Chrome Stains or Iron-FFA Complexes? *

Red Stains on Wetblue Leather

Staining is a common problem in the leather industry and can also be the cause of significant economic loss. The origin of the stains, how to remove them and perhaps most importantly how to prevent them, is of interest to the tanner. The more we know of the chemistry and causes of staining the easier it is to avoid stains completely.

On wetblue leather we often find various shades of green, yellow, red, pink, brown, and black stain. The shape, size, and ease of stain removal can be a clue to their origin and mitigation. A significant and recurring problem for wetblue producers however is red or pink stains. Chemical suppliers are often asked to help find the cause and suggest a remedy. The etiology and composition of these stains was therefore the subject of investigation at Buckman.

Red stains are typically associated with the presence of fat, chrome, and iron, and may be correlated with growth of microorganisms. Practical experience points towards a higher incidence in salted hides versus fresh hides and the problem appears to increase with direct chrome recycling systems. Stains are often associated with poorly preserved raw material. Generation of red stains has also been linked to fungal growth on wetblue[1]. It has been observed that there is greater hydrophobicity associated with the red stained area. Red stains are found in sheep and goat, but the predominant commercial problem is experienced with bovine wetblue. Mechanical operations such as splitting and shaving may enhance the prevalence of red stains and they are sometimes observed with greater intensity surrounding blood vessels. The stains are often not readily apparent on freshly produced wetblue stock, but can appear after a few days or weeks of storage – a source of frustration for the tanner. It is common knowledge that these stains can be difficult to remove in the wetblue.

The literature states that red stains involve chromium, iron, and fat, but the fundamental role of these components in forming the stain is not clear[2,3,4]. Authors refer to these stains as "chrome soaps" and this suggests necessary involvement of chromium for color generation. Also, it may be logically deduced that the frequent association of the stain with bacterial or fungal activity implies a greater involvement of the metabolites of fatty material and not necessarily with intact tallow. It is perfectly feasible that exogenous bacterial or fungal lipases degrade triglycerides present in the hide to form free fatty acids (FFA) which then react with metals to form red stains.

Investigation into Red Stain Components

A good starting point for the investigation was to try to confirm the levels of fatty materials and metals present in red stain. Cuttings of unstained wetblue and an adjacent area showing heavy red stain were analyzed for fat and iron – (we already know that chrome will be present and prior testing had not shown significantly higher levels of chromium detectable in the red stained areas). Standard fat analysis was performed using IUC/4 method. The samples were also analyzed for metal content using standard SEM-

* Based on a paper presented at the 31st IULTCS Congress in Valencia, Spain in Sept 2011 entitled: "*Investigation of Red Stains on Wetblue"* by Luis Zugno, Marilyn Whittemore and Elton Hurlow of Buckman International

EDX analysis. A spot test for iron, using an acidic potassium thiocyanate solution with dilute hydrogen peroxide, was also performed on both areas.

Figure 1: Analysis of unstained and stained wetblue for fat and iron.

