Vinegaroon – Never Dye Leather Again!

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Class description: Long before Fiebings or Eco-Flo leather dyes, people made deep black leather using this ancient mixture of iron scrap and vinegar. It works instantly, never rubs off, and never fades! Come see how it works, try it for yourself, and learn to make your own! Class will consist of a short talk about the historical plausibility of this method, a discussion of the chemical properties that make it work, a demonstration, and hands-on make-and-take of a simple key fob.

Tanning

The purpose of tanning a skin is to prevent decomposition, while stabilizing the structure of the skin to preserve the natural properties of the skin: soft, flexible, semi-permeable, and tough.

Humans have used vegetable tannins to tan leather since the beginnings of recorded history. For example, an 800 BC Sumerian account gave instructions for dressing a fresh ox hide:

"*This skin, you will take it, Then you will drench it in pure pulverized Nisaba flour, in water, beer and first quality wine, With the best fat of pure ox, the alum of the land of the Hittites, and oak galls, you will press it and you will cover the bronze kettle-drum with it.*" (Reed, 1975, p. 25)

Early tanners seem to have used simple alcohol baths to tan hides. The bath generally contained warm liquid solutions of vegetable matter consisting of stalks, leaves, twigs, nuts and fruit of soft green plants and/or wood, bark and galls of shrubs and trees. (Reed, 1975, p. 26)

This early process of tanning involves using vegetable tannins to bind to the collagens of the skin. It involves the insolubilization of protein by the formation of chemical bonds between the two polypeptide chains and an accessory molecule, usually an aromatic polyphenol. (Pearson, 2014, p. 48)

The term tannin (from *tanne*, an Old High German word for oak or fir tree[1], as in Tannenbaum; or from Latin *tannare*[2], meaning tan, dye a tawny color; or from Latin *tannum*[3], meaning crushed oak bark; or from Celtic/Breton *tann*[4], meaning oak tree) refers to the use of wood tannins from oak in tanning animal hides into leather; hence the words "tan" and "tanning" for the treatment of leather. However, the term "tannin" by extension is widely applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong complexes with proteins and other macromolecules.(Lancashire, 2013)

[1] Noun: tanne: 1: fir. https://en.wiktionary.org/wiki/Tanne. Retrieved 5/4/2017
[2] To tan leather. http://www.latin-dictionary.org/tannare. Retrieved 5/4/2017
[3] Oakbark for tanning. http://www.latin-dictionary.org/tannum. Retrieved 5/4/2017
[4] Noun: tann: 1: oak gall. https://en.wiktionary.org/wiki/tann#Breton. Retrieved 5/4/2017

