COMMERCIAL vs. FORMULATED: An Investigation of Artificially Produced Patinas Used on Copper in the Field of Jewelry Making

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INTRODUCTION: This study deals with studying the composition and aging properties of formulated and commercially produced patinas for use on copper that are available to contemporary jewelers in North America. In this experiment, commercial and formulated black, green, and brown colored patinas were applied on pure copper plates by using the cold patination technique. The samples were exposed to 80°C and 65% RH. Surface morphology, characterization of color, and adhesion strength of both types of patinas were examined using scanning electron microscopy, colorimetry, and ASTM Measuring Adhesion Tape Test (D3359-99), before and after treating.

EXPERIMENTAL

SAMPLES AND SAMPLE PREPARATION
- Electrolytic tough pitch copper (99.88%) C11000 plates were cut into several different sizes.
- The copper samples were prepared by abrading the surface of metal with SiC paper (up to 600 grade) and cleaned with ethanol.
- Two types of patinas were applied onto the copper surface using cold patination techniques.

<table>
<thead>
<tr>
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<th>Commercial</th>
<th>Formulated</th>
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<tbody>
<tr>
<td>Black</td>
<td>MIDAS Liver of Sulfur XL Gel®</td>
<td>Potassium sulfide, and distilled water</td>
</tr>
<tr>
<td>Green</td>
<td>JAX® Green</td>
<td>Cupric nitrate, ammonium chloride, calcium chloride, and distilled water</td>
</tr>
<tr>
<td>Brown</td>
<td>JAX® Brown</td>
<td>Sodium thiosulfate, ferric nitrate, and distilled water</td>
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</tbody>
</table>

- The samples were exposed to high levels of temperature (80°C) and RH (65%).

EXPERIMENTAL INVESTIGATION:
Tests performed on both groups of patinas, before and after exposure to high temperature and RH.
- Observe surface morphology of all the patinas and identify the elemental composition of the commercial patinas using a FEI Quanta MLA 650 FEG environmental scanning electron microscope and X-ray elemental energy dispersion spectroscopy (SEM-EDS)
- Studying color change using Minolta CR-300 chroma meter
- Investigate surface adhesion strength of patinas using ASTM Measuring Adhesion Tape Test (D3359-99)²

RESULTS

SURFACE MORPHOLOGY
- Both JAX® Green and the formulated green patinas exhibit the greatest difference in their morphological structure
- The surface of the unaged green patina shows high porosity consisting of fine grains and flakes while the aged surface is characterized by large homogeneously distributed, asymmetrical flakes.
- In contrast, patinas such as JAX® Brown exhibits a similar structure for aged and unaged samples. The only difference is noticed with higher porosity in the aged sample.

COMPOSITION OF THE COMMERCIAL PATINAS

<table>
<thead>
<tr>
<th>Patina</th>
<th>Elemental Composition</th>
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<tr>
<td>MIDAS Liver of Sulfur XL Gel®</td>
<td>Copper, sulfur, oxygen</td>
</tr>
<tr>
<td>JAX® Green</td>
<td>Chloride, copper, sulfur, oxygen</td>
</tr>
<tr>
<td>JAX® Brown</td>
<td>Copper, chloride, oxygen, selenium, carbon</td>
</tr>
</tbody>
</table>

SEM-EDS was used to identify the elemental composition of the commercial patinas. The spectrum presented shows the elements found in JAX® Brown.

COLOR CHANGE

- The ASTM Measuring Adhesion Tape Test (D3359-99) only determines the adhesion to the substrate where failure occurs between the patina coat and the substrate.
- Commercial black, formulated black, and formulated brown showed no adhesion failure between their layers and the substrate, therefore, the obtained value for those patinas equaled zero.

- The chart presented shows the CIE \( \Delta L^* \) values for commercial and formulated patinas from before and after aging with their respective standard error bars.
- The greatest change in CIE \( L^* \) values before and after aging is observed within the commercial patinas, as their color became lighter in value.
- The results show that the formulated patinas have the least change in CIE \( L^* \) values before and after exposure to extreme environmental conditions. The black and green became darker in color while the green became lighter.

CONCLUSION: Despite their positive aspects of readiness, easy application and fast drying time, some commercial patinas may not have good aging properties. The results obtained from this experiment proved that after exposure to high levels of temperature and humidity, JAX® Green and JAX® Brown had a large change in color and adhesion strength. In contrast, formulated patinas showed to be relatively stable. MIDAS® Liver of Sulfur XL Gel produced similar results with respect to the formulated black patina.

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