AN ON-GOING MYSTERY: COPPER KETTLES & CHILKAT BLUE

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ABSTRACT—While there had been reports by explorers and traders about the North West Coast native peoples for centuries—by the Spanish, the Russian (in French), by Canadians and American, Lt. Emmons stationed in a frigate in Alaskan waters took extensive notes about what he saw, the language, and customs of the Tlingit people. His curiosity led him to ask about the source of the dyes; his is the first popularized description of the dyeing. Inorganic and organic analysis of the Chilkat blue in Smithsonian museum collections supports the conclusion that this documentation was a misinterpretation of the processing of indigo and vat dyeing. A detailed review of 19th century dyeing materials supports this conclusion, but historic, economic, cultural, and social factors suggest a broader range of possibilities, as do analyses of Chilkat blankets from other institutions. This paper will report new findings that both support and contra-indicate for indigo as the source of Chilkat blue.

1. INTRODUCTION

The source of the blue colorant found in Chilkat blankets woven by the Tlingit peoples in NW Alaska has been a source of confusion for decades. In 1907, U.S Navy Lieutenant George T. Emmons (and anthropologist Franz Boas) wrote papers on the Chilkat blanket (Emmons 1993) suggesting that blue-green coloration was the product of fetid urine in copper vessels which was later supplanted by aniline dyes. The paper was reported by W.D. Darby (Darby 1917) to American industrial dyers, to Canadians by D. Leechman (Leechman 1932), and summarized again by Leechman (Leechman 1964). Emmons exact description is:

> The bluish-green, the most esteemed of all the colors, came from the oxidization of copper in urine and the boiling of the same. The yarn is introduced and boiled, removed, well washed in fresh water, and dried in the sun. The Tsimshian tell me that a blue clay-stone was used to produce this shade. The Tlingit use this same stone for the decoration of masks, houses, robes, etc. as a paint, but not as a dye. (Emmons 1993)

In 1982, Cheryl Samuel thoughtfully tried to update and accommodate this reportage with research of the Canadian Conservation Institute and the University of British Columbia, who found the blue to be indigo, free of copper; they also reported that urine treated copper was fugitive to wool (Samuel 1982). Yet, in 1988, colleagues at the Canadian Museum of History found all the dyes in an early 19th century Chilkat tunic were fugitive to water (Hughes et al. 1988). When four National Museum of Natural History Chilkat textiles were analyzed by portable X-ray ray fluorescent spectrometry XRF for mordants in 2009, the blue dyes, like the yellow colorants, lacked a mordant level of copper (Hacke 2009). Similarly, in 2012 various

levels of copper from strong to trace were detected blue fibers from three NMAI Chilkat blankets (Doroszczyk 2012). Recently these NMAI fibers were analyzed using direct analysis in real time mass spectrometry (DART-MS): urea, isatin, indoxyl, and indigo were found in all three (Newsome 2018; Baglia et al. 2018).

The impetus to resolve the mystery of the Chilkat blue pertains, in part, to the polychromatic palette of the Chilkat blankets and the proclivity of museums for long-term exhibitions. The durability of a dye is directly related to the nature of the dyestuff, its method of application to the fiber, and the choice of fiber. So, it is prudent to ascertain the identity of the colorants in order to estimate the potential stability of the dyes. Even without permission for destructive sampling/testing, portable XRF can be used to look for mordants, from which plausible mordant or non-mordant dyes may be deduced.

A re-reading of Emmons in reprint form included appendices of corrections for language, plant, and bird identifications. Amendments also seem relevant for the dyeing procedures he describes. Western dye literature by *dyers*, routinely describe about the *coppery green appearance* of the leuco (aka reduced, white) form of the indigo vat. Modern literature on lant and reduction reinforce the distinctive processes associated with the various forms of reductive fermentation (Pratt 1987; Hartl et al. 2015; Liles 1992; Trotman 1975). These were quickly superseded in the early 1900's by a newly available commercial sodium dithionite (Heerman 1901; Hummel 1906; Trotman 1975). By revisiting older literature, records, and dyeing procedures with a clearer understanding, and by returning to the actual objects with new technologies, some of the confusions about the colorants in Chilkat blankets now may be resolved. Yet, additional findings in treatment, analysis, and records from other institutions may support other claims.