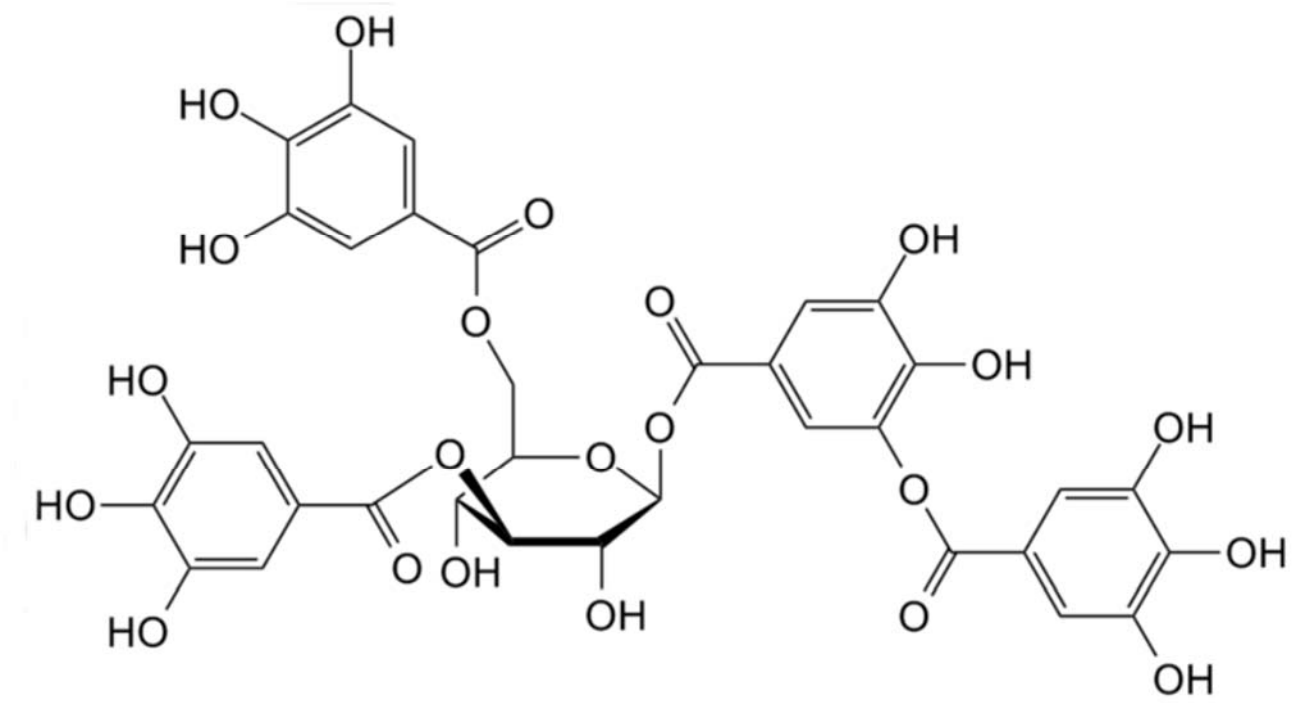

Fig. 1: The chemical structure of a (gallo)tannic acid, from oak galls (Lancashire, 2013)

There are also various methods of chemical tanning (chromium, alum, etc.), but they are not usually found in our period of study. Additionally, I don't know anything about brain tanning so please don't ask.

It is important to note that vinegaroon will only work on vegetable tanned leathers. It is vitally important that you use high-quality vegetable tanned leather. These days, there are chemical processes that can produce leather with properties nearly indistinguishable from vegetable tanning. Every piece of economy-grade "vegetable tanned" leather you buy from Tandy Leather Factory will be of this grade, as is almost every hide labeled "import" quality from other vendors.

These hides are tanned in India and Mexico, using very, very little actual vegetable matter. This tanning produces hides that superficially look like vegetable tanned leather, but in practice, they exhibit poor dye retention, poor tooling properties, poor plasticity for wet molding and water forming, poor consistency for carving, and poor leather finish, exhibiting numerous marks and scarring from insect bites, branding, and so forth.

While they are generally acceptable for the majority of hobbyist leather workers, and are sold at an excellent price point, if you wish to create a high-quality item, use vinegaroon, or both, you will need to purchase more expensive leathers. I recommend Hermann Oak leathers, made in Missouri, or Wickett & Craig leathers, made in Pennsylvania.

Vinegaroon

"Vinegaroon" is the name currently used by many leatherworkers to describe a process whereby vegetable

tanned leathers are turned black by a chemical reaction between iron steeped in vinegar, and leather. It is particularly prized by gun holster makers, as it will not ever leave dye residue on clothing. Woodworkers also use this process, known to them as “ebonizing”, to stain hardwood carpentry objects, and this process is readily visible in rural areas where board-and-batten construction is still common for sheds and small barns – you can see dark streaks extending downward on their walls from the construction nails, where rainwater pulls ferrous material from the exposed nail heads and runs down the walls, causing ebonization of the wood below the nails over many years.

The chemical reaction behind this happens in several parts: (Korycinski, 2017)

1. The vegetable tanning process binds carbon atoms to the collagens in the tanned skin.
2. The creation of the vinegaroon solution is a reaction between iron and acetic acid (vinegar is about 5% acetic acid to make ferric acetate.
3. Ferric acetate, when mixed with acetic acid (vinegar is about 5% acetic acid) has an effect of blackening some organics.
4. The acetic acid in the vinegar breaks down some of the carbon chains in the leather, which were created during the vegetable tanning process.
5. The ferric acetate replaces the carbon atoms the acetic acid is breaking down, and causes the indelible black color.