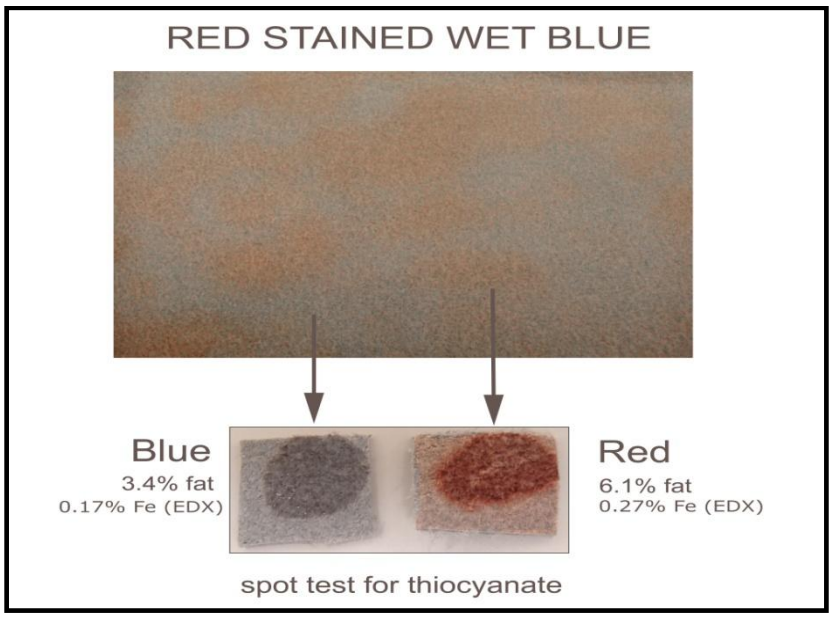

Figure 1 shows the fat content of the unstained wetblue was approximately half the value of the fat level in the red stained area. The amount of iron present, determined as a semi-quantitative ratio of the elements identified by SEM-EDX, was likewise approximately half the amount in the stained area. The KSCN spot test provides good visual confirmation of higher iron content. Clearly higher iron and fat levels are associated with the red stain.

Simulation reactions in the laboratory

The next step was to try and simulate generation of the red color complex. Relatively pure commercial bovine tallow was reacted with a pickle and a chromium tanning solution, as were the major free fatty acid (FFA) constituents of bovine tallow. Also tested was cholesterol and decanoic acid – see Table 1. The FFA's are listed by carbon chain length, number of unsaturated C-C bonds, and percentage present in tallow.

Table 1: Selected Fatty Materials reacted with Tannery Solutions

ID	Fatty Material / "Free" Fatty Acid	Carbon number : % Saturation	% in Tallow
A	*Decanoic or capric acid*	C10 : 0	0
B	*Cholesterol*	C27 : 1	0
C	*Linoleic acid*	C18 : 2	3.1
D	*Linolenic acid*	C18 : 3	0.2
E	*Myristic acid*	C14 : 0	3.2
F	*Oleic acid 99%*	C18 : 1	41.5
G	*Commercial Oleic acid 90%*	~ C18 : 1	~ 37

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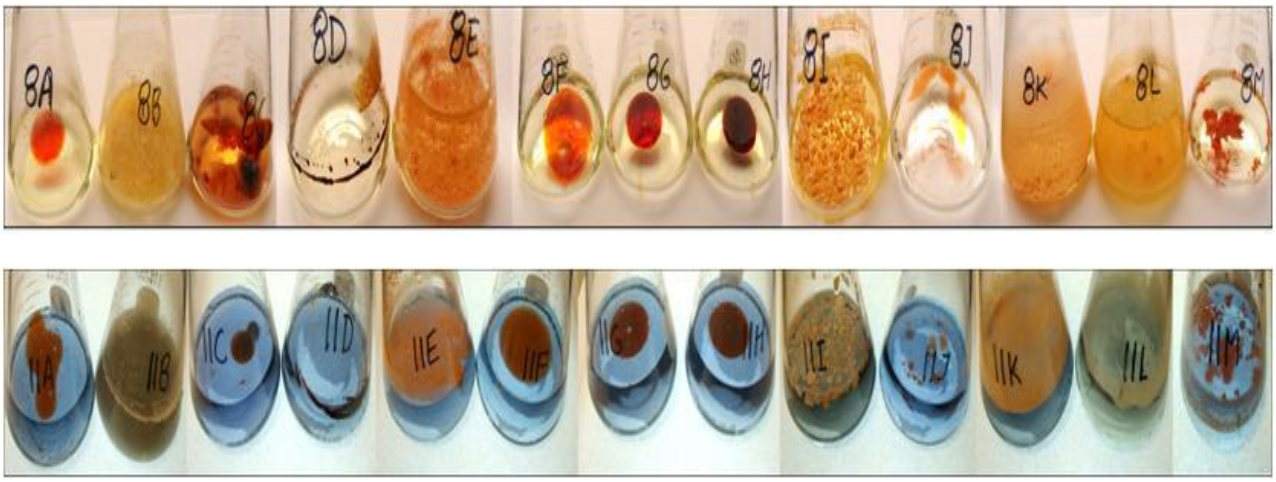
H	*Commercial Oleic acid 80%*	~ C18 : 1	~ 33
I	*Palmitic acid*	C16 : 0	24.6
J	*Palmitoleic acid*	C16 : 0	2.9
K	*Stearic acid*	C18 : 0	18.4
L	*Commercial Tallow*	Varies	~ 100
M	*Mix - oleic, palmitic, stearic, 33% each*	C18 : 1 / C16 : 0 / C18 : 0	~ 85

