PATINAS FOR SMALL STUDIOS



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Introduction

There has recently been an increased interest in patination and metal coloring. This may be seen as a response to the use of titanium, niobium and aluminum anodizing as well as the increased use of non-precious materials and metals in jewellery.

A trend towards object making in North America has produced large surface areas in base metals on objects which invite patination of various kinds. It is likely that the sculptural tradition of patinated bronzes has had an influence on surface treatment decisions in many of these works.

The publication of Richard Hughes and Michael Rowe's monumental work <u>The</u> <u>Colouring</u>, <u>Bronzing and Patination of Metals</u> in 1982 accelerated the interest in metal coloring in the international metal community. It provided a carefully researched compilation of coloring solutions and application methods superior to anything previously published on the subject for use by artists.

Many of the solutions and chemicals are however unsuitable for the average small studio. Some are toxic and corrosive and others impractical to make as large minimum quantities of expensive chemicals must be bought from supply houses while only a minute amount is used in making up a solution.

There is therefore a need for simple, fairly non-toxic solutions for small scale general purpose use. This paper, a revised version of a technical brief on patina and Lustersud I wrote in 1981, will address this need. For more specific colors, patinas and subtle surface effects I would refer one to the Rowe and Hughes book as well as to other sources listed in the bibliography. Since 1985, when the bulk of this paper was written, Ronald Young, his books and Sculpt Nouveau company have done a great deal to advance the availability of patination information. There are now numerous prepared patination solutions available from various sources. These were simply not available in the same way and breadth of choice in 1985.

There are literally thousands of solutions, pastes and atmospheres to choose from which affect metal surfaces. There is often more than one method of achieving the same or similar colors on a specific metal. I have chosen procedures that require small investment of money in chemicals, are reasonably non-toxic or are made with household chemicals. It is intended that the paper serve as an introduction to metal coloring. The colors dealt with are greens and blues, black, reddish brown and a simple interference coloring procedure.

It should be noted that it is not wise to have patinated surfaces next to skin or used in anything connected with food. Many are toxic if ingested or would cause skin irritation if in close and constant contact. Protective sealers are often used with patinas.

Paint Instead of Patinas

In order to use or have a patina in skin contact with people you have to seal the surface to protect the user. Thus you have essentially metal oxides and salts in a binder. Another way of describing such a thing is to call it paint. One might as well use paint then, where appropriate. 1980 Medium Green Chevrolet (GM 42) is a marvelous patina substitute on the right work. Car paint people know lots about durable finishes on metals. Museum folks can emulate any patina, any texture or surface using shellac and children's powder paints, as well as bits of fluff and dirt from the floor. The bias against painting metal is a Bauhaus thing as far as I can see. If the right answer is paint instead of patina then that is

what you should use. It is of course acceptable to choose patinas for philosophical reasons....

Natural green patinas

The natural green patina such as is found on roofs varies with the environment. In industrial areas it has a copper sulfate base, near the sea a copper chloride and in the mountains a copper carbonate base. With varying conditions it can be a combination of these. Some of the natural patinas and their colors include the following:

Black	Copper sulfide	Cu ₂ S.CiS
Blue	Copper hydroxide	Cu(OH) ₂
Green-blue	Basic copper carbonate	CuCO ₃ .Cu(OH) ₂
Green-blue	Basic copper sulfate	$CuSO_4^{3}Cu(OH)_2$
Green	Basic copper chloride	CuCl ₂ .3Cu(OH) ₂

These patinas develop in a time span from 4-30 years, depending on their location.¹ (footnote) All of them can be produced faster with various chemical solutions and treatments, but it has been found that the best durability and colors suitable for use on metal are artificially produced with some solutions that do not occur naturally.

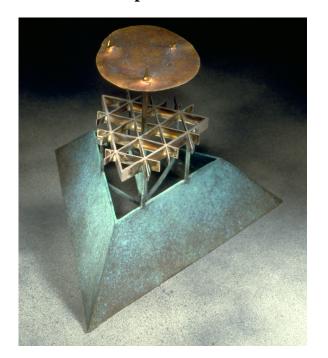
The simplest one that is easiest to use on small scale also has some of the best properties. This is a patina based on cupric nitrate. It holds well, is durable, has good color, is easy to mix up and keeps almost indefinitely. Its drawbacks include the need for a good fume hood and avoidance of skin contact or exposure to its fumes when applying it with heat.

This patina is used for roofs in Germany and when I visited the British Museum Research lab for a conference in 1990 Rowe and Hughes were demonstrating patination to the assembled delegates. This very one was the patina solution they chose to use and when I asked them why they were using it (as it is not particularly stressed in their monumental book) they replied "Because this one works". I felt rather vindicated.

This patina will produce a range of greens, olives, browns and blacks on most metals. It can be modified to turquoise, brown, white, yellowish etc.

When purchasing chemicals it is best to buy commercial or technical grade rather than reagent grade. The price difference can be staggering.

General Purpose Green Patina.



Cupric Nitrate Distilled Water photo-flo* 300 grams 1000 ml (fill <u>to</u> 1000 ml level) 1-2 drops (wetting agent)

*One can substitute household liquid detergent or 1-4 drops methyl alcohol.

Safety precautions: effective fume hood for complete breathing protection, gloves, eye protection.

Mixing

To make up, place the cupric nitrate in a container, pour in water to the 1000 ml level, add the wetting agent and shake until the cupric nitrate is dissolved. Warm water will dissolve it faster. Use plastic containers for it with a plastic lid, not a metal one.

The solution is applied more easily to brass but holds a little better on copper. It may be used on silver, nickel silver, brass, bronzes, steel and iron. It may even be used on gold. It is a surface covering and providing it adheres well (mechanically roughened surfaces, copper containing alloys) and is not used next to skin or to eat from it is a very good general purpose patina.

As in all metal coloring the end result is greatly dependent on the care put into the cleaning and preparation of the metal surface before beginning. If one wishes to develop a perfectly even patina an absolutely grease free surface is necessary. Most problems in patination may be traced to inadequate cleaning or to insufficient patience in application.

The more time and attention given to repeated applications of the patina the more even a finished surface will be obtained. Developing the ability to produce a perfect finish at will allows one the conscious choice of various qualities and imperfections of finish.

Basic tools for using this patina

Hot plate or Bunsen burner and/or a torch A piece of steel or thick metal above the burner or hot plate to act as a device to transfer heat evenly to the flat metal being patinated. A thick short bristled brush with natural bristle A stiff scrubbing brush Pumice or Ajax type cleanser Clean sponge or felt in a plastic container with a lid Spray bottle (if this is used the solution may need to be filtered) Fume hood Rubber gloves Chemical filter face mask

The use of a fume hood with excellent drawing power is recommended for this patina application. Use rubber gloves and the face mask. There is no point to unnecessary exposure to chemicals. Plans for the construction of a small scale, inexpensive fume hood for patination designed by Theo Jansen and James Evans are available from the Ontario Crafts Council in Canada.

For patinating three dimensional objects one can use a torch or a heat gun to heat the object or resort to the slow application method described later. In a fume hood the cooling effect of the draft of air being sucked in can be very pronounced. You can make a windbreak just in front of the object in the fume hood with a brick. This makes a huge difference.

Procedure

- 1. Prepare the metal. Rub it well with pumice to completely remove the oxide layer on the surface and to provide small scratches for better adhesion of the patina.
- 2. Clean the metal as described in the Appendix to remove greases and oils from the surface.
- 3. Place the flat work on the heated metal plate. If the work is not flat place it on a clean fire brick on a turntable and heat it evenly with a torch flame in the fume hood.
- 4. Dip the brush in the solution, wipe it partly dry on the newspaper and dab it on the metal until it is covered with green. A better alternative is to moisten a piece of sponge in a jar and dab the brush on it to keep the brush barely moist (almost dry) when applying the solution. If one is spraying the solution on, a light touch is suggested and a large shield constructed around the work to prevent solution being sprayed over everything. A chemical mask and fume hood are especially necessary when spraying the solution on to hot metal. Don't apply too much in one go, too wet and the newly applied material dissolves the patina already there on the surface.

- 5. Let the metal heat up to the point that the surface turns darker, to brown. Expose it to a flame, burning the layer on, turning it black. Do not heat it too much however as it may lead to adhesion problems.
- 6. Using a stiff brush under running water remove as much of the surface coating as will come off easily and then repeat steps 3-6 until the surface is covered evenly. If you are wanting things done fast don't scrub as hard and count on 'gluing' the surface down at the end with a sealer. However, the slower you apply it and more time you take the more even and subtle the final effect is.
- 7. When an even blackish greenish layer is formed on the metal repeat the process dabbing with an almost dry brush (or use a sparing spray) to build up the green patina. When the surface is evenly covered in green cool it and scrub gently under running water to remove all that can be removed. Repeat this until the desired thickness and color are reached. One can build it up extremely thickly with time.

