Iron Acetate Solution Prepared from Steel Wool and Vinegar for Ebonizing Wood

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Research Article

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Abstract

Woodworkers darken wood by reacting iron in solution with tannins in the wood to form blue-black phenolate complexes, a process called ebonizing. According to the literature, the darkness and color are controlled by the tannin concentration (higher, darker) and the counterion of iron (acetate, darker). Iron acetate is not readily available, so woodworkers prepare it in the woodshop by reacting steel wool and vinegar. This reaction was studied. Products were ferrous acetate $Fe(CH_3COO)_2.4H_2O$ (and H_2) and subsequently basic iron acetate $[Fe_3O(C_2H_3O_2)_6(H_2O)_3](CH_3COO)$ by air oxidation, giving a red-colored solution. Both inorganic phosphate and air (O_2) were required for maximal reaction rate. A volume of 85 mL of distilled white vinegar per gram of super fine (#0000) aged steel wool provided a final reaction mixture with fully dissolved steel and no precipitated products. Maximal darkening of cherry and red oak wood with minimal application of iron solution was attained by applying a 0.125 M iron acetate solution at a rate of 1 mL per 125 cm^2 of wood surface. A protocol for creating and using an iron acetate ebonizing solution is described and was demonstrated to be a much-improved version of the one currently promoted in the woodworking literature.

Introduction

In the craft of woodworking, the process of darkening wood in furniture and other wood pieces to make them appear to be ebony (*Diospyros ebenum*) is called *ebonizing* (Gomez 2016; Hanlon 2022). Chemical ebonizing relies on the reaction of wood tannins, polyphenols, with iron (or other metallic) salts to produce brown and blue-black amorphous complexes that remain trapped in the wood fibers. Tannins can form chelates with iron through hydroxyl groups in ortho position, yielding mono-, bis-, and tris-type compounds (Hider 1981). The reactions give rise to a variety of colors depending on the wood and the iron counterion, as depicted in Fig. 1.

The typical amounts of tannins in the four wood species listed in Fig. 1 vary from lower concentrations in birch and maple to higher concentrations in cherry and red oak (Bianco 1994; WWGOA 2022). The tannin concentration strongly affects the color of iron-treated wood. At low concentrations, iron simply hydrolyzes to the oxyhydroxide Fe(III)OOH which subsequently is slowly reduced to gray-colored magnetite $Fe(II)Fe(III)_2O_4$, a reduction coupled to oxidation of the tannin phenol group (Jaen 2003). Indeed, Yamauchi (2011) detected Fe(III)OOH in Japanese cedar on exposure to iron nails, but found higher amounts of Fe(II) in ancient trees exposed to iron because of the longer reaction time. At higher tannin concentrations the darker, more stable iron-phenolate complexes predominate (Jaen 2003). Comparison of ferrous acetate-treated birch & maple with cherry & red oak in Fig. 1 demonstrates the point clearly.

The anion of the iron salt also plays a significant role in the color of ebonized wood. Yamauchi et al. (2017) studied four trees (Japanese cedar, chestnut, oak, zelkova) buried or submerged for long periods, called *umoregi*, and found colors due to reaction with environmental iron that fell into two pairs. One pair (chestnut and oak) contained no chloride and displayed black colors due to Fe(III) complexes with octahedral geometry. The second group (cedar and zelkova) displayed lighter colors and lower iron content, indicating lower tannin content, with one member having an olive green color and a higher amount of chloride. The geometry of the complex was undefined, not clearly octahedral and possibly tetrahedral. Figure 1 demonstrates the same finding – a green color in woods with low tannin content and chloride as the anion of the iron salt. In addition, iron(II) polyphenol complexes oxidize in air (O_2) to the more stable Fe(III) complexes, and the rate of this autooxidation depends on the anion of the iron salt (Perron 2009). With ferrous sulfate, the autooxidation is slow, Fe(II) persists (Dagher 2022), fewer deeply-colored Fe(III) complexes form, and the colors of ebonized woods are lighter (Fig. 1). With ferrous acetate, the opposite is true, with Fe(III) the predominant oxidation state in treated wood (Dagher 2022). As a consequence, darker colors develop (Fig. 1).

Based on the previous discussion, true *ebonization* – making wood black like ebony – only occurs when wood with a high concentration of tannins is treated with an Fe(III) salt or an Fe(II) salt that can undergo rapid autooxidation. So, woodworkers can blacken cherry and oak and walnut, among the hardwoods with higher tannin content, or do the same with other species that have been pretreated with aqueous solutions of tannins, such as quebracho tea (Boggs 2022). The choice of iron salt is restricted since only a few are readily available to woodworkers: ferric chloride solution is a chemical etchant for printed circuit board and photoengraving processes and can be ordered from online retailers; solid ferrous sulfate can be found at garden centers as a soil acidifier and as a nutritional supplement at drug stores; iron complexed with glycinates or gluconates is used to add iron to lawns and other plants. As noted above none of these iron compounds are completely satisfactory, and ferrous acetate, which does nicely blacken wood, is not easily obtained.

As a consequence, woodworkers must prepare their own ferrous acetate, most commonly by mixing steel wool from the hardware store and vinegar from the grocery store. This concoction has been not-so-affectionately called a “witches brew” and “liquid nightmare” (Woodweb 2022). The terms are apt, since many recipes exist (Chemistry Stack Exchange 2022; CutTheWood 2022; Robbins 2022), many different outcomes have been reported (Boggs 2022), and the whole process seems to woodworkers more magic than chemistry (WWGOA 2022). Neither the woodworking literature nor the scientific literature offers an in-depth study and explanation of the reaction of steel wool with vinegar. To fill this void, we set out to better understand the reaction and to design a foolproof, reproducible method for preparing and using the resulting solution for ebonizing wood.

