The Layered patination of copper

Ronald VanOstrand
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By

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INTRODUCTION

This thesis was a pragmatic exploration into the patination process of copper. Two particular process elements were researched; patina layering and manipulation of the environment in which patination occurs. The success of the process will be determined by the permanence, consistency, durability and aesthetic worth of the resulting patina.

The primary process element, that of patina layering, was comprised of a hot immersion process followed by compatibility tests with a subsequent exposure to fumed, sprayed, and saturated suspension processes. Initial and subsequent surface preparations were required.

Additionally the process element of environment and its effects, both visually and texturally on the metal being patinated, was explored. Environmental factors manipulated and introduced were comprised of, but not limited to, temperature and suspension/drying medium (sawdust, wood-chips, cat litter, rolling or chewing tobacco, marbles, steel slag, iron fillings, etc.).

A body of work comprised of vessels, functional and non-functional, provided an outlet for exhibition of the resultant patinas.
PATINATION AND THE METAL ARTS

The term patina traditionally refers to the greenish layer that forms on copper and its alloys over time. The modern definition has grown to include any deliberate or natural change in surface coloration due to a chemical change in surface composition. In copper this is the result of the formation of copper oxides and sulfide as well as inorganic and organic copper salts (Hughes and Rowe 1982).1 The process of obtaining a patina is referred to as patination.

Patination occurs primarily as the result of one of two conditions. The first is that of a natural exposure to the elements over time. A patina generated in this way is not intentional or controlled, but rather the natural result of the atmosphere and its various pollutants. Intentional reproduction of the natural patination effects of time is the second condition. In the 19th century western collectors were interested in older classical works thus forgeries complete with artificial patinas were produced. Even earlier, Eastern forgers artificially produce aged effects on metal. As early as the Song (AD 1137-1279) and Ming (AD 1368-1644) dynasties, imitations of the works from the earlier Chinese bronze age were produced (Kerr 1990).

The application of a chemical solution to patinate copper is done not only to imitate long term effects of slow processes, but also to minimize color change in the future. Even with a wax coating2 copper will continue to deepen in color over time. By

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1 Oxides, sulfides and salts most common are cuprite, chalcocite, brochanite, atacamite, antlerite, posnjakite, gerhardite, malachite, azurite, formates, acetates, and oxalates. (Hughes and Rowe 1982)
2 Paste wax is often applied as a last step in finishing copper work to retard further oxidation.
forming a deliberate layer of oxidation or a mineral layer on the copper followed by a layer of wax or clear acrylic spray, a more stable appearance over time can be achieved.

Modern metal artists utilize natural and artificial processes to generate surface effects for their work. In the metalsmithing studio of Thomas Markusen his copper hollowware is treated by chemical and heat oxidation processes to produce a deliberate visual effect. On the other hand, Albert Paley using cor-ten steel, is known to allow his work to naturally oxidize.\(^3\) Commercial patinas for copper and its alloys are produced and commonly available from jewelry material suppliers.

**PATINATION PROCESS**

Three steps must be followed in the formation of a patina if consistent results are to be obtained; surface preparation, exposure, and finishing. Omission of surface preparation is possible but various contaminants on the material may hinder results, or render them inconsistent. Finishing techniques typically end any reaction and attempt to preserve the patina in its current condition.

Before the metal is exposed to a patination process it must first be prepared. Oxides, dirt and grease must be removed from the surface of the material. The material may be heated to burn off grease\(^4\) or a chemical degreasing agent may be applied to the surface. Oxides may be removed with abrasives or immersion in warm chemical bath

\(^3\)"Genesee Passage," 1996, Bausch & Lomb, Inc., Rochester, New York, is an example of Albert Paley’s use of weathering steel.

\(^4\)Heating of copper to remove grease may result in the softening of the metal if the temperature reaches the annealing point (1110-1290°F depending on particular copper alloy).
known as pickle.\textsuperscript{5} Patinas that develop a crusty mineral layer may benefit from a sandblasted or scratched surface; the increased surface area will allow better mechanical adhesion of the newly formed mineral. Prepared material must be handled carefully to avoid contamination by grease (such as oil from fingers) which may be initially invisible but appear later when it retards a developing patina or causes oxides to develop.

In the process of chemical patination, the method of applying the chemical solution to the prepared copper has a substantial effect on the resultant patina. In this exploration four methods were used to apply chemical to the surface: boiling immersion, fuming, brushed, and saturated suspension. Length of exposure and relative temperature were controlled to allow resultant patinas to be replicated.