In the experiment, iron was omitted from half the series, but a small amount of Fe^{3+} (10 mg) was added to the second half. The fatty materials were then introduced to all the samples and reacted by shaking for 72 hours at 35°C to ensure good mixing and interaction of insoluble fatty materials with all components in the simulated pickle and tanning solutions.

Reaction of the solutions where no iron was present resulted mostly in colorless solutions. This included the tanning solutions which contained chromium. No red or brown stains were observed in any of these samples. This is an indication that chrome may not play a role in color formation.

By contrast, reaction of the fatty materials in both pickle and tanning solutions where Fe^{3+} was present resulted in a number of highly colored solutions. Figure 2 shows a brown to slightly orange color in the cholesterol and tallow samples (B & L), and a more orange colored solution with the saturated FFA's myristic, palmitic, and stearic acid (E, I & K). However, a more intense orange to red coloration was observed in the samples of decanoic and palmitoleic acid (A & J), and especially the unsaturated fatty acids linoleic, linolenic, oleic acid (C, D, F, G, H) and the mixture of the three most common FFA's present in beef tallow (M). It is interesting to note that a more intense color evolves with increasing level of unsaturation.

Figure 2: Top row showing Fe^{3+} and fatty material in pickle solution and bottom row with Fe^{3+} and fatty material in chrome tanning solution



No significant difference in the intensity of the color or the sequence of color formation was observed from samples with chrome and/or those without chrome. This is a further indication that chromium may not play an important role in the development of red stain coloration.

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Simulated breakdown of tallow and reactions with iron

Although FFA's occur naturally in animal hides or skins, they are typically present at low levels. This will however change with saponification reactions that occur during leather processing. FFA levels can also increase with microorganism activity, i.e. bacteria and fungi, where lipolytic enzymes degrade triglycerides to generate FFA's. Simulated breakdown of bovine tallow and interactions with iron was investigated next.

Mixtures of tallow, oleic acid, soda ash, and lipase enzymes were made and spiked with iron as follows:

A. Tallow + soda ash, run 24 hours on shaker, drop pH to 3.5 with acid, add 20 mg Fe^{3+}
B. Tallow + soda ash + lipase, run 24 hours on shaker, drop pH to 3.5, add 20 mg Fe^{3+}
C. Tallow + soda ash + lipase + surfactant, run 24 hours on shaker, drop pH to 3.5, add 20 mg Fe^{3+}
D. Tallow + soda ash + surfactant, run 24 hours on shaker, drop pH to 3.5, add 20 mg Fe^{3+}

Results after 24 hours show a separation of phases with the top fatty layer exhibiting a pink color in samples B and C and a slight color in sample D (see Fig. 3). The acidic aqueous phase was reasonably clear. The aqueous phase in Sample A remained yellow in color indicating that iron remained in solution. The samples were then put back on the shaker for a week to simulate aging of the reaction. The intensity of color in samples B, C, and D were similar after one week. This indicates that the iron present is sequestered by the insoluble FFA layer forming reddish complexes. Surfactant does little to delay or prevent the formation of the complex. The aqueous phase of sample A remained intense yellow. This implies that the triglyceride is not involved in sequestration of the iron and does not appear to remove Fe^{3+} from solution. Saponification of sample D takes place over time, as indicated by the final color.

Figure 3: Simulated formation of FFA's with samples after 24 hours and 1 week aging.