Materials And Methods

Materials

Steel wool

Steel wool was obtained from local hardware stores or by ordering online. Single pieces of steel wool were cut from steel wool finishing pads (Super Fine #0000 grade from Rhodes America company) or from a continuous roll of oil-free steel wool (Extra Fine #0000 grade from BriWax company). Each Rhodes steel wool pad could be unfolded to show 6 segments, with each segment weighing between 1.5 g and 2.2 g. No further cutting or shredding of the steel wool in preparation for reaction was performed.

Vinegar

Heinz-brand Distilled White (DW) vinegar (5% acidity), Multi-Purpose (MP) vinegar (6% acidity), Apple Cider vinegar, and other brand and type vinegars were purchased from local grocery stores.

Reagents

Water, purified by reverse osmosis, was obtained from the laboratory faucet. Glacial acetic acid, iron wire, potassium hydrogen phosphate monobasic, various iron salts, and other chemicals were ACS grade or better and purchased from chemical supply companies.

A stock inorganic phosphate solution (10.00 mM) was prepared by dissolving 136 mg pure KH_2PO_4 in water and diluting to exactly 100.0 mL. Standard solutions of phosphate were prepared by volumetric dilution of the stock solution with water. Aliquots of the same stock solution were added to acetic acid solutions to adjust their phosphate concentrations.

A stock iron solution (250 ppm) was prepared by dissolving 0.250 g pure iron wire in 20 mL concentrated nitric acid in a 250-mL Erlenmeyer flask. The reaction solution was heated until all of the solid was dissolved and all of the brown gaseous nitrogen oxides were removed. The solution was cooled, diluted to exactly 1.000 L, and stored in a polyethylene bottle. Standard solutions of iron were prepared by volumetric dilution of the stock solution with 1 vol% nitric acid.

Wood Veneers for Ebonizing

A pack of wood veneers (heartwood) with 0.60 mm thickness were purchased from a woodworking supply. Birch (*Betula alleghaniensis*), maple (*Acer saccharum*), cherry (*Prunus serotina*), and red oak (*Quercus rubra*) veneers were studied. The veneer was sanded on one face to a final sanding with 180-grit paper. Any dust was blown off with a jet of air, wiped with a damp (water) cloth to raise the grain, allowed to air dry, and then sanded again with 180-grit paper. Any remaining dust was removed with a jet of air. A 5.0 cm^2 area (2.0 cm x 2.5 cm) was marked on the veneer, and 50 µL (or other volume) of iron solution was applied. The solution was spread out evenly over the entire area using a plastic pipette tip. After 24 hours the area was rubbed lightly for 10 s with a damp cloth and then for 10s with a dry cloth to remove loose solid.

Methods

Titration for Total Acid Concentration

The acidity of the vinegars was determined by titration with standardized (against potassium hydrogen phthalate) sodium hydroxide solution (0.1090 M) to a phenolphthalein endpoint (Harris 2020). It was assumed that acetic acid was the only significant titratable acid present in the vinegars, so the titration gave the concentration of acetic acid. The acidity of the reaction mixture at the conclusion of the reaction was determined in the same way, except that iron interfered with the endpoint. Excess sodium hydroxide was added first to precipitate green ferrous hydroxide and then to change the phenolphthalein to red (easily seen against the white stir bar). The excess hydroxide volume was computed by knowing the mass of iron (steel wool) to start, and the volume correction was made to give the true acid concentration.

Flame Atomic Absorption Spectrophotometry (FAAS) for Total Iron Concentration

A Perkin-Elmer AAnalyst 700 instrument was used to measure atomic absorbance and determine total iron in the reaction mixtures. A multielement hollow cathode lamp emitted the characteristic wavelength of 248.3 nm for iron, no background correction was employed, and a lean air-acetylene flame was used for atomization. Standard concentrations ranged from 1.00 ppm to 7.00 ppm to prepare a best-fit linear calibration line.

Visible Spectrophotometry for Total Inorganic Phosphate

The method used for determining inorganic phosphate involved the formation of phosphomolybdates and their reduction with ascorbic acid to a blue-violet species, solubilized with sodium lauryl sulfate (Patton 2021). Reagent volumes were scaled up by a factor of 40 from the published method: sample 4.00 mL; Mo/Sb reagent 0.400 mL; ascorbic acid 0.600 mL; total volume 5.00 mL. The reagents were added in the order listed in the prior sentence, the mixture briefly vortexed after each addition, and the absorbance was measured after a wait time of 15 min. The absorbance spectrum had two peaks in the 500 nm – 1000 nm range: 710 nm (lesser absorbance) and 890 nm (wavelength of measurement). Standard concentrations ranged from 2 μM to 20 μM to prepare a best-fit linear calibration line.

Redox Potential Measurement for the Ratio of Fe(II) / Fe(III)

An Orion combination Pt and Ag/AgCl reference electrode was used to measure the potentials of solutions with varying ratios of $[Fe^{2+}] / [Fe^{3+}]$. Aqueous standards of $FeCl_2.4H_2O$ and $FeCl_3$ were prepared by dissolving pure solid in DW vinegar. Aliquots of each solution, summing to 1.00 mL, were added to 10.0 mL aqueous 1.0 M KCl to prepare each of a series of solutions with varying concentration ratio from 100:1 to 1:100. A best-fit linear calibration line was constructed by plotting potential in mV versus log $[Fe^{2+}] / [Fe^{3+}]$.

Capillary Electrophoresis Measurement for the Ratio of Fe(II) / Fe(III)

The method of Gotti, et al. (2015) was modified slightly to determine [Fe^{2+}] / [Fe^{3+}] by capillary electrophoresis (CE). Standard or sample (50 µL) was mixed with 50 µL of 1,10-phenanthroline (20 mM in water) for 3 min, then 50 µL of CDTA (20 mM in 0.10 mM NaOH) was added and mixed for 3 min, and finally 50 µL sodium tetraborate buffer (50 mM, pH 9.2), the background electrolyte (BGE), was added and mixed. All reactions were performed at room temperature. Separations were performed on a Sciex P/ACE MDQ Plus system with a 40-cm long x 50-µm i.d. fused silica capillary, integrated UV detection module at 254 nm, and 32-Karat software. Separations were accomplished using a constant voltage of 25 kV and were completed in under 5 minutes.