2. INDIGO

Many of the historically important stable natural dyes on wool were "mordant" dyes (Adrosko 1971; Bemiss 1973; Schweppe 1986). Less well known is that lant (stale urine) was a major commodity in the 18th and 19th centuries, an important auxiliary for the natural dyeings of lichens, for 'orchil' and for indigo (Pratt 1987). This chemistry, familiar to our ancestors familiar to our ancestors, to American Indians, and to most cultural groups and continents in the past. Yet it is foreign to modern sensibilities. The Conservation Laboratory of the National Museum of the American Indian held an internal indigo workshop in September 2018 focusing on cotton and paper dyeing using natural indigo (primarily *Indigofera tinctorial* L.*)* and woad (*Isatis tinctorial,* L.). Indigo dyeing can be quite tricky, dependent on time, temperature, reagent activity, and exposure to oxygen (Hartl et al. 2015; Cardon 2007; Liles 1992). For this reason, the process will be divided into steps.

2.1 PREPARATORY PROCESSING OF PLANT

The first step extricates the indigo from the plant itself. Some cells of indigo and woad leaves contain indican, a compound composed of indoxyl—the precursor to indigo--and a sugar, while other cells hold the enzyme that cleaves the two components apart, when the leaves are cut and mashed in water (fig. 1). Gradually, in the water, two indoxyls combine to form one indigo ("indigotin") molecule. Yet, these indigo molecules are not readily water-soluble, the mixture is a mash of aggregated indigo particles suspended in water (fig.2).(Cardon 2007; Hartl et al. 2015)

2.2 VAT DYEING

In order to make this indigo mash soluble in water, the indigotin must be reduced to its leuco state, "deoxidizing" it, lowering its oxidation state. A strong chemical reaction is required. This is the second step: forcing the double bonded oxygen to add a hydrogen and form hydroxy groups (fig. 3). For this process, urine is especially suitable as the agent that promotes bacterial fermentation to take place.

Fundamentally, urine is the chemical urea in water, with trace amounts of vitamins, minerals, and sugars removed by the human kidneys (Liles 1992). As seen in Figure 4, when urea, diluted further with water, is decomposed by warming in the sun or by proximity to an oven, it transforms slowly to form ammonium hydroxide and carbamic acid. The addition of more sugar, in the form of molasses, madder, bran, or dates can enhance indigo fermentation (Liles 1992; Cardon 2007; Hartl et al. 2015). This is the perfect environment to shift indigo to its leuco-form (upper chemical equation of figure 5). Just as seen in figure 3, the indigotin has changed into its leuco form with hydroxyl groups. Zollinger describes the reaction in this manner:

> …vat dyes contain a chain of conjugated double bonds with two keto groups in the end positions…carbonyl groups can be sited in the E-position to the ethylene group …As diols ('vat acids') the leuco derivatives are very sparingly soluble in water, but, since the hydroxyl groups have an enol character, they are acidic (pK_a=9-11) and dissociated in alkaline media to form soluble enolates (Zollinger 1991).

This is known as "indigo white" although it is yellowish-greenish. In order to make this form of indigo truly soluble, it needs to be transformed into a soluble salt (Step 3, figure 5). Again, urine is the perfect answer. With heat, the urine is further altered into ammonia and carbon dioxide (seltzer water) which evaporates with tiny bubbles (fig. 6). That is, the presence of bubbles in a vat dye liquor can also indicate active fermentation rather than boiling water (Liles 1992). The indigo is now a soluble salt—as easy to dissolve in water as table salt, because of an excess ammonia has replaced the hydroxyl group in the reduced indigotin with a NH^+ cation. Thus, with urine, two different chemical reactions are available from one chemical reagent. It can provide

the essential steps two and three for indigo processing. As to the indigo, the presence of bubbles indicates that the indigo has entered step 3 also since the disassociation of the carbonic acid to carbon dioxide in water [1] also means the indigotin must now be in the leuco salt stage. As to the dyeing itself, Bemiss cautioned as follows:

> The symptoms of the dye being fit to work, may be known by the rising of a fine copper-coloured scum, on top of the dye, and likewise, a fine froth rising, called the head; your dye will look green, and your cloth dipt [sic] in it, before it comes to the air, will look green also. (Bemiss 1973)

When the vat is working, it takes on a yellow-green or green appearance. (fig 7; Balfour-Paul 1998). This fermentation vat dyeing of indigo has distinct characteristics: it can be slow, taking place over several days; the urine and indigo can be added at the same time—or not; the bath benefits from benign neglect in order to avoid the accidental introduction of oxygen at key points; the bath can be amended to retard or to accelerate the activity. Not much heat is required (50^{o} C.) and not too much alkali; stirring disturbs the reduction process.

On the other hand, a fair amount of skill and practice may be necessary to achieve a good vat. Liles enumerates several difficulties: that the vat stays blue even after several days (step 1) because the vat is too cool, some heat may be required, and/or the proper micro-organisms may not be present: synthetic indigo will have no microorganisms. A little dried woad (processed), madder root, or dry cake yeast are suggested. If it seems weak, additional sugar in small amounts may help. When the vat smells ‘sour’ and the fermentation has been ‘heavy,’ i.e. active, there may have been enough ammonia released to reduce the indigo to its leuco state (step 2) but not enough to turn the vat greenish, to its salt. It may appear counterintuitive, but the remedy is to add *slightly more ammonia* to reduce the rate of fermentation and concomitantly, supply the alkali to ‘salt’ the reduced indigo, and slightly neutralize the bath—achieving step 3 (Liles, 1992).

2.3 RELATED DYEING BY TLINGIT

Indigo containing plants are not indigenous to Alaska, but there is a Tlingit dyeing tradition that would lend itself to indigo dyeing. The earliest records of Tlingit blankets from the third quarter of the 18^{th} century, had a palette of yellow, brown, and black colors (Holm 1982). Wolf moss (*Letharia vulpine* L). is a lichen dye. It is found in northern, forested snow-covered regions of North America and Europe, and was widely used by native peoples for a bright yellow (Samuel 1982; Cardon 2007). Urine or ammonia is required to transform its precursor into β-orcinol and to build amalgamations that are chromophores, dyes (fig. 8; Cardon 2007). Ideally, the protein fiber is boiled in the alkaline solution for one hour. Tlingit dyers were entirely capable of adjusting their hearth dyeing from wolf moss to indigo-tinged wolf moss (i.e. green) or to an indigo dyeing by itself.

2.4 COPPER SALTS

Copper salts occur in several forms. A basic copper acetate (Blue Verditer, $2CuCO_3$) varies in color as a powder depending on its ratio of cupric acetate to cupric hydroxide to water. A proportion of 1:1:5 will produce blue verdigris while a 2:1:5 will yield an emerald colored green verdigris [3]. These precipitate out in water and are soluble in acids and ammonia. Chalcanthite, a hydrated copper sulfate ($CuSO_4 \cdot 5H_2$), was found inland where the Tsimshian dwelt (Cardon, 2007; Mindat.org 2019; Emmons 1993). It has been used as a mordant for dyeing cotton or wool (Liles 1992; Schweppe 1986); its common names were 'blue stone' or 'blue vitriol.' Copper sulfate can be converted to copper acetate by boiling in water with lead acetate or by immersing in vinegar (Knecht and Fotheringill 1936; Cardon 2007). Copper sulfate is soluble in water, but after mordanting onto wool, less so. At room temperature deionized water, the color-change between control yarns mordanted with copper sulfate and the same lot wetted out and allowed to dry was ΔE of 1.75 (Fury, Little, and Ballard 2018).