Chemical reactions are generally ceased by rinsing in water (hot water for boiling immersions and cold water for all other exposures), and drying in air or suspended in sawdust. When dry the work may be coated in paste wax or a clear acrylic spray. Paste wax tends to leave the metal with a more natural appearance; however, application of the wax may cause the patina layer to be rubbed away in spots. A clear acrylic spray will not remove material, but may actually help bond crusty mineral deposits to the base material. The short coming of the acrylic is that the material may appear glossy, resulting in a plastic or painted look. Additionally, if care is not taken in the application of the acrylic then streaks or drips may develop.

\textsuperscript{5}Pickle is typically a solution comprised primarily of sodium bisulfate.
STRUCTURE OF EXPLORATION

Test plates were first exposed to an immersion or brushed on patina process. There were eight plates in a series exposed in this manner; and eight different process exposures, additionally there was one control group. One plate from each series and one from the control group were then exposed to one of seven secondary patina exposures with an additional control group. The result was eight groups of nine plates bearing a two letter designation on each plate. Each letter relates to a process or control as follows.6

<table>
<thead>
<tr>
<th>FIRST LETTER (A-I) DESIGNATION:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Rokusho Immersion</td>
</tr>
<tr>
<td>B. Copper Sulfate, Ammonium Chloride Immersion</td>
</tr>
<tr>
<td>C. Copper Sulfate &amp; Acetate, Sodium Chloride, Potassium Nitrate Immersion</td>
</tr>
<tr>
<td>D. Copper Sulfate, Ammonia (.880) - Immersion</td>
</tr>
<tr>
<td>E. Copper Nitrate - Successive Brushed Exposure</td>
</tr>
<tr>
<td>F. Bare Copper - Control Group</td>
</tr>
<tr>
<td>G. Ammonium Carbonate, Copper Sulfate &amp; Acetate, Oxalic &amp; Acetic (10%) Acid - Immersion</td>
</tr>
<tr>
<td>H. Copper Nitrate, Ammonia (.880) - Immersion</td>
</tr>
<tr>
<td>I. Copper Acetate, Ammonium Chloride, Acetic Acid (6%) - Immersion</td>
</tr>
</tbody>
</table>

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6Complete patina recipes and material safety data sheets are located in the appendices.
SECOND LETTER (S-Z) DESIGNATION:

<table>
<thead>
<tr>
<th>Letter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.</td>
<td>Copper Nitrate - Suspension Medium</td>
</tr>
<tr>
<td>T.</td>
<td>Ammonium Chloride &amp; Carbonate - Suspension Medium</td>
</tr>
<tr>
<td>U.</td>
<td>Copper Nitrate, Ammonia (.880), Acetic Acid, Ammonium Chloride - Suspension Medium</td>
</tr>
<tr>
<td>V.</td>
<td>Ammonia (.880) Fume Exposure</td>
</tr>
<tr>
<td>W.</td>
<td>Copper Nitrate, Sodium Chloride - Suspension Medium</td>
</tr>
<tr>
<td>X.</td>
<td>Ammonium Chloride, Copper Acetate - Suspension Medium</td>
</tr>
<tr>
<td>Y.</td>
<td>Ammonium Chloride, Sodium Chloride, Ammonia (.880) - Suspension Medium</td>
</tr>
<tr>
<td>Z.</td>
<td>No Exposure - Control Group</td>
</tr>
</tbody>
</table>

Patinas that have aesthetic merit and appear to be durable were repeated to determine if the effects were able to be replicated. For all initial suspension medium exposures cedar wood chips and shavings were used. Where texture appears to have a dramatic effect on the resultant patina, the suspension medium was changed to test alternate effects.

PATINA EVALUATION

In most of the second letter series of test plates the results were similar. One of three conditions were created; either the base patina created an underlying color that showed through the second layer, the base patina was covered and obscured by the second layer, or the base patina retarded the reaction of the second exposure to a varying degree to the others in the series. For the most part the more interesting effects were created when the base coat showed through setting a richer tone to the overall patina.

The U, W, X, and Y series produced the best results. In particular the W series allowed a good portion of the base to show through, although slightly altered; and only
the contact points of the suspension medium reacted with the second patina exposure. The X series produced a change in all of the underlying patinas, but to varying degrees of warmth. Both the U and Y series allowed a minimal amount of underlying patina to show through, and that which showed through darkened with the exposure to the second patina.

Etching to some degree occurred in the T, U, X, and Y series. In the X series the etching was uniform and slight resulting in a raw clay-like surface texture. The U series produced aggressive etching at the point of suspension medium contact. The pattern of etching in the U series does appear to be evenly distributed over the surface of the copper.

Suspension medium in some cases, particularly in the T series, was bonded to the surface of the plates during exposure as the resulting mineral grew around the medium in contact with the copper surface. Evidence of some degree of suspension medium bonding occurred in the U, W, and X series; however, in these series the bond was weaker than in the T series and was able to be broken during rinsing after exposure.