Steel Wool – Vinegar / Acetic Acid Reaction

All reactions were carried out at room temperature (21 ^{o}C – 25 ^{o}C) in air or under nitrogen (as specified), in ambient light, and without agitation. An exact mass of steel wool was placed in the reaction vessel, and an exact volume of either 5 vol% acetic acid or vinegar was added. The steel wool was pushed to the bottom of the vessel several times to remove trapped air. The reaction mixtures were sampled at various reaction times by removing 1 mL, centrifuging to remove any unreacted steel wool, and then quantitatively diluting an aliquot (10 µL – 100 µL) of the supernatant in 1 vol% nitric acid to provide a solution within the standard iron concentration range for FAAS. For potentiometry, 1.00 mL of the reaction solution was taken and centrifuged, and then the supernatant was mixed with 10.0 mL of 1.0 M KCl. Prior to each sampling, the reaction mixture was stirred with a glass rod to homogenize the solution.

Reaction Residue

After the reaction was judged complete, the entire reaction mixture was centrifuged and then filtered (Whatman #42 paper) to remove solid. Any unreacted steel wool was separated from other solids by using a strong Nd-Fe-B magnet to hold the steel in the centrifuge tube as the rest of the mixture was poured from the tube and filtered. The supernatant was stored in a capped, glass bottle. The brown-black solid on the filter paper was rinsed with a small amount of cold vinegar before allowing it to thoroughly dry on the paper at room temperature. The mass of the solid was recorded.

X-Ray Powder Diffractometry

Powder X-ray diffraction (PXRD) data were collected using CuK_a radiation on a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry with a scan rate of 4° 2q per minute.

X-Ray Crystallography (Single Crystal)

The data were collected from a shock-cooled single crystal at 150(2) K on a Bruker AXS D8 Quest three-circle diffractometer with a fine focus sealed tube X-ray source using a Triumph curved graphite crystal as monochromator and a PhotonII charge-integrating pixel array (CPAD) detector. The diffractometer was equipped with an Oxford Cryosystems low temperature device and used MoK_α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT, and a multi-scan absorption correction using SADABS was applied (Bruker 2022; Krause 2015) The structure was solved by dual methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 using ShelXle (Hübschle 2011; Sheldrick

2015) All non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon-bound hydrogen atoms were refined isotropically on calculated positions using a riding model with C-H distances of 0.98 Å. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. U_{iso} values were constrained to 1.5 times the U_{eq} of their pivot atoms.

Optical Reflectometry

The color and brightness of ebonized wood was measured using a hand-held reflectometer (Chroma Meter, model CR-400; Konica Minolta). Values were produced in the CIELAB / L*A*B color sphere system (Whetzel 2022) and standardized against an ultra-white disk provided by the manufacturer.

Results And Discussion

Characterization of Reactants

Steel Wool Steel wool is usually produced from low carbon steel that contains iron, carbon (up to 0.3 wt%), manganese (up to 1.5 wt%), copper (up to 0.6 wt%), silicon (up to 0.6 wt%), and possibly other metals (Total Materia 2022). FAAS analysis of the two steel wools studied here showed the following contents after dissolution in nitric acid. The Rhodes steel wool (statistically identical values for unwashed and washed): 100 ± 4 wt% Fe, 0.73 ± 0.05 wt% Mn, and no Cu. The BriWax steel wool: 98 ± 4 wt% Fe, 0.56 ± 0.04 wt% Mn, and no Cu. Carbon and silicon were not determined. The two steel wools had nearly identical compositions in terms of the measured metals and were essentially pure iron.

Steel wool available in the hardware store comes in different grades, from coarse (#2) to fine (#0) to super fine (#0000). The wire diameters were measured with an optical microscope, giving values nearly identical to the nominal values: 40 μm for Rhodes fine and 25 μm for Rhodes super fine. Measurements of both newly purchased and two-year-old Rhodes steel wool gave the same values. The newly purchased BriWax steel wool was composed of a steel ribbon, rather than wire, of approximate dimensions 5 μm x 20 μm.

Vinegar Two different Heinz brand vinegars were used in this study. Multi-Purpose vinegar (MP) is labeled as the most acidic at 6 wt% acetic acid, while the Distilled White vinegar (DW) nominally contains 5 wt% acetic acid. The measured (by titration) acetic acid concentrations (and wt% acetic acid) were: 1.031 M ± 0.002 M (6.2 wt%) for MP, and 0.872 M ± 0.002 M (5.2 wt%) for DW. The actual and nominal acidities matched very well.

The measured amount of inorganic phosphate P_i in the vinegars was 1.88 ± 0.02 mM (MP) and 1.62 ± 0.02 mM (DW). Two other brands of distilled white vinegar had similar P_i concentrations. It is reasonable to find phosphate in vinegar, since phosphate is added as a nutrient for the acetobacter organism that is used to catalyze the oxidation of alcohol to acetic acid in the vinegar-making process (Biology Discussion 2022). No iron was found in either of the vinegars.

Reaction Products

Primary Reaction Product / Reaction Stoichiometry The reaction of steel wool and vinegar produces ferrous acetate tetrahydrate. Within 2–7 days, depending on factors discussed below, the reaction goes to completion. In every case, except when product precipitated out of solution (solubility exceeded), the mass of steel wool to start was not significantly different from the mass computed from the total iron solution concentration determined by FAAS at the end of the reaction. And after 7 days of reaction only a trace of dark material (bits of steel wool) was collected from the surface of a strong Nd-Fe-B magnet added to the reaction solution.

