How to Make Verdigris Pigment

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What is Verdigris?

Verdigris is the greenish blue patina most often found on copper structures. It is created by the oxidation "rusting" of copper which creates Aerugo rasilis (copper acetate). Verdigris is also created by a deliberate corrosion of copper with heat using organic materials, such as the lees of wine (residual yeast from the fermentation process), stale vinegar, curdled milk, urine, salt, and honey. Lead paint turns verdigris brown overtime. Salt can change the color of the verdigris by changing copper carbonate (Cu2CO3(OH) to copper chloride (Cu2(OH)3Cl).

Brief History of Verdigris:

Verdigris has been used as a pigment for centuries; recipes to make verdigris can be found dating back to the Ancient Greeks. Verdigris crystals have been found in both paint and wax seals on documents. I've included a few examples of famous paintings such as: The Last Supper (1306) by Giotto, the Mond Crucifixion by Raphael (1502), and some photos of verdigris in wax seals. (See color photos on page 2)

Verdigris was also used as medicine; however, while copper is an essential element for health, the patina is toxic. Its use for both a pigment and medicine was phased out by the 19th century due to its toxicity. Do not to eat or drink out of rusty copper cookware. Be sure to use gloves and other protective gear when handling and grinding the pigment. **Do not lick the science!**

Disclaimer: This class is about making the pigment itself and not how to make period paint. I don't work with period paints, but I do make period wax which includes verdigris pigment for wax seals. This is about making your own pigment so you don't have to buy it or to be able to control the shade of blue/green you produce.

Experimental Archaeology

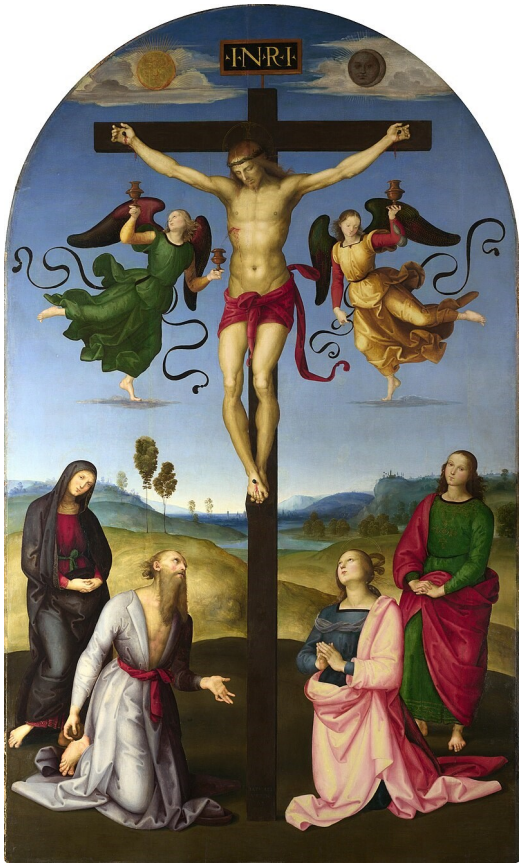
For a Tournament of Arts event, I did an experiment with 4 different types of vinegar. One batch of just vinegar, one with salt, and one with honey - 12 jars in total.

Things I learned from my experiments with different types of vinegar with salt, and honey:

- Most recipes called for copper sheets, but I used tubing. The copper tubes produce a lower yield/less surface area, but they are cheaper than sheets.
- Make sure your sheets are 100% copper or impurities may ruin the color.
- Filtered apple cider vinegar 5% acidity produced the most consistent amount of verdigris.
- Adding salt without heat only slightly altered the color of the pigment.
- Adding honey without heat did not yield significant amounts of verdigris and made the tubes tacky and difficult to scrape off pigment.
- You can use vinegar to clean your copper tubes before submerging them.
- Vinegar will also strip the patina off the tubes if submerged after it starts to patina.
- The "mother" in unfiltered apple cider vinegar can alter the color of the verdigris.
- Heating the vinegar or placing the jar in a heated place may change the color of the verdigris.
- Make sure your area is well ventilated when heating vinegar. It stinks.
- 30% acidity vinegar (commonly used as weed killer) does not patina well. Stick with the 5% stuff.
- Make sure you explain that you are making verdigris before you ask someone for their kid's urine. Awkward!

If you would like to see my experiments in full color, I can send you a pdf via email.
Please sign up on my list.

