Chemistry of Indigo

Indigo is extracted from plants such as Woad (Isatis tinctoria, a member of the Cruciferae, related to cabbages) and Japanese Indigo (Polygonum or Persicaria tinctoria, a type of knotweed) in addition to “true” Indigo, Indigofera, a member of the Leguminosae (related to beans and peas) that has several species, including tinctoria and suffruticosa. In fact many plants will yield indigo, but only a few yield it in sufficient quantity to be of any use in dyeing.

Indican, the compound that yields indigo blue, is a glycoside: a sugar (in this case a form of glucose) bound to another molecule, indoxyl. When the glycosidic bond is broken, the indoxyl is freed. When the indoxyl compound is oxidised, it becomes blue: indigo blue.

The indigo-bearing leaves are harvested. In Japan the Indigo leaves are dried in the sun and stored for later use. Elsewhere the leaves are then physically damaged – chopped, pounded or trampled – presumably to release larger quantities of indican. This is the point at which woad was traditionally made into balls of leaf matter and dried for easier storage and transport. In West Africa the pounded leaves might also be dried and stored at this stage. Alternatively (in West Africa and elsewhere) the mass of fresh leaf material might be fermented; in Japan the dried leaves are later moistened and fermented; in Europe the woad balls are moistened and fermented (a process known as couching). In other words, bacteria are encouraged to consume the glucose in the indican, leaving the indoxyl molecules as highly reactive free radicals. The bacterial breakdown of glucose may be an aerobic process in which the bacteria consume oxygen, creating the reducing (low oxygen) environment necessary for the next stage of the process, or an anaerobic process in which the bacteria release hydrogen that acts as a reducing agent in the next stage.

The indoxyl free radicals bind to each other to form indigo. If an alkali is present (pH is above neutral), this takes the form of water-soluble leuco-indigo (leuco means white), also known as white indigo or white indigotin. The “white” refers to the compound’s relative lack of color: the leuco-indigo solution is a clear yellow or yellow-green. This is the form in which indigo dyes, so at this point it is possible to convert the fermentation vat to a dye vat, or to continue the process to extract indigo from the solution. Extraction is simply a matter of converting the soluble leuco-indigo to its insoluble blue form by adding oxygen: straining the fluid off the leaves, then pouring it back and forth between two containers may be sufficient, after which the blue particles of indigo can then be filtered out of the liquid.

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How does indigo dye?

Water carries the soluble form, leuco-indigo, as it soaks through the material in the vat. When the material is exposed to the air (or another source of oxygen such as well-oxygenated water) the leuco-indigo oxidises to blue indigo particles that physically lodge in the material. Unlike many other dyes, the particles are not chemically bound to the material, just wedged into cracks and crevices. This means that dense, smooth materials or those that are not easy to wet will not hold a lot of dye or will not be easy to dye. Indigo is one of the most light-stable natural dyes, but the way in which it dyes means that materials dyed with indigo “fade” in two ways: as particles of indigo are dislodged and fall away from the material, and as the dyed material itself wears away to reveal undyed material. Taken together, these largely explain the classic fading of denim.

Making leuco-indigo: reducing the vat to remove oxygen:

Whether they’re based on synthetic or natural indigo (including plant material that contains indigo), all indigo vats work on the same basic principle: convert the blue indigo into soluble leuco-indigo, then allow that solution to penetrate the material to be dyed. As leuco-indigo only maintains that form in the absence of oxygen, the vat must be reduced (the oxygen removed) in some way. Traditional vats use bacterial fermentation: the vats contain organic matter on which bacteria feed, such as the nutrients in urine, rice bran, the plant material that contains the indigo compounds, or even the skin flakes, sweat and manure held in a sheep fleece. Chemical vats use raw chemistry - compounds, including sodium hydrosulphite or thiourea dioxide, or reducing sugars, such as fructose - to remove oxygen from the vat.

pH – the acidity or alkalinity of the vat – is important, as the conversion to leuco-indigo requires an alkaline environment. It’s easiest to predict and maintain in a chemical vat, with recipes calling for measured amounts of lye (sodium hydroxide) or washing soda/soda ash/soda crystals (sodium carbonate) or calc (calcium hydroxide, a.k.a. slaked lime). It’s just as important in a biological vat, but much trickier to maintain because the fermentation process produces byproducts, such as lactic acid, that lower the pH. Dyers in the past learned to manage their vats by tasting the fluid or feeling it between their fingers, trying for something that’s slippery (alkaline), but not too slippery.