The acetic acid concentration in vinegar at the start of the reaction and at the conclusion of the reaction with steel wool was measured by titration. We found that 2.11 ± 0.04 mol of hydronium ion was consumed per mol Fe. On a per gram basis, iron (steel wool) requires 0.036 mol acetic acid or 41 mL of DW vinegar for full reaction {1.0 g / 55.85 g/mol) x 2 = (0.872 M)(0.041 L)}.

The volume of hydrogen gas produced by the reaction was measured by water displacement and converted to moles using the ideal gas law. We found that 0.85 ± 0.04 mol H_2 was produced per mol Fe. This value was corrected for gas collection efficiency, as measured from the known reaction of zinc metal and hydrochloric acid to produce hydrogen gas. However, the zinc reaction was completed in a few hours, while the steel wool reaction went on for several days, and this could have led to more loss of hydrogen gas and a coefficient of less than 1. In addition, oxygen in the air may play a role as a reactant (see below), thus decreasing the total volume of gas collected. In any case, the reaction equation of iron (steel wool) and acetic acid (vinegar), as determined to the nearest whole number stoichiometry, was: $1\ Fe + 2\ CH_3COOH + 4H_2O \lozenge Fe(CH_3COO)_2 .\ 4H_2O + 1\ H_2$. This was as expected.

Oxidized Reaction Product Throughout most of the reaction time the reaction mixture was colorless, reflecting the colorless / light green color of solid ferrous acetate. As the reaction reached completion, the solution color turned greenish yellow, then orange. At reaction end, all of the iron and about half of the acetic acid was consumed, so the solution pH increased. Without Fe^0 present the disproportionation reaction $Fe^0 + Fe^{3+} \lozenge 2Fe^{2+}$ was no longer possible, and with a rise in pH, the air (O_2) oxidation rate likely increased (Morgan 2007). So, the concentration ratio Fe(II) / Fe (III) decreased, and a dark red complex $[Fe(II)_1\ Fe(III)_2\ O(OH)]^+$ (Misawa 1974) likely formed to impart color to the solution. See Fig. 2 for a visual representation of these changes. Potentiometry and capillary electrophoresis were applied to the determination of Fe(II) / Fe(III) over the course of the reaction. Both techniques demonstrated that Fe(II) predominated during most of the reaction time, and Fe(III) grew in relative concentration as the reaction reached completion and beyond. For example, in one reaction mixture the measured ratio was 15:1 three days after completion of the reaction, 1:1 three weeks later, and 1:2 three months later.

Controlled evaporation of a red-colored iron acetate solution in air over a week yielded a few semi-transparent, light red-brown crystals (Supplementary Information). By crystallography, the solid was identified as the mixed-valence trinuclear Fe(II,III,III) acetate-aqua complex $[Fe_3O(C_2H_3O_2)_6(H_2O)_3]^+$, also known as basic iron acetate. Basic iron acetate has three iron centers each of which are octahedrally bound to six oxygens, including an oxide at the center (Sato 1996a). The counterion is likely acetate in our structure. The data (Supplementary Information) matched well two previously published structures (CSD ref codes ZUSJEC and ZUSJEC01; Sato 1996b). They differed by the content of the solvate molecules which are ordered water molecules for the published structures and are highly disordered unidentified molecules for the current data set. The metal complex was unchanged among the three structures. In summary, we believe the reaction product solution of steel wool and vinegar contained both ferrous acetate and basic iron acetate, tending toward the latter as the solution aged. As further proof, rapid evaporation in air of some of the product solution left a brown-red solid that gave an X-ray diffraction pattern that was nearly identical to a library spectrum of basic iron acetate (Supplementary Information). We conclude that any ferrous acetate in the reaction solution oxidized to basic iron acetate during solution evaporation. The term “iron acetate” will be used below to indicate this mixture of ferrous acetate and basic iron acetate.

Factors Affecting the Reaction Rate

Factors involved in the reaction that could affect the reaction rate were investigated using 2.00 g steel wool and 170 mL of vinegar. The reaction was followed by measuring the amount of dissolved iron in solution by FAAS. Results are given in Table 1 as the reaction rates over the first 48 hours of reaction and discussed below.

Table 1
Mass Fe (g) reacted in 48 hr relative to the value for the first item in the list. *

Vinegar (type); Heinz brand	**Distilled White**	**Multi-Purpose**	**Apple Cider**
	1	0.94	0.19
Steel Wool (dimensions)	Ribbon; 5 µm x 20 µm	Wire; 25 µm	Wire; 40 µm
	1	0.44	0.38
Steel Wool (wash)	Unwashed	Detergent wash	Hexanes wash
	1	0.94	0.86
Steel Wool (age)	Old (2 yrs)	Heat treated	New
	1	0.61	0.59
Container	Canning jar	Plastic cup	Erlenmeyer flask
	1	0.91	0.77
* Uncertainties estimated to be ± 0.03			

Vinegar The results with Apple Cider vinegar were inconsistent with only 2 of 6 mixtures showing complete reaction by day 7, but in all cases the reaction was much slower compared to DW and MP vinegars. Perhaps proteins and other ingredients of the cider coated the steel, decreasing the contact between the reactants. Because the reaction was usually incomplete, Apple Cider vinegar was not further studied. DW and MP vinegars reacted quite similarly with steel wool. The more common DW vinegar was selected as the vinegar for further study.

Steel Wool Recall that Rhodes steel wool was made of wire of 25-µm diameter, and BriWax steel wool was made of 5 µm x 20 µm ribbon. Smaller dimensions should provide a larger surface area per gram and a higher reaction rate. Experiment confirmed this hypothesis. The BriWax #0000 reacted more than twice as fast as the Rhodes #0000, and the BriWax reaction was complete on average in 2.5–3 days compared to 6–7 days for the Rhodes.

