

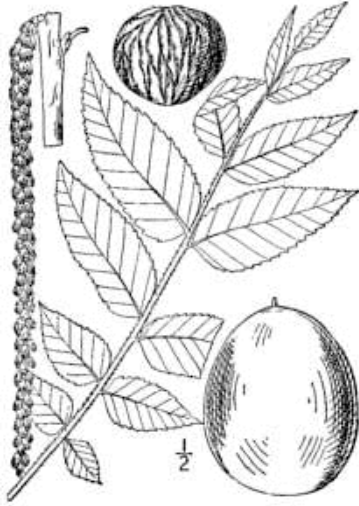
## Dyeing with Tannic Acid and Iron: Walnut Husks



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## I. Introduction

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This paper discusses the use of walnut to dye fabric. As far back as Roman times black cloth was produced by dyeing of fabric or skeins in dye baths of tannic acid and iron salts; including using black walnuts. It is mentioned in Pliny and there is evidence of it in the dyeworks at Pompeii.<sup>2</sup> Walnut was also known as a dye during the Viking Age.

From the 13<sup>th</sup> C. to 16<sup>th</sup> C. much of what we know about dyeing comes from the accounts of the Guilds and the laws concerning what they were permitted to do. Many plants contain tannic acid in their bark, leaves, stems, or fruit. Some are mentioned in the *Plictho de larte de Tentori che insegna tenger pani telle*

*banbasi et sede si per larthe maggiore come per la comune* written by Giovanventura Rosetti and printed in 1540<sup>3</sup>. This book was written to popularize dyeing in the 16<sup>th</sup> C and contains numerous recipes.

Unfortunately while there is much information on the process, there are few details of the exact order or amounts to be used in historic texts. Thus, there is room for a wide variety of interpretations of these “recipes”.

## II. Historical Notes on Dyeing

Dyeing black from a combination of tannic acid and iron salts was common in Roman times. Various plant materials were used including all portions of nut trees. The walnut (*Juglans Nux Regia*) was brought by the Roman to the European continent and England.<sup>4</sup> The iron mordant was made from dissolving iron in vinegar. The fabric, if it was wool, was then dyed by the *infectores* and *offectores*. Each step in wool production was handled by a separate company.<sup>5</sup>

As dyeing moves into the Middle Ages the Guilds take over the various steps of processing various fabrics. In Germany there is even a specific group for dyeing

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<sup>1</sup> Line Drawing of *Juglans nigra* L

<http://plants.usda.gov/>

<sup>2</sup> Brunello pg. 110

<sup>3</sup> Brunello pg. 181

<sup>4</sup> Brunello pg. 110

<sup>5</sup> Brunello pg. 110-111

black called the *Schwartzfarber*. This group is less prestigious than one that dyed colors.<sup>6</sup>

In 15<sup>th</sup> C York the dyers set out ordinances; as other dyeing guilds had done in prior centuries. There is a specific reference that dyeing may be done at any time.<sup>7</sup> Thus, the dyeing may occur with the raw fiber, after the fiber is spun, or after weaving. The cover illustration of this paper from Rosetti's *Plictho* shows skeins being dyed. Jost Amman's *Book of Trades*, originally published in 1568, has an illustration of the dyeing of fabric.

### Der Schwartzferber.



During the Viking Age there is some evidence of dyeing with walnut shells. In addition, there are a couple pieces "that were intentionally dyed very dark brownish-black with walnut shells and iron (Hagg 1984, 289)."<sup>8</sup>

Both Brunello<sup>9</sup> and Rogers<sup>10</sup> comment that while there were naturally produced dyes they were not used in commercial production of cloth. Brunello further comments that this may have been due to the preference for brighter colors than those produced by natural tannic acids.

*Ich bin der schwarz Farber in Sächet/*

Various documents have recipes for black dyes. The Innsbruck Manuscript was written around 1330 and contains a number of German recipes.<sup>11</sup> The manuscript notes using both alum and iron as mordants. One recipe specifically refers to using nuts and it has been thought that the reference was to walnuts.<sup>12</sup>

Nim grün nusschaln vnd stozz die vnder einander vnd lazze das sibentag vaulen in einem hevelein vnd da mit verb schwarcz varb.

<sup>6</sup> Brunello pg. 152

<sup>7</sup> Rogers pg. 1770

<sup>8</sup> Dorman <http://www.cs.vassar.edu/~capriest/vikdyes.html> - reference to Hägg, Inga. 1984. *Die Textilfunde aus dem Hafen von Haithabu*. Berichte über die Ausgrabungen in Haithabu, Bericht 20. Neumünster: Karl Wachholz Verlag.