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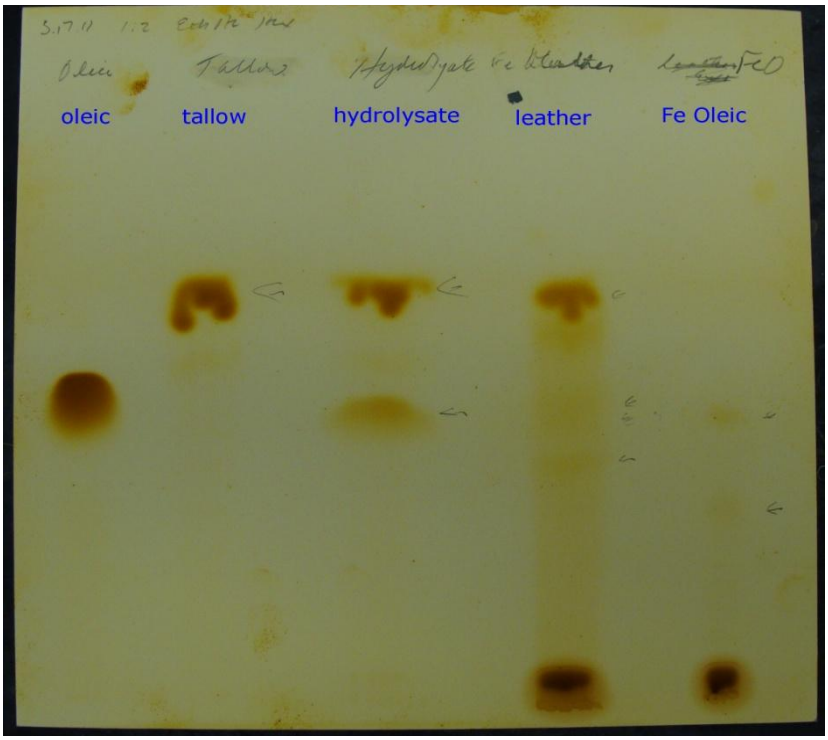
Separation of Simulated and Real Red Stain Components

Having identified possible sources of the red stain, further steps were taken to try and separate specific mixtures and correlate these with compounds extracted from tannery wetblue with red stains. The following mixtures were evaluated using TLC:

A. Oleic, palmitic, and stearic acids – commercial sample
B. Bovine tallow – commercial sample
C. Wetblue leather extract - Stained wetblue was extracted using standard method for fats (IUC/4).
D. Bovine tallow hydrolysate (TH) – The TH was prepared by reacting bovine tallow with lipase enzyme.
E. TH + iron – A sample of D above was reacted with Fe^{3+}.
F. Oleic + iron – A sample of oleic was reacted with Fe^{3+}.

Selected results of different TLC scans are shown below. In Figure 4a, the first two samples (silica plate) show good mobility (ethyl acetate / hexane) and separation of the fatty material oleic and tallow, with the tallow travelling furthest from origin and close to the solvent front. The center sample shows partial hydrolysis of the tallow with good separation of the components into two distinct bands aligned with oleic acid (FFA's) and intact tallow (triglyceride). When oleic is reacted with iron (last sample), the oleic + iron complex remained immobile near the origin. The extracted sample of red stain leather separated into three components. There was an immobile band similar to the oleic + iron complex near the origin, a diffuse band with similar mobility to the oleic or FFA's, and distinct band in line with the tallow. All three of these components may be expected in the fatty extract from the stained wetblue leather.

Figure 4a: TLC separation of oleic acid, tallow, tallow hydrolysate, leather extract, and oleic reacted with Fe^{3+}



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Using a less polar cellulose plate and suitable mobile phase, it was possible to get the hydrophobic Fe^{3+} complex to migrate. Figure 4b shows the developed plate where the tallow hydolysate + iron and the red stain leather extract show a diffuse pattern near the origin but distinct and comparable spots that move near the solvent front. To visualize these spots, the first plate is shown sprayed with acidic potassium thiocyanate enhanced with dilute hydrogen peroxide to visualize iron, and the second plate is then exposed to iodine to highlight fat material. It is assumed that the indicated spots are an "iron + FFA" complex.