Oils as lubricants are commonly used in steel wool manufacture, so some woodworkers try to remove the oil before reaction with vinegar in hopes that this speeds the reaction. Rhodes steel wool was washed with detergent in tap water and then rinsed thoroughly with tap water. Or it was soaked in hexanes, squeezed to remove hexanes, and residual hexanes allowed to evaporate. Washed steel wool reacted with vinegar at about the same rate as unwashed steel wool. So, washing /removing oil proved to be unnecessary and was not further included in our protocols. Note that BriWax steel wool is produced without the use of oil, according to its manufacturer.

A difference in reaction rate was noted when a new package of Rhodes steel wool was purchased for use in the midst of the study. The age of the steel wool had a positive effect on the reaction rate that could not be reproduced by artificial aging (heating steel wool in a moist atmosphere; 20 min at 218 ^{o}C in a toaster oven). See the next section for a discussion of this aging effect.

Surface Reactions and Phosphate Iron has a complex surface chemistry. In air and in solution, the surface of iron quickly forms a layer of iron oxides and oxyhydroxides, the main components of iron rust (Misawa 1974). More specifically at low pH, the large number of possible chemical species include Fe^{2+}, $Fe(OH)^{+}$, green rust, Fe^{3+}, and forms of FeOOH (Misawa 1974). Green rust I (GRI) is $[Fe(II)_4Fe(III)_2(OH)_{12}]CO_3$, where the planar carbonate coordinates with a mixture of ferrous and ferric ions (Benali 2001). $Fe(OH)^{2+}$, forms of Fe_2O_3, and Fe_3O_4 can be found upon further air oxidation (Music 1993). Rhodes steel wool was exposed to DW vinegar for 3.0 min, thoroughly washed with distilled water, and air dried. The newly purchased wool did not change in measured diameter (25 µm), but the two-year-old wool after treatment had a reduced diameter of 15–20 µm. This demonstrated that an iron oxide/oxyhydroxide layer, soluble in acetic acid, had formed over time. In addition, we found that more iron was removed by vinegar from aged steel wool in 48 hr (1.0 relative amount) than from new steel wool (0.59), due to the greater solubility of the surface layer and the resulting smaller wire diameter.

That steel wool reacted very slowly in 5 vol% glacial acetic acid in water in comparison to the same reaction in DW vinegar was puzzling. Compare the top and bottom reaction progress curves of Fig. 3. Knowing the content of typical enzymatic reactors that convert ethanol to acetic acid (Biology Discussion 2022; See Supplementary Information for details) and applying a factorial design to screen the major components for their effect on the reaction rate (Supplementary Information), we determined that inorganic phosphate acted as a catalyst. Indeed, the addition of 1.0 mM P_i brought the reaction rate in acetic acid in line with that in vinegar (Fig. 3).

The likely reason for the catalytic effect of phosphate was revealed by careful reading of the relevant literature. GRI oxidizes to ferrihydrite, an amorphous hydrated form of FeOOH, that in turn can crystallize into goethite a-FeOOH (Deng 1994). Geothite is x1000 less soluble in aqueous solution than ferrihydrite (Jang 2007). Thus, once goethite forms on the surface of steel wool the iron underneath would become much less available for attack by acetic acid. However, phosphate can form an inner sphere complex with ferrihydrite at low pH, binding via two Fe-O-P covalent bonds (Kim 2011; Shi 2010) and thereby inhibiting the conversion to goethite (Benali 2001). As a consequence, the iron oxyhydroxide layer on the surface of the steel wool remains highly soluble, the iron surface is easily exposed to acetic acid as the ferrihydrite dissolves, and the reaction proceeds at a faster rate. This process appeared to continue throughout the course of the reaction since the accelerated rate extended to reaction end.

Air (oxygen) / Reaction Vessel As described above, the oxide / oxyhydroxide layers on steel wool are slowly formed in an air / oxygen-rich environment as steel wool ages on the shelf and appear to continue to form and play a role in the steel wool – vinegar reaction in solution. Therefore, we hypothesized that oxygen is necessary for the dissolution of steel wool in vinegar.

Reaction vessels of different dimensions and different air-liquid interfacial areas were studied for their effect on reaction rate. The vessels and their characteristics were:

Pint canning jar glass top area 30 cm^2 air-liquid interfacial area 45 cm^2

200-mL Plastic cup polystyrene top area 40 cm^2 air-liquid interfacial area 30 cm^2

250-mL Erlenmeyer flask glass top area 6 cm^2 air-liquid interfacial area 40 cm^2

The air-liquid interfacial areas were measured when the vessels were filled with 170 mL of liquid. The canning jar had the highest diffusional area and, thus, could likely provide the most oxygen to the reaction. Indeed, the reaction rate in the canning jar was slightly higher than in the plastic cup and significantly higher than in the Erlenmeyer flask, whose top restricted air flow above the solution. This demonstrated that air (O_2) was an important component of the reaction. As further evidence, experiment showed that nitrogen-sparged 5 vol% acetic acid was slower to react with steel wool than air-saturated 5 vol% acetic acid (Fig. 3). Likewise, N_2-sparged vinegar was slower to react (not shown).

Protocol for Preparing an Iron Acetate Ebonizing Solution

Volume of vinegar per gram of steel wool The goals for preparation of an iron acetate solution for use in the woodworker's shop are (1) a solution that is as concentrated as possible and (2) little need at reaction end for filtering out solid – leftover steel wool and iron acetate that exceeds its solubility.