Commercially, for printing these copper salts were often mixed with pastes to act as reserves or resists to protect cloths, previously dyed with indigo, from taking up a second pass of the dyeing. Once these reserves were removed after the oxidizing rinses, the cloth would have a lighter blue pattern on deeper blue field from the second dipping (Knecht and Fothergill 1936).

3. CONTEMPORANEOUS EVENTS

All these technical aspects of dyeing would seem to confirm that the dyeing Lt Emmons described was indigo, that Lt. Emmons wrote exactly what he saw, but as a layman, as an accurate observer or reporter, but not a dyer: he mistook the bubbles of carbon dioxide for boiling water, and the container as the source of the colorant. One Tlingit elder interviewed in 1907 says as much: "the making of the was carried on with much ceremony, after all but the dye maker had gone to bed, at night" (Wickersham 1907). In fact, Emmons amended his original notes in 1891 with the postscript "Latterly, this color [blue or green] has been obtained from blue blankets, boiling the wool with pieces of blanket." [2] (Emmons 1991) In other words, the commercial blue blankets sold by traders were the source of the indigo as early as 1891. The lighter shade could easily be due to the lower efficacy of the re-vatting and re-dyeing. While this method might well be more difficult than having a cake of indigo, it would certainly be feasible for Tlingit dyers.

Yet this also suggests the Chilkat blankets from the late 19th and early 20th centuries were not the "classic" period typical for the Tlingit people despite a sketch that might be as early as 1826-9 depicting a Tlingit with a yellow, black, and blue dyed patterned blanket (fig 9; Holm, 1982).

The world of the Tlingit had been disrupted over the half century prior to 1907 (fig. 10; Jones 1914). Russia had taken possession of Alaska as early as the 16th century; it was an outpost for traders. Alaska, including the area where the Tlingit lived, was purchased by the United States in the aftermath of the Civil War (1867). The presence of the United States Navy in Alaskan waters--Emmons's deployment to Alaska from 1874 to 1899--was undoubtedly related to this territorial expansion.

While it might once have been a quiet backwater, cataclysmic changes were developing. Nearby, the province of British Columbia and then the entire Canadian government outlawed the Potlach in its territory in 1885: native ceremonies like weddings were banned until 1951, though they remained legal in the American Alaskan coastline. In the Canadian Klondike, the Gold Rush started in 1896, and American prospectors came up through Skagway (Klondike Gold Rush National Park 2019). Beyond the Aleutian Islands, the Sino-Japanese war in 1894-5 involved the control of Korea. In its aftermath, Russian, English and German forces took up positions in Korea; these troops joined with those of five other nations to crush the 'Boxer Rebellion,' based in northern China and Manchuria. Russian occupation of Manchuria in the aftermath exacerbated tensions; the Russo-Japanese war was fought in 1904-5. The expansionist Japanese were victorious over the Czar's forces, a feat that shocked the European powers and formalized the control of Korea and Manchuria by the Japanese (*Ploetz'* 1925).

Industrially, a pathway to synthetize indigo had been patented in 1880; its chemical structure, in 1883; synthetic indigo was successfully manufactured in 1897, and, by 1913, natural indigo was no longer an important commodity (Vetterli 1951). In only sixteen years, the world market was irrevocably altered. Furthermore, in 1901 the alkali-fusion reaction used by chemical engineers to produce synthetic indoxyl, was used to fuse two 2-aminoanthraquinones together, producing Indanthren Blue (C.I. Vat Blue 4), the first of the synthetic vat dyes for cotton—close in hue to indigo, dyed the same way, but with superior light- and wash-fastness. Similarly, Hydron blue (C.I. Vat Blue 42), born an amalgamation of organic and sulfur containing compounds, was synthesized and gave rise to the class of sulfur dyes (SDC 1971; Seefelder 1994; Allen 1971; Abrahart 1972). Urine, as a reagent, was already being replaced by sodium dithionite and an alkali at the end of the 19th century. (Heerman 1901; Hummel 1906)

4. CONCLUSION

What began as a straightforward issue of identification and misidentification is now a bit more curious. In the present investigation, research data has all led to examples of indigo dyed weft yarns. This may be happenstance, based on the time frame of the collectors, the popularity of the blankets, and/or the building of museum ethnographic collections. Already, one Chilkat blanket outside this cache was reported as *having dyes soluble in water* (Hughes 1988). Even Lt.