Botticelli's *The Mystical Nativity*, 1500

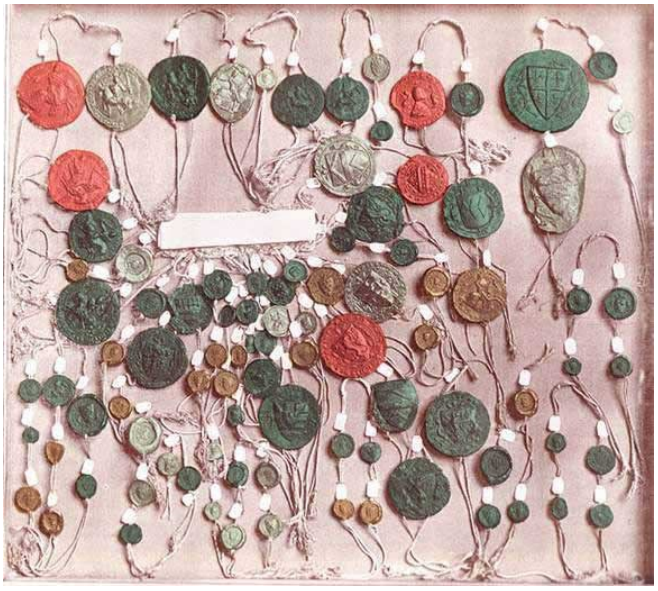


Mond Crucifixion by Raphael, 1502—1503

The Last Supper by Giotto, 1306

Why we don't leave scrolls in hot cars!
http://www.dellacivetta.org/lorenzo/tag/sealing_wax/

https://media.nationalarchives.gov.uk/index.php/materiality-matters-new-approaches-medieval-wax-seal-studies/



Seals detached from Barons' Letter Copy A, 1301 (catalogue reference: E/26 2)

Making Verdigris ~ No Heat Version

Most medieval verdigris recipes do not specify what type of vinegar was used, so experiment with whatever you have in your kitchen. If you want to get fancy, you can make your own vinegar using medieval techniques and ingredients. Today, we are using modern store bought filtered apple cider vinegar as it yielded the most verdigris in my science experiments. We are not heating the vinegar in class, but you may do so at home.

Ingredients Used in Class

- **Meijer filtered apple cider vinegar 5% acidity**
- **Ace Hardware 3/4 inch copper pipe**
- **Embroidery floss**
- **Ball smooth half pint jar**

Day 1

Step 1: Fill jar with enough vinegar to cover the tube

Step 2: Cut copper tubes into 2 inch lengths

Step 3: Wipe tube with vinegar to clean off any impurities, and pull a long piece of thread/twine/floss through the tube

Step 4: Place clean tube in the jar - keep the excess string outside of the jar. The tube should be submerged in the vinegar

Step 5: Replace the lid tightly keeping the excess string outside the jar - store in the dark at room temp (aprox 67-69 degrees)

Day 2

Step 6: After 24 hours, open the lid - keep strings on the outside

Step 7: Pull the strings tight across the lid opening - secure the strings either by holding them in one hand or taping the strings to the sides of the jar

Step 8: Carefully replace the lid - you want to have the tube suspended over the vinegar without touching the vinegar, the lid, or the sides of the glass
Store in the dark at room temp (aprox 67-69 degrees)

Day 27

Step 1: Open lid and remove the tube from the jar. Do not let the tube slip and touch the vinegar.

Step 2: Hang tubes for 24 hours to dry completely.

Day 28

Step 3: After 24 hours - remove string from tubes

Step 4: With a knife/razor, scrape off crystals into a mortar

Step 5: Use a pestle to grind the verdigris into a fine powder

Step 6: Bottle powdered verdigris for future use as paint or pigment for seal wax.

Making Verdigris ~ Medieval Period Recipes

ON THE CHARACTER OF A GREEN CALLED VERDIGRIS.
CHAPTER LVI

A color known as verdigris is green. It is very green by itself. And it is manufactured by alchemy, from copper and vinegar. This color is good on panel, tempered with size. Take care never to get it near any white lead, for they are mortal enemies in every respect. Work it up with vinegar, which it retains in accordance with its nature. And if you wish to make a most perfect green for grass . . .,[1] it is beautiful to the eye, but it does not last. And it is especially good on paper or parchment, tempered with yolk of egg.

Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte'*, trans. by Daniel Thompson (New York: Dover, 1960).

RECIPE 21 VERDIGRIS "PIGMENT" FROM THE RICITTE PER FAR OGNI SORTE DI COLORI

"In this recipe from the Ricitte perfar ogni sorte di colori (University of Padua, MS 992, recipe 17), both sides of a piece of copper foil were covered with honey, after which the copper foil was attached to the inside of the lid of a glass jar filled with hot balsamic vinegar. The heat from the vinegar caused a lot of condensation to collect at the top of the jar and on the foil, and this may have dissolved much of the honey. The jar was left in an oven at 40 °C for 1 month. At the end of this time, the surface of the copper was tarnished in some areas and had developed a green patination in others. There was no bulk corrosion. The experiment was repeated as above but without heating the vinegar. This second piece of copper ended up covered lightly with a blue green corrosion of varying texture. A sample from the second experiment was identified as a mixture of two types of copper acetate. This method, however, appeared more likely to create a patina than to be a useful means of producing verdigris pigment."