Ammonia fumed exposure in the V series proved too aggressive and resulted in a near black dark green film over all the plates. During rinsing the film flaked of in some places on C, E, H, and I plates of the series. Masking of the vapor appears possible as contact points with the wooden rack holding the plates during exposure appeared to be unaffected by exposure.

All test plates were finished with paste wax on one side and clear acrylic spray on the other. Paste wax worked best for the W series and on plates CZ, FZ, and IZ of the

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7 In many of the tests a fuming reaction seems to have accompanied the direct contact exposure to the suspended medium resulting in a change to the underlying base patina.  
8 Care must be taken when using this particular solution on thin metal and at low points were the solution may settle. Allow for run off of solution.
second exposure control group. Spray clear acrylic produced the best results overall on the tests. Spray acrylic when applied to warm metal generally produced a less plastic or painted look. A hand held hair dryer was used, on vessels prepared for the thesis exhibition, to warm the metal before coating with clear acrylic.

Marbles, steel slag, plus-shaped floor tiling spacers (plastic), fish tank gravel, cat litter, and iron filings were used as suspension medium for a series of plates exposed to the U series solution. Iron filings and steel slag produced an orange rusty coating along with the expected patina which primarily washed away with water, with only traces reappearing after air drying. Cat litter produced a similar film residue (from the clay of the cat litter) along with the expected patina. This clay film washed entirely away with water. Marbles, fish gravel, and tiling spacers produced similar results to the wood chip medium.

**VESSEL FORMATION**

The vessels, that have been created to allow an outlet for exhibition of the resultant patinas for this investigation, are intended to work as a series. For unity, all forms at least allude to the same function of vessel, and possess similar characteristics. Formal elements common to each vessel are linear tendrils, a sense of mushroom-ness, and marks of both a machined and that of a hammered process.

The nomenclature used in the title of each vessel is intended to allude to process and form of the objects. The word “Mycrian” is based on the word “mycology,” the study of fungus (i.e. mushrooms), and the suffix “-rian” alludes to ancient times and cultures,

\(^{9}\)CZ developed flaking with prolonged exposure to gallery lighting. Further test showed that humidity and direct sunlight sped up deterioration of the patina. Clear acrylic offers more protection to this patina.
such as Macedonian. Besides starting with the word “Mycrian,” each title also includes a description of the work such as plate, bowl, vase, or simply vessel.

Patina selections for each vessel, or in some cases which section of vessel, are based on the individual requirements of each form. Larger less detailed sections are given a more textural patina to create movement. Areas of more surface detail are allowed a thinner patina to allow the surface texture of the metal to show through. Color and textural contrasts are also used to create movement within the work.

Two pieces in the series are deficient in some of the formal elements of the series. The most blatant of these is “Mycrian Plate #1,” which has a stylized linear element in the form of a gold leafed and embossed design within the inner rim of the center of the plate. This piece relates to the others to a lesser degree as a result of the stylized element. The other notable variant is “Mycrian Bowl,” which had its linear elements removed from the interior of the bowl as their movement detracted from the overall simplicity of the vessel.

CONCLUSIONS

The patinas recreated on the exhibition vessels were all initially successful. After the work was removed from the gallery however, flaking of one patina (CZ) was discovered. Two vessels, “Mycrian Bowl” and “Mycrian Vase #1”, were effected by the flaking. In both cases paste wax was used as a final treatment. Subsequent tests showed acrylic coating as a
hardier finish for this particular patina. The test plate for CZ maintained its patina for both finishes after six months duration. Exposure to harsh gallery lighting and humidity is suspected to have caused the damage. The flaking was the consistency found in the oxidation that commonly appears on annealed copper. There was no significant loss of surface texture or detail, and repatination with an acrylic final coat was successful.

The patina that appears to have been the most successful in terms of aesthetic value as well as durability, is that of the HU designation. This patina appears in “Mycrian Plate #1”, and “Mycrian Three Hole Vessel.” In both cases this particular patina was chosen to cover a large smooth surface. The pattern of the suspension medium left on the surface reduced optical stagnation while being viewed.
“Mycrian Three Hole Vessel” is one of three vessels that were constructed in two sections that were patinated separately and then joined afterwards. A lighter coloration was chosen for the underside of the vessel to counter the shadow of the two inch overhang of the upper portion of the vessel. Patina CW while being lighter in color, still possesses a textural similarity to patina HU. A paste wax finish was applied to the patina HU portion while an acrylic spray finish was used to seal the patina CW portion.