An extremely wide range of finished effects is possible. Perfectly even green, speckled, patchy, yellowish, brownish, tones of green to turquoise, rough textured or almost smooth, patterned colors and areas of reddish-brown are possible on copper.

If any problems in adhesion occur dipping in a mild (2%) solution of hydrogen peroxide between applications improves its adhesive properties. This also tends to give the patina a slight brownish tinge. Use only synthetic brushes with hydrogen peroxide solution, if brushed onto the patina.

After the final scrubbing and rinsing, dip in alcohol and dry in the air, with a fan, compressed air or in resin free sawdust. This last method is fast and avoids water spots. Gentle blotting also works.

Slow Application Method

This is best done outside in the sun in hot dry weather. The solution is sprayed or painted on in a thin film and let dry. A light brushing under running water may be used to remove loose material between coats. The process may take a day or more. Many kinds of patina lend themselves readily to such a slow applications procedure.

Color Variations with the Cupric Nitrate Patina.

Yellowish tone: remove the metal from the heat before the patina turns green.

- Brownish yellow on green: expose the finished surface to a light flame. Some experiment is necessary here to obtain even tones of brown. On textured surfaces the high areas will turn brown first which may be useful in emphasizing patinated heavy texture. The blue portion of the flame will work well. You have to move fast to avoid burning the patina.
- Greener: add a few drops of acetic acid. <u>Do not</u> add more than a few as too much may ruin the solution.

Blue-green: dip in a weak lye solution.

Bluish-green to turquoise: expose the surface to ammonia fumes or paint on or wash the surface in dilute ammonia (non-detergent household clear types are good). Patina that has been heavily treated with ammonia to obtain a turquoise color may lose some adhesive strength. When applying ammonia do it to cool metal as it will tend to dissolve the patina if dripped on while it is very hot. The color may be made to revert to green from turquoise by gentle heating.

Pattern Development

Scraping:

Areas in bright metal may be obtained by scraping through the patina layers. Paint, inks or gold leaf may be laid into the scraped areas and lines. Planned raised areas can be scraped clean leaving recesses patinated. Hard felt buffs may be used to high polish such raised areas.

Blue-green (turquoise) on green:

When the base color is satisfactory one can paint or draw with ammonia to develop blue where the ammonia wets the surface. The process is accelerated if the work is warmed slightly. Several applications on the same place may intensify the blue. Depending on the strength of the ammonia used and its evaporation time a deeper blue outline to the affected area may be developed.

White (very pale green) on green:

Vinegar (acetic acid) can be painted or drawn with. After a minute or so working time it is rinsed off leaving its location bleached.

White (to metal surface) on green:

A 1:2 solution of nitric acid when drawn on the surface will bleach the patina and if left long enough will eat into the surface providing some surface relief and the brown of the metal beneath showing through. Make sure and neutralize it afterwards with baking soda.

Dark brown on green:

Bleach is painted on. Where it is turns brown after 30 seconds or so. This is accompanied by a nice shade of deeper green that unfortunately washes off with water and disappears as the patina dries. The brown however remains. If the surface is suspended in bleach a mottled brown and green results. When oiled or waxed this becomes darker. It seems possible that resists might be used with the foregoing color modifications.

Green areas with brown outlines:

A pattern is laid out on the surface with water, preferably beaded up slightly. A gel made from gelatine and water or a lubricating jelly such as KY or Lubafax would be excellent for this purpose. A torch flame is rapidly played once over the surface and the areas protected by water will remain green, the exposed areas turning brown. There will be a brown outline to the protected areas.

Modifying the color with other solutions.

You can for instance, change the green patina by using ammonia on it or adding ferric chloride solution and letting it dry before rinsing it off.

One can make a mixture of cupric nitrate, salt and water which produces azures and hints of orange on the metal's surface. This can be applied hot like the cupric nitrate solution.

Rowe/Hughes 3.129 Cupric Nitrate 200 g Salt 200 g Water 1000 ml

Burning with resists

You can wrap the object in string or cloth or tie plants to it. Then use a torch on it. I have also soaked the string in lighter fluid and set fire to it (outside of course), which caused the exposed patina to blacken from the smoke and leaves green x-ray like patterns where the plants or string protected the patina.

Fuming or smoke effects

This requires a good fume hood or outdoor use. The patina surface may be exposed to the smoke of burning leaves, straw or wood to modify the color. Burning straw, twigs, leaves, pine needles, resinous shavings, etc. may be placed directly on the patina or the patinated metal dropped into burning materials for random or semi-random carbonized effects. This can be done to almost all metal colorings including smooth ones. Tape resists can be used when smoking surfaces. Afterwards smooth finishes can be rubbed with a soft cloth to remove loose soot and a gentle scrubbing with water may do the same for more porous ones. If doing this use good sense and follow fire-safety rules.

Applied finishes

Spray applications of acrylic sealers, lacquers, silicone lubricants and oils may be used with tapes, wrapped string or organic materials as resists to obtain patterned or mottled areas. One makes a color palette, that is a long strip with different finishes on it so you can choose what effect the finish will have.

Protective Coatings

The finished product may also have some form of protective coating, although this patina is tough and not liable to damage if applied correctly. If a patina is brought near skin it should be sealed in some manner.

Traditionally these would include waxes, Vaseline and oils. Also available are the spray sealers and lubricants mentioned above. These work as water does in intensifying perceived color on the patina surface. The exact effect will depend upon the refractive index of the coating involved, its evaporation rate, viscosity, etc. One should make samples with various colors and different coatings for reference. Oils and waxes tend to

darken the color. The spray acrylics tend to make the patina resemble green paint and I usually use them sprayed from a distance for a thinner more subtle effect. I like transparent auto enamel, sprayed on from a distance, allowed to dry, a light second coat blotted while drying seems to work. Some people like a sealer called 'Dead Clear Flat Matte Lacquer" from Start industries. Many goldsmiths use "Nicholas" lacquer and swear by its longevity. I happened to talk to someone who began using it after asking what the high school band used on its instruments to keep them shiny and protected. One can have transparent powder coating done on metal objects. They are pretty good against wear. The opaque powder coating however looks like paint in which case paints for metal might be an option instead.

Note: Avoid dry sanding cupric nitrate patina surfaces, wet sand only under water. I had a student experience breathing and other problems when they foolishly dry sanded such a surface.

Small Studio and Household Chemical Patinas

The oldest traditional method of obtaining green patinas on copper alloy surfaces was to expose them to urine, preferably aged to develop a stronger ammonia content. Works have been buried in manure, coated with urine containing pastes or sealed in an atmosphere of urine fumes. I have heard of a Korean goldsmith who had forty or so jars of aged urine in his workshop, each labeled with its date and quality, the older ones being more prized. While ammonia (presumable more hygienic) works well as a substitute for urine one would expect that diet and physical condition would add minerals, salts and complex chemical compounds to the solution and so affect metal surfaces in more subtle ways than straight ammonia does.

Burial in alkaline or acidic earths has also been used to create patinas and may be considered a kind of paste application. These procedures in common with others outlined here take time for the effects to develop, from a period of days to months. Adhesion is not as good as with Cupric Nitrate patina.

Application Methods

As previously, extremely clean metal surfaces give better results.

Cold fuming:

Generally speaking exposure to a fume or atmosphere results in a more even effect except where condensation causes pooling of moisture on the surface. A simple method for doing this is to place the object on a small platform (to keep it out of the patination agent) in a large plastic container or bag and pour the agent out on the bottom of the container. It is then sealed and left to affect the metal.

Painted solutions:

The solution is painted on with a brush or swab. It may be necessary to use a tiny amount of soap or some alcohol in the solution to act as a wetting agent in order to obtain an even surface. The metal is allowed to dry and the application repeated a number of times until the color development is satisfactory. Often this may be done outside to aid in drying and eliminate fumes from the workshop.

Sprayed on:

This serves as a method for obtaining an even or evenly speckled effect on the surface. It works well for three dimensional objects. Again, repeated applications and time yield the best results. Keep applications light. If using a spray bottle the solutions may need filtering before use. In the case of ammonia which decomposes rapidly in air one should spray the surface and then seal it off from the air in a closed (plastic) container.

Bound materials:

Where a material moistened with a patination agent comes in contact with a surface etching, reaction takes place more readily at the point of contact. An object can be wrapped in cloth or string to take advantage of this. Organic materials such as feathers and plants may be bound to the object.