Vinegaroon is prepared by taking a gallon jug of vinegar (I have always used white vinegar, but any kind or quality of vinegar *should* work), pouring out a cup or so of it (to make room in the jug), and adding any kind of iron or steel scrap. It is important that you do not use galvanized steel, as the galvanization process coats the iron in zinc, and prevents the vinegar from coming in contact with the iron. Likewise, any type of chromed steel will also not work. Stainless steel will work, but not as well, due to the high nickel content. You want to use ferric material as pure as you can get. Old nails, scrap from cutting knife blanks, swarf (sharp chips and spirals from drilling metal), untreated steel wool (this works particularly well, as the large surface area puts a lot of the steel in contact with the vinegar and creates ferric acetate faster), used razor and utility knife blades, and scraps from making period hinges are all things I have used to successfully make vinegaroon.

Once you have added as much iron material as you can to your bottle of vinegar, put the cap back on, and POKE A HOLE IN THE CAP! The chemical reactions in the jug will produce some hydrogen gas[5], which if not vented will blow the cap off your jug and spray your vinegaroon mixture everywhere. If you’re like me, and were storing your mixture in your leather shop, where you store all your leather, this can be particularly troublesome. (If you ever catch me at a camping event, ask me how I know this – preferably after I’ve had a few drinks.) Also, hydrogen gas is highly flammable. While the creation of a gallon of vinegaroon doesn’t produce a dangerous amount of hydrogen at one time, care should be taken not to leave your steeping jug near an open flame[6].

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[5] The chemical reaction of the acetic acid dissolving the steel wool is:

$$Fe + H + OAc^{+} \longrightarrow Fe^{2} + OAc_{-2} + H_2$$

[6] I’m not sure how this could happen, but I can imagine a nightmare scenario where someone leaves a jug of vinegaroon to steep in their basement shop next to their gas water heater with a pilot light, and forgets to poke a hole in the top, and the jug explodes and the hydrogen gas ignites and their house burns down and sets alight the surrounding city and then aliens see that and decide that humanity is a threat to the universe and so they reroute an enormous comet to impact the Earth and that’s the end of life as we know it. Or something. It is possible my imagination is overactive – but please don’t somehow manage to burn something up while making your vinegaroon.

Let this jug sit for at least a month, then test it. Pour a small amount – perhaps a quarter cup – into a shallow dish and stick in a scrap of vegetable tanned leather. The leather should turn almost immediately black. If it does not turn completely black, then you have one (or both!) of the following two problems:

1. Your vinegaroon hasn't steeped long enough. Pour it back in the jug, put the cap back on, and leave it alone for another month, then try again.
2. Your leather is of poor quality.

If it works, you can begin coloring leather with it immediately. You can either brush it on, or pour it into a bowl and immerse the leather. Immersion is best, as it completely colors the leather, front and black. The longer you immerse the leather, the deeper the penetration of the black color will be.

The next, and VERY IMPORTANT step, after coloring all your leather, is to neutralize the acetic acid in the leather from the vinegar. **If you do not do this, it will corrode any metal hardware it comes in contact with.**

Neutralizing the acetic acid is very simple: get a bowl of warm water, and stir baking soda into it until the powder stops dissolving. Now immerse your leather into this solution, for the same amount of time you immersed it in the vinegaroon. Baking soda is sodium bicarbonate, and with water creates a weak alkaline solution, which will neutralize the acetic acid in a safe manner.

Once you have neutralized the acetic acid, if your leather needs to be water formed or wet molded, do it now. It's already soaked through from the immersions, so this is a perfect time. If you do not need to do any forming or shaping, be sure to dry your leather flat, or it will take whatever form it dries in. Either way, you'll need to let it dry thoroughly before use.

The final step is to oil your leather. The immersion in acetic acid, followed by immersion in sodium bicarbonate solution, will leach much of the natural oils out of the leather, causing it to become dry and brittle. A thorough oiling with neatsfoot oil, mink oil, Olbenauf's Leather Preservative, Montana Pitch Blend, Leather Honey, or a combination of these (or any other leather preservative) is needed to restore the suppleness of the leather.