With “Mycrian Three Lobe Vessel” a change in form was introduced to the series. Instead of the traditional multiple tendril lids, the tendrils were thickened and reduced in number. Additionally, the lower section abandoned the strict spun form for one that was hammered into three equal lobes. With the increased activity in the lower section, a medium toned patina DU was
used. The upper dome was patinated with CW. Both sections were treated with a clear acrylic spray. The copper tendrils piercing the upper dome were left unfinished bare copper. The lack of protection allows the metal to oxidize naturally.

The final two section vessel is “Mycrían vase #3.” Patina DZ, a single exposure patina, was used on the lower section of the vessel to allow the spun pattern to show through. On the upper section, patina IS was rubbed from the high points of the highly textured surface and allowed to remain in the valleys created by the texturing hammer blows. Colorful heat oxidation accents the tendrils of the lid.

An unanticipated, but never the less successful, effect was that generated from patina CX combined with a heavy hammer texture. The result of the mild etching of the patina was a hand-worked clay effect. This patina arguably rivals that of HU. The transmuted coloring of the initial patina was significant in that the base effects of patina X varied along with the initial patina. A random pattern of etching and mineral deposition
occurred over the surface, depending on solution strength variability within the suspension medium. This effect was greater where the solution was allowed to concentrate; low areas were more likely to be etched and acquire mineral deposition.

“Mycrian Lidded Vessel” was positioned in the suspension medium in an inverted orientation. The result was that an increased frequency of mineral deposition occurring under the overhang of the top portion of the vessel. Sterling silver and solder seams do not appear to react in the given exposure time of either patina.

Several vessels were included in the series that were not direct results of the investigation into layering effects. One such vessel was “Mycrian Vase #4.” This vessel when initially exposed to patina D yielded an unexpected result; sterling silver when exposed to this solution turns a bright red. This effect was interesting enough that a further planned exposure for this vessel was not carried out.
Also included in the series was a vessel that was the precursor to the series and the exploration into layered patination. The elements of this vessel served as a model for the other vessels. Additionally the patina on the upper surface was the result of three commercially produced patina solutions applied in several separate misted exposures. The success of this vessel lead to the formation of the premise of this thesis.

The final vessel in the series was “Mycian Plate #2.” This vessel acquired the desired patina effects on the back side of the plate. The face of the plate developed in a more inconsistent manner. Patches of flaking and an overall translucency were two of the major variations from the test plate for patina BY. While the effects of the front side of the plate were not those that were intended, they still possessed an interesting visual quality, that of variability. Contrasting high polished bare copper brought order to the work.
In summation, several new patina effects were generated during this investigation. By introducing a different base patina, a secondary patina could be generated with variation in base color, texture, and intensity. It was also discovered that the second patina exposure tended to be the dominant patina, in several cases removing the effects of the primary exposure entirely. In regards to environmental manipulation, it was determined that the suspension medium held minimal influence on the textures of the patinas tested. Temperature variation resulted in predictable results, the hotter the exposure the faster the reaction. Patinas generated at room temperature had exposures measured in hours, and boiling immersions were measured in minutes.

Through this investigation I acquired more knowledge into exactly how patination occurs and which environmental factors play a significant role in patina development. I also learned what features a metal studio will require for carrying out safe and effective patination. The investigation yielded a few new patina effects that will be added to my repertoire and used in future works. Next I will likely investigate patina effects on silver-copper alloys, particularly sterling silver. Increasing the amount of copper in the silver to copper ratio in the alloy may be necessary for the variety of effects that I would wish to achieve.

A definitive style has begun to emerge with my work, which was a goal that I had set for myself for graduate school. As I see and experience more, I am sure my work will continue to evolve; but for now, my work has defined itself in a unique manner. Vessels, functional or not, currently hold my favor as the means of expression for my art. A continued investigation into the possibility of vessel, its form and essence, will occupy me for quite some time.
BIBLIOGRAPHY


APPENDICES A.
PATINA RECIPES

A. Rokusho

- 6.5 grams Copper Acetate
- 2.25 grams Sodium Hydroxide
- 2.25 grams Calcium Carbonate
- 150 milliliters Distilled Water

Allow solution to sit for one week and then drain off the supernatant. The remaining mixture is allowed to dry out. The dry cake is ground into powder which is mixed in equal amount with copper sulphate in 1 liter of water for hot (boiling) immersion coloring. A small quantity of diluted acetic acid (1-5 ml of a 6% solution) is added to the hot solution just prior to exposure.

B. Semi-Matt Red

- 25 grams Copper Sulphate
- 1 liter Water

Bring Solution to a boil and expose copper for 15 minutes. Remove material and quickly add .5 grams of Ammonium Chloride and reimmerse copper for an additional 10 minutes. Rinse in hot running water and allow to dry in sawdust.

