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The Indigo Blues:
A Comparison of Dyebaths

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Introduction

Indigo blue is one of the most challenging and, in my opinion, rewarding, colours to dye. Not only is the historical method of making this dye difficult, but the chemistry behind the indigo plant is a fascinating look into the mystery of nature and the creativity of humanity. It is for these reasons, as well as the personal challenge to myself, that I decided to submit a process piece looking into the production of indigo dye for Tir Righ Arts and Sciences A.S. 53.

While my original vision was to complete several dye vats using both indigo powder and indigo plant matter, due to some hiccoughs with growing my own plants I was forced to scale back the project and focus on comparing a modern chemical vat with a historical fermentation vat. This still provided a worthy challenge and plenty of opportunity for experimentation with different fiber types.

The final product of this project was the dyeing of Egyptian linen in two different shades of blue to be used in my second project: a process piece on the re-creation of a knitted Egyptian sock motif.

A Brief History of Dyeing

Humankind has been adding colour to their lives for centuries. Whether trying to accurately depict the real world in cave paintings, or mimic natural colours in their wardrobes, we have borrowed colour from natural sources from prehistoric times up to, and past, when we discovered the ability to synthesize those colours and dozens of others.

There are extant examples of dyes being used as far back in our history as Ancient Egypt (an indigo garment was excavated in Thebes, dating back to 2500 BCE[1]), as well as literary references to dyed fabrics in the Christian Bible (Exodus 35:25[2]) and in the works of the ancient Greeks and Romans (Herodotus, writing in about 450 BCE[3] or Pliny the Elder in his Naturalis Historia around 78 CE[4]). Over time, sources for different colours were discovered, colours were mixed to learn new ones, and many different types of fibers and fabrics were dyed according to various methods. This was a universal process that occurred over and over across the entire world as humanity's natural curiosity pushed previously known limits and we continued to learn bigger and better ways of doing things.

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[1] Anne Mattson, "Indigo in the Early Modern World," University of Minnesota Libraries, accessed September 06, 2018, https://www.lib.umn.edu/bell/tradeproducts/indigo.
[2] And all the women that were wise hearted did spin with their hands, and brought that which they had spun, both of blue, and of purple, and of scarlet, and of fine linen.
[3] Cynthia Clark Northrup, *Encyclopedia of world trade. from ancient times to the present* (Abingdon, Oxon: Routledge, 2015), 506.
[4] "Pliny the Elder, The Natural History," Book 35, Chapter 27, accessed September 06, 2018, http://www.perseus.tufts.edu/hopper/text?doc=Perseus:text:1999.02.0137:book=1.

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While dyeing textiles and the use of colour in cosmetics was common across the globe for centuries, European dyers reached the height of their skill in the thirteenth century, mainly due to the guild systems which maintained a high standard of quality. In some places it was forbidden to possess, let alone use, major dyestuffs unless you were a member of a guild. In Germany, the dyers and woad workers were regulated by the guilds, with each grower having to present his crop to a "sworn dyer" to determine its quality, weight and condition before it could be sold.[5] English producers of woad had fewer restrictions: mainly that of a proclamation first made in 1585 (though it was amended later) to ensure that no woad mills were sited within four miles of any market or clothing town, or within eight miles of a royal residence, because of the highly offensive odor they emit.[6]

In 1377, dyers in Florence, Italy founded the Dyers' Guild after they refused to work with the Weavers' Guild and their rulers acknowledged that the "craft of dyeing was of equal important with other crafts."[7] However, even with that proclamation, the dyers remained under the "strict and often cruel jurisdiction of the weavers and cloth merchants,"[8] and the 1377 guild was dissolved in 1382. The Florentine dyers often emigrated to other Italian cities such as Venice, which were more sympathetic and had their own flourishing dyers' guilds.[9] One of the long-lasting products of a Venetian dyers' guild was the 1540 publication of Giovanni Ventura Rosetti's *Plictho de Larte de Tentori*[10] which contained the recipes of the Venetian Dyers' Guild and was a working reference for dyers until the end of the 17th century.[11]

According to Stuart Robinson, author of *History of Dyed Textiles*, the dyers were formed into three groups:

> The first and largest was that of the black or plain dyers who worked from 4 p.m. to 7 p.m., had three years' apprenticeship, five as a workman and three of travel before passing stringent tests to become a master craftsman in a guild system. They specialized in black and all simple colours. The second was reserved for the individual dyers of high colours on expensive materials using rarer dyestuffs. They were the outstanding masters of the craft and relatively few in number. The final group was a specialist one for the dyers of silk, particularly strong in France and Italy; they were regarded as individual artists and not of a guild.[12]

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[5] Su Grierson, *Dyeing and Dyestuffs* (Aylesbury: Shire, 1989), 8-9.
[6] Frederic A. Youngs, *The Proclamations of the Tudor Queens* (Cambridge: Cambridge University Press, 1976), 151.
[7] Stuart Robinson, *A History of Dyed Textiles: Dyes, Fibres, Painted Bark, Batik, Starch-resist, Discharge, Tie-dye, Further Sources for Research* (London: Studio Vista, 1979), 28.
[8] Ibid.
[9] Ibid.
[10] Spelling and date as per Robinson, 28 - other sources write it as *Plictho de L'arte de Tentori* or *Plictho del Arte de Tentori* and give a date of publication of 1548.
[11] Robinson, 28.
[12] Robinson, 28.

