Antiquing:

A Process That Never Grows Old

The aesthetic appeal of jewelry with antique finishes has produced strong consumer demand for these items for many years.

Many different metal substrates, including brass, copper, bronze, gold, silver and pewter, as well as many plated metals, can be treated to produce strikingly attractive antique effects.

The term “antiquing” actually refers to a combination of two different processes, one of which is chemical in nature and the other mechanical. The first process (chemical) involves the artificial or accelerated coloring of metal surfaces. The second step deals with the highlighting or “relieving” of antiqued surfaces by mechanical means.

The second process enables dark coloration to remain in recessed areas while the high areas have the coloration removed, leaving the original substrate or bright, plated surface exposed.

The first process – the artificial or accelerated coloring of metal surfaces – is achieved by using one of two techniques: non-conversion coating or conversion coating.

Non-Conversion Coating

The term “non-conversion” alludes to a straightforward coloring or blackening that is done with coatings such as lacquer or paint that act as a top coat over the metal substrate or surface. In most cases, the antiquing agent is applied by immersing parts in a tank that uses either a rack or basket. Occasionally, the top-coat material will be applied by spraying the parts.

The relieving or highlighting of parts is a subsequent operation, usually performed in an oblique tumbling barrel with non-abrasive, hardwood, pre-formed media (wooden pegs). Hardwood media is an ideal vehicle for this operation since its block-like shape reaches and exposes high areas while leaving coloration in recessed areas. The absorbent quality of this media also is useful for collecting excess antiquing or blackening liquid, and for simultaneously performing a parts-drying process.

Following the relieving operation, parts are customarily sprayed with a clear top coat to preserve the antiqued finish.

Conversion Coating

Conversion-coating technology is more complex than non-conversion coating. It differs in that the plated surface or metallic substrate is actually “converted” to another substance by chemical means (oxidation), as opposed to being coated. This tech-
The three stages of producing an antique finish in jewelry using non-conversion coating (left to right): First, the part is plated. Second, it is dipped in a black lacquer. Third, the part with black lacquer is "relieved" using hardwood peg media in an oblique tumbling barrel. The jewelry designs and highlighting were done by Alan Jewelry (a Danecraft company) in Providence.

Technology has been utilized widely by manufacturers who require black oxide finishes for functional reasons.

Conversion coatings are popular in non-decorative applications because of their strong resistance to corrosion and the fact that they are non-dimensional in nature. They can be used for manufactured parts or components that have precise dimensional tolerances that electroplating or other coating methods would alter. Again, this is because the parts’ surfaces are not really coated, but “converted” with a finish that has a uniform, negligible thickness.

Another reason that oxide-coating technology is valuable is that it can provide a wide variety of weathered or antiqued surface effects on demand. Contrast this with “antiqued” surface effects that are produced by lengthy natural processes.

For example, natural processes will oxidize copper surfaces to a patina green in approximately eight years. During this time span, copper will oxidize through a variety of colors such as: statuary bronze, light Flemish brown, chocolate brown, black and, finally, patina green.

Conversion-coating technology makes it possible to focus on any of these naturally occurring colors, and permanently fix it to the part’s surface by using differing oxidation compounds, concentrates, immersion times, etc.

There are four primary types of formulations for conversion coating that will provide specific color finishes on specific metals:
- Sulfide/Sulfur (Sodium Polysulfide) Formulations.
- Aqueous Acidic-Selenium Formulations.
- Alkaline-Oxidizing Formulations.
- Electrolytic-Nickel Cyanide Formulations. (This is not strictly a non-conversion-coating process, but is grouped with the other three because of its similar sequential methodology.)

Conversion-coating processes generally involve using a series of tanks into which the parts are immersed for a specified time, in sequence. This is prompted by the need for cleaning and pre-treating the parts prior to the actual oxidation procedure, as well as post-treatment rinsing and cleaning. (Refer to the “Conversion-Coating Flowchart” on page 96.) Although we used a selenium-based product in the flowchart, each of the four major formulation types has advantages and disadvantages:

Sulfur-based compounds: At one time these were the most-common formulations for producing antique finishes. These low-cost compositions can produce a wide assortment of colors that can be induced by varying process parameters such as temperature, solution concentration and
immersion time. These have an added advantage of creating copper-sulfide surfaces that are relatively easy to highlight or relieve. On the negative side, careful monitoring is required to maintain consistent solution strengths. Otherwise, inconsistent batch-to-batch coloration may result, which often requires adjustments by dumping and recharging tanks. Additionally, some of these formulations produce objectionable odors.

