Indigo (substantive vat dye)

Recipe for a 7 Gallon Indigo vat

Supplies needed

Indigo (natural or non-synthesized)	Thiourea dioxide (Thiox)
Lye	Synthrapol or other textile detergent
Soda ash	*Large 7 gallon vat
One quart mason jar with lid	Wooden sticks for stirring
Rubber gloves	Scissors

*I use a plastic trash can (kitchen sized) for this, measure off 7 gallons and mark it on the side. Choose a trash can with as narrow a top opening as possible. This means less oxygen introduced over time. If you can find one with a close fitting lid, that will work well. If not, a towel clamped over the top will also work.

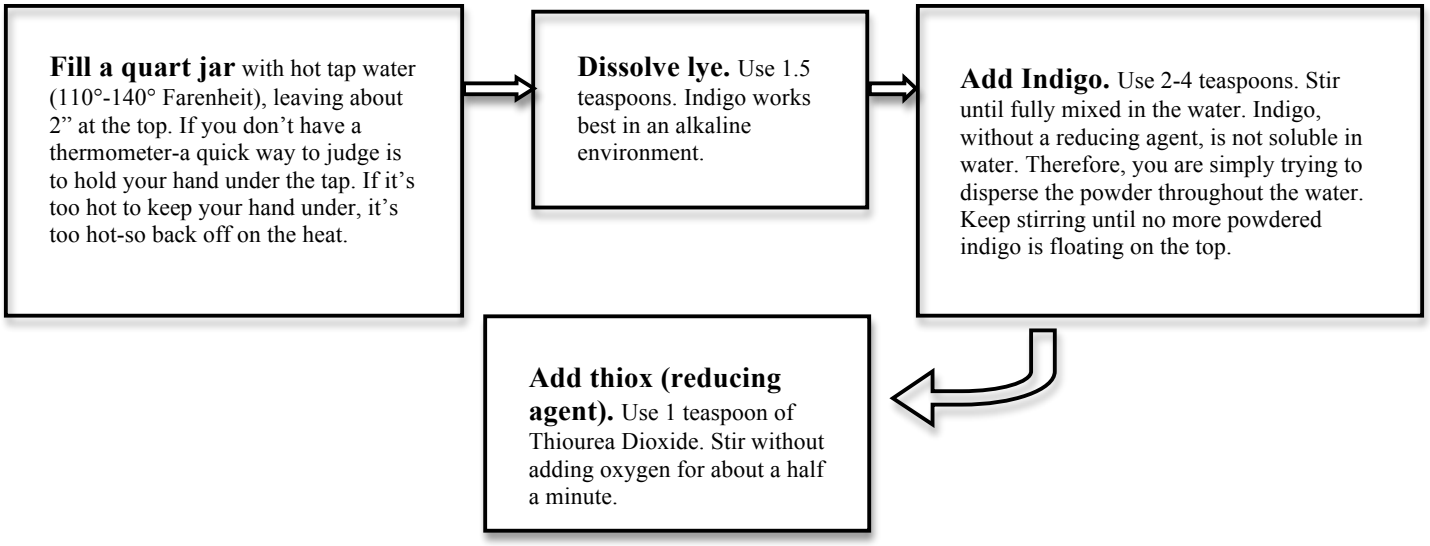
SAFETY CONCERNS:

CAUTION! Wear a mask when possible to avoid inhaling lye, thiox or the dye itself!! Keep vats in VERY well-ventilated places!

Search the web for MSDS (Material Safety Data Sheets) information on indigo, thiox and lye. It's good practice to read and keep MSDS copies (Label a Notebook for this purpose!) on every chemical in use during dyeing. In case of an accident, these sheets help you understand the safety issues and proper disposal methods for chemicals. Please DO read them in advance of working with the chemicals.