C. Red

- 6.25 grams Copper Sulphate
- 1.25 grams Copper Acetate
- 2 grams Sodium Chloride
- 1.25 grams Potassium Nitrate
- 1 liter water

Bring solution to a boil and expose copper for one hour. Rinse in hot water and allow to dry in sawdust. Towel drying may remove some color revealing a yellowed underlayer. Similar removal of color may result from aggressive application of paste wax.

D. Purple

- 25 grams Copper Sulphate
- 3 milliliters Ammonium Hydroxide (.880 solution)
- 1 liter Distilled Water

Combine copper sulphate and water when water begins to steam. When the solution begins to boil add the ammonium hydroxide and the copper to be colored. Exposure time is 30 minutes or until color reaches desired level. Use of water other than distilled will likely not produce coloration. Sterling silver immersed with copper will turn red.
E. **Blue-Green Frosting**

200 grams Copper Nitrate  
1 liter Water  

Dip object into solution or mist object with solution two times a day for one week. A blue green frosting will develop where solution is allowed to settle while drying. Useful for edges but poor for larger areas.

F. **Bare Copper**

Copper for the control group is heated to the point of annealing and quenched in pickle to remove oils and grease. Under running water the material is further cleaned with an abrasive pad and a degreasing dish detergent; rinsed the material is dried with paper toweling and not exposed to bare hands.

G. **Medium Brown**

180 grams Ammonium Carbonate *(add in small amounts to acetic acid)*  
60 grams Copper Sulphate  
20 grams Copper Acetate  
1.5 grams Oxalic Acid * (do not allow contact to skin or eyes)  
1 liter Acetic Acid 10% solution  

Combine dry ingredients to acetic acid in order, taking special care with the ammonium carbonate which must be added in small quantities to the acetic acid. Oxalic acid is a skin irritant and is poisonous if taken internally; extra caution is warranted in dealing with this ingredient. The solution is brought to a boil and the copper is exposed for 25 minutes. Apply hot solution with a brush to even the surface and allow to air dry. A light blue residue way develop which can be lightly washed away with a damp towel.

H. **Reddish Purple**

80 grams Copper Nitrate  
1 liter Distilled Water  
5 milliliters Ammonium Hydroxide (.880 solution)  

Add the copper nitrate to the distilled water as it nears the boiling point and follow with the ammonium hydroxide. Expose the copper to the boiling solution for 30 minutes. Wash the copper thoroughly in warm water and dry in sawdust.

I. **Orange**

7 grams Copper Acetate  
3.5 grams Ammonium Chloride  
100 milliliters Acetic Acid (6% solution)  
1 liter Water  

Bring solution to a boil. Expose copper for 10 minutes. Rinse well in warm water and dry thoroughly with a paper towel.
S. **Mottled Red and Brown**
   200 grams Copper Nitrate
   1 liter Water
   Rest copper in solution moistened medium for 3 days. Gently rinse in cold water and allow to air dry.

T. **Blue-Green Stipple**
   100 grams Ammonium Chloride
   150 grams Ammonium Carbonate
   1 liter Water
   Rest copper in solution moistened medium for 24 hours. Gently rinse and remove any medium that may adhere to copper under cold water and then air dry.

U. **Blue-Green Stipple on Black**
   100 grams Copper Nitrate
   200 milliliters Water
   gradually 400 milliliters Ammonium Hydroxide (.880 solution)
   400 milliliters Acetic Acid (6% solution)
   100 grams Ammonium Chloride
   Combine ingredients in order using adequate ventilation and a respirator suitable of ammonia vapors. Use of eye protection for ammonia fumes is also recommended. Rest copper in a solution moistened medium for 24 hours. Gently rinse and remove any medium that may adhere to copper under cold water and then air dry.

V. **Dark Green to Black**
   200 milliliters Ammonium Hydroxide (.880 solution)
   Suspend copper over solution in a near air tight container for 24 hours, less time for lighter results. When removing copper from the container do so using adequate ventilation and a respirator suitable of ammonia vapors. Use of eye protection for ammonia fumes is also recommended. Gently rinse with cold water and allow to air dry.

W. **Bronzing with Etched Green Stipple**
   200 grams Copper Nitrate
   100 grams Sodium Chloride
   1 liter Water
   Rest copper in solution moistened medium for 24 hours. Gently rinse and remove any medium that may adhere to copper under cold water and then air dry.
X. **Red Brown with Green Stipple**
   - 350 grams Ammonium Chloride
   - 200 grams Copper Acetate
   - 1 liter Water
   Rest copper in solution moistened medium for 20 hours. Gently rinse and remove any medium that may adhere to copper under cold water and then air dry.