If tightly bound they will to some extent prevent surface activation by the patination agent and their outlines will be visible on the finished surfaces. When one binds with dry materials with or without organic materials and exposes the surface to cold fuming they act as resists and use can be made of this in developing pattern. In the case of ammonia it soon permeates the binding medium and begins etching and reacting with the surface at the contact points.

Pooling:

If the agent is pooled on the surface it reacts where it is pooled. Fingerprints can be used as a grease source to force pooling to occur. Pooling will result in a variegated effect as the edges of the puddles will act differently upon the metal than the centers.

Immersion:

The object is immersed in the solution. This tends not to work quite as fast with the agents recommended here but can produce even finishes. In some cases (as ammonia on brass) strong etching of the surface can take place. Immersion can be used as a method of coating an object with a solution by dipping it, removing it and allowing it to dry. This can tend to produce a concentration of effects where the liquid has run down the piece while drying.

Moistened shavings

Moistened (not wet) wood shavings or other porous materials work very well for differential patination/etching of surfaces. Again, contact points are the focus of action on the metal and very interesting surfaces are possible. Using ammonia or vinegar etching takes place producing texture as well. Possible media for this include resin-free sawdust and shavings, peanut shells, kitty litter, Styrofoam balls or chunks, crushed cork, sisal or other coarse fibers, pine needles, grass clippings, organic materials such as leaves, feathers and so on. Use them in a sealed plastic container to prevent evaporation. The piece may be shaken up in them to obtain an even effect. Rowe and Hughes suggest making a dam of modeling clay to contain the most media in order to obtain pattern

development or block areas of such effects on a piece.² It should be noted in this context that modeling clay has a high sulfur content and will attack and etch silver while turning copper alloy surfaces black where it contacts them. This too could be used in developing pattern. The cat box or hamster cage could provide a good medium for patination in this technique.

RECOMMENDED AGENTS (For use on copper alloys)

Household Clear Ammonia: produces greens and blues, olive green on bronze. Can produce bright blues with brass especially when used as a fuming agent. It affects the structure of brass if left in contact too long (possibly reacting with the zinc) and the brass may crumble or fall to pieces with light pressure. Therefore if using brass and ammonia the structural elements of the piece should be in copper or another metal. An ammonia and salt fumed blue can be converted to a greener color by brushing a flame over it in the same way as with the cupric nitrate patina.

- Vinegar: produces dark greens, blues and will also affect brasses in the same way as ammonia.
- Salt solution: Varying strengths of salt solution may be made up and applied to the metal. Colors formed include some tones of red on copper. Deep green is common.
- Dry salt: This can be sprinkled on the metal surface. It draws moisture to itself in a humid atmosphere and will react with the surface over a period of weeks. When finished the loose material may be brushed off leaving a variegated surface of greens, browns and possible orange-reddish patches.
- Borax: Left on the metal in a humid place with react over weeks to make nice azure crusts and other greens.
- Baking soda: Left as a moist paste on the metal will attack it and produce greens.
- Iron filings: In combination with any of the above they will react to produce localized dark mottled surfaces.
- Combinations: Various combinations of the foregoing are effective for patination. There are also other household chemicals which will produce patinas on metal.
- Nitric acid: Although not a household chemical most studios have some. A strong (1:3) solution of nitric acid will turn copper a reddish-brown color if left to dry. If a film of it is maintained over the surface for a week or so a deep even green is produced. When ready the surface is rinsed for a long time in running water and loose material is scrubbed off with a toothbrush and baking soda solution to neutralize it. Great care and safety precautions should be used when working with acids (always pour acid into water) and cleaning up carried out right away. If the metal reacts to release brown fumes the acid is too strong. Use a fume hood for this procedure.

Resists

Wax, tape or lacquer resists may be used with many of the above agents. Vinyl sign makers have lots of free scrap peel and stick vinyl material which makes great resists for patinations and platings. Thinned rubber cement (just roll it up when done). Ironed on Xerox. Sharpie markers.

A table of application methods suitable for these chemicals is included in the appendix. Protective coating procedures would be the same as for the previous patina.

Greens on silver

For greens and blues on silver one will have to approach it by covering up the surface with something that is green or blue because in sterling and higher there is not sufficient copper to produce these colors by corrosion and reaction with the metal. This approach of attacking a copper alloy to produce colors is a Western approach. In Japan they have often approached coloring by varying the alloy and using a similar chemical solution to produce long lasting, durable colors, though not to my knowledge much on silver beyond grays, browns and similar effects-I may be wrong on that.

One can in fact fume sterling in an ammonia or vinegar atmosphere and you will get light blue stains, usually associated with puddling or pooling. This is rather thin and pale except at the edges of the pools. One can also copper plate the silver and then react that with ammonia or vinegar.

The cupric nitrate patina solution will work on silver alloys and you have a full range of greens, yellowish green, turquoise, black, olives etc. available. It works best on a roughened, clean surface so you increase mechanical adhesion. The surface is sealed as well with a clear auto lacquer. It does cover up the silver unless you scrape it off, etch it preferentially down to the silver with vinegar or an acid or use some kind of a resist during application. The patina is absorbent so if you want to polish part of the silver next to it you have to seal the patina first otherwise it absorbs polishing compounds and looks dirty.

Dyes and Paints

One can use all kinds of dyes as well on metals. Ron Young sells a good kit. I believe Swest sells some too. Auto paints are intended for metals and some paints may make an excellent solution to this problem. GM42 1980 medium green Chevrolet (which any body shops should be able to make up for you) and 1976 Thunderbird blue both make excellent patina substitutes which work extremely well if rubbed into recesses on a metal surface and then the high points wiped off with a rag.

A student of mine, Gary Honig, had applied taxidermy dyes usually used on fish (trout?) to a number of metal surfaces, they provided great transparency and were almost like a shiny tint to the surface. They held very well and so far I have not heard of any damage to them with time, though he used them all in pieces not subject to wear, wall pieces, sculptural objects etc. There was no need to wax them.

Layered Metals

Plated, mokume and doublee surfaces may be used with these agents also, that is with layered metals of varying susceptibility to chemical attack one can emphasize the different layers by the appropriate use of chemicals. A gold plate on copper can be engraved through leaving the copper exposed to turn green in an ammonia atmosphere. There will also be significant reaction at the many pin-holes that characterize a gold plate unless there has been a nickel strike beneath it. Liver of sulfur can be used effectively here to emphasize the difference between the metals.

I use resist plating sometimes in my work. A resist (I like thinned rubber cement) is applied to the copper sheet, then plated in nickel (gray), then more resist plated in silver (white), then more resist and plated in gold. If I have left some copper surfaces exposed these will go green and blue when fumed thus producing a complex series of colors on the work.

Kieth Lewis came up with an interesting method of darkening high copper content brasses like Nugold[®] or 'jewellers bronze'. He used a fusion inlay (see Gold Applications paper) to inlay patterns of gold marks into a high copper content brass. Then he cleaned the surface, placed it into hot water to stabilize its temperature and then held it in hot household ammonia fumes for 30 seconds or so. The Nugold[®] turns a lustrous purplish black while the inlaid gold stayed bright. The color is very similar to Niello so much that at a conference I introduced Kieth to Phil Fike, America's master of

Niello and asked Kieth to show his work. Phil thought the surfaces were niello which says a lot about what the surface looks like.

There are a number of easily accomplished coloring procedures which are worth mentioning.

Liver of Sulfur

This is a mixture of potassium sulfides which has traditionally been used to darken or 'antique' silver and bronzes. This is usually called 'oxidizing' the surface though it has nothing to do with oxygen, what is really happening is that sulfur is reacting with the surface to produce the grays and blacks. So if you call it 'oxidizing' as most jewelers do just remember that is untrue. Most people who make jewellery are quite familiar with its use.

Usually a piece about the size of one's little finger nail is dissolved in a cup or more of warm water. One may shake the jar it comes in to obtain small flakes which will dissolve quickly. In my opinion more dilute solutions give better control, repeated dippings and rinsing building up to the desired surface.

The fumes are dangerous and it should be used with good ventilation and covered right after use. It must not be allowed to come in contact with acids as a toxic gas is then rapidly evolved. It decomposes with exposure to light and air and so should be kept in a dark bottle that is sealed tightly. It is possible to keep for months if poured in hot. As the hot air contracts after sealing and cooling less air is available to decompose it inside the bottle.