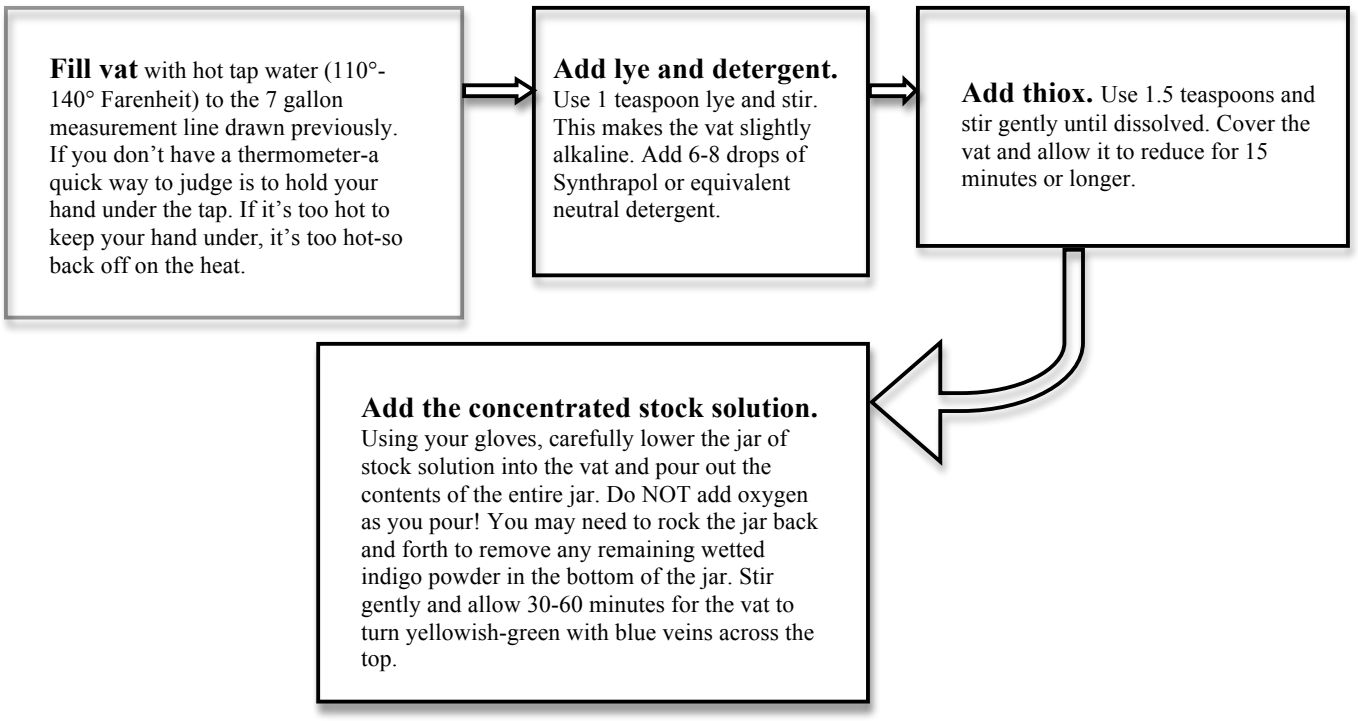
FLOWCHART for preparation of the stock solution: (Do in advance of using-at least 60 minutes)

Prior to dyeing, a stock solution must be made. It may be used right away or stored. In either case, be sure NOT to shake the jar.



Cap the jar tightly and set aside in a warm water pan for an hour. As the indigo becomes reduced, a coppery sheen will develop on the top and the solution will change from an opaque blue to a translucent brown, yellow green. If you don't get reduction right away, the stock solution may need to develop longer. Once reduced, the stock solution can be used now or kept for an extended period. If you store the jar, some oxidation will occur over time, allowing the indigo to settle in the bottom. To reverse this, heat the jar in a water bath, stir gently and add more thiox if needed.

FLOWCHART for preparation of the vat:



Dyeing in the vat:

1. Add wetted, scoured fabric to the vat carefully, avoiding splashing and air bubble accumulation.
2. With rubber gloves on, work the fabric through the vat gently allowing about 3-10 minutes for this first dip. Be sure you get 100% penetration of the vat liquid onto the fabric.
3. To remove the fiber from the vat, squeeze the fiber out underneath the indigo-laced water as much as possible. Press the fiber against the side of the vat and remove without dripping into the vat. Open the fiber up as much as the design allows and expose it to the air. The color change will go from yellow-green to blue. Allow the fabric to completely oxidize before re-dipping. If green is still on the cloth, complete oxidation has not taken place. Many sources recommend at least 30 minutes of oxidation time.
4. Successive re-dippings darken the shade. To demonstrate how darker shades are achieved and to test the strength of the vat, use your scissors to cut a strip off of the fabric and redip the remaining fabric, continuing to do this each time you dip in the vat. This is a good way to track how many dips it might take to get the shade you desire.
5. After you have achieved the desired shade and allowed 24 hours for final oxidation, rinse in water with a pH neutral detergent like synthrapol. However, expect to lose some indigo during this process. You can add a teaspoon of vinegar to help bring the cloth back closer to neutral, too. Finally, rinse well until the water runs clear, ring out (gently with rayon) and dry. The piece can then be washed normally.

Keeping the vat active over time and/or discarding the vat:

If you desire to keep your vat active for some time, purchase an aquarium heater to keep the temperature somewhere around 70°-80° Farenheit. If possible, add boiling water to the vat to raise the temperature just prior to dyeing. However, take care not to raise the temperature too high (110°-140° Farenheit). If a blue green reduced color is not visible, you may need to add more thiox OR adjust the pH up or down (using lye for up or vinegar for down). A typical vat pH is between 9-10, which is quite a bit of difference since pH is a logarithmic scale. However, I find vats work well in this range.