Y. **Black Green and Blue on Dull Pink**
   - 16 grams Ammonium Chloride
   - 16 grams Sodium Chloride
   - 30 milliliters Ammonium Hydroxide (.880 solution)
   - 1 liter Water
   Combine ingredients in order using adequate ventilation and a respirator suitable of ammonia vapors. Use of eye protection for ammonia fumes is also recommended. Rest copper in a solution moistened medium for 24 hours. Gently rinse and remove any medium that may adhere to copper under cold water and then air dry.

Z. **Control Group**
   Designation for no secondary exposure to a patination process.

**Notes on Patina Recipes:**
Patina recipes are based on formulas presented in “The Colouring, Bronzing and Patination of Metals” by Richard Hughes and Michael Rowe, and modified for ease of replication in a studio environment. Use of distilled water is essential in recipes calling for it. Tap water was used in recipes calling for just water. Contaminants in tap water seemed to have a greater influence in recipes that called for a lesser mass of reagent to be added to water, as in recipe D where 25 grams of copper sulphate is added to every 1 liter of water.

In selecting what patina recipes to explore for layering, formulas were chosen for a variety of effects they could produce, and for what reagents were used. Reagents that could not be safely used in a studio environment were immediately rejected. Formulas that produced questionable health situations such as powdery residues that could be dangerous were similarly rejected. Ammonia vapors were a concern, but use of proper ventilation/respiration and handled in times when few or no other persons were in the studio seemed to address health issues.
APPENDICES B.
LIST OF REAGENTS

Acetic Acid
Liquid.
Acetic Acid 5.9%, Water 94.1%
Skin and eye irritant.

Ammonium Carbonate
Crystals.
Ammonium Carbonate 100%
Eye, skin, and mucous membrane irritant. Harmful if swallowed.
Avoid exposure to vapors.

Ammonium Chloride
Crystals
Ammonium Chloride 100%
Eye and skin irritant. Harmful if swallowed.

Ammonium Hydroxide
Ammonia 28-30%, Water 30-32% (a .880 specific gravity solution)
May cause burns to eyes or skin. Harmful or fatal if swallowed. Vapors are
very irritating to eyes and mucous membranes. Were appropriate respirator
and use in a ventilated hood.

Calcium Carbonate
Powder
Calcium Carbonate >97%
Skin irritant.

Copper Acetate
Powder
Cupric Acetate, Monohydrate 91-100%
Eye and skin irritant. Harmful if swallowed or inhaled.

Copper Nitrate
Crystals
Cupric Nitrate, Trihydrate 100%
Eye, Skin, and Mucous Membrane irritant. Harmful if swallowed or
inhaled. Strong oxidizer.
**Copper Sulphate**
  Powder
  Cupric Sulphate, pentahydrate (1:1:5) >99%
  Eye, Skin, and Mucous Membrane irritant. Harmful or fatal if swallowed.
  Corrosive.

**Potassium Nitrate**
  Crystals
  Potassium Nitrate 100%
  Harmful if swallowed. Strong oxidizer: avoid combustible materials.
  Do not use with tin solders.

**Oxalic Acid**
  Crystals
  Oxalic Acid 100%
  Severe eye, skin, and mucous membrane irritant. Harmful or fatal if swallowed.
  Corrosive.

**Sodium Chloride**
  Crystals
  Sodium Chloride 100%
  Common salt.

**Sodium Hydroxide**
  Pellets
  Sodium Hydroxide 90-100%
  Severe eye and skin irritant. Harmful or fatal if swallowed. Do not inhale dust or mist.

**Notes on Reagents:**
  It is advised that anyone attempting to replicate patinas used in this thesis refer to the material safety data sheets (MSDS) found in Appendices D for any reagents contained in the patina recipe duplicated. All reagents are dangerous and proper ventilation, eye and skin protection, respiration, and safety precautions should be strictly followed. Storage of reagents should separated by category.
APPENDICES C.
SAFETY

General cautions are included with recipes and in the reagents list. Refer to the material safety data sheet for a given reagent for full disclosure of health risks, handling precautions, and disposal requirements. A proper working environment, working precautionary equipment, and first aid supplies should be addressed prior to embarking on any exploration or replication of patinas.

A proper working environment should be one with adequate space, ventilation, general cleanliness, and away from interruption by those not properly attired or prepared. Proper attire includes chemical goggles, a smock, rubber gloves, and a respirator for particles as well as fume filters when dealing with ammonia based chemicals. General cleanliness should constantly be addressed. Chemical spills must immediately be neutralized and cleaned up. Measuring of reagents should be in a manner that the reagents do not come in contact with each other. Measuring papers should be used on scales to avoid contamination or reaction.