Ferrous and ferric salts precipitate in neutral to basic solutions because their hydroxides have very low water solubilities. Thus, it is important that the hydrogen ion concentration does not drop too much as acetic acid is consumed during the reaction. For example, if too much steel wool is added to a volume of vinegar, the product might not be ferrous acetate tetrahydrate but instead ferrous and ferric hydroxides. Ferrous hydroxides are green in color (See Fig. 2), and a green color has been observed in poorly designed steel wool – vinegar reactions. To maintain an acidic pH excess acetic acid should be used in the reaction. Since 41 mL of DW vinegar {0.872 M x 0.041 L = 0.036 mol} are required for full reaction per gram of steel wool {(1.0 g / 55.85 g/mol) x 2 = 0.036 mol}, then about 20% more or 50 mL of vinegar should suffice to fully dissolved the steel, keep the pH below 3, and prevent iron precipitation.

When the ratio of vinegar to steel wool was just above 50 mL per gram, a solid residue – some as flat crystals floating on the solution and some as particles on the sides and at the bottom of the reaction vessel – developed toward the end of the reaction. More solid was found as the volume of vinegar relative to the amount of steel wool (3.00 g) decreased: 0.02 g / 250 mL; 0.80 g / 200 mL; 1.1 g / 150 mL. Saturation of the solution with iron acetate explained these results. In a separate experiment, solid, reagent-grade ferrous acetate was added in excess to a known volume of DW vinegar, and the mixture was shaken for 7 days. Excess solid was removed by centrifugation and filtering, and the supernatant was tested for total iron content by FAAS. Repeated trials gave a solubility of ferrous acetate tetrahydrate in vinegar of 0.25 M ± 0.02 M, and the solubility did not vary significantly upon dilution of the vinegar with water up to a dilution of 20:1. To prevent precipitation of iron acetate toward the end of the reaction, a sufficient starting volume of vinegar is necessary. The required volume is 72 mL per gram of steel wool {0.018 mol / 0.072 L = 0.25 M}, but to allow for evaporation over a 3- or more-day reaction about 20% more or 85 mL vinegar per gram of steel wool should be used. Note that this volume is more than necessary to also fully dissolve the steel and keep the pH low, as described above.

Concentration and volume of iron acetate solution for ebonizing Aliquots (50 µL) of iron acetate solution were spread evenly across 20 mm x 25 mm pieces of prepared cherry and red oak veneer. Decreasing concentrations of iron solution, diluted in vinegar, gave rise to progressively lighter wood. See Fig. 4. The maximum darkness, indicated by a minimum in the L value from the reflectometer, was obtained using solutions of 0.125 M and higher. A second application of iron solution did not significantly increase the darkness, though it did fill in some lighter areas.

Increasing volumes of 0.125 M solution produced darker veneer until a maximum was reached at a volume between 25 µL and 50 µL. See Fig. 5. The required amount of iron solution was estimated to be about 40 µL since excess solution on the surface of the wood was noted upon addition of 50 µL. Thus, 5 µmole or more of iron added to 5 cm^2 of wood (cherry and red oak) was expected to give the lowest L value, the most darkening.

Of course, the iron solution seeps from the wood surface and into the pores and lower layers. Optical microscopy gave an estimate of the depth of penetration of the iron solution by measurement of the dark layer of the wood viewed edge on and along the grain (Fig. 6). The dark layer was not of uniform color or thickness and difficult to judge in some samples. Our best estimate of the average ebonized layer thickness was 100–120 μm for cherry and 60–80 μm for red oak wood in the 600-μm thick veneer. Since cherry wood 630 kg/m^3 is less dense than red oak 740 kg/m^3 (Engineering Toolbox 2022), the measured deeper penetration of the iron solution in cherry is reasonable. Canevari (2016) reported treatment of popular wood with gall dyestuff and found penetration of high iron concentrations to 30 μm. They, like us, also found SEM-EDX data for iron to be “rather noisy” and inconsistent. Thus, we did not report those data here.

With a surface area of 5 cm^2 and an average depth of 0.0070 cm, the volume of penetration of iron solution in red oak was 0.035 cm^3, per 40 μL of applied 0.125 M iron acetate, giving an iron concentration in the wood of 143 $\mu mol/cm^3$ {(0.125 M)(40 μL) / (5 cm^2)(0.0070 cm)}. Dagher (2020) reported that the concentration of di-substituted phenolics in red oak (500 μmol per g wood) was well correlated with wood color after ebonization. Assuming the same tannin content of our red oak sample, we can make a rough estimate that the mole ratio of phenolics to iron in the dark layer of our treated red oak was 2.6 {(500 μmol / g)(0.74 g / cm^3) / (143 μmol / cm^3)}. This indicated the likelihood that mostly bis-phenolate and tris-phenolate complexes formed, an observation that is quite reasonable and supported by the report of Perron (2009).

Conclusion

Our recommended protocol for making iron acetate solution for ebonizing in a woodworker’s shop is given in Table 2. The protocol yields an approximately 0.125 M solution from steel wool pads (*e.g.* Rhodes) or an approximately 0.25 M solution from wool made from ribbon (*e.g.* BriWax), both in 3-days time. Only about half of the steel wool pad will dissolve in 3 days, while the wool made from the smaller ribbon should be fully dissolved. See Fig. 7.

Our findings and recommendations differ considerably from the information that is currently available to woodworkers. In a wikiHow (2022) article on ebonizing wood, representative of the content of woodworkers’ sites on the internet, the following mistaken notions are espoused. [1] “Steel wool usually has an oil coating that you’ll need to remove before making the solution.” We found that the reaction rate is not significantly changed upon washing in water or rinsing in nonpolar solvent. [2] “New steel wool is best.” We found that aged steel wool has an oxyhydroxide coating that is easily dissolved in vinegar leaving a smaller dimensioned wire that reacts at a faster rate. [3] “Apple cider vinegar works better.” We found that apple cider vinegar reacts inconsistently and at a slower rate. We recommend distilled white vinegar. [4] “Fill a glass jar with steel wool and vinegar.” No metrics are given. We found that the relative amounts of vinegar and steel wool are quite important – 85 mL per g is best. And the shape of the glass jar has an effect. [5] “Let the steel wool and vinegar sit for a week.” We found that an effective iron ebonizing solution can be created in just 3 days.