<sup>9</sup> Brunello pg. 110

<sup>10</sup> Rogers pg. 1766

<sup>11</sup> Brunello pg. 152 and <http://costume.dm.net/~drea/dyes/>

<sup>12</sup> <http://costume.dm.net/~drea/dyes/>

Take green nutshells and grind them together and let them rot seven days in a (stoneware?) pot, and therewith make a black dye. <sup>12</sup>(translation by Drea Leed)

In the mid-16<sup>th</sup> C., with the advent of the printing press, there are a profusion of books published on diverse topics. One is Giovanventura Rosetti's *Plictho: Instructions in the Art of the Dyers which Teaches the Dyeing of Woolen Cloths, Linens, Cottons, and Silk by the Great Art as Well as by the Common*. It contains 108 recipes for dyes of which 20 are for black.<sup>13</sup> A number of these are tannins mixed with iron salts.<sup>14</sup> Included are several that use various parts of nut trees.

Vitriol or Vitriol Romano (green vitriol) is ferrous sulfate. It has other names such as Pisa green copperas and was commercially manufactured in Italy.<sup>15</sup> Recipes in the Innsbruck Manuscript request rusty iron, while recipes in Theophilus and Rosetti refer to vitriol. Iron acetate (also called ferric acetate) can be produced by soaking iron filings in vinegar<sup>16</sup>.

Vitriol, tannic acid, oak bark and a number of other acidic compounds were banned from the workshops of Master Dyers by decree in 1480 by Doge Giovanni Mocenigo. These had been found to be destructive to fibers.<sup>17</sup>

In addition, there were years of scandal in the Italian silk industry over a process for dyeing black, called *in goro* that was alleged to make the fabric heavier and wear poorly. The controversy led to a decree in 1580 that only gallnut be used. It was an attempt at enforcing the earlier degree of 1546. This debate continued through to the beginning of the 17<sup>th</sup> C. <sup>18</sup> From the description, this sounds suspiciously like the dyers using metallic salts and then not washing the excess out thoroughly. Both of which would add to the weight of the fabric or thread and cause deterioration over time.

If we lack extant examples of tannic acid dyes, it can be attributed to a couple problems. One problem is that the dyes from such natural dye stuffs as nuts, barks and oak galls are similar to those acquired in the course of fabric being buried. Then too the acid in the dyes may have had a destructive effect on the fabrics. In addition, overdyeing was practiced and so an item identified as being

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<sup>13</sup> Brunello pg. 188 & 190

<sup>14</sup> Brunello pg. 190

<sup>15</sup> Brunello pg. 190

<sup>16</sup> Smith pg. 92

<sup>17</sup> Brunello pg. 190-1

<sup>18</sup> Mola pg. 134-7

dyed with madder may not reflect a prior dyeing with a tannic acid, for example.  
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### III. The Project Notes

-- **Project 1** – March 16, 2005: Walnut Hulls alone and with Post Mordanting—  
A. Preparing the Dye Bath:

Take black walnut nuts and break up with a mallet. Remove the nut meat.

Take 4 oz of the walnut hulls and place in cheese cloth and tie shut. Place into 1 gallon of water in a stainless steel pot – sufficient to cover fabric and dyestuff package. Let soak 1 hour to soften up the shells. The pot was chosen as it would impart few if any impurities into the dye bath.

B. Preparing the Fabric:

Take 6 skeins of wool\* and 2 silk swatches and immerse in a container of room temperature water. (fiber weight is approximately 4 ounces) Let soak 1 hour to ensure that the fibers are well opened up.

*\* 1 skein for this project is approximately 10 yards of Robin and Russ undyed but cleaned (scoured wool) which has been spun loosely.*

C. Adding Fiber to Dye Bath:

Add the fiber to the dye bath. Bring to a boil. Turn off heat and let sit. Historically they may have boiled or simmered the fabric longer. (See Project 2 below)

At 14 hours remove 2 skeins of wool and 1 silk swatch. Rinse well. These will show what a “days” sitting in the dye vats would have produced from the natural color provided by the tannic acid from the hulls alone.

Also remove 1 quart of dye liquid. Immerse 2 skein of wool in container. Leave in an additional 10 hours. Remove and rinse well. This quart and skein was designed to show the natural color provided by the resulting tannic acid from the hulls alone and if the skeins were left in a longer period of time.

The tannic acid from the walnut hulls is self mordanting. Thus in the Innsbruck recipe, there is no additional mordant added. However, the green walnut outer skin has a lot of fresh tannic acid and may produce a deeper tint than the hulls alone.

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<sup>19</sup> Crowfoot: Appendix by Penelope Walton pg. 201

#### D. Post Mordanting:

Bring pot back to a boil. Add 1 teaspoon ferrous sulfate (iron). Stir well and simmer for 30 minutes to ensure that the Iron is dissolved and the material is thoroughly infused with the Iron dye so the chemical reaction can occur. The chemical reaction between tannic acid and the tannic acid creates the black.

