Formation of patina on a copper surface in polyacrylate gels with gold nanoparticles

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Abstract. The experimental research demonstrates the effective use of patination of the copper and copper alloys in containing gold nanoparticles in order to increase their protective properties. The copper samples were examined by cyclic voltammetry method, optical microscopy, and X-ray analysis. It has been shown that patinas obtained in the polymer gel solution have a better corrosion resistance in comparison with the patinas obtained with chemical methods.

1. Introduction
There are many architectural and culturally valuable objects made of copper metal and copper alloys [1], which require the restoration. Such objects are covered by the layer of patina to make the decorative painting and keep the surface protection against external influence [2–5]. However, even if patination recipes are well-known it is highly difficult to achieve reproducible phase composition on the surface of pure copper and copper alloys. Therefore, the search for new methods of patina creation on the copper surface of culture and art objects is still an issue of concern. In this work, we propose to use the polymer a gel, the mixture of homopolymers of polymethyl methacrylate and polymethacrylic acid, polyethylene glycol containing gold nanoparticles.

2. Experimental part
The polymeric gels were based on copolymer of methyl methacrylate and methacrylic acid filled with polyethylene glycol. The reagents were immediately put into a polyetilen polymerization form and solidified by thermal polymerization at 60°C; benzoyl peroxide was used as an initiator. In experiment we obtained films with thickness of 0.5 mm by two approaches. The first method included the films formation by thermal pressing, and the second one – films formation from the solution of the polymeric gel in composition solvents [6, 7]. Methylcelllosolve, butylacetate, toluene (in ratio 75:15:10) were used as the composite solvents [8]. The nanoparticles in gel solution were obtained by the method of laser ablation.

Chemical patination was used for the creation of some resistance layers as the reference standard (table 1).

Table 1. The solutions for patination

| Solution | Composition |
|----------|-------------|

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The solutions were placed on the surface of the 1x1 cm samples. The morphology analysis of the samples was carried out by means of an optical microscope “Metam PB-21-1” (Russia). Surface phase transformations after contact “metal – gel” were examined by the method of X-ray diffraction (XRD-7000, Shimadzu). Corrosion resistance of the coatings was evaluated using a cyclic voltammetry method with the help of a potentiostat-galvanostat IPC-Pro MF (Russia). The cyclic current-voltage curves registration (CV) was performed in the three-electrode cell: the reference electrode (chloride saturated silver electrode), the auxiliary electrode (graphite rod), and a test samples (copper plates, 5x5 mm). Patina obtained on the surface was used as the indicator electrode. Registration of the cyclic current-voltage curves was performed in potential change range at $1000 \ldots 700$ mV with scan rate of $10$ mV/c in three media: HCl, KCl, NaOH.

3. Results and discussion
The figure 1 presents the results of X-ray analysis after patination of copper. All X-ray diffractograms (XRD) show the signals of the elemental copper. Most of patinas contain cuprite. The patina obtained in polymer gel solution also contain phase of tenorite ($\text{Cu}_2\text{O}_2\cdot \text{H}_2\text{O}$).

![Figure 1. X-ray diffractograms of copper objects after patination.](image)

The figure 1b shows the XRD of patinas formed in polymer solution with nanoparticles at different temperatures. It can be seen that the patina formed at $40$ °C is the most stable because the copper peaks were weaker; it means that the patina is homogeneous, that proved optical images (figure 2). Patina formed at $80$ °C has a higher copper XRD signal, which indicates a thinness of the film. The areas with green color point of copper carbonates on the surface, which are generally have less corrosion resistant than cuprite.

Values of the potential and the corrosion current are shown in the table 2. Among the chemically produced patinas only one has the best protective properties in all three aggressive mediums: the patina formed in the solution of copper and silver nitrate (solution #3). This patina has the lowest value of the current and the highest value of corrosion potential. The patina formed in gel solution
(MMA, MAA, PEG) has stronger protective properties. When the polymeric gels include the gold nanoparticles, the reproducibility of patina increases as shown by the error value.

Most informative data are received after overnight exposure in the electrolyte solution. Patina’s amperage has increased by an order, but patinas prepared by the polymer gel electrolyte have smaller corrosion current than chemically prepared patinas. The results demonstrate that the addition of gold nanoparticles into the gel solution increases the corrosion resistance of patina. However, increasing the number of particles in the volume of the gel has low effect on the properties of patina.