Table 2
Protocol for preparing an iron acetate solution for ebonizing

• **Collect steel wool (#0000, super/extra fine); no need for washing the wool**	
(A) Rhodes steel wool pad (aged is better than newly purchased):	(B) BriWax steel wool roll (newly purchased is fine):
Unravel pad to reveal 6 segments	Unroll and cut
Collect 4.0 g or 2 segments	Collect 4.0 g or 3.8 cm (1.5 in)
• Add steel wool to a 1-pint glass canning jar or similar non-metallic, wide-mouthed vessel	
• Add 340 mL or 1.5 cups of Distilled White vinegar to the same jar	
• Stir the mixture with a glass or plastic rod (*e.g.* plastic knife) and repeat every 24 hours. Leave the mixture uncovered	
• After 3 days filter the mixture to remove any remaining steel wool and other solids; pour the mixture through a coffee filter or fine cloth	
• Collect the liquid and store it in a glass or plastic bottle with cap. The liquid is colorless to orange at first and then becomes more red to red-brown with time	

In the WoodWeb forum (2022), ferrous sulfate was said to produce the same results as iron acetate. We found that to be incorrect, that the colors produced are markedly different (Fig. 1), and that the literature suggests that the sulfate anion slows the rate of conversion of Fe(II) to Fe(III), minimizing the production of dark Fe(III) phenolate complexes, in contrast to what happens with an acetate counterion. Finally, we recommend applying the iron acetate solution at a rate of 1 mL per 125 cm^2 or about ¼ cup of liquid per 7 ft^2. This seems to be a much lesser application than is typically shown in woodworking videos on the internet (WWGOA 2022). Using excess iron solution does nothing but leave surface residue to clean up after the solution evaporates. By following the protocol in Table 2, 340 mL of ebonizing solution are prepared, providing coverage for about 40 ft^2 of finished lumber.

By way of this work, we hope to have improved the theory and practice of ebonizing wood by chemical means and added important knowledge and protocols to the woodworker’s toolkit.

Declarations

FUNDING

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COMPETING INTEREST

The author has no competing interests to declare that are relevant to the content of this article.

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Figures

Figure 1

Birch (*Betula alleghaniensis*), maple (*Acer saccharum*), cherry (*Prunus serotina*), and red oak (*Quercus rubra*) veneers treated with iron solutions. The iron-tannin reaction produces a variety of colors in the *ebonized* wood: light green (chloride with birch and maple); light gray (sulfate and gluconate with birch and maple); light brown (acetate with birch and maple & sulfate and gluconate with cherry); dark gray (sulfate and gluconate with red oak); dark brown to black (chloride and acetate with cherry and red oak). Veneers were photographed one week after treatment

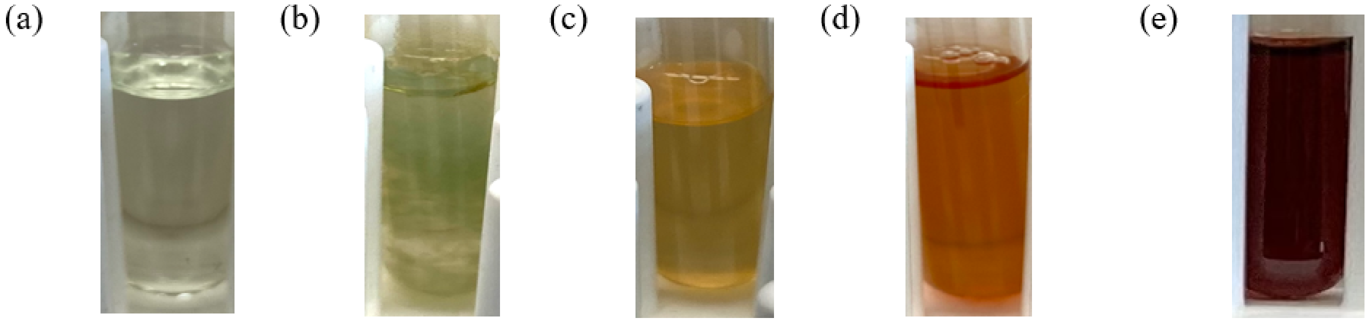

Figure 2

Liquid portion (supernatant) of a 4-day reaction mixture of aged Rhodes steel wool and DW vinegar: (a) Colorless reaction solution not treated further; (b) With added NaOH (enough to neutralize half of the acetic acid in the vinegar), green precipitates of presumably ferrous hydroxide and GRI form; (c) With added NaOH, shaken, and allowed to stand for 2 min, ferric ion forms, producing a yellow-orange color;

(d) With added NaOH, shaken, and some Fe(III) chloride added, the dark red complex is likely formed. (e) Dark red-brown liquid portion (supernatant) of a 14-day reaction mixture of aged Rhodes steel wool and DW vinegar