To obtain black a number of repeated applications alternated with rinsing and brass brushing with a little soapy water is effective. A lustrous blue-black to steel gray may be produced on silver this way, and a purplish black on copper. Painting with the solution on specific areas accompanied by heating the object gently works well. An excellent black on sterling is obtained by sand blasting immediately before dipping into the solution. (don't touch it with your fingers-any grease will interfere with an even coloring. This surface is fairly durable, particularly if gently brass brushed with some soapy water as a lubricant.

Liver of Sulfur does not take well on brass. Repeated heating and pickling or the introduction of iron to a pickle solution will coat the piece with copper which can be darkened. This is good for emphasizing recesses. This same idea is sometimes used on gold jewelry that has to be 'antiqued'. Because gold alloys do not react to most sulfur solutions one can take some used pickle solution, place it into a bowl with the object and (wearing gloves) blot the object with some medium steel wool. This will contact plate the object and its recesses with copper. Then rinse, use the liver of sulfur solution to darken the plating to the desired level and buff off the surface with a rouge buff. The darkened recesses will be untouched by the buffing and so remain, everywhere else is bright.

Another way to work with it is to use rubber gloves and hold a small lump of liver of sulfur and draw on the metal surface with it while it is held at an angle under cold running water. This gives some interesting effects even on brass.

Liver of sulfur (potassium sulfide) powder is not the best way to obtain it. Lump form lasts longer. Light and air will destroy it so keep it shut and in the dark. Use gloves. Don't mix it with or place it next to acids dry or when mixed up (no pickle in your objects if you are coloring them) as this can release hydrogen sulfide gas which is very bad for you. Use ventilation with it.

Most people tend to use too much and too strong. Only mix up as much liquid solution as you need to just cover your object, more is wasteful. put hot or warm water into a glass or Pyrex or corning ware container. I take my clean object, put it under running hot water (to raise its temperature so differential coloring does not occur on the areas to heat up first when placed in the solution), then dip it in the solution for a moment or two, take it out, rinse and repeat until the darkness you want is achieved. A brass brushing with soapy water as a lubricant in between rinsings will render a shiny, uniformly dark metallic surface. By going slowly you have a lot more choice in color, tone and surface qualities.

While it is usually used to obtain gray and black colors on silver and copper there are a number of intermediate interference colors formed, particularly if a weak solution is used. These include yellow, reddish brown, purple and blue. Some people add a small amount of household ammonia to the solution claiming it intensifies the lovely blue-green-red-purple interference colors one gets when using a dilute solution and slow approach. These pretty colors are not very stable over time because they continue to react with sulfur in the air and darken. You can sometimes 'save' them by spraying an appropriate lacquer over them. They may be retained if the surface is properly sealed. Acrylic resin is the recommended sealer for durability and resistance to darkening in light. Some jewelers lacquers also work. Envirotex® works very well for this. It is usually best in my opinion to continue darkening to the grays and darks which will last indefinitely.

For grays and blacks on silver one can also react the surface with sulfur compounds to form black silver sulfide. Plasticine (Plastilina) modeling clay for example contains some sulfur compounds and it can be used to create patterns of darkness where it has been stuck on in contact with the silver for some time. A soak in bleach will turn silver a gray color, sometimes with a sheen to it. (Remember never to mix bleach and ammonia!)

Hughes/Rowe solution 5.2 (orange to red to brown on brass)

Copper sulfate	25 grams
Ammonia (.880 solution)	3-5 cm ²
Distilled water	to 1000 ml level ⁴

A stainless steel pan is used for this solution. While various ruddy browns can be produced on brass and copper with mixtures of copper sulfate and water this solution has rather rich tones to the colors produced.

As the ammonia is added a dense turquoise colored precipitate forms and this seems to be the effective agent in the solution. It is important not to add too much ammonia and that the metal is absolutely clean. Brass is the intended metal for this solution and the color progression is mustard to orange towards a brown with purple tones. One can increase the copper sulfate content (and ammonia) to affect copper more readily. The Hughes/Rowe solution for a similar color on copper is (3.2):

Copper sulfate	120 grams
Ammonia (.880)	30 cm^2
distilled water	to 1000 ml level ⁵

As one can see from this there is a certain latitude available in mixing the solution. It is noted that too much ammonia stops it from working. As the solution does have some leeway in its formula one can avoid the more dangerous .880 ammonia and use household clear ammonia instead. Ideally one must take the specific gravity of the household clear ammonia and compensate by adding more and less water. In practice an educated guess will suffice to produce a usable solution providing too much ammonia is not added. A ventilation system should be used primarily to vent the ammonia fumes.

Selenic acid

This is available in the form of photographic print toners, as 'hobby black' for model railway use and as a main ingredient in many gun bluings. It is simply painted on the metal and turns it black with hits of blue-gray or brown depending upon the formulation. It works on silver, steel, brass and bronze.

It too will cause a progression of interference colors to occur on silver, especially if diluted. One method of dilution is to paint some parts to blacken them and then to place the metal in some warm water. Some will be liberated from the already darkened area and go into solution. The still clean areas will begin to be affected, starting by turning a gold color.

Selenic acid, often sold in gun shops for gun-bluing or browning steel will work on silver, depending upon dilution one can get rainbow colors (interference colors-probably not too permanent or scratch resistant) to grays and blacks. Selenic acid is also available at photography shops as 'selenium print toner'. Selenic acid is I understand it being withdrawn from use because it can be very toxic. I would check this out at an MSDS web site like:

gopher://atlas.chem.utah.edu/11/MSDS

Iodine

Tincture of iodine will turn metals brown, including gold. The color is fairly difficult to remove and holds up well in recesses. It can be a good addition to recesses.

Bleach

Bleach will turn silver a light gray color, sometimes with a hint of red-orange iridescence. It has little effect on brass and copper besides leaving an outline of where the drop edge was on the metal. this is brown in brass and grayish with copper. Prolonged immersion turns brass an uneven brown.

Red oxide on copper

A very tough red/purple oxide layer can be developed on copper by plunging it red hot into boiling water. In practice it is difficult to achieve an even coating. A 50% mixture of borax flux and water does a pretty good job as a quench to produce a uniform red.

A piece of copper that was excessively heated with an oxy-acetylene torch was a very even rich red color after quenching. The ability to control oxygen supply to the metal with such a torch could be useful in developing consistent results. There are commercial red (and purple) metal dyes and even patina solutions now for reds and oranges on copper based alloys.

Linseed oil and Beeswax

This is a blacksmith's method of giving a protective black coating to iron and steel. The metal is cleaned and roughened slightly with emery or a file. A mixture of one part linseed oil and two parts beeswax is warmed gently until homogenous. This is painted on the metal and the metal warmed until it just begins to smoke. As it dries the procedure is repeated and slowly a textured black surface that is slightly glossy is built up. This can be built up to a thick layer on the surface. Painted on oil finishes which were heated to bake them used to be standard fare for iron and steel objects. Quite durable if you think about how a standard baking tray or cookie sheet can look after a while if it not vigorously cleaned.

It is worth noting that a number of metal coloring procedures and patinas like this last one and the cupric nitrate patina build up a layer of material over the surface, effectively hiding it. The only difference between them and say, the use of suitable paints, is recent historical context. There is no reason why paint, sealed color pencil, plastic resins and other durable surface coloration methods not be used on jewellery and metal surfaces save tradition. Rodin's sculptures were routinely finished with colored pencils after patination.

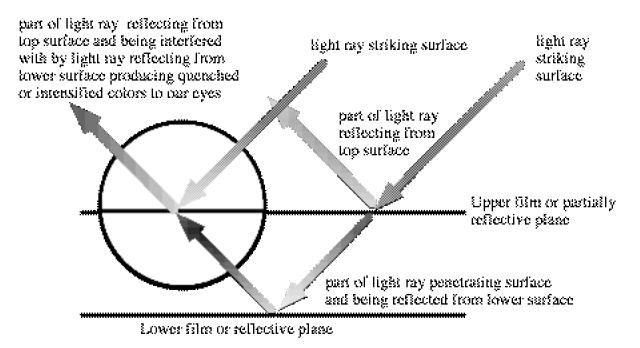
Where intent and aesthetic choice demand it and a durable medium is available it should be used to solve the aesthetic problem posed if appropriate to the intent.

Ferric Chloride: This etchant for copper base alloys is available at any Radio Shack[®] Store. It leaves remarkably durable yellowish to brownish, almost brown black stains on metals. I noticed it when I realized how permanent the stains on a stainless steel sink were from the etchant. The colors are most of those found in rusts. The control factor is dilution. You might want to add a little alcohol or a drop of dishwashing liquid to the solution to make it sheet better. Remember that it contains hydrochloric acid and so all precautions normally taken when handling acids should be done, goggles, rubber gloves and apron and good ventilation.