Let cool and remove the 2 skeins and silk swatch from the dye bath. Rinse thoroughly.

The choice of powdered Iron was to both a question of safety and convenience. See section above on historical choices. The amount chosen was to reflect the least amount sufficient to affect the necessary chemical changes as I was aiming to not have long term fiber deterioration.

My choice to post mordant was generated by a comment in another of the Innsbruck black dyes - oak gall. It says that if you want it darker add more black. In this case I opted for the ferrous sulfate to create a darker result.

#### E. Project Conclusions:

The non-mordanted fiber took on a color similar to tea dyeing which is another tannic acid dye. The color is a very light tan. When checked at the 1 hour and 3 hour points, it had taken very little color, nor did it darken overnight. The chemical reaction of the tannic acid and the ferrous sulfate produced a light gray/black.

The lightness of color could be due to either the lack of heat or the dye product to water ratio.

-- **Project 2** - March 21, 2005: Walnut Hulls alone and Post - Mordanting with Iron - over heat

#### A. Preparing the Dye Bath:

Take black walnut nuts and break up with a mallet. Remove the nut meat.

Take 4 oz of the walnut hulls and place in cheese cloth and tie shut. Place into 1 gallon of water in a stainless steel pot - sufficient to cover fabric and dyestuff package. Let soak 1 hour to soften up the shells.

#### B. Preparing the Fabric:

Take 4 skeins of wool and silk swatch. No pre-wetting was done to see if the dye would take differently.

#### C. Adding Fiber to Dye Bath:

Add the fiber to the dye bath. Bring to a boil and then reduce to a simmer.

At 2 hours remove a skein of wool. Rinse well.

At 4 hours remove a skein of wool. Rinse well.

At 8 hours remove a skein of wool and silk swatch. Rinse well. These will show what a “days” simmering in the dye vats would have produced from the natural color provided by the tannic acid from the hulls alone.

#### D. Post Mordanting:

Bring pot back to a boil. Add 1/4 teaspoon ferrous sulfate (iron). Stir well and simmer for 30 minutes to ensure that the Iron is dissolved and the material is thoroughly infused with the Iron dye so the chemical reaction can occur. The chemical reaction between tannic acid and the tannic acid creates the black.

Let cool and remove the skein from the dye bath. Rinse thoroughly.

Although the tannic acid from the walnut hulls is self mordanting, and the color was a deep brown, I was curious to see the effect of adding the iron (additional “black”) as in the Innsbruck Manuscripts and in others for doing oak galls.

#### E. Project Conclusions:

Keeping the heat on the dye bath both allowed more tannic acid to be released from the hulls and the fibers to absorb more of the dye. The 2 hour skein is a nice medium brown with the 4 hour skein being slightly darker. The 8 hour skein and silk swatch is a rich “walnut” brown. Adding the iron created an almost instant reaction and the result is a deep rich black.

### -- **Project 3:** Walnut Hulls with Pre-Mordanting --

#### A. Preparing the Dye Bath:

Take black walnut nuts and break up with a mallet. Remove the nut meat.

Take 4 oz of the walnut hulls and place in cheese cloth and tie shut. Place into 1 gallon of water in a stainless steel pot – sufficient to cover fabric and dyestuff package. Let soak 1 hour to soften up the shells.

Bring to a boil and let simmer until level of preferred color depth is reached. This took about 8 hours.

There were 3 skeins of wool that were removed at 2 hours, 4 hours and 8 hours. This was used to determine the depth of color obtained in the dye bath.

#### B. Pre-Mordanting:

In a separate pot take 2 quarts water (a sufficient amount to cover the fiber) and bring to boil. Add 1 teaspoon of Ferrous Sulfate (Iron) and stir to dissolve. Add in 6 oz of fiber – 6 skeins of wool and silk swatch. Simmer for 30 minutes to ensure that the Iron is dissolved and the material is thoroughly infused with the Iron dye.

Remove 1 skein and wash thoroughly. This skein will show the amount of iron coloration alone.

#### C. Adding Mordanted Fiber to Dye Bath:

Remove skeins and silk to the dye bath. Bring dye bath to a boil. Let simmer.

After 1 hour remove 2 skeins and silk swatch. Rinse well.

After 4 hours remove 2 skeins and rinse well.

#### D. Project Conclusions:

The dye bath this time was not yielding quite the same depth of color as in Project 2, however the browns were close enough to use the same timing sequence as in the prior project.

The premordanted fiber reached a depth of brown color similar to the walnut alone at the 8 hour level, but at the 1 hour mark. While it has a bit of a blacker tinge to it, it is not the rich black of the post mordanted fiber. At the 4 hour mark, the fiber was a little bit darker and a bit blacker, but still lacked the richness of the post mordanted skein.

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