**Selenium-based compounds:** Like the sulfur-based compounds, selenium-based compositions are capable of producing a variety of surface colors including reddish brown, brown and black. The resulting copper-selenide surfaces have approximately the same hardness as those produced by the sulfur-based compounds, and are easy to mechanically relieve. Selenium-based operations are noted for bath stability and life, which contribute to strong batch-to-batch uniformity of color. These formulations are operator-friendly, emitting little odor and fumes, and have the ability to process parts at room temperature. Selenium

All of these crowns except the 'yellow' one on the far left were immersed for various lengths of time in a selenium-based conversion coating. Then, the two on the far right were mechanically finished and clear-lacquered to remove the excess antiquing agent and bring out the highlights. These samples were prepared by Eric Olander of EPI in New Berlin, WI, a supplier of metal-finishing chemicals.

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compounds require a waste-treatment regime similar to that of electroplating compounds.

**Alkaline oxidizers:** These compounds can create very durable, consistent, highly adherent, black finishes that are quite economical to produce. The surfaces they generate are much harder than those produced by other formulations, which means they are often not good for mechanical relieving. In addition, workers are somewhat more exposed to risk, since these formulations are used at high temperatures and are strongly caustic with potentially hazardous fumes.

**Electrolytic black finishes:** These are most suitable for existing plating operations with the waste-control technology needed to deal with cyanide-bearing wastes. The strong advantage of black electroplating solutions (commonly nickel/cyanide combinations) is that parts fabricated or assembled from different metal compositions can be colored to a consistent finish. If relieving is necessary, a pre-plating operation may be required so exposed surfaces have a uniform color. Continued on page 96.
Highlighting Processes

Some experts have said that the relieving and finishing portion of the total antiquing process is among the most critical to achieving desired final finishes.

The type of relieving process you select is determined by the size of the parts to be processed. In most small-part relieving operations, mass-finishing methods such as barrel or vibratory finishing will be used to process parts in bulk. Larger, more-awkward parts can be processed with abrasive or non-abrasive wheel buffs. Scratch-brushing also can be performed with pads. But since most jewelry antiquing is concerned with small-part finishing, we will concentrate on mass-finishing techniques for relieving and highlighting.

The two major factors in selecting a relieving/mass-finishing process are equipment and media. Here, there are four primary types of equipment-driven processes:
- Barrel Finishing
- Vibratory Finishing
- Centrifugal-Barrel Finishing
- Centrifugal-Disc Finishing

These types of equipment typically are used to abrasively refine jewelry-part surfaces and, in some cases, create near-buff surface finishes in preparation for final mass-relieving finish or assembly operations. Most operations are performed in barrel- or vibratory-finishing equipment, but each type of equipment has advantages and disadvantages. The table on page 98, titled “Mass-Finishing Equipment Selection Considerations,” illustrates the pros and cons of various types of mass-finishing equipment used for abrasive operations such as deburring, smoothing, and polishing.

Media for Highlighting

Selecting the correct media is as important as choosing the right mass-finishing equipment for relieving and highlighting. The effects of media on the parts’ surfaces are governed by four media factors: size, shape, abrasiveness and bulk-density (weight).

Size and shape are important

Conversion-Coating Flowchart

This example of a line-production conversion-coating process employs an aqueous acid-selenium formulation to oxidize the jewelry parts’ surfaces and produce an antique finish. Note that each of the first seven steps takes place in a separate dip or immersion tank. The tanks are constructed from acid-resistant materials such as PVC, polypropylene, Fiberglas or a rubber-lined metal.

TANK ONE
Process: Cleaning.
Purpose: Remove oils, grease, fingerprints, etc., from surfaces.
Material: Soak cleaner (caustic base).
Concentration: 8-10 ounces/gallon.
Temperature: 150°F.
Immersion Time: 2-10 minutes, depending on soils to be removed.

TANK TWO
Process: Cold-water rinse.
Purpose: Prevent dragout contamination in subsequent cycles.
Material: Water.
Temperature: Ambient.
Immersion Time: 30-60 seconds.

TANK THREE
Process: Deoxidize/surface activation.
Purpose: Remove residual oxides from surface to ensure uniform oxide coating from primary oxidizing treatment.
Material: Acid dip.
Temperature: Ambient.
Immersion Time: Variable, 30 seconds-2 minutes.

TANK FOUR
Process: Cold-water rinse.
Purpose: Prevent dragout contamination of subsequent cycles.
Material: Water.
Temperature: Ambient.
Immersion Time: 30-60 seconds.