If you will not use the vat again, make sure that indigo in the vat has been completely used up OR fallen out of solution. You can encourage oxidation of indigo by simply vigorously stirring the vat. Leave it for a few days for all indigo to fall out of solution into the bottom of the vat. Pour off the water into a drain OR onto a grassy substrate, using a different location each time. Take care that your vat is not at an extreme pH (11-12) when you do this or you may be killing off organisms as you dump it. If so, dial the pH down with the addition of vinegar. I do NOT recommend this for large scale dyeing houses. However, for a hand dyer who does not do large scale work, this method is acceptable. Also, you may notice indigo grains in the vat as the water is poured off. I have kept those after drying and reused them!

Indigo background (written specifically for South Carolina teachers)

Natural, non-synthesized indigo was known and used several thousand years before the start of the Christian era. Many different cultures used indigo as a dye. With the possible exception of iron buff and tannins, indigo has probably seen longer continuous use than any other dyestuff.

Well over 20 species contain the precursor molecule that becomes indigo upon fermentation and oxidation. These species are members of at least five different plant families, the most well known being the Fabaceae or pea family. Natural indigo can be obtained from indigo bearing plants, the most significant ones being *Indigofera tinctoria* and *Indigofera suffruticosa*. These plants grow wild and are in cultivation in Asia (chiefly India) and South American, respectively, though they have been grown worldwide. South Carolina has a naturally occurring Indigofera species (*Indigofera caroliniana*) that was used as dyestuff in the 18th century, though it fell out of favor rapidly.

Eliza Lucas Pickney is most often credited for creating a market for indigo from South Carolina during a boom period between 1740-1790 and she certainly played a major role. Of course, Pickney did not achieve this alone. Recent research indicates significant contributions by enslaved peoples. Certainly, West African peoples are skilled dyers and many enslaved Africans arrived in the New World from this region. It is not known if slave traders sought out people with these skill sets, as happened with rice.

The economics of the crop literally transformed South Carolina. This was partly due to a bounty paid by the English. Indigo was grown throughout the state. However, in the lowcountry, growers had the option of growing both rice and indigo in the lowland and upland areas of the land, respectively.

The plant material does not contain the blue dye directly, but instead produces a colorless glucose-based substance called **indican** (and other chemical precursors are found that are specific to species). When the plant is fermented, a bacterial enzyme consumes the glucose leaving **indoxyl**. Several anaerobic bacteria species have been found to naturally occur in indigo vats. As molecules of indoxyl leave the plant and become suspended in water, a dimer of **indigotin** is formed. Indigotin is soluble in water. To retrieve the indigo from this solution, lye was added to create an alkaline environment. The water was then beaten to add oxygen in the vat. At this stage, the indigo is insoluble in water and falls out of solution to the bottom of the vat. As the top water is drained off, the indigo mud is formed at the bottom and can be dried, ground and used later. This is the procedure that was used in the 1700's to form indigo cakes for shipment to England.

Indigo must be chemically reduced before it can be used in dyeing. As ground indigo is added to an alkaline vat with a reducing compound (Thiourea dioxide, hydrosulfite, diothionite or others), the compound is called **indigo white or leuco indigo** which quickly transforms into a soluble salt compound. When the fiber is immersed in indigo vats, which is amber to yellowish green, it will be penetrated by the soluble indigo white. When the fiber is removed from the vat into the air, the indigo white salt compound exchanges its bond with the salt for a bond (van der Waals forces) with the fiber as it oxidizes into the familiar blue indigo form. From here, it remains in relative permanence lightly bound into the fiber. However, in the case of cellulose fibers, indigo doesn't penetrated a single fiber very deeply. It mostly attaches to the frayed edges of cellulose microfibrils. Microfibrils are multiple cellulose strands wound into a cable-like structure. Thus, when blue jeans fade, it is likely because of the loss of some indigo, but also because friction has exposed the inner parts of the cellulose microfibril which are still white.

Animal, plant and some synthetic fibers can be dyed with indigo. However, all cloth must go through a chemical treatment (scouring) prior to dyeing to 1) help the fiber become slightly frayed so that the molecule can enter the fabric more easily; 2) remove any surface chemical treatments. Most clothing/fabrics that are purchased come with surface treatments to help them look less wrinkled, more polished and therefore, more marketable. These treatments can spoil an indigo vat in a hurry, as the reaction is dependant on pH and a reductive environment.

Some questions to think about:
Why do repeated dips in the vat result in darker dyes? *Hint: Think about the movement of molecules in solution from higher to lower concentration.*
Why do blue jeans fade? *Hint: Think about the strength of van der Waals forces and the structure of cellulose and cellulose microfibrils*
Why is indigo blue? *Hint: Think about absorption spectra*
What other types of reduction/oxidation reactions are found in nature? *Hint: Think mitochondria and chloroplasts*
What does the glycosidic indican do for the indigo plant? *Hint: Think pest control*