Historical Plausibility of Vinegaroon

I have no hard evidence of the use of vinegaroon in period yet. There are a number of problems with proving its use:

1. The colloquial name itself: "vinegaroon". This is clearly a modern reference to the nocturnal carnivorous whip scorpions of the Thelyphonida order of arachnids, many of which are both solid black, and discharge an offensive liquid when threatened which contains acetic acid. They are found in tropical and subtropical areas worldwide – and notably not present in Europe[7]. This modern name makes it difficult to search for in period manuscripts, and there were undoubtedly many colloquial and regional terms and names for this process in antiquity.
2. A number of additional chemical reactions take place in buried or submerged leathers, all of which may alter or obfuscate the chemical reactions that happen during the vinegaroon chemical reaction.

[7] http://arachnology.org/arachnology/orders/thelyphonida.html, retrieved 4/17/2017

3. Very little chemical analysis of extant leathers is done. Admittedly, I have not delved into this research too deeply yet, but my first few hours of searching have yielded no results.

Fig. 2: A vinegaroon whip scorpion

However, there are a number of reasons to believe this process to color leather was not only known, but widespread:

1. Readily accessible materials. Iron has been available since approximately the 11th century BC in Europe[8]. Vinegar is mentioned in the book of Bamidbar in the Torah[9], part of the Pentateuch (what modern Christians would call the book of Numbers, the 4th book of the Old Testament), which Orthodox Judaism says dates to 1312 BC[10].
2. Vegetable tanned leather was common.

Once you have those two pieces in place, all it would take for someone to figure out that iron turns leather black would be for that person to leave an iron tool laying on a piece of wet leather for a few minutes. Just a little experimentation would lead them to vinegar as an accelerant.

However, we also have additional evidence for the widespread use of black leather from period illustrations and art. For example, the very first panels of the Bayeux Tapestry show two horses with black tack.

Fig. 3: Excerpt of the Bayeux Tapestry. Red circles show black horse tack.

[8] "Iron working was introduced to Greece in the late 11th century BCE, from which it spread quickly throughout Europe."

[9] Bamdibar/Numbers 6:3: "He shall abstain from new wine and aged wine; he shall not drink [even] vinegar made from new wine or aged wine, nor shall he drink anything in which grapes have been steeped, and he shall eat neither fresh grapes nor dried ones." (Chabad.org)

[10] "Rabbinic writings indicate that the Oral Torah was given to Moses at Mount Sinai, which, according to the tradition of Orthodox Judaism, occurred in 1312 BC. The Orthodox rabbinic tradition holds that the Written Torah was recorded during the following forty years…" (Wikipedia)

Continuing on through the tapestry, there are numerous similar examples.