Indigo itself was used in Ancient Egypt circa 2500 BCE, and was common throughout India and Asia. In Europe, the colour was derived from the woad plant (Isatis tinctoria) instead. There are “records written in Sanskrit, describing various methods of preparation, [and] has been known to the people of Asia both as a dye and as a cosmetic, for over 4000 years.”[13] However, for centuries, any kind of blue pigment was called indigo. The real characteristics of indigo were not widely known until the 14th century,[14] particularly in Europe, and people continued to believe indigo was a mineral, as shown by a British patent granted in 1705 for obtaining indigo from mines.[15] Much of this was due to the fact that influential woad growers and distributors lobbied successfully to prohibit indigo importation in Europe for more than a century. In 1577, an English local governing body declared that indigo was “prohibited under the severest penalties”[16] and it was described as “the newly invented, harmful, balefully devouring, pernicious, deceitful, eating and corrosive dye known as ‘the devil’s dye,’ for which vitriol and other eating substances are used instead of Woad.”[17] The proclamation was renewed in 1594 and again in 1603. Other countries made their own proclamations against indigo, but such measures proved futile and it quickly superseded woad as the preferred source of indigo blue.

The art of dyeing was accidentally revolutionized in 1856 by a chemical student named William Henry Perkin, who, while experimenting with aniline,[18] made the first artificial dye: mauveine.[19]

These first synthetic dyes, when compared to the natural dyes that preceded them, were found to be “hard, coarse, crude, and very inartistic.”[20]This was often remedied by mixing shades to soften them. However, these first dyes were not terribly light fast and did not fade true - a bright red might, after a few days, fade yellow, or white, or become a darker shade.[21] By 1868, however, two German chemists manufactured alizarine[22] and created a whole new class of dyestuffs that were fast to both light and washing.[23]

With the advent and development of colour fast synthetic dyestuffs, natural dyeing became less common, and for some colours non-existent, as it was more expensive and difficult to replicate on a large scale. However, it is experiencing a resurgence as people find an interest in it once again.

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[13] William F. Leggett, *Ancient and Medieval Dyes* (Brooklyn, NY: Chemical Publishing, 1944), 17.
[14] Ibid. 20-21.
[15] S. L. Kochhar, *Economic Botany a Comprehensive Study* (Delhi, India: Cambridge University Press, 2016), 525.
[16] Leggett, 27.
[17] Ibid.
[18] A colourless, oily liquid made, in this case, from distilling indigo (Pellew, 40).
[19] Charles E. Pellew, *Dyes and Dyeing* (New York, NY: McBride, Nast & Company, 1913), 40.
[20] Ibid. 41.
[21] Ibid. 42.
[22] A compound prepared from madder and used as a synthetic dye.
[23] Pellew, 42.

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Indigo Varieties

Indigofera Tinctoria (True Indigo)

Found originally in India, Indigofera tinctoria prefers tropical climates and can also be found in China, Indonesia, and parts of Northern South America.[24] Early English buyers focused their attention on western Indian (Gujarat mainly[25]), which Marco Polo described in his *Travels*:

> They have also abundance of very fine indigo. This is made of a certain herb which is gathered, and [after the roots have been removed] is put into great vessels upon which they pour water and then leave it till the whole of the plant is decomposed. They then put this liquid in the sun, which is tremendously hot there, so that it boils and coagulates, and becomes such as we see it. [They then divide it into pieces of four ounces each, and in that form it is exported to our parts.][26]

Due to the fact that the indigo pre-cursor, indican, is contained solely in the leaf of the plant, and that only a small amount is obtained from each leaf, the processing and making of indigo dye was one of the most expensive form of dyeing in the medieval world.[27]

I attempted to grow and harvest my own Indigofera tinctoria, but despite several different seed batches from several different suppliers, it refused to even sprout. Perhaps I overwatered it, or the soil was unfavourable. Either way I was unable to obtain a crop this year. Next year I will try to sprout the seeds first in wet paper towel before planting.

Persicaria Tinctoria (Japanese Indigo)

Also known as Polygonum tinctoria,[28] dyer's knotweed,[29] or *tadeai*[30] this variety of indigo is common in Eastern Europe and Asia, particularly the Tokushima prefecture of Japan,[31] where there are still studios that dye using historical methods. The plant matter can be used fresh, dried, or fermented and made into sukumo[32] or aidama[33] to be used at a later date.