Working precautionary equipment includes that for proper attire, ventilation, fire extinguishers, spill clean up materials for reagents being used, eye wash station, first aid kit, a phone and list of emergency numbers, and proper chemical storage facilities. Storage of chemicals should be in polypropylene containers rather than glass which could break. No food should be stored or consumed in the work area.

When dealing with hot or boiling immersions it should be realized that temperature is now a consideration. Also the vapors being released as a result of the increased temperature are potentially more dangerous since they are often in greater concentrations. Proper ventilation in the form of a ventilation hood is essential.
The preparation of solutions should always be performed with the utmost caution. Always add reagent to water not the reverse, especially when dealing with acids and alkalis. When measuring dry reagents use a clean scoop or spatula. Clean up spills immediately and completely. Reagents are strongest in their dry form as they are not yet diluted by water.

Copper patinas are usually oxides, sulphides, or mineral deposits that can pose extra health concerns. Potential toxins, in the form of gases, can be released when the patinated copper is heated. Furthermore a patina may flake off or leave a powdery residue that might be inhaled or ingested. Proper precautions should be taken when handling such patinated pieces of copper so as not to break loose particles or deposit them on hands or clothing. Sealing a patinated material with a clear acrylic spray often helps bond a patina together that might otherwise continue to degenerate.

In some cases solutions can be neutralized and disposed of easily. Many chemicals still pose health or environmental dangers and should be disposed of by incineration or in a chemical landfill. Consult the material safety data sheet, local and federal regulations, and a chemical disposal facility before dumping chemicals down the drain.
APPENDICES D.
MATERIAL SAFETY DATA SHEETS

Material safety data sheets or MSDS’s should be provided by any chemical supplier. They provide basic safety precautions, contain known hazards involving the particular chemical reagent, and spill or leak procedures. It is advised that anyone using a particular chemical in a patina recipe acquire an MSDS for the reagent they are using from their supplier and read it thoroughly. MSDS’s contained in this thesis are for the reagents used specifically in this thesis investigation, they are not thought to be standard for any similar reagents.
Other Precautions

In handling & storing:

- Avoid prolonged breathing of dust or gas/mist/vapors.
- No special personal protection equipment needed.
- Inhalation, respiratory, skin, eye, & ingestion protection equipment should be used.
- Avoid high pressure contact with affected material.
- Use a respirator to avoid gas exposure.

Other Precautions

In case of contact:

- Wash thoroughly with soap & water.
- Use a water spray to cool spilled material.
- Use a water spray to neutralize spill.

Other Precautions

In case of fire:

- Extinguish fire with water, foam, or a dry chemical.
- Do not usehigh intensity heat or flames.

Precautions for Safe Handling & Storage

- Store in cool, dry, well-ventilated areas.
- Do not store in proximity to incompatible materials.
- Do not store in direct sunlight.

Precautions for Safe Handling & Storage

- Proper labeling of containers.
- Keep away from heat, sparks, and sources of ignition.
- Avoid contact with skin and eyes.
- Wear appropriate protective clothing.

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**Material Safety Data Sheet**

**Product Name:** ALCOR

**Alcohol Corporation**

**Date:** 5/20/11

**Material:** 99W-7.0

**Wt%:** 0.5

**Hazardous Component:** Ammonium carbonate (CAS No. 508-7-6)

**Flash Point:** 308-7-6

**Material Fire Fighting:**

- **Material is combustible.**

**Health Hazards Data:**

- **LD₅₀:** 450 mg/kg

**Chemical Name:** Ammonium carbonate

**Physical Data:**

- **CAS No.:** 508-7-6

**Material Handling:**

- **Storage:** Keep dry and cool.

**Emergency and First Aid Procedures:**

- **Eye Contact:** Rinse with water.

**Reactivity Data:**

- **Stability:** Stable.

**Material Compatibility:**

- **Compatibility:** Good.

**Inert Gas Data:**

- **Flash Point:** 308-7-6

**Inhalation Data:**

- **LD₅₀:** 450 mg/kg

**Experimental Data:**

- **Flash Point:** 308-7-6

**Material Description:**

- **Appearance:** White, crystalline solid.

**Material Safety Data Sheet**

**Section VI**

**Emergency and First Aid Procedures:**

- **Eye Contact:** Rinse with water.

**Material Compatibility:**

- **Compatibility:** Good.

**Inert Gas Data:**

- **Flash Point:** 308-7-6

**Inhalation Data:**

- **LD₅₀:** 450 mg/kg

**Experimental Data:**

- **Flash Point:** 308-7-6

**Material Description:**

- **Appearance:** White, crystalline solid.