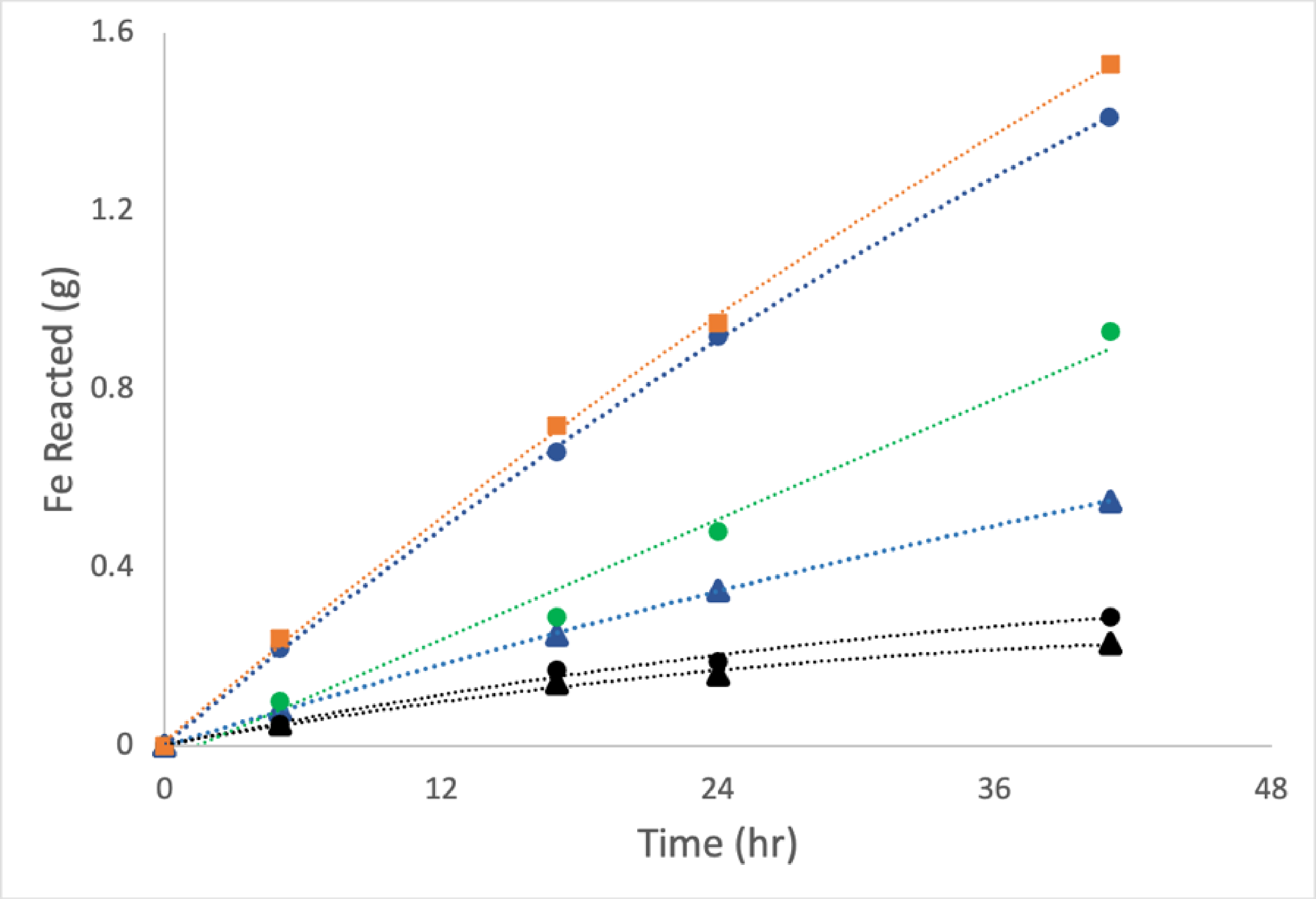

Figure 3

Reaction progress curves. Aged Rhodes steel wool (2.0 g) reactions with 170 mL DW vinegar (squares), 5 vol% acetic acid (circles), nitrogen-sparged 5 vol% acetic acid (triangles). Reactions with no added phosphate (orange and black; top line & bottom two lines), 0.10 mM phosphate added (green; 3rd line from top), and 1.0 mM phosphate added (blue; 2nd line from top & 4th line from top)

Concentration	CHERRY L	color	RED OAK L	color
None	64		76	
0.025 M	40		39	

Figure 4

Cherry and red oak veneer treated with 50 µL of varying concentrations of iron acetate solution, the product of aged Rhodes steel wool – DW vinegar reaction. The brown to black color of the *ebonized wood* was measured by reflectometry using the CIELAB system. That system is diagrammed to the right of the table (Whetzel 2022). Values of a (green-red scale) decreased slightly and values of b (blue-yellow scale) decreased by about 12 units (bluer). The largest changes, as reported, were along the L axis

Concentration	CHERRY L	color	RED OAK L	color	Comments
None	63		75		
10 µL	36		38		Difficult to spread over entire space
25 µL	34		33		Just enough to spread over entire space
50 µL	29		29		Plenty to spread; some excess liquid
100 µL	30		31		Lots of excess liquid

Figure 5

Cherry and red oak veneer treated with varying volumes of 0.125 M iron acetate solution, the product of aged Rhodes steel wool – DW white vinegar reaction. The brown to black color of the *ebonized wood* was measured by reflectometry using the CIELAB system. The largest changes, as reported, were along the L axis

Figure 6

Cherry (left) and red oak (center) veneer treated with iron acetate solution, the product of aged Rhodes steel wool – DW vinegar reaction, and viewed edge on along the grain (vertical axis) by optical microscopy. The average thickness of the veneer was 600 µm. The *ebonized wood* layer is the slightly darker band on the left side, and its thickness was estimated by ruler measurement of the photo. The third photo (right) is of the holder used to secure the veneer edge perpendicular to the optical path of the microscope. The edge of the wood (and top of the holder) was sanded to 4000 grit prior to microscopy

Figure 7

At left are two photos of pairs of reaction mixtures. Each pair has newly purchased Rhodes steel wool in DW vinegar (left) and BriWax steel wool in DW vinegar (right). The photo at left is the reaction after 1 day and at right after 3 days. After 3 days, nearly all of the BriWax steel wool was consumed, but about half of the Rhodes steel wool remained. At right are two photos of the filter paper used to remove the small amount of solid remaining and the filtrate of the BriWax-DW vinegar reaction mixture on day 3 and again one day later (far right). The filtrate initially contained mostly ferrous acetate (greenish brown solution) and then began to be oxidized in air to basic iron acetate (red-brown solution)

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