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[24] Gösta Sandberg, *Indigo Textiles Technique and History* (Asheville, NC: Lark Books, 1989), 19.
[25] Ibid. 22.
[26] Marco Polo, *The Book of Ser Marco Polo, the Venetian, concerning the Kingdoms and Marvels of the East*, trans. Henry Yule, vol. 2 (London: John Murray, Albemarle Street, 1871), 312.
[27] Leggett, 19.
[28] John Marshall, *Singing the Blues* (Covelo, CA: Saint Titus Press, 2018), 12.
[29] Ibid.
[30] In Japanese - Ibid.
[31] Ibid. 9.
[32] Ibid. 9 - the moist version of aidama.
[33] Marshall, 9. - dried cake made from composted material.

I was more successful in my attempts to grow Persicaria tinctoria than Indigofera tinctoria, as the plant seems to be more forgiving, but still require more leave production in the future to attempt a dye-vat made solely of plant matter. From what I was able to harvest this year, I have begun the process to make sukumo on a very small scale.

Isatis Tinctoria (Woad)

Woad is what was common in Europe before the Europeans discovered Indigofera tinctoria. However, even though it finds the growing conditions in Europe more favourable than true indigo, Isatis tinctoria contains the indigo pre-cursor isatan B as opposed to indican and in much weaker concentrations.[34] It was a common cosmetic, particularly for the Celts[35] and was used as a textile dye by the Anglo-Saxons and Vikings.[36]

I did not attempt to grow my own crop of woad at this time, as I was more focused on true and Japanese indigo, but it would make for an interesting comparison in the future.

Other Varieties

Indican is found in many other plants, such as Indigofera suffruticosa[37], common in the tropical and subtropical areas of the Americas from the southern United States all the way down to Argentina. There is also Indigofera bracteolata[38] from West Africa, Marsdenia tinctoria[39] which is common in subtropical regions like Nepal, Thailand, Burma, and Indonesia, or the other varieties in Japan such as Mercurialis leiocarpa and Strobilanthes cusia[40]. Finally, there is the synthetic indigo that was developed in 1897 and is still produced and used today.[41]

[34] *Indigo and Wood*, PDF, Vancouver: Maiwa Handprints.
[35] A body of a Celtic chieftain was discovered to have preserved tattooed skin and dates to approximately 500 BCE - John Edmonds, *The History of Woad and the Medieval Woad Vat*(Little Chalfont: J. Edmonds, 2006), 12.
[36] Ibid. 14.
[37] Marshall, 11.
[38] Ibid.
[39] Ibid. 12.
[40] Ibid.
[41] Ibid. 13.

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Indigo Dyeing Methods

The Basics

According to a blog post by Maiwa Handprints Ltd.,[42] there are three things you need for an indigo vat: indigo, a base, and a reducing agent.[43] The indigo can come from either the living/actual plant or as a powdered extract. However, in order to utilize the indigo properly, since it is not water-soluble, there needs to be a reducing agent that diminishes the oxygen in the solution, which thereby encourages the indigo to dissolve. A base turns the solution alkaline (as opposed to acidic) and allows the reducing agent to work.[44]

Fermentation Vats

A fermentation vat is an older form of indigo vat in which the "dye-stuff was made soluble in water with the help of micro-organisms [*sic*] and alkaline substances…[t]he bacteria, whose metabolism produced the required reduction, were often assisted with some food-stuff that enhanced their effect, such as sugar, honey, molasses, etc."[45] When using fresh or dried indigo leaves, the leaves themselves contain sugar, though more is often added to promote the fermentation (however, if you add too much you risk the fermentation getting out of hand). When dyeing from an indigo powder, the fermentation can come from a variety of sources including: fruit, madder, or even stale urine. In order for the fermentation to work, it needs to be kept at a consistent temperature of about 40° C.[46] This keeps the microorganisms alive and working to reduce the oxygen within the vat.

Urine Vats

A, historically, very common form of fermentation vat was the urine vat. It has been in use for thousands of years[47] and even Pliny the Elder describes dyeing fabric Tyrian purple in much the same way, as "the liquid is mixed with water and human urine in equal parts, one-half only of the proportion of dye being used for the same quantity of wool."[48] Urine has a tendency to be acidic (with a Ph of around 6[49]), but can be alkaline if the proper foods have been eaten. When urine is allowed to stand for

[42] The natural dyes store in Granville Island, Vancouver BC, considered experts in the field.
[43] "Natural Dyes - About The Organic Indigo Vat," The MAIWA BLOG, accessed September 06, 2018, http://maiwahandprints.blogspot.com/2013/08/natural-dyes-about-organic-indigo-vat.html.
[44] For a more in-depth discussion of the chemistry behind indigo vat dyeing, see Appendix A.
[45] Sandberg, 40.
[46] Ibid.
[47] Ibid.
[48] Pliny the Elder, Natural History, Book 9, Chapter 64.
[49] Sandberg, 139.