Scott, David, A., Copper and Bronze in Art: Corrosion, Colorants, Conservation, (Los Angeles: Getty Publications, 2002) Index
Original Source: Ricitte perfar ogni sorte di colori (University of Padua, MS 992, recipe 17)

"In his famous work, De materia medica, the first-century Greek physician and pharmacologist Dioscorides records one of the earliest accounts of the preparation of aerugo rasilis (copper acetate) using vinegar and a brazen (copper) vessel from which the product is scraped off and put to use, most likely as a medicinal preparation:

> But Aerugo rasilis is thus prepared. Pouring it into an hogshead, or some such vessel, ye sharpest vinegar, turn upon it a brazen vessel : it is good ifye hollow look downward, if not, let it be plane. But let it be made clean and having no breathing space. Then after ten days take off ye cover and scrape off ye Aerugo that is come on it ; or having made a plate of ye brass itself, hang it in the vessel, so as not to touch ye vinegar, and after ye like number of days, scrape it off."

Scott, David, A., Copper and Bronze in Art: Corrosion, Colorants, Conservation, (Los Angeles: Getty Publications, 2002) pg 279
Original source: Dioscorides, De materia medica, translated by Lily Y. Beck (Hildesheim: Olms, 2017)

Making Verdigris ~ Medieval Period Recipes

"How to make the green from brass which is called Greek or common green
If you wish to make the copper-green which is called Greek, take a new jar, or any other concave vase, and put it into the strongest or most acid vinegar, so as not to fill it and put strips of very clean copper or brass over the vinegar, so as that they may not touch the vinegar or each other, being suspended to a stick placed across the vase. Then cover the vase and seal it, and put it into a warm place, or dung, or underground, and leave it so for six months, and then open the vase and shake out what you find in it, and on the strips of metal, into a clean vase, and put it in the sun to dry."

Merrifield, Mary P., *Original Treatises Dating from the XIIth to XVIIIth Centuries on the Arts of Painting*, 2 vols (London: John Murray, 1849), vol. 1, pg. 124.

95. *To make good green.*—Take honey and strong vinegar of each as much as you like, and incorporate them very well together; then put the mixture into a well-luted copper vase, place the jar a foot deep in every direction in warm dung, in a place where the sun shines strongly, and let it remain so for a fortnight; then take it out, and you will find all the matter converted into fine verdigris of a perfect kind.

Merrifield, Mary P. *Original Treatises, Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introduction; with Translations, Prefaces, and Notes*. 2 vols. London: J. Murray, 1849.

"106. The recipe for verdigris
Take very clean copper leaf and hang it over very sharp vinegar. Leave it undisturbed in the sun for 14 days. Open it up, take away the leaf and collect the efflorescence; and you will make the cleanest verdigris."

Smith, Cyril Stanley, and John G. Hawthorne. Mappae Clavicula: a Little Key to the World of Medieval Techniques, Transactions of the American Philosophical Society. Philadelphia: American Philosophical Society, 1974. *p. 42.*

Making Verdigris ~ Medieval Period Recipes

"If you want to make verdigris, take a new pot, and put sheets of the purest copper into it; and so fill that pot with very strong' vinegar; and cover it thus, and seal it. And place that pot in some warm place, or in the ground, and put it away thus for six months; and then open that pot, and put what you find in it on to a wooden panel, and set it in the sun to dry."

Thompson, Daniel Varney, George Heard Hamilton. An Anonymous Fourteenth-Century Treatise: De Arte Illuminandi, the Technique of Manuscript Illumination; Translated from the Latin of Naples Ms. Xii. E. 27. New Haven, London: Yale University Press; H. Milford, Oxford University Press, 1933. *Endnote 26, p. 29.*

"157. *Also, How to make verdigris for writing.*- Whoever wishes to make a green colour for writing, let him pour into a copper or brass vessel equal quantities by weight of honey well mixed with vinegar, and then bury the vessel in horse-dung, in the hottest part of the heap. After 12 days are passed, he may take the colour out of the vase, scraping it out ; then dry it in the sun, and keep it for use."

Merrifield, Mary P. *Original Treatises, Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introduction; with Translations, Prefaces, and Notes. 2 vols.* London: J. Murray, 1849. *"Manuscripts of Jehan Le Bègue",* p. 126.

15 century recipe for green ink:

"To make verdigris green. Take one pound of copper filings or scraps and wash it a little through a linen bag. Take ground egg yolks, quicklime, tartar sediment, common salt, strong vinegar, and boys' urine, and mix everything in the vinegar and urine and put half of it in a copper vessel and stir four times a day, then put it over heat or in the sun to dry."

Raymond Clemens, Timothy Graham . "Introduction to Manuscript Studies" Cornell University Press, 2007. p 27

https://distillatio.wordpress.com/2015/09/26/making-blue-and-green-ink/

Making Verdigris ~ Bibliography

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Raymond Clemens, Timothy Graham . "Introduction to Manuscript Studies" Cornell University Press, 2007. p 27.

Ricitte perfar ogni sorte di colori (University of Padua, MS 992, recipe 17)

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Thompson, Daniel Varney, George Heard Hamilton. *An Anonymous Fourteenth-Century Treatise: De Arte Illuminandi, the Technique of Manuscript Illumination; Translated from the Latin of Naples Ms. Xii. E. 27*. New Haven, London: Yale University Press; H. Milford, Oxford University Press, 1933.