Emmons spoke to the different dye sources during his time in Alaska. Following his paragraph on the copper kettle dyeing of blue in 1907, his published text reads:

> The native dyes give very pleasing effects; and in the older blankets soft, dull bluish-green and yellow harmonize beautifully with the slightly discolored white and reddish-black. But some fifteen years ago the trading-stores flooded the country with colored wools, and the demand from tourists for blankets induced the weaver to supply all of the colors from those foreign yarns. This resulted in coarsely woven blankets in discordant shades of yellow and blue, which overstocked the market, and discounted their values. When the weavers recognized their mistake, they returned to primitive methods; and to-day the few blankets produced are on aboriginal lines, except that the blue coloring is more often procured from aniline dyes than from the copper mordant. (Emmons 1993)

In other words, over a twenty-five-year period Emmons saw at least three different types of dyeing qualities in response to external forces. Cheryl Samuel found different palettes among examples among American and European museums associated with earlier explorations (Samuel 1985; Holm, 1982). The original intent and colorway appears to have shifted between 1874-1914; analyses of earlier collections and later collections may provide a better understanding of the effect the perturbations of modernity had on the Tlingit weavers and dyers.

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NOTES

[1] Sometimes referred to as carbonic acid, CH_2O_3.
[2] Cheryl Samuel is reported to have found this hand scripted note by Emmons dated 1891 among the British Columbia Provincial Archives, Victoria (BCPA) which was merged with the Royal Museum of British Columbian in 2003. See p. 225-6 Emmons 1991 for Chapter 8 "Art and Industries: Women's Work by Jean Low pp. 210-233.
[3] From the French, *vert de Grece*—green of Greece

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ADDITIONAL READING

If you would like to direct readers towards publications that are NOT cited directly in the text, they go in this section, and are formatted like other references.
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LIST OF FIGURES

Fig. 1. Indican is the precursor to indigo; it is composed of indoxyl (β-hydroxy indole) linked to a sugar.

Fig. 2. Two indoxyl molecules are combined to form indigotin or indigo; they lie ‘trans’ to each other to form indigotin.

Fig. 3. The oxidation-reduction reaction for indigo; for this reaction n=1 (after Zollinger 1991)

Fig. 4. Urea in water gradually breaks down to form ammonia and carbamic acid, forming step #2.

Fig. 5. The chemical activity associated with vat dyeing indigo. Step #2 reduces the indigotin to its leuco state; step #3 forms the water soluble leuco-salt (after Cardon 2007).

Fig. 6. In step #3, further breakdown of urea doubles the quantity of ammonia and the carbamic acid is degraded to carbon dioxide.

Fig. 7. The indigo vat in its leuco-salted state. Where the cloth has floated into air (oxygen) the fabric has turned blue (credit Balfour-Paul 1998).

Fig. 8. Lichen dyeing in a bath of boiling degraded urea and water first splits lecanotic acid (I) into orseillinic acid (II) and down to orcinol or β-orcinol before these precursors are recombined to produce the chromophores that attach to the fiber (credit Cardon 2007).

Fig. 9. Watercolor depicting (left to right) Aleut, Kodiag, and Tlingit men in ceremonial garb. Attributed by Holms to Aleksandr Filippowvich Postels artist documenting expedition 1826-29 for Czar Nicolas I (Holms 1982).

Fig. 10. Plate from a book on the Tlingit people (Jones 1914).