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some time, it develops the micro-organisms whose "metabolism produces the ammonia which is a necessary reducing-agent."[50] This does take some time, and some recipes for an indigo dyebath will specify that the urine must be quite old.[51] In later works, even more specifications were noted, such as that the urine must come from men,[52] or as in Cajsa Warg's work in 1762 which states to "take urine, preferably of those who drink strong drinks."[53] However, the pros of this type of dyebath (simple ingredients that are easy to collect), may be outweighed by the cons (smell, and the need to collect urine and keep it for up to several months), depending on the individual. I, personally, chose a different method of fermentation.

Modern Substitutions

There are several opportunities to use modern substitutions in the pursuit of an indigo dyebath if a pure fermentation bath proves too time-consuming or finicky to work with. For the most part, these are chemicals that have been discovered to work as a base or a reducing agent that are not found in nature or were not used historically. These are compounds such as sodium dithionite or thiourea dioxide, both effective reducing agents, or calcium hydroxide (calx) which is used as a base.

It is also helpful to test the alkalinity of the solution with a digital Ph reader to make sure your dyebath is on the correct path. Historically, the alkalinity could have been tested by feel, as the more alkaline a solution, the more 'slippery' it feels.[54]

Dye Vat One

For the first dyebath, I chose to replicate a more modern, chemical vat, while still using natural indigo powder. For the recipe, I followed the one provided by Maiwa, from whom I purchased the indigo powder. The base is calx (calcium hydroxide) and the reducing agent is thiourea dioxide.

Materials

- Calx (calcium hydroxide)
- Thiourea Dioxide
- Indigo Powder
- Rainwater/Distilled water

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[50] Ibid.
[51] Rosetti (1548) *Plictho* - Recipe 43 reads (English translation): "The more the urine is old, the better."
[52] Sandberg, 139.
[53] English translation from Sandberg, 171.
[54] Due to the fact that bases react with the fatty acids in your skin - this is how soap is made ("The Observable Properties of Acids and Bases," ChemTeam, accessed September 06, 2018, https://www.chemteam.info/AcidBase/Acid-Base-Properties.html.).

Method

First the fibers must be scoured to remove any grease, wax, pectic substances or oil. This will help the dye to infuse the fiber evenly. For wool and silk (protein fibers) you can use a gentle soap in warm water, leaving it overnight, and being careful not to agitate the wool so much that it felts. For linen and cotton (cellulose fibers) this is best done with a pot of hot (simmering) water and washing soda, agitated gently and left for at least an hour. The water will turn a yellow-brown, and you can repeat this process as many times as you feel is necessary or until the water remains clear. I only needed to scour the cotton and linen, as the wool and silk I had were sold ‘ready for dyeing.’ When the dyebath was ready, the fibers were put in already damp to provide consistency.

Next, Maiwa recommends mixing a stock solution:[55]

1. Fill a quart size wide mouth mason jar with hot water. Dissolve 1 to 1.5 teaspoons of lye.
2. Add 2 - 4 teaspoons finely ground natural indigo and stir for 2 minutes.
3. Add 1 teaspoon of thiourea dioxide or 2 teaspoons of sodium hydrosulfite and stir for about a minute.

If reduction of the indigo starts properly, the colour of the surface of the liquid should change to a purplish violet with at coppery sheen. Place a lid on the jar and set aside in a warm room (or place in a pan of warm water) for about 60 minutes. The solution will change from an opaque blue to a translucent brown-yellow as it reduces. Check the stock solution to see if it is ready by dribbling some solution on the side of a white cup. Note the change from clear yellow to opaque blue as the indigo is reintroduced to the oxygen in the air. At this point the stock solution may be used or kept up to a week. If kept longer the solution may need to be revived. Heat gently to about 50°C (120°F) and add some more reducing agent (thiourea or hydrosulfite) and stir well.

Then it’s time to prepare the vat itself:

1. Put 5 gallons of hot water 110-140°F (45 - 60°C), in a plastic pail or garbage can.
2. Add 1/8 teaspoon of lye into the water and stir until dissolved. This makes the vat slightly alkaline so that the reduced indigo from the stock solution does not re oxidize when added.
3. Add 1/2 teaspoon of detergent. This will help the indigo penetrate the fiber and will break up oxidized indigo on the surface of the vat.
4. Add 1 teaspoon of thiourea dioxide or 2 teaspoons of sodium hydrosulfite and stir gently until dissolved. Cover the vat and allow it to reduce for about 15 minutes. 5. Carefully lower the jar of stock solution into the vat and pour out the contents (avoid pouring from above as this adds

[55] The following instructions are from *Indigo and Woad*, PDF, Vancouver: Maiwa Handprints.

oxygen). Use all the stock solution for cotton or half for the same weight of wool. 6. Stir gently and allow 30-60 minutes for the vat to turn yellowish green.

Finally, the scoured fibers can be added to the dyebath. They will be submerged and agitated slightly in order to facilitate dyeing as evenly as possible. Then the fiber is left for an amount of time, in this case I opted to let the fiber dye for 10 minutes. For a much lighter shade, the dyeing time can be drastically reduced, with an immediate rinse upon removing the fiber from the dyebath.