Interference colors

They are encountered in pools of water and oil, tarnished metal, liver of sulfur coloration and in the oxidation colors seen on steel when tempering.

The phenomenon is caused when extremely thin sheets or layers of different materials are placed over one another in such a way that a light ray entering the top layer is partially reflected away and partially refracted into the layer and reflected form the bottom of the lower layer(s). The ray in reflecting back into the air coincides with and interferes with another ray being reflected from the top surface. In the process some of the wavelengths (perceived colors) in the second ray are quenched and some intensified. When this happens simultaneously with countless light rays and with multiple layers and the play of observed light can be very complex.



With oxidation colors on steel, copper and other metals the oxide thickness works in this way and providing it is an even development of oxidation it 'filters' out all colors except the one observed. As the oxide layers thicken the observed color changes.

Liver of sulfur and other interference colorations work by building up layers of sulfides or other compounds which work in the same way.

Heat can therefore be used to obtain colors on metals by oxidation. They are fragile and must be protected from abrasion and further oxidation. This can be done with acrylic coatings and some lacquers. Waxes may destroy the clarity of the effect by changing the way light enters and is reflected from the oxide layers. It can be difficult to obtain even results with heat.

Lustersud, the particular luster coloring described here works by creating interference with layers of lead sulfide crystals on the metal surface. Because it is an additive technique like the cupric nitrate patina the colors can be produced on almost any metal including gold. They can be separated into yellow-gold, copper-red, violet, dark blue, bright blue, chrome, gray and gray with a hint of red. These colors repeat themselves if the metal is left in the solution but are not usually as bright the second time around. The sulfide layers are however tougher and thicker.

This solution is potentially dangerous because of the lead acetate used in it. Great care and proper chemical safety should be used if the solution is tried out. This one is not recommended without chemical lab level precautions!

The colors are fairly fragile and need some sort of protective lacquer, acrylic resin, wax or surrounding walls to prevent abrasion. They were used industrially in watch dials and were protected by lacquers and the watch glass.

The usual solution working temperature is between 50 and 90° C but by adding certain acids as in the one cited here the effective temperature drops to room and above and the

layers become denser, thicker, finer in structure and so tougher and more durable. The best durability is found at the blue color.

The colors appear in sequential order. This is approximately:

5+ seconds	gold/yellow
15 seconds	bright red-violet
25 seconds	deep blue
30 seconds	bright blue
60+ seconds	gray

These times will vary with temperature, concentration of the solution and so on. Colors may vary as the base metal modifies them slightly.

<u>Lustersud</u>	Temperature: Room to 60 ^o C	
	Sodium Thiosulfate	240 grams
	Lead acetate (Very Toxic!!!)	18 - 25 grams
	Potassium Bitartrate (cream of tartar)	30 grams
	Distilled water	1000 ml (fill <u>to</u> 1 L)

It must be mixed and used in a glass or corning container, not a metal or enamel one. The container should be large enough to allow movement of the metal to be colored as agitation is necessary for an even coloration.

When mixing it a suitable mask <u>must</u> be worn as lead acetate dust is **very** toxic. Once it is in the solution it is much safer to deal with. It should still however be used in a fume hood.

The solution can be kept in an airtight container for some time without deteriorating. Keep it out of the light. It is best to operate with a thermometer in the solution (not resting on the bottom) as a temperature guide and a check on the water level in the container if it is not marked. If it falls below 1000 ml it can become too concentrated and will not work. Add distilled water as necessary.

The work is best held in the solution by a wire attached to it, preferably on an out of the way spot. It is essential that all tools used be perfectly clean and that the metal to be colored be completely grease and oxide free. A polished surface will produce a more reflective finish.

Tools

Tweezers Thermometer Pyrex or similar container Heat source Fume hood

Procedure

- 1. Clean with pumice (not if polished surface).
- 2. Follow cleaning procedure in Appendix. Electrocleaning (procedure 2.0 2.5) is recommended.

- 3. Immerse in the hot solution, moving the object in an even manner in the solution. If it is large it should be preheated to a little more than the Lustersud temperature in a water bath to equalize temperature effects on the edges and to obtain an even coloring. Room temperature use avoids this problem.
- 4. When it reaches the desired color remove it and stop the progress of coloration by placing it in water.
- 5. Rinse well, in running water 6 10 times.
- 6. Dip in alcohol, dry in resin free sawdust, pat dry or use compressed air.
- 7. Put protective coat on. Acrylic resin, waxes, etc.

APPENDIX I

Application Method Table

Recommended	Sealed	Painted	Sprayed	Bound	Pooling &	
Agent	Moistened <u>Fuming</u> <u>Shavings</u>	<u>On</u>	<u>On</u>	<u>Materials</u>	<u>Puddling</u>	
Household clear ammonia	yes	yes	yes	yes	yes	2
Vinegar	yes	yes	yes	yes	yes	2
Household Ammonia: 2 parts Vinegar: 1 part	yes	yes	yes	yes	yes	2
Salt solutions	N/A	yes	yes	yes	yes]
Dry salt crystals	N/A	sprinkle	N/A	N/A	N/A	2
Iron filings in combination with the above	N/A yes	yes	N/A	yes	yes	
Nitric acid: 1 part Water: 3 parts	yes yes*	yes	NO!	yes*	yes	
Rowe/Hughes 3.129 Cupric Nitrate 200 g Salt 200 g Water 1000 ml NB: can be applied hot like the General purpose patina.	N/A (Produces a	yes variegated gre	yes en/orange surf	yes face. Green ha	yes as an azure bia	ls)

*The organic materials will be damaged by the acid. Disposal may present a problem.

Cleaning Metal Surfaces

1985-91©

For all metal coloring and electroplating a clean metal surface is essential. The cleaning process must remove mineral oils, organic oils and greases as well as traces of chemicals on the surface. It must remove oxidation which might interfere with the metal coloration or plating adhesion and it should possible activate or roughen the metal surface to better receive the treatment.

Cleaning may be accomplished using mechanical (abrasive), chemical (heating, solvents, pickling with acids) and electrolytic (electrocleaning, electrostripping) means. Examples of easily achieved clean surfaces include bead-blasted ones and ones scrubbed well twice with rinsings using Fantastic®. A pumice rub followed by scrubbing with dishwashing liquid and ammonia on a toothbrush does pretty well. Best of all is electrocleaning.

A simple procedure is:

- 1.0 Anneal and pickle in suitable acid.
- 1.1 Rinse 3-5 times in running water.
- 1.2 Dip into simmering ammonia and detergent solution and scrub well.
- 1.3 Rinse well 5 10 times.

NB: electrocleaning can be used after step 1.3. While steps 1.0-1.3 produce a quite clean surface by themselves if one is electrocleaning it is not a bad idea to pre-clean using steps 1.0-1.3 so as to make the electrocleaning solution last longer and lower it's work load in cleaning the metal surface.

A much better and surer procedure is:

- 2.0 Remove oxides with pumice
- 2.1 Rinse well.
- 2.2 Electroclean for 1.5 2.5 minutes, object as cathode, then reverse the polarity for a few seconds.
- 2.3 Rinse 3- 5 times in running water.
- 2.4 Dip in 1:10 sulfuric acid to neutralize the electrocleaning solution and activate surface. (15 seconds or so).
- 2.5 Rinse 3 5 times in running water.

After cleaning, the metal should be placed in running or circulating water (preferably distilled) to avoid oxidation until it is plated or coloured. One can of course plate or colour immediately after cleaning. In all cleaning methods the piece must either be wired to suspend it in the solution or held with tweezers. It must afterwards be very well rinsed to remove all traces of cleaning chemicals. <u>Do not</u> touch the surface once it is free of grease.

Abrasive blasting may be substituted for steps 1.0 and 2.0 above.

Sample Electrocleaning solution:

Sodium carbonate Trisodium phosphate	50 grams 25 grams	Current density: 1-3A/dm ² Polarity: 1 - 3 minutes
Thisodiani phosphate	25 grunns	Cathodic(of work)
Sodium Hydroxide	25 grams	5 - 10 seconds Anodic
Water	2000 ml	
Operating Temperature	60-70 ⁰ С	

APPENDIX II

FOOTNOTES

- 1. <u>Chemische Farbungen von Kupfer und Kuperlegierungen</u>, Deutsches Kupfer Institut, Berlin, 1974, p. 36.
- 2. <u>The Colouring, Bronzing and Patination of Metals</u>, Hughes, Richard and Rowe, Michael, Crafts Council, London, 1982, p. 41.
- 3. <u>Chemische Farbungen von Kupfer und Kuperlegierungen</u>, Deutsches Kupfer Institut, Berlin, 1974, p. 31.
- 4. <u>The Colouring, Bronzing and Patination of Metals</u>, Hughes, Richard and Rowe, Michael, Crafts Council, London, 1982, p. 270.
- 5. <u>Chemische Farbungen von Kupfer und Kuperlegierungen</u>, Deutsches Kupfer Institut, Berlin, 1974, p. 18.

