Sustainably Reduced Indigo and Woad Dye Application with Porcupine Quills

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Literature Review. The fashion industry uses large quantities of water, fuel and various chemicals in the manufacturing process (Desore & Narula, 2018). Over a third of chemicals, some are nonbiodegradable and potentially carcinogenic, can be linked to textile dyeing (Thiry, 2011; Manzoor & Sharma, 2020). Exposure to such compounds can lead to respiratory issues and skin irritation for consumers (Manzoor & Sharma, 2020). Awareness of potential health and sustainability issues are prompting interest in natural dyes for textiles (Haar et. al., 2013).

Woad and Indigo share indigotin as a coloring compound. However, indigotin is not immune to sustainability concerns. Strong reducing agents, such as sodium dithionite (hydrosulfite, $Na_2S_2O_4$), as well as alkaline conditions in the dyeing vat are needed (Kombonchoo et. al., 2009). $Na_2S_2O_4$, is most commonly used with indigo due to its ability to quickly reduce color and ability to provide a stable dyebath (Saikhao et. al., 2018). However, there can be unstable in alkaline solutions at elevated temperatures and have toxic, corrosive sulfite and sulfate ion reaction by-products (Saikhao et. al., 2018; Blackburn et. al., 2009; Meksi et. al, 2012).

Woad, or *Isatis tinctoria*, is a native plant to Eurasia, now a noxious weed in North America, and a source of blue dye (Britannica, 2015; Washington State, 2023). Historically important as a source of blue dye in Europe, woad contains indigotin, and must be reduced to its soluble, leuco form in order to be used to dye textiles (Edmonds, 1998). The methods can be nearly identical to those used for indigo, including sodium dithionite and strong alkali agents (Edmonds, 1998).

Indigo, *Indigofera tinctoria,* remained the critical source of this blue dye and an important industry in India, up until the beginning of the 20th century (Petruzzello, 2016; Schwarcz, 2019). As synthetic color equivalent dyes gained prominence, they largely displaced natural dyes. Natural indigo dye managed to maintain a small market share. For millennia, indigo was rare and exceptionally valuable, driving the development of global trade networks (Mayes, 2023).

Every culture active in producing textiles has found a source of indigotin, a water insoluble compound which must be reduced in an oxidation reduction chemical reaction to yellow leuco form using various agents under alkaline conditions (Edmonds, 1998; Komboonchoo et. al., 2009; Saikhao et. al., 2018). Once material is introduced to the reduced form, it is re-oxidized during air exposure, which converts the leuco dye back to the water-insoluble indigo, trapping the color in the material's fibers (Saikhao et. al., 2018). Though more recent research has explored sustainable reducing agents for indigo (Saikhao et. al., 2018), less work has investigated woad outside of fermentation reduction (Osimano et al., 2012).

Porcupine quills are a complex material, often coming from the North American porcupine. These white quills are composed of keratin protein. The hard nature of the quill is the highest at the inner quill layer (Chou et al., 2012). This multidimensional structure will likely impact the amount of dye saturation of the quills. Quillwork is one of the oldest forms of Native American embroidery in which porcupine quills are soaked to make them more pliable and then flattened before the application of dye (Museum of Native American History, 2023). Few sources exist describing the dye and dyeing procedures used to color the quills (Cole & Heald, 2010). Studies that have examined dyes and mordants present in Native American textiles have found the presence of trace amounts of copper and tin metallic mordants, goldthread for yellow color, alizarin or purpurin for red. Some had traces of carminic acid from cochineal, and indigotin was in the majority of blue or purple quills (Troalen, 2013; Cole & Heald, 2010). The present research explored coloration options with blue natural dyes for porcupine quills.

Experiment Methodology. The quills that were used in this study were obtained from *The Wander Bull LLC*, a family owned and operated Native American Craft Supply, Antique and Art store. Quills were in a natural state. Quills were prepared for dyeing by putting the quills into a simmering (180 F) container of distilled water for 30 minutes, stirring every 5 to 10 minutes. Quills were then put into the dyebaths. Indigo was purchased from Maiwa and Woad from YarnTreeUSA. Dyebath conversion took place through the addition of a sodium hydroxide alkali agent from Fisher Scientific to adjust the dye vat ph to 10.5 before the introduction of one of three reducing agents, thiourea dioxide (TD), fructose (F) or glucose (G). Distilled water was heated to 50 degrees C and had 25% weight of dry quills was dye powder, 12g/l of sodium hydroxide and 1.33g/l of thiourea dioxide added and thoroughly mixed. Alternatively, 10 g/l of fructose or glucose were used as sustainable reducing agents. The liquor ratio of dyebath solution to dry goods was 50:1. After reduction, the dyebath was heated to 30 C, and the quills were added for 20 minutes. Quills were then exposed to the air for 60 minutes. This was repeated 2 times. Quills were cooled slightly and lanolin was applied to the surface to prevent cracking.

Results. *Colors Simulations*

Natural *Indigo TD* *Indigo F* *Indigo G* *Woad TD* *Woad F* *Woad G*

Two evaluators rated the conditioned samples in a light box set to daylight setting using either the AATCC EP-2 Staining Scale for Color Change or AATCC EP-1 Grey Scale for Color Change, using .5 rating gradations. *Colorfastness to Crocking*: Dry and wet crocking evaluation was done in accordance to AATCC 8. For each of the reducing agents, woad performed better, on average, in wet and dry crocking than indigo. Values for wet and dry crocking in the wood samples ranged from 4 to 5, while values for indigo ranged from 3 to 4.5. *Colorfastness to Artificial Light*: AATCC 16.2 was used as an evaluation guide with a custom built light exposure device modeled after Australian test method 2001.4.21. Samples were mounted in the circular lamp and exposed to continuous light for 72 hours. Additionally, Woad and Indigo samples ranged from 4 to 5, indicating good to excellent colorfastness. For both Woad and Indigo, all samples reduced with thiourea dioxide scored a 5. *Colorfastness to Laundering*. AATCC 61-2013 Test No. 1A was used. Samples were air dried. All Indigo and Woad samples scored 4 to 5, with all Woad samples reduced with thiourea dioxide scoring a 5.

Conclusion. Both Indigo and Woad showed sufficient colorfastness to crocking, light exposure and laundering when reduced with the sustainable compounds used in this research.

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