The product is then removed from the dyebath carefully, in order to prevent oxidizing the bath more than necessary, and any excess liquid is squeezed out (preferably while still submerged). The fibers are allowed to oxidize for 30 minutes and can be dyed again if required. The only fiber I put into the dyebath for a second time was the cotton, as it required more time and more dye to reach a shade similar to the wool, silk, and linen.

When the dyeing process is finished, the product is left to oxidize and dry for 24 hours. If a darker shade is desired, the process may be repeated (without the need to scour the fibers again) as many times as necessary. Once happy with the results, the fibers are washed and rinsed.

Challenges

The main challenge with a chemical dyebath is the proportions. By following a recipe developed by experts in the field, I was able to easily create the conditions needed for the indigo to work properly, but to guess at the proportions would be difficult. Once the vat was showing the ideal conditions, it was easier to adjust it to maintain those conditions. It was also difficult to start from a stock solution and transfer to a vat, as I was working in a space that was smaller than I would have liked

Results

The dyed fibers were all very consistent in colour, and brighter than I anticipated, though the cotton needed a second dye to reach that same level.

100% Merino wool
Worsted weight

100% silk
Lace weight

100% Cotton
4 ply of 8/2

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100% linen
2/4.8 NM

Dye Vat Two

For the second dyebath, I chose to attempt a fermentation vat made with natural indigo powder. For the base, I used soda ash; for the reducing agent, I used a combination of madder and wheat bran; and I made sure to use collected rainwater, topped up with distilled water when I needed more.

Materials

- Wheat Bran
- Soda Ash
- Madder
- Indigo Powder
- Rainwater/Distilled water

Method

For this vat, I applied a slightly less scientific, but a more historically accurate method. Instead of following an exact recipe, I used a recipe as more of a guideline and as a place to start, adding more ingredients as required. Fermentation vats are, by their very nature, fluid and difficult to maintain and therefore a recipe cannot be considered a way to achieve a perfect vat each and every time. As such, I am unsure of exactly how much of each ingredient I used in the end.

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First the fibers (cotton and linen) were scoured as per the method in Dye Vat One. The wool and silk were purchased ready for dyeing and did not need to be scoured. Again, the fibers were damp when they were added to the dyebath.

Then I followed a recipe from Sandberg's *Indigo Textiles* that appears to be a translation from a book from 1759:

> - with which you can dye blue
> wool, linen and cotton
> from: An honest and reliable dye-book 1759
>
> Take a wooden vessel large enough for 8 jugs of water; then take a copper-kettle, into this pour 7 jugs of water and 8 weights of coarse madder, a stoup of bran, 1 pound of grey potash, allow the kettle to come to a boil and let it boil for a quarter of an hour, then pour it into the firkin in which the dye shall be, lay something over it so that it keeps warm; take 4 weights of Indigo in a small pot with a quarter of a gallon of water, 4 weights of potash, allow it to boil for half an hour, while it is boiling pound gently on the bottom of the pan with a pestle so that the indigo becomes as fine as powder, when it is boiled, take the pan off the fire and allow it to cool somewhat, and also pound evenly so that the indigo becomes truly small, then pour from the firkin what is clear and with the pestle pound the thickness on the bottom of the pan until it becomes quite fine: then pour all into the firkin and rinse the pan clean, and stir well the content of the firkin and allow it to stand 12 hours, then stir again, and so continue until 24 hours have passed, then the dye is ready to dye.
>
> NB All woollen yarn that is to be dyed blue must first be washed in warm water and dyed wet. But linen yarn is dyed dry. All cotton yarn is boiled for half an hour in pure water and dyed wet.
>
> 1 jug = 2.6 litres
> 1 weight = 13.3 g
> 1 stoup = 1.3 litres
> 1 pound = 425 g
> 1 bucket = 49 litres[56]

[56] Sandberg, 170.

I used that recipe in conjunction with the following, similar one from a website that allowed me to substitute some of the ingredients and measurements:

> - 4 oz. ground Indigo
> - 2 oz. ground Madder
> - 2 oz. wheat bran (buy at any health food store)
> - 12 oz. washing soda ("soda ash")
>
> Combine these ingredients in about a three gallon pot of warm water. Always add these amounts in proportion. A larger vat can be made, for example with: 1 lb. ground indigo, 1/2 lb ground madder, 1/2 lb ground bran and 3 lbs washing soda in about a 10 gallon plastic tub. However, I advise starting small, till you are comfortable with the process. The size of the pot is determined by the amount of fibre you need to dye at one time. A three gallon pot is good for yarn skeins of 4 to 6 oz., while a 10 gallon or larger tub will be needed for yards of fabric.
>
> WARMTH: It is necessary to keep the vat warm, but not hot, around 100 - 110° Fahrenheit. It is the same temperature for raising bread or making yogurt. It should feel pleasantly warm to the hand.
>
> To keep it warm, a light bulb in a reflector can be put under the vat, with a blanket over it to keep in the heat. (See illustration, next page.) In a warm climate no additional heat is needed, but be sure the vat is out of direct sun so it does not overheat.
>
> TIME is very important. It takes time for the vat to ferment and it does no good to try to rush the process. The first time, it takes about a week for the vat to ferment and be ready to dye. With "renewals" the time needed is a bit less, four or five days.[57]