TANK FIVE
Process: Oxidation.
Purpose: Oxidize parts to desired color.
Material: Aqueous selenium-dioxide solution (acid bath).
Concentration: 5%-25% by volume.
Temperature: 70°-100°F.
Immersion Time: 30 seconds-2 minutes.

TANK SIX
Process: Cold-water rinse.
Purpose: Rinse to clean parts’ surfaces.
Material: Water.
Temperature: Ambient.
Immersion Time: 30-60 seconds.

TANK SEVEN
Process: Hot-water rinse.
Purpose: Helps facilitate drying for storage of parts for next step.
Material: Water.
Temperature: 120°-150°F.
Immersion Time: 30-60 seconds.

STEP EIGHT
Process: Spin-dry or oven.
Purpose: Produce dry parts.
Temperature: 150°-300°F.

STEP NINE
Process: Relieving/mechanical finishing.
Purpose: Produce final “antique” effect by removing coloration from high areas and leaving coloration in recessed areas of the parts.
Methods: Barrel-finishing; vibratory finishing; scratch-brushing; buffing wheel and brass wheel.
Media: Non-abrasive types: hardwood preforms (pegs); corn cob; porcelain; ceramic burrishing; steel. Abrasive types: resin-bonded plastics.

STEP TEN
Process: Clear-lacquer/clear-powder coating.
Purpose: To set and preserve antique finish.
Process Notes: The particular type of coating selected can have an important effect on overall appearance. Clear-lacquer and clear-powder coating compositions are not crystal clear. The resins and polymers used in the formulations may have yellow, red, green and gold hues that will affect the overall color of the parts.

NOTES
If the parts being oxidized have been plated, it is important that plate thickness be maintained at a minimum of 0.0003 to 0.0004 inches. Plating of insufficient thickness will be dissolved by the oxidation process, thus exposing the original metal substrate and producing inconsistent surface color.

Source: Eric Ghaderian of En. New Berlin, WI.
<table>
<thead>
<tr>
<th></th>
<th>Horizontal Barrel</th>
<th>Oblique Barrel</th>
<th>Round Vibrator</th>
<th>Tub Vibrator</th>
<th>Centrifugal Barrel</th>
<th>Centrifugal Disc</th>
<th>Spin/Spindle Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time Cycles</td>
<td>Very Long</td>
<td>Very Long</td>
<td>Medium</td>
<td>Medium</td>
<td>Short</td>
<td>Short</td>
<td>Very Short</td>
</tr>
<tr>
<td>Media Wear</td>
<td>Slow Large</td>
<td>Very Slow</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High</td>
<td>Very High</td>
<td>Very High</td>
</tr>
<tr>
<td>Media Size</td>
<td>Large</td>
<td>Large</td>
<td>Medium</td>
<td>High</td>
<td>Very High</td>
<td>Very High</td>
<td>Very Small</td>
</tr>
<tr>
<td>Equipment Cost</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Typical Kinds of Processes</td>
<td>Heavy radiusing,</td>
<td>Drying part</td>
<td>Deburring,</td>
<td>Deburring,</td>
<td>Micro-finishing,</td>
<td>Aggressive</td>
<td>Aggressive</td>
</tr>
<tr>
<td></td>
<td>burnishing, dry</td>
<td>on part</td>
<td>smoothing,</td>
<td>stock</td>
<td>polishing, fast</td>
<td>deburring, stock</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polishing</td>
<td>finishing</td>
<td>removing,</td>
<td>removal,</td>
<td>stock removal</td>
<td>removal, no</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pre-plate</td>
<td>large</td>
<td></td>
<td>impingement</td>
<td></td>
</tr>
<tr>
<td>Port Size Limitations</td>
<td>Medium</td>
<td>Small to Medium</td>
<td>Restricted by bowl diameter; flat parts nest</td>
<td>Almost unlimited; very large - one per machine</td>
<td>Small to moderate; fixture or compartments possible</td>
<td>Port length severely restricted by size of chamber</td>
<td>Some part geometry restriction</td>
</tr>
<tr>
<td>Type of Energy</td>
<td>Rotational;</td>
<td>Rotational;</td>
<td>Kinetic;</td>
<td>Centrifugal;</td>
<td>Centrifugal;</td>
<td>Centrifugal;</td>
<td>Spin; media</td>
</tr>
<tr>
<td></td>
<td>gravity slide</td>
<td>gravity slide</td>
<td>vibratory</td>
<td>pressure</td>
<td>toroidal</td>
<td>toroidal</td>
<td>resistance</td>
</tr>
<tr>
<td>Continuous or Batch</td>
<td>Batch</td>
<td>Batch</td>
<td>Continuous</td>
<td>Batch</td>
<td>Batch</td>
<td>Batch</td>
<td>Batch</td>
</tr>
<tr>
<td>Liquid Compound Usage</td>
<td>Low</td>
<td>Low</td>
<td>High with flow-through systems</td>
<td>High with flow-through systems</td>
<td>Low</td>
<td>High with flow-through systems</td>
<td>Medium</td>
</tr>
<tr>
<td>Working Capacity</td>
<td>50%</td>
<td>35%</td>
<td>80 - 90%</td>
<td>80 - 90%</td>
<td>60% WET 80 - 90% DRY</td>
<td>30 - 40%</td>
<td>N/A Fixtured</td>
</tr>
<tr>
<td>Exterior or Interior Part Areas</td>
<td>Concentrates on exterior corner, edges</td>
<td>Concentrates on exterior corner, edges</td>
<td>Interior and exterior</td>
<td>Interior and exterior</td>
<td>Exterior and interior similar</td>
<td>Exterior and interior similar</td>
<td>Dependent on fixture orientation</td>
</tr>
<tr>
<td>Media/Parts Material Handling</td>
<td>Awkward w/ external separation</td>
<td>Easier unloading than horizon barrel</td>
<td>Automated internal separation</td>
<td>Discharge chute to external separation</td>
<td>Manual load; machine unload</td>
<td>Manual or Automatic</td>
<td>Manual or Robotics</td>
</tr>
<tr>
<td>In Process Inspection?</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>YES usually</td>
<td>NOT usually</td>
<td></td>
</tr>
</tbody>
</table>

