace of earth, purified seven times".

Cleaning was needed for erasing debris of a precious metal object, and this activity does not diminish the value of the object and does not affect the holiness obtained by it by means of sacred usage.

A lot of non-conventional methods have appeared in the field of art objects cleaning. The restoration specialists are considering them as part of the non-destructive treatment category. Among these, the ultrasound cleaning seems to gain more importance in the last time. Researches have proposed the ultrasound usage in conservation and restoration of art works, for the removal of

* e-mail: bradeail@yahoo.com

the surface debris which are in less accessible areas [1, 2]. This method can be used for metal objects with different adornments, flawless and sometimes is preceded by a chemical treatment. Ultrasounds are also used for removing the traces of the older restorations and also for removing the consolidations and the protecting layers from the object.

Ultrasounds are elastic vibrations of the fluid or solid particles of environment, with frequency over 20 kHz, a frequency considered as the minimum limit of receiving vibrations by mean as ultrasounds. The generating equipments are mechanic or electro-acoustic, the latter being considered more efficient. Generally, the parts of the electro-acoustic equipment are [3, 4]:

- The source of energy, which is an electronic generator of frequency that changes the energy of industrial frequency into high frequency, in order to charge the ultrasound transductor. The generator frequency is different depending on the utilization field. For example, the objects cleaning requests ultrasounds with frequencies between 20-40 kHz.
- The ultrasound sources or the ultrasound transductor, which changes the energy received from the source into acoustic energy. The frequency of the generator should be in agreement with the basic frequency or on that of first harmonics of the transmitter. There is a large variety of transmitters; among them the most common are the piezoelectric and the magnetic-limitative ones.
- The concentrators or the amplifiers of acoustic energy are elements which achieve the concentration of the acoustic energy in a reduced volume and, hence, obtaining high intensity ultra-acoustic waves.
- The elements of transfer for the acoustic energy are linking the concentrators and the radiating environment with ultrasounds, and the chargers of waves are converting a type of wave into another one.
- The acoustic adaptation and coupling elements are assuring an optimal energy transfer between the elements of the equipment.
- The systems of mechanical placing and acoustic isolation used in order to transfer more efficiently the ultrasounds.

Recently discovered, the Tube Resonator is a unique omni-directional ultrasonic cleaning device that can be easily retrofit into existing or new cleaning systems to enhance the overall cleaning efficiency. Tube Resonators are available in operating frequencies ranging from 20 kHz to 40kHz and it works with a high-energy output and reduced maintenance costs [5].

Due to their high frequency, ultrasounds have some specific peculiarities, among them the cavitation phenomenon. This aspect means the “breaking” of a fluid in certain areas and its immediate re-making under the action of high pressures appearing as a consequence of the necessary relaxations and pressures of the environment, due to the transmission of the wave.

The fluid and the gases dissolved in the fluid are directed toward the appearing cavities. The subsequent compressions lead to the minimizing of the cavities volume and, hence, to the increase of the pressure inside them (up to thousands of atmospheres), leading finally to their implosion, resulting thus very strong hydraulic shocks or shock waves.

The implosion of cavity spheres leads to the increase of the environment temperature (material), but also influences the electrochemical potential and the metal passivity, facts that generate chemical effects [6-8]. On the other hand, the pressure increase when the cavity implodes (10^{-6} atm) leads to the appearance of electric shocks and ultraviolet radiations in the cavity sphere producing ions, free radicals or ionised molecules of high energy, achieving thus chemical reactions [9-11].

The high pressures that appear as a consequence of implosions generate the corrosion of a submerged solid body. The corrosion degree depends on many elements, among them the wave frequency and intensity, the length of ultrasound shock, the nature and temperature of the fluid and the type of gas dissolved in the fluid, etc.

The cleaning of the metal objects with ultrasounds leads to the fragmentation of the covering layer made of corrosion elements, dust or varnish, into thin particles, without affecting the main surface.