**Material Safety Data Sheet**

**Section VII**

**Emergency and First Aid Procedures:**

- **Eye Contact:** Rinse with water.

**Material Compatibility:**

- **Compatibility:** Good.

**Inert Gas Data:**

- **Flash Point:** 308-7-6

**Inhalation Data:**

- **LD₅₀:** 450 mg/kg

**Experimental Data:**

- **Flash Point:** 308-7-6

**Material Description:**

- **Appearance:** White, crystalline solid.
### Material Safety Data Sheet

**Albunin 29**

**DOT**

**UN**

**NA**

**I.C.**

**CAS** No.

**Product Name**

**Product Classifications**

**Hazardous Substance**

**Uses and Applications**

**Safety Precautions**

**First Aid Procedures**

**Emergency and Aftermath**

**Hazardous Data**

**Physical Data**

**Section IV**

**Section V**

**Section VI**

**Section VII**

**Section VIII**

**Section IX**

**Section X**

**Appendix**

**References**

**Note:** This document contains information about the material safety data sheet for Albunin 29. It includes sections on material hazards, physical properties, handling and storage, and emergency procedures. The section on health hazards provides information on the potential health effects of exposure to the material. The section on physical properties includes data on density, flash point, and vapor pressure. The section on handling includes information on safe handling practices and environmental considerations. The section on emergency procedures includes information on first aid procedures and emergency response actions.
SECTION IX
Specific Hazards to Precautions

SECTION X
Inhalation Routes

SECTION XI
Ingestion

SECTION XII
Environmental Exposure Routes

SECTION XIII
Physical and Chemical Properties

SECTION XIV
Stability and Reactions

SECTION XV
Toxicological Information

SECTION XVI
Ecological Information

SECTION XVII
Disposal Considerations

SECTION XVIII
Transport Information

SECTION XIX
Regulatory Information

SECTION XX
Other Information

SECTION XXI
Administrative Information

SECTION XXII
Other Safety or Handling and Precautionary Information

SECTION XXIII
Other Information, Not Included in Other Section

SECTION XXIV
Technical Information

SECTION XXV
Other Information
This is a continuation of the hazardous materials information sheet.

**SECTION III: PHYSICAL DATA**

- **Appearance:** Clear liquid
- **Odor:** Sodium in water
- **Boiling Point:** 25°C (59°F)
- **Vapor Pressure (mm Hg):** 0.5
- **Decomposition:** 0.006 (2.3°C) Rate
- **Specific Gravity:** 1.02 (62°F)
- **Flash Point:** 10°F

**SECTION IV: FIRE AND EXPLOSION HAZARD DATA**

- **Fire Extinguishing Agents:** Water, foam, dry chemical, carbon dioxide
- **Explosive Limit:** 0.6-4.2% in air
- **Autoignition Temperature:** 150°F
- **Flammable Range:** 0.6-4.2% in air
- **Spontaneous Ignition:** No
- **Sensitivity to Knock-Down:** None

**SECTION V: REACTIVITY DATA**

- **Stability:** Stable
- **Incompatibility:** Oxidizers
- **Decomposition Products:** Hydrogen fluoride, hydrogen chloride, hydrochloric acid

**SECTION VI: ACIDIC REACTIVITY**

- **Reactivity with Water/Other Materials:** Reacts exothermically with water to form hydrofluoric acid, which can cause severe injury to eyes, skin, and mucous membranes.

**SECTION VII: SPILL OR LEAK PROCEDURES**

- **Spill or Leak Procedures:** Use personal protective equipment. Wear gloves and protective clothing.

**SECTION VIII: HANDLING PROCEDURES**

- **Stability:** Stable
- **Incompatibility:** Oxidizers
- **Decomposition Products:** Hydrogen fluoride, hydrochloric acid

**SECTION IX: STORAGE**

- **Stability:** Stable
- **Incompatibility:** Oxidizers
- **Decomposition Products:** Hydrogen fluoride, hydrochloric acid

**SECTION X: TRANSPORTATION**

- **Stability:** Stable
- **Incompatibility:** Oxidizers
- **Decomposition Products:** Hydrogen fluoride, hydrochloric acid

**SECTION XI: SPECIAL PRECAUTIONS**

- **Spill or Leak Procedures:** Use personal protective equipment. Wear gloves and protective clothing.

**SECTION XII: SPECIAL PROTECTION METHODS**

- **Spill or Leak Procedures:** Use personal protective equipment. Wear gloves and protective clothing.

**SECTION XIII: DISPOSAL METHODS**

- **Spill or Leak Procedures:** Use personal protective equipment. Wear gloves and protective clothing.