In the end, my measurements were likely not the same as stated here. I started with the ingredients and measurements in the second recipe (as I was working on a smaller scale), and then tested the Ph of the solution and adjusted as necessary. Once the indigo was added, it became easy to tell whether the vat was ready simply by immersing something (a length of yarn, or a finger) to see if the dye would stick to it. This particular vat never attained the look of the chemical vat, but it seemed to work fine all the same.

Once the vat was set, I dyed each of the fibers for approximately 10 minutes, same as with the chemical vat, and then I let them oxidize. The cotton, again, was the only fiber that needed a second 10 minutes in the dyebath to obtain the same colouring. They were then left to dry.

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[57] "Indigo Natural Fermentation Vat," Aurora Silk, accessed September 10, 2018, http://www.aurorasilk.com/tutorials/how_to_natural_indigo_dye_vat.html.

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Challenges

There were several challenges with the fermentation vat - namely, getting the fermentation started. As I live alone and did not wish to risk burning my house down, I was unable to maintain a situation where the vat could remain at a high enough temperature to keep the fermentation process active, despite trying many different methods. As such, I did end up needing to jump-start the fermentation by adding a small amount of a chemical reducing agent (thiourea dioxide). This quickly set the vat in order and allowed me to proceed with dyeing the fiber.

Results

The results of this vat were interesting. The colour was a much darker and duller blue than the chemical vat, possibly due to the addition of madder as a fermentation agent. Since the madder did not ferment as anticipated, it may be that the colour dissolved in the water and mixed with the indigo to obtain this different shade. In addition, when the yarn was withdrawn from the dyebath, it oxidized much faster than the indigo from the chemical dyebath. The final interesting difference was that the fermentation dyebath never took on the coppery sheen like it was 'supposed' to, yet it dyed perfectly well.

100% Peruvian Highland Wool
Worsted weight

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100% silk
Lace weight

100% Cotton
4 ply of 8/2

100% linen
2/4.8 NM

Conclusion

Indigo is complicated. From the basic chemistry behind indigo's behaviour, to the intricacies of a fermentation vat, that is the crux of what I learned with this experiment: indigo is complicated. By comparing and contrasting two different indigo vats over four different types of fiber, we can see that there is quite a difference between a modern chemical vat and a (mostly) historical fermentation vat, not only in the results that were produced, but in how the vat behaved. Granted, some of those inconsistencies can be explained by a modern inability to perfectly recreate a medieval setting, but you would still expect some similarities in how the vats functioned.

In the future, I would also like to experiment with vats made with fresh or dried plant matter from the indigo-producing plants, or even to include woad as a contrast to the true indigo I used here. The foundation for obtaining indigo straight from the plant matter is the same as from indigo powder, but it would be interesting to see if and how the results are different.

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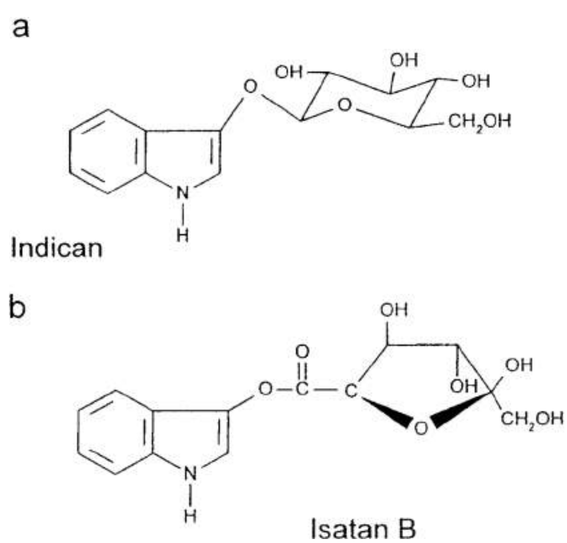
Appendix A: The Chemistry of Indigo

While indigo's chemistry is known and utilized today, it is unknown whether dyers in pre-17th century Europe and Asia knew exactly why indigo acted the way it does. It is more likely they learned how a dye vat was 'supposed' to look, feel, or smell, passing traditions down for hundreds of years after many trials and mistakes were made. However, as the science behind it is fascinating, and explains why dyeing with indigo can be difficult, I opted to include it here.

Indigo begins as a molecule known as 'indican' (in Indigofera tinctoria and Persicaria tinctoria, but the indigo precursor in woad is isatan B);[58] however, it is actually the molecule 'indoxyl' that is able to penetrate the fiber within the indigo vat. When the indoxyl is exposed to oxygen outside of the vat, whether or not it is attached to a fiber, it forms bonds and becomes indigo.