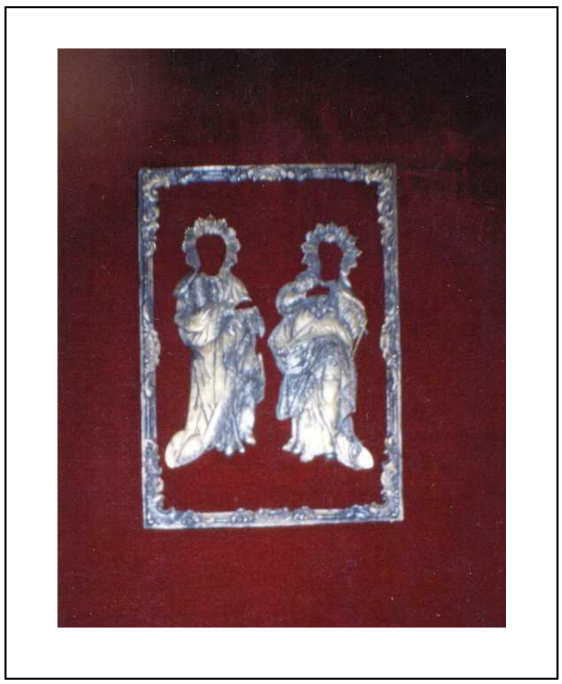


Figure 1. Silver covers of 'St. Ecaterina and St. Varvara' icon

2. Experimental

The experiments were conducted on silver icon works handcrafted at the beginning of the 20^{th} century. These silver covers belong to an icon ('St. Ecaterina and St. Varvara'), which was separately restored by the specialists of the "Ressurectio" Centre of Conservation and Restoration of Art from the Metropolitan Church of Moldova and Bucovina in Iassy. (Figure 1)

First of all, the icon silver works were analysed by means of Scanning Electronic Microscopy (SEM), using a TESLA BS 800 microscope, in order to determine the types of degradation. Prior to these analyses the covers were firstly cleaned of dust and disinfected.

Later on it was performed the physical cleaning with ultrasounds, the objects being submerged into a bowl with fluid (water and 1% detergent). The ultrasound bowl was filled with water through which there are propagated the ultrasound waves, having an effect all over the object. During the experiments the icon works were exposed to a 20 MHz ultrasonic field. The experimental programme is shown in the Table 1.

Table 1. Experimental programme of cleaning with ultrasounds of some silver samples

Time of exposure to ultrasounds (minutes)	10	30	60
The temperature of the bowl (^{0}C)	80	80	80

A dithionite-alkaline classical cleaning followed the process of removing the corrosion products by the ultrasounds activation of the chemical treatments. The dithionite-alkaline solution contained 40g of sodium hydroxide, 50g of sodium dithionite and 1liter of distilled water. A witness sample was subjected only to the classical chemical cleaning. The electronic microscopy offered information on the efficiency of the proposed method.

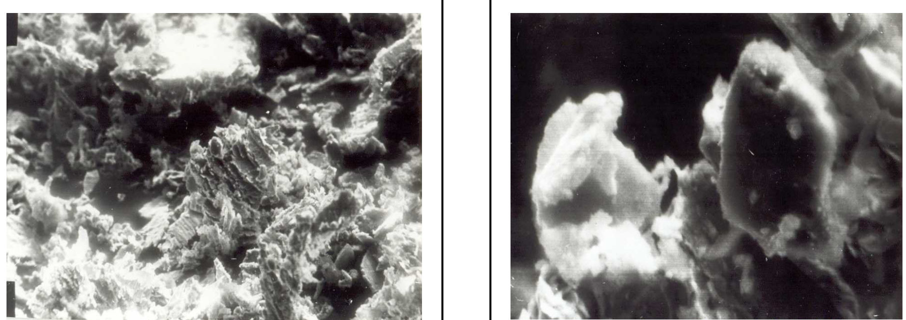
3. Results and discussion

By means of the electronic microscope there were gathered information about the type of degradation products present on tarnish silver objects. It is known that silver objects of art are sensitive to the action of sulphur gases in the modern polluted atmosphere and to moist resulting in the following type of reactions:

$$2Ag + H_2S + 1/2O_2 \rightarrow Ag_2S + H_2O \qquad (1)$$

The resulting corrosion product, silver sulphide Ag_2S, the principal components in tarnish, is the main cause of darkening the silver objects in museums [12]. The icon and old book works, having incorporated silver, are also sensitive to sulphur gases in atmosphere, but also to hydrogen sulphide from other sources (the degradation of protein materials, sulphur dyers, glues with aluminium sulphide, etc.). In the case of the studied sample there were firstly detected trigonal crystals, of corrosion essence, perpendicularly placed on the surface of the material (Figure 2).