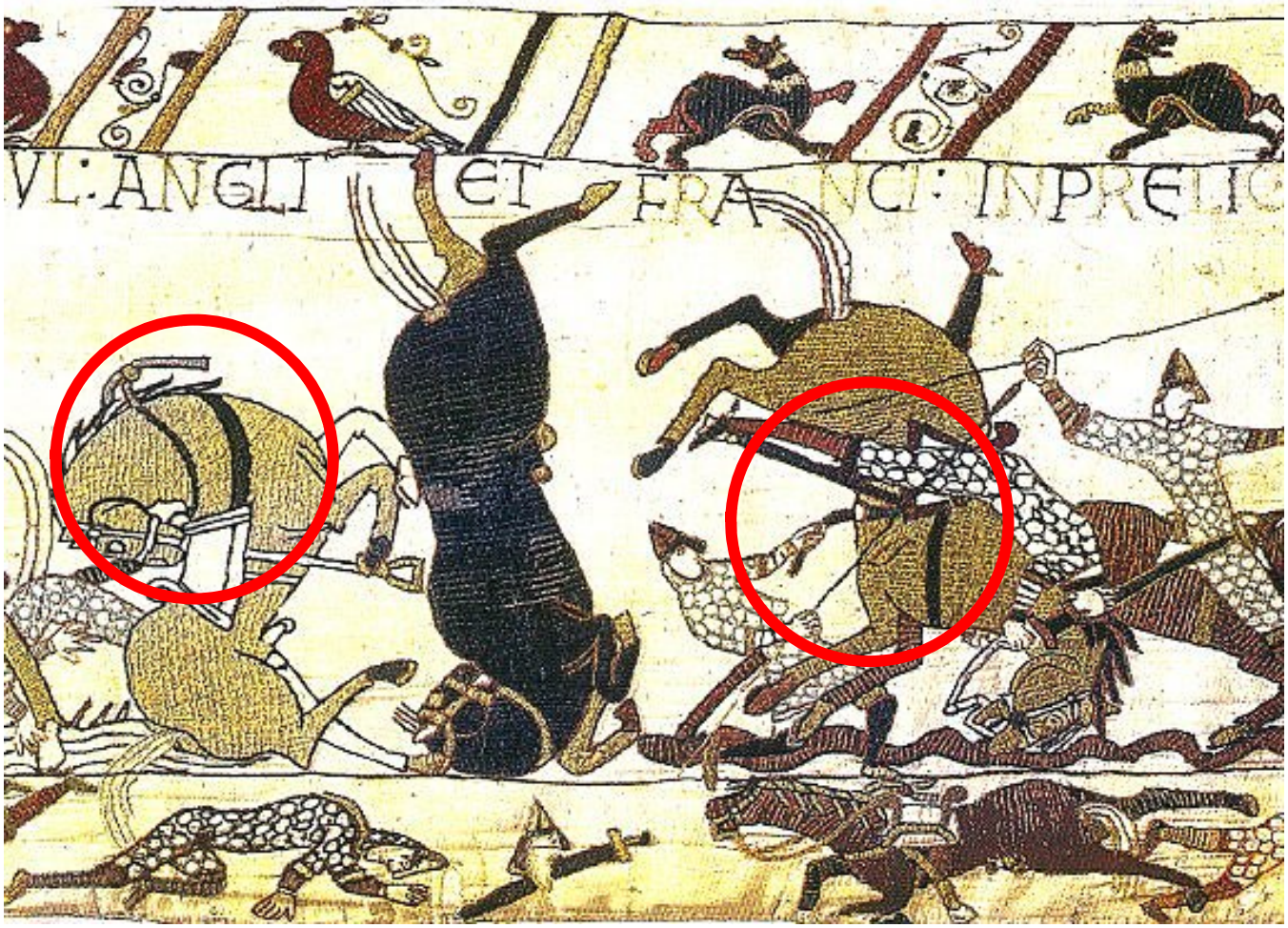

Fig. 4: Another excerpt of the Bayeux Tapestry. Red circles show black horse tack.

And careful examination of high-resolution photographs of the complete tapestry shows sword scabbards and belts of black as well, albeit in fewer quantity than black horse tack is shown.

Another example, from a continental European Book of Hours in the L. Tom Perry Special Collections section of Brigham Young University, thought to be from 1450-1480, clearly shows a black sword scabbard in an illustration of Judas Iscariot giving Jesus a kiss during his betrayal.

Fig. 5: Black sword scabbard from a 15th Century illumination.

Earlier examples are also easily found, for example, Figure 6, a picture from the Vespasian Psalter, from 8th century Kent, England, in which everyone is wearing black shoes.