Below are the skeletal formulae of these molecules. Skeletal formulae are common in organic chemistry and look quite bare as they simply show the carbon 'skeleton' without the requisite hydrogen atoms attached. However, they enable us to briefly glance at multiple molecular structures and see how they are similar. I have also included each molecule's molecular structure.



[59]

Indican ($C_{14}H_{17}NO_6$) is what is called a glucoside,[60] or a glucose molecule that is bound to another molecule, in this case, indoxyl.

Isatan B ($C_{14}H_{15}NO_6$) is also a glucoside, just with a slightly different molecular composition. It has the exact same indoxyl molecule attached to a different sugar molecule.

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[58] "Indigo: Recreating Pharaoh's Dye," Science in School, accessed September 06, 2018, https://www.scienceinschool.org/2012/issue24/indigo.
[59] K. G. Gilbert et al., "Qualitative Analysis of Indigo Precursors from Woad by HPLC and HPLC-MS," *Phytochemical Analysis* 11, no. 1 (2000): 18, doi:10.1002/(sici)1099-1565(200001/02)11:13.0.co;2-x.
[60] Glucosides are subsets of glycosides. A glycoside is a molecule in which a sugar is bound to another functional group via a glycosidic bond. A glucoside is when that sugar is specifically glucose.

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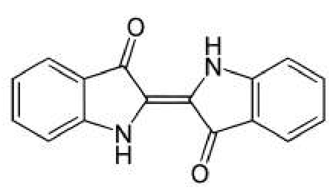
When starting with fresh indigo or woad leaves, obtaining indoxyl is easy: just remove the glucose molecule. This is done through a process called hydrolysis,[61] and can be done naturally or chemically. While there are a variety of ways to achieve this chemically, it can be done organically in a fermentation vat, where the yeasts from the fermentation will eat the sugar molecules, leaving behind the indoxyl dissolved in water. Then the indoxyl can be used to dye fibers or precipitated[62] out to form powdered indigo.

[63]

This is an indoxyl molecule (C_8H_7NO).

Once indigo is in its powdered form, it is stable and can be traded or shipped, but it is no longer water-soluble. The indigo must be converted back into a water-soluble form in order to use it as a dye.



[64]

This is an indigo molecule ($C_{16}H_{10}N_2O_2$).

This is where the dyeing process can get tricky. In order to achieve this reduction, an alkaline vat and a reducing agent are needed. The reducing agent provides electrons that are able to bond with the excess oxygen to form alcohols, which are water-soluble. This also leads to an excess of hydrogen ions.[65] When there is an excess of these ions in a solution, that solution is said to be acidic. By providing an

[61] The chemical breakdown of a compound due to reaction with water.
[62] To create a solid from a solution.
[63] "Indigo-a-go-go: Better Dyeing through Chemistry," Sheep Cabana, accessed September 06, 2018, http://www.sheepcabana.com/?p=1180.
[64] "Indigo-a-go-go: Better Dyeing through Chemistry," Sheep Cabana, accessed September 06, 2018, http://www.sheepcabana.com/?p=1180.
[65] H^+ ions, or simply just the hydrogen nucleus with no electron.

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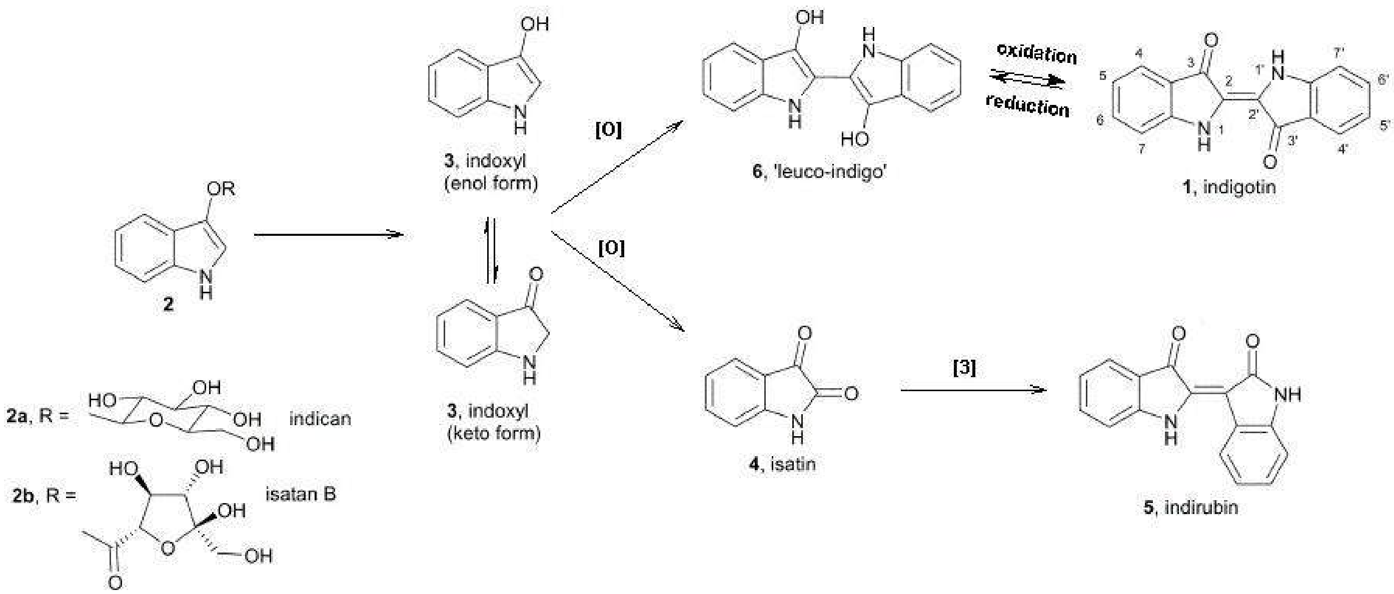
alkaline solution to begin with, one that has an excess of OH ions,[66] the solution will balance out through the production of sodium salts and water.