because they determine what areas will be accessed for relieving and highlighting. Abrasiveness is important because it determines how quickly material is removed. It also determines the appearance of the exposed surfaces, which can be left as a matte finish or a highly reflective one. And the bulk-density of the media per given volume can have an enormous effect on final surface appearance and process-cycle times.

Bulk-density can vary widely among types of media. Here, for example, are the bulk densities of various media:

- Hardwood is 22-27 lbs./cu. ft.
- Corn cob is 32-35 lbs./cu. ft.
- Walnut shell is 43-45 lbs./cu. ft.
- Plastic is 55-57 lbs./cu. ft.
- Ceramic/porcelain is 90-100 lbs./cu. ft.
- Steel media is 300 lbs./cu. ft.

Plastic media, as well as non-abrasive ceramic/porcelain media and steel media, are generally run in conjunction with aqueous-compound solutions. The non-abrasive media, with their heavy bulk-density, can produce compressively induced, burnished surfaces at the same time of the actual scrubbing away of conversion coatings.

Natural media such as wood and crushed corn cobs or walnut shells is used in dry environments. Hardwood media is especially favored in dry-relieving and highlighting operations, since it is available in a variety of pre-
formed shapes that can determine the amount of part-surface area accessed. Both corncob and walnut shell media are of a random, granular shape, and may remove more material from recessed areas than is desirable.

Process Development

Despite the large number of variables addressed here, developing successful antiquing processes need not be fraught with difficulty. Many of the OEMs (Original Equipment Manufacturers) and coating-industry suppliers have capable technical-service staffs that can help you define the best processes for your applications. These resources are often overlooked by jewelry manufacturers. However, suppliers can provide important technical assistance. With their assistance and expertise, antiquing can be a process that's used in your business for a long time.

David A. Davidson of Colville, WA, is a consultant to the mass-finishing industry and serves as executive director of the Mass Finishing

Various types of plastic media used in 'wet' relieving processes in both barrel- and vibratory-finishing operations. The media are supplied by PBGCO Process Laboratories in Bartlett, NH.

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Job Shops Association. Previously, he was vice president and technical director of PEGCO Process Laboratories in Bartlett, NH, which provides finishing equipment and supplies to jewelry manufacturers. He will be available for consultation at PEGCO's booth at the Expo Providence show, May 1-3.

Davidson's technical articles on finishing have been published by "Products Finishing," "Plastics Engineering," "Metal Finishing," "The Fabricator," "Finisher's Management," and other periodicals. He has delivered technical papers on finishing subjects for the Society of Manufacturing Engineers, the Society of Plastic Engineers, and the American Electroplaters and Surface Finishers Society. He is currently adapting high-speed, non-polluting Russian "Turbo-Finish" technology to the U.S. industrial and consumer item markets. Davidson can be reached at (800) 723-4554.

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References for Further Reading