Similar crystals, referred to as "whiskers", have been grown on silver under laboratory special conditions (high levels of hydrogen sulphide). It was observed that whisker grown at relative humidity below 100%. The sulphide crystals are thought to originate at sites, such as crevices, where water condenses by capillary action. Crystal growth is encouraged by the high mobility of silver atoms in pure silver and in silver sulphide crystals and by the higher concentrations of reduced-sulphur gases [13].



(a) (b)

Figure 2. The corrosion products on the surface of a silver icon, as seen by SEM: (a) magnification x1000; (b) magnification x10000.

The macroscopic analysis of the sample subjected to the mixed treatment revealed that the ultrasounds have activated the chemical cleaning, the treated surface having a reduced quantity of remaining corrosion products. It seems that the higher efficiency of cleaning with ultrasounds, unlike the exclusive chemical treatment, is the result of the cavitation phenomenon.

Later on the above sample was analysed by SEM. The microscopy analysis confirmed what was macroscopically observed. The corrosion products detected on the surface of the sample treated with ultrasounds are much more fragmented and non-adherent to support comparing with the initial non-treated sample (Figure 3). It was also observed that this fragmentation phenomenon increased with the time of ultrasonic exposure.

The qualitative analytical analysis, performed with specific solutions of corrosion products, showed that the main corrosion product is the silver sulphide [14].


(a)


(b)

Figure 3. The corrosion products on the surface of the silver work, after the treatment with ultrasounds for 60 minutes, as observed by SEM: (a) magnification x1000; (b) magnification x10000.

4. Conclusions

The hereby study concerns the silver objects degradation and the removing of the corrosion products by means of ultrasounds.

This type of treatment, combined with a cleaning chemical agents, is efficient and recommended to specialists in the field of metal objects restoration, especially for well enough preserved objects, with less accessible areas.

References

[1] C. Dignard, R. Douglas, S Guild, A. Maheux, and W. Mc. Williams, Journal of the American Institute for Conservation, **36** (1997) 127.
[2] W.Mourey, *Conservarea antichităților metalice*, Ed. Tehnică, Bucureşti, 1998, 50.
[3] V. Vasilescu and I.Nagy, *Ultrasunetele în medicină şi biologie*, Ed. Medicală, Bucureşti, 1984, 5.
[4] E. Bădărău, M. Grumăzescu, *Ultraacustica fizică şi tehnică*, Ed. Tehnică, Bucureşti, 1967, 7.
[5] ***, available at www.telsonicusa.com/cleaning.htm
[6] R.G. Compton, J.C. Eklund, F. Marken, T.O. Rebbitt, R.P. Akkermans and D.N. Waller, Electrochim. Acta, **42** (1997) 2919.
[7] H.N. McMurray, D.A. Worsley and B.P. Wilson, Chem. Comm., **8** (1998) 887.
[8] J.L. Hardcastle, J.C. Ball, Q. Hong, F. Marken, R.G. Compton, S.D. Bull and S.G. Davies, Ultrason. Sonochem., **7** (2000) 7.
[9] K.S. Suslick, Science, **247** (1990) 1439.
[10] B.E. Flint and K.S. Suslick, Science, **253** (1991) 1397.
[11] K.S. Suslick and G.J. Price, Annu. Rev. Mater. Sci., **29** (1999) 295.
[12] C. Degrigny, M. Wery, V. Vescoli and J.M. Blengino, Studies in Conservation, **41** (1996) 170.
[13] C. Sease, L.S. Selwyn, S. Zubiate, D.F. Bowers and D.R. Atkins, Studies in Conservation, **42** (1997) 1.

[14] D.O. Dorohoi, N. Melniciuc–Puică and C. Nicolescu, *Tehnici de investigare a obiectelor de patrimoniu*, Ed. Vasiliana 98, Iaşi, 2000, 133.