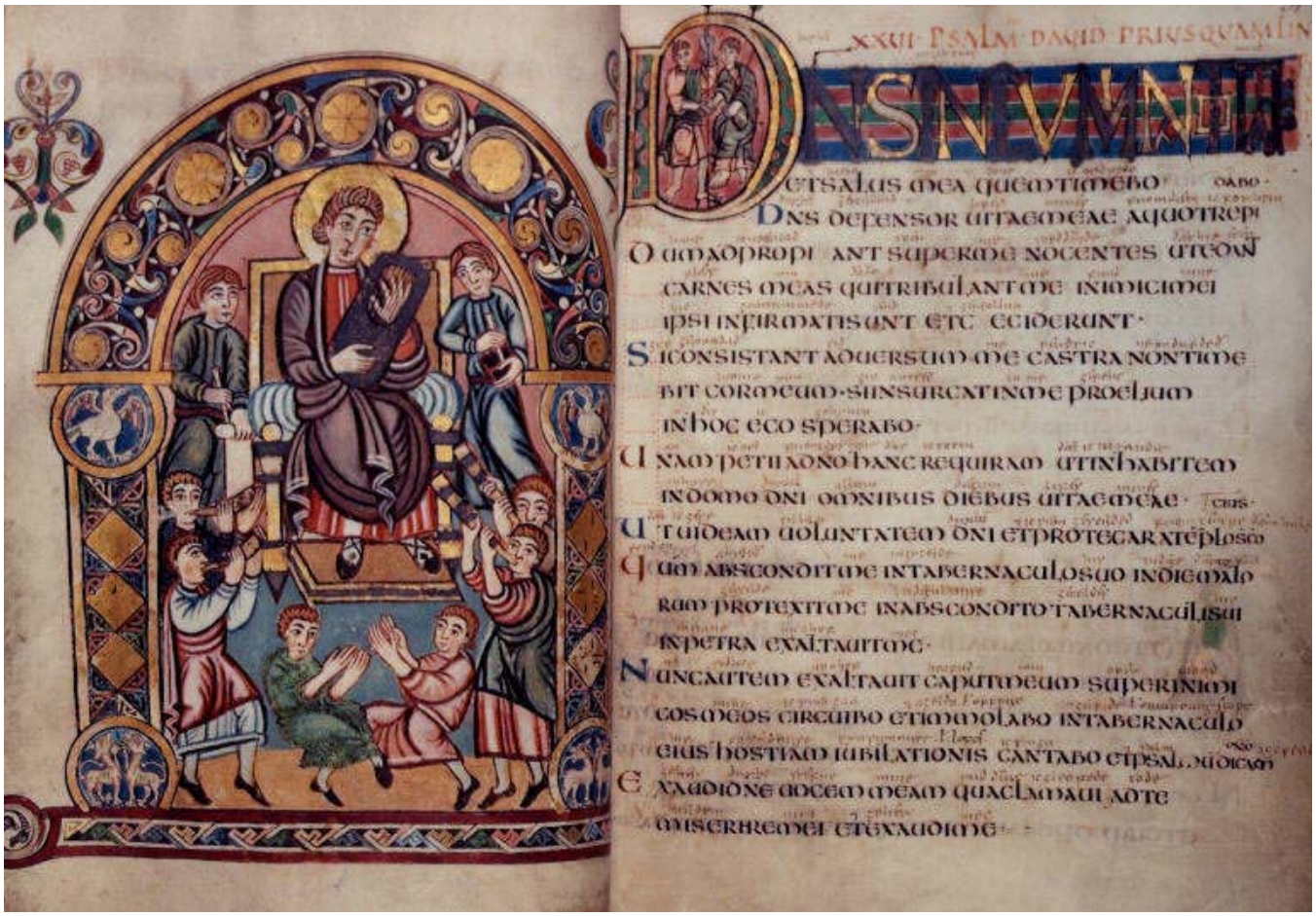

Fig. 6: Illumination from 8th Century England, showing black shoes.

I was able to find these examples with very little research; an extensive search is beyond the scope of this paper, however these few examples, spread over hundreds of years and several countries, I feel are sufficient to prove my point that widespread use of black leather is not just plausible, but demonstrable.

Chabad.org. Bamdibar – Numbers – Chapter 6.
http://www.chabad.org/library/bible_cdo/aid/9934/jewish/Chapter-6.htm. Retrieved 4/28/2017

Korycinski, Craig. Conversation on April 27, 2017. Mr. Korycinski is a personal friend who is a Bachelor of Science in Analytical Chemistry from Utica College and a Bachelor of Science in Computer Information Systems from the State University of New York Polytechnic Institute. He worked for two decades in the electroless metal plating industry.

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