Table 2. Corrosion potential and current of some patinas

| Solution | $I_{\text{corr}}$ A·$10^{-9}$ | $E_{\text{corr}}$ mV | $I_{\text{corr}}$ A·$10^{-9}$ after 24 hour in 0.1M KCl | $E_{\text{corr}}$ mV after 24 hour in 0.1M KCl |
|----------|-------------------------------|----------------------|-------------------------------------------------|----------------------------------|
| Solution #4 | 31±11                         | 206±11               | 113±59                                           | 138±22                           |
| Solution #5 | 62±31                         | 192±72               | 130±98                                           | 133±44                           |
| Solution #6 | 70±38                         | 174±50               | 106±59                                           | 149±31                           |
| Solution #7 | 53±23                         | 193±78               | 107±34                                           | 174±27                           |
| Solution #6 | 40 °C 63±38                   | 253±23               | 75±63                                            | 121±121                          |
| Solution #6 | 80 °C 92±59                   | 185±15               | 88±25                                            | 96±22                            |
| Solution #1 | 23±6                          | 206±24               | 132±86                                           | 198±23                           |
| Solution #2 | 73±61                         | 215±86               | 183±51                                           | 129±12                           |
| Solution #3 | 28±29                         | 291±10               | 113±38                                           | 247±64                           |
| Solution #4 | 45±18                         | 304±5                | 42±13                                            | 238±73                           |
| Solution #5 | 47±12                         | 270±76               | 77±29                                            | 256±19                           |
| Solution #6 | 21±2                          | 219±61               | 27±5                                             | 202±59                           |
| Solution #7 | 14±2                          | 220±15               | 89±24                                            | 182±48                           |
| Solution #6 | 40 °C 18±7                    | 322±15               | 105±92                                           | 231±49                           |
| Solution #7 | 69±16                         | 280±9                | 156±71                                           | 238±53                           |
| Solution #6 | 80 °C 40 °C 18±7              | 322±15               | 105±92                                           | 231±49                           |
| Solution #1 | 32±7                          | 351±12               | 32±28                                            | 230±15                           |
| Solution #2 | 38±23                         | 243±24               | 24±17                                            | 258±45                           |
| Solution #3 | 18±4                          | 257±12               | 62±7                                             | 265±15                           |
| Solution #4 | 34±6                          | 97±7                 | 39±8                                             | 80±16                            |
| Solution #5 | 25±2                          | 117±11               | 105±56                                           | 155±152                          |
| Solution #6 | 29±8                          | 47±5                 | 44±21                                            | 111±9                            |
| Solution #7 | 38±5                          | 83±6                 | 17±3                                             | 91±10                            |
| Solution #6 | 40 °C 43±11                   | 112±80               | 66±30                                            | 109±87                           |
| Solution #7 | 80 °C 21±20                   | 118±10               | 87±13                                            | 178±102                          |
| Solution #1 | 39±10                         | 88±18                | 114±3                                            | 118±17                           |
| Solution #2 | 32±3                          | 53±44                | 183±51                                           | 129±12                           |
| Solution #3 | 40±36                         | 128±7                | 160±9                                            | 191±21                           |
The figure 3 shows the cyclic voltammetry curves of the patinas obtained by the chemical method in solution of silver and copper nitrate. Also there is a patina formed by the polymer gel electrolyte on the figure 3. According to the data, the oxidant reduction passes more actively on the surface of patina formed in copper and silver nitrate. It testifies the presence of juvenile-free areas of copper, that may be seen on the optical images on the figure 2. However, the oxidant reduction passes not actively on the surface of patina formed in the solutions of MMA, MAA, PEG polymer gels with gold nanoparticles (figure 3).

Thus, patinas formed by polymer gel electrolyte solutions with the addition of gold nanoparticles at the temperature of 40 °C showed the greatest stability.

4. Conclusion
Cathode reduction of oxidants on the surface of patina, formed by chemical method, extends at a
higher rate. Patinas obtained by polymer gel electrolytes have stronger protective properties than the patinas formed by the chemical methods. The adding of gold nanoparticles in polymeric gel increases the stability of the patina and its reproducibility. The most stable patina is formed in the MMA-MAA-PEG gel with gold nanoparticles at 40 °C.

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