[67]

Indican/Isatan B becomes indoxyl (2 forms), which then becomes leuco-indigo[68] and finally indigotin[69] when introduced to oxygen
Alternatively, the indoxyl can become isatin[70] and indirubin[71] through a slightly different reaction

For example (using urine):

$(12\ C_{16}H_{10}N_2O_2(s) + (C_6H_{12}O_6(aq)) + 9H_2O(l) + (CH_4N_2O(aq)) = (12\ C_{16}H_{10}N_2(OH)_2(aq)) + (7\ CO_2(g)) + (2\ NH_4^+) + (2\ OH^-)$[72]

Indigo (solid), plus glucose (aqueous), plus water (liquid), plus urea (aqueous) equals leuco-indigo (aqueous) plus carbon dioxide (gas) plus ammonium hydroxide (the $NH_4^+ + OH^-$)

[66] OH^- or hydroxide, an oxygen and hydrogen atom held together by a covalent bond that carries a negative electric charge.
[67] "Unit - Chemistry of Textiles: Dyeing Fibres," accessed September 06, 2018, http://wwwchem.uwimona.edu.jm/courses/CHEM2402/Textiles/Dyeing_FibresJ.html.
[68] AKA indigo white - for the fact that it is colourless in an alkaline solution.
[69] The chemical in indigo that produces the blue colour.
[70] A reddish-orange crystalline compound made by oxidzing indigo.
[71] A chemical compound most often produced as a byproduct of bacterial metabolism.
[72] Extrapolated from "Chapter 12: Dyes," Caveman Chemistry : Hands-on Projects in Chemical Technology, 12.2, accessed September 06, 2018, https://www.cavemanchemistry.com/cavebook/chdye2.html.

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To break it down into its component parts:

$C_6H_{12}O_6(aq) + 6\ H_2O(l) = 6\ CO_2(g) + 24\ H^+ + 24\ e^-$
Glucose is oxidized into carbon dioxide and hydrogen ions with free electrons

$12\ C_{16}H_{10}N_2O_2(s) + 2\ H^+ + 2\ e^- = 12\ C_{16}H_{10}N_2(OH)_2(aq)$
Indigo takes some of those hydrogen ions and free electrons and becomes leuco-indigo

$CH_4N_2O(aq) + H_2O(l) = CO_2(g) + 2\ NH_3(g)$
Urea plus water is converted by the bacteria into carbon dioxide and ammonia

$2\ NH_3(g) + 2\ H_2O(l) = 2\ NH_4^+(aq) + 2\ OH^-(aq)$
Ammonia is soluble in water and deprotonates[73] a small amount of the water to obtain ammonium and hydroxide

While the above equation is balanced, it is not perfect, as the amount of ammonia that converts into ammonium (NH_4^+) and hydroxide (OH^-) depends on the Ph of the solution, which is also dependent on how much ammonium (acidic) versus hydroxide (alkaline) there is. If another alkaline ingredient, such as sodium hydroxide or washing soda, were used, the by-products of that reaction would be different. Not only that, but fermentation itself can create by-products that alter the equation. So this particular version is not as important as the basic idea behind the equation: that combining these ingredients causes a chemical reaction to occur, and that due to this reaction, hydroxide and hydrogen ions will form and solid indigo will be changed to leuco-indigo.

Eventually, the reducing agent gets used up and the sugar gets turned into an acid, therefore no longer reducing the oxygen in the vat and changing the overall Ph back towards neutral and halting the fermentation.

This is part of why it is so difficult and exacting to create and maintain a fermentation indigo vat, and why it is so impressive that peoples from pre-17th century societies figured it out. Everything needs to remain in balance so that the correct chemical reactions can occur.

[73] The removal (transfer) of a proton.