The Colouring, Bronzing and Patination of Metals contains an exhaustive bibliography of sources dealing with patina and metal coloration.

Gun bluing equipment and chemicals from Brownells. Their bluing catalogue contains a lot of information on procedures.

Brownells, Inc.	Ronald Young at: http://www.sculptnouveau.com/
Route 2, Box 1	(patina solutions, dyes, books etc)
Montezuma, Iowa	
50171	

A Method of Patinating Brass Alloys Using Contact Plating 1990©

Recently I have been presented with the problems of repairing or changing the color of Indian made polished brass objects, usually to brown or grey tones. In one case the object was a Shiva which was about three feet high and across.

It was cast brass in a hollow core technique and had a number of parts separately cast and then brazed together and the surface finished. This was not immediately evident and occasioned some slightly irritating moments when pickling liquids (which I now do not recommend using) were trapped in several different sections and had to be first driven out through tiny holes with heat and then neutralized and rinsed. The Shiva had been partly ground at by the owner which had removed a darkened copper plating on the cast brass and revealed the bright yellow core. The request was for a grayish patina, fairly bright with a hint of bluish green. As nothing would match reactions on both surfaces and in order to start with a uniform metal type I decided to plate the object. The same technique worked well later on a pair of 5' brass cobras destined to be part of a lighting company's offering. They asked me to change the patina on the snakes from a tan brown to a glossy reddish black with blue hints.

The first time I mixed up a plating solution and used a (DC) wired brush and rectifier to plate with. While this worked I found that precipitating the copper on the cleaned brass surface was easier using a contact plating technique and steel wool as the precipitating agent. Zinc would also be electrochemically active in this regard.

I found that the fineness of the steel wool made a difference. The finer the steel wool the faster it precipitated the copper. Because it had a great deal of surface area most of the available copper ions were used up in reacting and plating out onto it leaving little behind in the solution to be precipitated onto the brass.

The best grade I found that caused the plating reaction without using up too much of the copper solution on itself was medium grade Bulldog® steel wool. Wearing goggles, rubber apron and gloves I would pour some of the plating solution onto a steel wool pad and slowly wipe the wool with slight pressure over the surface of the brass. Several passes were necessary to effect a good plating. It was very important to be clean beforehand; to have properly cleaned the base metal and rinsed it well. A good deal of rinse water was also used after applications of the copper plating solution.

In my case having got the plating on I sprayed on a dilute liver of sulfur solution onto the plating and rinsed afterwards to blend coloring areas and keep the pace of coloration uniform. One can brass brush the surface with soapy water in between coloring applications to achieve a more glossy result. When the color was correct I placed the objects inside a polyethylene tent (a garbage bag will work) with some household ammonia in a pan in the bottom of the tent. The fumes affect the surface giving blue hints which gather in the recesses of the work. This occurs starting at about one hour and continues with time. I generally use six hours or so. As the contact plating is thin it is possible that too long an exposure would use up the copper metal and begin attacking the brass. Brass in ammonia fumes for long periods of time may crumble when bent even with hands or fingers and becomes very weak and brittle. The surface can then be waxed or sealed. In one case the client requested no protection, he wanted the patina to advance further slowly with time. In the other I used a clear auto enamel which produces a shiny, more metallic surface.

Contact Plating Solution Recipe

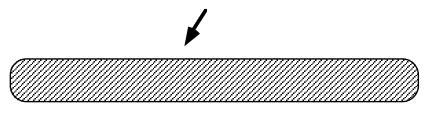
All safety warnings apply. <u>Always add Acid to Water!!</u> <u>Goggles/Gloves</u>!

250 grams copper sulfate (CuSO₄) Technical grade chemicals for this solution is fine. 42 cc sulfuric acid Distilled water to the 1000 ml level.

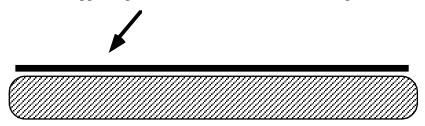
Put about 800cc water into plastic or glass container after marking the 1000cc level on it. Add the copper sulfate and stir to dissolve. Slowly pour a thin stream of acid into the swirling water. Heat is evolved-be aware of this. Rinse the acid container with distilled water and top up the mixture with it to the 1000 ml level. This solution can also be used as an electroforming solution for growing copper. Remember, acids are dangerous.

A dust mask is suggested around chemicals. Work cleanly. Copper salts are toxic and irritant and should be handled with care. Dispose of properly.

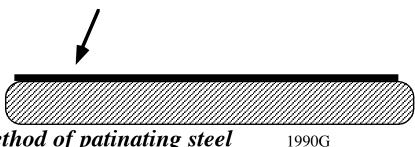
The metal surface is well cleaned. I often use Fantastic® and rinse well.



The copper is plated onto the brass substrate using medium steel wool.



The surface is then rinsed and fumed in a sealed environment using household ammonia fumes for a period of one hour or longer as required to convert some of the copper plating to blue-green copper hydroxide-a bluish wash-like patina.





As part of a large scale patination project in which I patinated a steel roof surface 24 by 48 feet on both sides I performed some 40 experiments to find out how to patinate the steel which was a requirement for structural reasons. In doing so I also experimented with paint, buying over \$350.00 worth of spray paint, eventually finding one single color which for all intents and purposes is green patina. When placed in recesses and the high areas are rubbed off it is indistinguishable from a cupric nitrate patina. It is a car paint: GM 42, 1980 Chevrolet Medium Green. While this is ideal for smaller surfaces my

paint experiments did not produce the surface effects I required on the large scale work. I reasoned that if I could plate the steel with copper and then convert the copper to patina in a fume not only would the job be easier but it would also be safer than dealing with solvents or corrosive patination techniques (such as a cupric nitrate patination) over large surface areas. I was dealing with $4 \ge 8$ foot sheet steel to be equally patinated on both sides simultaneously. Other types of objects might be easier to deal with. 'Tents' of polyethylene plastic sheeting stapled to a framework of 'economy' studs were built. The construction of such a tent requires that it be sealed (draped onto the floor from the frame and then weighted down). The object inside is positioned on supports of some kind so that it is suspended off the floor in the air inside the tent. Then pans of household ammonia are placed underneath the object. The fumes attack copper or copper based alloy surfaces. Under normal conditions one can activate a copper containing surface with a dilute salt solution to speed up the procedure and obtain a blue patination but this proved too corrosive for dealing with steel. The final procedure chosen was as follows:

- 1) The steel was cleaned well. Sandblasting would be ideal but was impractical for the project. Solvents were also out for safety reasons on such large surfaces without good ventilation. We ended up using Fantastic® cleaner. Two scrubbings with Fantastic® on large sponges and good rinsings in between and after were adequate most of the time. The surfaces were then left damp with the rinse water. Only the edges were handled to avoid contamination of the cleaned surfaces.
- 2) A contact plating solution for copper plating was prepared (see below) and this was applied to the steel using paint rollers (*goggles/gloves!*) Brushes work also but the paint roller is a bit more gentle. Plating occurs instantly. Several passes may be made over the same area, without pressing hard, which can remove the delicate plating. The surface was then rinsed very well. If areas of the plating lifted grease residues were the cause and a further local Fantastic® sponging and good rinsing sufficed to allow plating to take place. After final rinsing the steel (held by the edges) was taken to the tent. One moves fast to retain the surface moisture.
- 3) The steel was then placed in the tent and pans of ammonia enclosed under it. The tent was sealed. The centers of the thin sheet sagged causing pooling, therefore we built a wooden support with a single nail pointing upwards to support the sheet. More stable objects would not need support, though pooling may be factor to consider depending upon the surface relief. The time required to convert the copper plating was optimal at about 1-1 and a half hours.
- 4) The steel was removed and gently rinsed as scrubbing or hard spraying can remove the delicate patina surface. It will be a mixture of blues, greens and hints of brownish red where pooling has occurred and the surface dried. In my case I chose to reintroduce pink spatter marks to the surface by spattering droplets of the contact plating solution onto the patina surface where they instantly went pinkish-brown. The steel was then dried with fans and immediately sealed using clear automobile enamel paint. I then went back with stencils and gold spray paint to further modify the surface.