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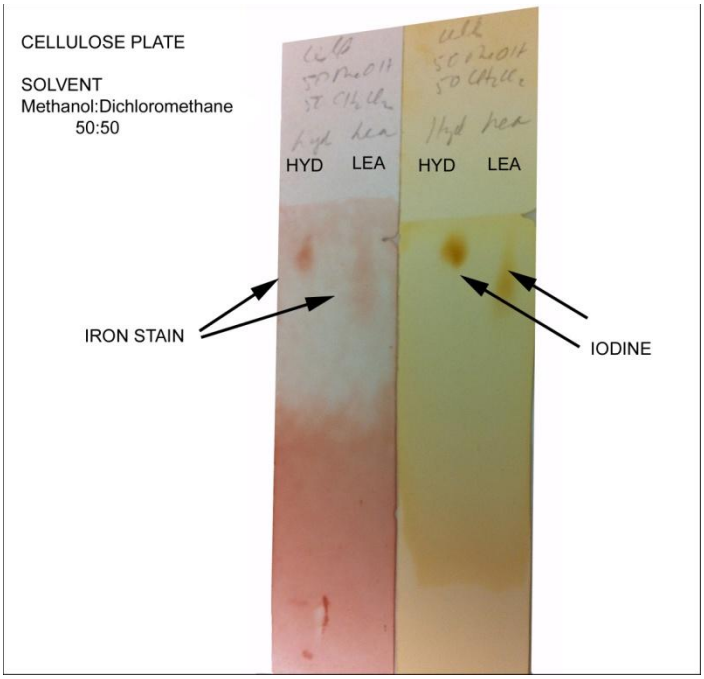
Figure 4b: TLC separation of HYD (Tallow hydrolysate + iron) and LEA (leather extract)



Implications of these Studies

It is clear that FFA's and iron form red stains. Other components tested did not produce red or pink colors on their own. It is proposed from this work that the red stains in wetblue are present primarily as hydrophobic clusters of FFA's coordinated with iron. The literature suggests these types of complexes are not simple. For example, the stable pink iron complex formed with stearic acid is a trimeric nuclear compound with 6 coordinated stearic acid ligands[5]. We also cannot categorically exclude the involvement of chromium, as various heteronuclear metal complexes that involve Fe and Cr are known[6], but chrome presence could be coincidental. It is unlikely that tallow (triglycerides) form part of the color complex.

From practical experience, once red stains are present in wetblue, they cannot be washed out using surfactant, they are only partially removed with strong oxidizing agents or bleach, and do not respond well to traditional sequestrants such as EDTA, phosphonates, or oxalic acid. In general they tend to be less noticed after retan, dye, and fatliquor operations, but it is likely that they are responsible at some level for uneven uptake of chemicals and non-uniform dyeing. It is suggested that part of the problem is the hydrophobicity of the complex and difficulty in rewetting the stained area.

Mitigation of Red Stains

It would appear that the best solution for mitigation is operational control and prevention.

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FFA's are naturally present in hides and skins at low concentration, but the breakdown of triglycerides through action of bacterial exo-enzymes, addition of lipases, and saponification during processing will increase the amount present. Good washing after liming and deliming is normally sufficient to effectively remove FFA's to levels that are not a significant problem for red stain formation. Post production formation of FFA's from natural fat in wetblue by action of fungal organisms is prevented by appropriate use of fungicides.

Eliminating iron from chemicals used, removal of iron from process water, and reduced contact with iron from machinery is also useful to help minimize red stains. This is especially important in recycle systems where metals can concentrate.

As shown in this work, chrome may be found associated with the stain area, but it cannot be concluded that chrome is indeed part of the iron + FFA complex. So it is suggested that these common red or pink stains on wetblue, heretofore called "chrome-soaps" by the leather industry should in future be more accurately referred to as "iron-FFA complexes".

References:

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