The steps in the procedure are then: *Clean, rinse, plate, rinse, fume, rinse, dry* and *seal*. *The conversion process*

The copper on the surface is attacked by ammonia liquid, not as much by the fume which has a different chemical composition than the liquid. The water dampened surface slowly takes in ammonia fumes where they are converted to ammonia liquid in solution so that they can attack the copper. The purpose of the pans of ammonia below the object is to provide a constant *vapor pressure* which replenishes the ammonia on

the surface at a constant rate as it is used up in converting the copper to patina. This system therefore ensures better overall constant dilution control than beginning with ammonia on the surface.

Control Factors:

- *Resists*: Resists may be used to prevent plating or to prevent the plating from being converted to patina by the fumes. Resists to plating may be a greasy material (lithocrayon, oil) or thinned rubber cement. Other resists require too much cleaning time and may need solvents for removal. Resists to patination may be a protective spray through stencils (Pam®) or thinned rubber cement. Pattern control through resists is easy.
- *Time*: Time is a factor in all fumings. Experiment with various times on sample pieces to have a palette of process marks (colors, tones, effects) to choose from.
- *Pooling*: Where pooling occurs variations in color will result. Pooling can be encouraged and controlled by local application of greases before or during patination and by the position and shape of the object. Various liquid thicknesses cause surface variations.
- Sealers: Sealers will each have a characteristic effect on the surface. I recommend making a palette of various sealing options over a patinated surface. Examples of sealers include waxes, oils, lacquers, transparent acrylics, enamels, varnishes and so on. They often have a tendency to darken the colors on the surface. I prefer clear auto enamel or *Spray-Lac number 1473 professional Finish Clear Dead Flat* lacquer. It is available from Star Chemical based in Hinsdale Illinois, Deerfield Beach, Florida and Dallas Texas. It is an industrial quality spray and requires good ventilation. It is very unobtrusive on a surface. With any spray the surface chosen can be glossy, like paint (in which case why not use paint?) or shortly after spraying can be matted down with a cloth pad for better surface control.
- *Other Chemicals*: I mentioned dilute salt solutions earlier. Many chemicals will modify surfaces. (Remember never to mix bleach and ammonia). Experimentation and sample making will offer the user control choices. Suggestions for initial investigations include salt, vinegar, baking soda and local heating. There are a number of patination books available including one I sell on patinas for small studios.

Contact Plating Solution Recipe

All safety warnings apply. <u>Always add Acid to Water!!</u> Goggles/Gloves!

250 grams copper sulfate (CuSO4) Technical grade chemicals for this solution is fine. 42 cc sulfuric acid

Distilled water to the 1000 ml level.

Put about 800cc water into plastic or glass container after marking the 1000cc level on it. Add the copper sulfate and stir to dissolve. *Slowly* pour a thin stream of acid into the swirling water. Heat is evolved-be aware of this. Rinse the acid container with distilled water and top up the mixture with it to the 1000 ml level. This solution can also be used as an electroforming solution for growing copper. Remember, acids are dangerous.

A dust mask is suggested around chemicals. Work cleanly. Copper salts are toxic and irritant and should be handled with care. Dispose of properly.

Black-C is a Korean patination solution for copper. It's composition was recently analyzed in Calgary by a Dr. Chiu as part of a research project by a student at the Alberta College of Art. The formula seemed surprisingly simple and is reported here, along with some background information.

In 1985 I was studying at SUNY New Paltz in New York State. There were some nine of us in the graduate program, three of whom were Korean. Professor Bob Ebendorf invited Professor Kang from Seoul, South Korea to visit the school and one of my colleagues, Chung Hoo Kim, who had been a student of his in Korea. During his visit Professor Kang gave a lecture about the making of a huge, intricate bronze bell for a temple and showed his work to us. Among his pieces were several that were made of copper and had silver inlaid into their surfaces. The surface finish however seemed unusual in that the silver showed the dead white we are used to seeing in repeatedly pickled sterling but the copper was a lustrous black as if liver of sulfur had been applied and brass brushed a number of times. When asked how one can oxidize copper black without affecting the silver he spoke of a Korean solution called either 'Black-C' or 'Ebony-C'. This mysterious solution when applied would leave the silver white and only affect the copper. He did not know what was in it and others I asked also could not tell me. I then began to ask the Korean goldsmiths I met to bring me some. Twice Koreans who were bringing me some (including Chung Hoo Kim) were stopped at the border and the Black-C was confiscated by customs.

In 1987 Professor Kang responded to a letter again requesting some Black-C by mailing me a liter of it labelled 'Chemical Medicine' which somehow avoiding exciting any suspicions among Canada Customs and so I received it unopened and unchecked by them. It did indeed seem to do what it was supposed to, in that it turned copper black and left the silver almost unaffected. I applied it by warming the work and painting it on, though I have since heard from Koreans that it may be applied by a boiling or simmering immersion. In practice I had little personal use for the mixture but wanted to have it analyzed as it was to my knowledge an unusual effect to have on these two metals.

As part of a 4th year class called Technical Research I have every student prepare a short (5-7 pages) technical paper on a subject of their choice. As part of this they have to take illustrative photographs, do descriptive drawings and write as if writing an article so that others (their fellow students) could duplicate the procedure they have chosen to investigate or describe. The papers are kept on hand to help future students deal with technical problems. I have then sent copies of the papers out to Lapidary Journal which has a readership of some 100,000 people. To this point in time they have chosen to publish almost all the papers I've sent to them which among other things is useful to the student's resumes and their self confidence. The 4th year class last year was having problems deciding upon subject matter and I suggested several ideas. One suggestion was to get Black-C analyzed, with the stipulation that the student who undertook the project, Annette Nelson, find a way to get the \$350.00 analysis done for free (practice for the real world). She called several University and Technical College Chemistry departments and a number of private companies, most of whom rejected her request fairly vehemently. Finally her persistence paid off and Doctor Chiu agreed to do the analysis providing that no private commercial advantage was to be gained and that the analysis be shared. He was also intrigued by the action of the chemical and wondered, as I did, what reaction occurred. His assistance in the project was greatly appreciated. Some time later he called me with the analysis results. They had tried a number of approaches assuming the stuff had a complex chemical structure but had eventually eliminated almost all the likely chemical candidates. Dr. Chiu noticed that the solution was caustic and slippery which is a sign of a strongly basic solution. The eventual result of the tests turned out to be very simple: Black -C is an 18% sodium hydroxide solution, nothing more.

Sodium hydroxide is available as lye at most supermarkets. It is an extremely strong base and *splash goggles*, *protective clothing* and *gloves* must be worn when handling it or solutions made from it. It should also be used with *appropriate ventilation*. To make the solution 18 grams of sodium hydroxide are dissolved in 100 cc of distilled water. The solution should be kept in a plastic container, correctly labelled and safely stored which includes always being aware that pressure can build in sealed bottles of chemicals and this may in some cases cause a splash upon opening. The solution may be painted on and the object is heated or may be immersed in the hot solution. It offers another color palette choice for the metalsmith working with surface design. It should be noted that this effect on copper has probably been recognized in Western metal finishing as a choice, but not perhaps in this combination with unaffected silver. And so we tried it. Well, Dr. Chiu forgot to test for chlorides (ie salt) and the solution as described above doesn't work unless you patiently and persistently apply it. I think it might work a little better with a dash of salt as well.... Haven't tried it yet personally.

Related finishes.

Some gun bluing solutions are lye based. A method using lye for removing spotty fire scale is reported by Doug Zaruba, (one I've not yet tried) which is to use a thick aluminum pot and simmer a lye solution in it. After a polishing operation that still leaves blotches of fire scale on the surface the object is suspended in the pot for some time and the residual fire scale is removed by the solution in the presence of the aluminum. The pot eventually dissolves, hence the suggestion for using a thick one. While this is not a surface finish as such it is evident that there is some effect on the copper oxide contained in the sterling alloy if in fact the solution removes the fire scale. Kieth Lewis, a goldsmith from Delaware reported and demonstrated an interesting finish with a similar effect to Black-C during a workshop with me in Pennsylvania. He used Nu-Gold® (a high copper content brass with about a 15% zinc content) as a base or 'host' metal and applied gold and silver to the surface in a fusion inlay technique. The metal was then finished and cleaned extremely well. Household ammonia was heated in a sealed container and the pre-warmed metal (for example dipping in hot water) was held in the ammonia vapors in the container. The Nu-gold® turned a lovely black, rather like niello in tone with the unaffected gold in the surface showing up brightly. This too would be a technique to use goggles and ventilation with.

<u>Black-C</u>

Sodium Hydroxide (lye), NaOH18 grams (and just maybe some salt)Distilled Water, H2OTo the 100 ml level

After placing the sodium hydroxide into a container with the 100 ml level marked on it the distilled water is added until it reaches the mark. The solution is mixed (swirling is good) and left. Store in a chemical cupboard.

<u>Remember</u>: *splash goggles*, *protective clothing* and *gloves* must be worn when handling lye or solutions made from it. Use with *appropriate ventilation*.

Some Tools to have around for playing with patinas.

This list gives some of the tools and equipment it is useful to have when experimenting with different basic patination techniques.

A small can of GM42 1980 Medium Green Chevrolet car paint-a patina substitute

A can of clear auto enamel to seal surfaces with. Nicholas lacquer is liked by jewelers. Cupric nitrate CuNO₃

Sulfuric Acid

Distilled water for the cupric nitrate solution

A graduated cylinder or measuring container.

Some solvent alcohol or methyl hydrate as a wetting agent for the cupric nitrate solution Dishwashing liquid, ditto and for cleaning surfaces.

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A bottle of household ammonia for fumed patinas

A small amount of table salt to accelerate fumed patinas

Plasticine, as a sulfur containing patterning paste.

Liver of sulfur (potassium sulfide) for darkening copper alloys and silver.

Rubber gloves

Rubber apron

Proper eye protection from chemicals

Fume hood or equivalent ventilation for the cupric nitrate solution. If none is on hand a good substitute can be made with sheet metal, a medium to large window fan, extension cord and an openable window.

A gold or silver ink pen.

Some large glass or plastic lidded jars or yoghurt or freezer containers for fuming.

Some coarse sawdust or wood shavings, enough to fill one of the above plastic containers for damp patterned fumed applications.

Tweezers.

Brass brush or pumice.

Used toothbrush.

Small plastic bristled cheap paint brush or welders flux brush.

Beaker or similar glass container.

Paper towel or rag.

Torch, fire brick, striker, to place by fume hood. A hot plate and metal plate to cover the burner surface may be used instead if preferred. This is safer when a fume hood is used.

Sink and running water.

Here's a web site or two with patina information

http://plains.uwyo.edu/~metal/patinas.html

http://gopher.tmn.com:70/1/Artswire/csa Michael McCann's Arts Safety and Hazards site (Center for Safety in the Arts).

http://ourworld.compuserve.com/homepages/brnzcaster/ Bronze casting and metalsmithing site: lots of very good information. Also a really strong metal oriented links page and lots of book sources.

http://www.finishing.com/ The metal finishing folks home page, lots of links concerning metal finishing

There is an article of mine on cupric nitrate patinas on the tips page at:

http://www.ganoksin.com/borisat/tree.cgi

under the 'surfaces' heading. Also the Artmetal site and the Metal web news have some patina info, as well as others:

http://wuarchive.wustl.edu/edu/arts/metal/ArtMetal.html The ArtMetal Project-a must visit for metals people.

http://www.mindspring.com/~wgray1/ The Metal Web News, an essential visit for metals folks. Check the metal oriented links.

http://www.finishing.com/ The metal finishing folks home page, lots of links concerning metal finishing

The Artmetal Site http://plains.uwyo.edu/~metal/patinas.html Artmetal archive, Cleaning metals and patination information

Here are some other books that deal with patinas:

La Niece, Susan, and Paul Craddock, eds. Metal Plating and Patination: Cultural, Technical and Historical Developments. Oxford:: Butterworth-Heinemann, 1993.Patination/Colouring

Deutsches Kupfer-Institut. Chemische Färbungen von Kupfer und Kupferlegierungen. 4. Auflage. Berlin: Deutsches Kupfer-Institut, 1974.

Hebing, Cornelius. Vergolden und Bronzieren: Untergrund - Arbeitstechniken -Werkstoffe: Ein Handbuch für die Praxis. 14. Auflage. München: Verlag Georg D.W. Callwey, 1985.

Hughes, Richard, and Michael Rowe. The Colouring, Bronzing and Patination of Metals: A Manual for the Fine Metalworker and Sculptor. London: Crafts Council, 1982.

Kramer, Oskar P. Rezepte für die Metallfärbung und Metallüberzügeohne Stromquelle. 5th ed. Saulgau/Wttbg: Eugen G. Leuze Verlag, 1977.

Walker, John R. Modern Metal-Working: Materials, Tools and Procedures. South Holland, IL: Goodheart-Willcox, 1973.

I recommend highly 'Contemporary Patination' by Ron Young. He sells metal dyes as well.

Ronald Young, Sculpt-Nouveau, 21 Redwood Drive, San Rafael, California, 94901, USA

Charles Lewton-Brain

Charles Lewton-Brain studied and worked in Europe and North America. He lectures and publishes in a number of countries on his research into rapid methods of manipulating metal and it's surface for artistic and manufacturing reasons. He thinks of himself as an artist who works primarily in the context of body ornament and creates performance art pieces dealing with the body. Jewellery/Metals program head, he has taught at the Alberta College of Art and Design since 1986 as well as writing, exhibiting and working in his studio. He is known internationally for inventing Fold-Forming, an original system of working sheet metal using simple tools that is a new way of working metal. He and his partner Dee Fontans opened The Lewton-Brain/Fontans Centre for Jewellery Studies in 1991 in Calgary where they teach jewellery making, exhibit innovative work from elsewhere in Canada and offer information on contemporary art jewellery. In 1994 he founded Brain Press to publish 'Cheap Thrills in the Tool Shop', a book of inexpensive tool options and bench tricks for goldsmiths. Other books include 'Small Scale Photography' and 'Hinges and Hinge-Based Catches for Jewellers and Goldsmiths'.

His collaborative site with Dr. Hanuman Aspler, Ganoksin.com, is currently the largest site in the world on the net for jewelry education.

http://brainpress.com/

Brain Press Publications

This list describes monographs for sale which detail the results of my research in various directions. As titles at the \$15.50 retail price range are revised and updated their prices are subject to change. Binding is on the primitive side: acetate covers and plastic slides. Shipping is extra. Current titles:

Forming using Metal Characteristics: Fold Forming Fold forming is a system of sheet metal forming which emphasizes forming using the metal's characteristics. Forms are derived from the natural plasticity, ductility and elasticity of the metal. The system is internationally recognized as a new approach to working metal. It is extremely efficient and rapid. Tools are simple: fingers, hands, hammers, mallets, anvil and rolling mills. The paper has a theoretical introduction and step - by - step recipes for quickly working sheet metal. 45 pages, over 70 B/W line drawings. 1985/90© \$15.50

Fold Forming Video This half - hour video serves to introduce fold - forming as a system. Made in 1986, it covers the basic folds of the system and includes a set of notes on developments since 1985. \$23.50

Patinas for Small Studios This paper describes safer, easy patination methods for metals that involve easily obtainable and kitchen chemicals to produce blues, greens, browns, blacks, grays and reddish tones on metals. Application methods and options for pattern and surface control are described. 34 pages, 5 color pictures, 1985© \$15.50

Gold Surface Applications: A Technology Review. The results of a research project for the Society of North American Goldsmiths. It describes fusion applications (gold painting), doublée, Keum - boo, depletion gilding (tumbaga, guanin), inlay and overlay procedures and has a discussion of fire gilding. Control factors for free compositional choice are defined and demonstrated. 27 pages. B/W diagrams, one color picture. 1985© \$15.50

Depletion Gilding: a historical and technical introduction. It describes the approaches that goldsmiths have used historically in various cultures to remove base metals from gold alloys for refining or "coloring the gold": depletion gilding. There is an extensive listing of recipes from many historical and contemporary sources designed to foster contrast and comparison to deepen understanding of the subject. This paper is intended for information only and is not a "how to" for depletion gilding. 20 pages. 1990© \$15.50

Shareware Book: This wide ranging, truly eclectic book is chock full of sources, suppliers, technical information, patinas, stonesetting, bench tools and thoughts on metalsmithing. About 175 pages and lots of diagrams. This is also used as a handout for Brain Press workshops. \$24.95

Cheap Thrills in the Toolshop This is a loose, eclectic collection of short cuts, bench tricks and alternative equipment options for goldsmiths. Cheap tool making, tool conversions and unexpected sources for tools are all described. Sections include shop machines, tools, setting tools, soldering and more. Lots of drawings, lists and reviews of sources round out the book. A good index and table of contents make finding information easy. 80 pages crammed full of information. 82 line drawings. 1996© \$24.95

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