

The stability of metal-tanned and semi-metal tanned collagen

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Abstract

The metal tanning and semi-metal tanning potency of the first row transition metals was studied using hide powder. Transition metals show different levels of synergistic hydrothermal stabilisation in semi-metal tanning. Measurement of hydrothermal stability was carried out regularly in order to monitor the stability and permanence of tanning interactions in metal tanned and semi-metal tanned leathers.

The results indicate that the physico-chemical properties of leather can be altered as a result of redox interactions, in which certain transition metals play the role of a catalyst. The extent of metal catalysed oxidative degradation of leather can proceed to the extent of complete destruction of the tanning matrix as well as the collagen itself. A proposed mechanism of metal catalysed autodegradation in semi-vanadium (IV) leather is discussed with regard to experimental results and a review of earlier research on the interaction of vanadium salts with phenolic compounds.

Keywords: semi-metal tanning, polyphenol, cyclic redox, catalyst, hydrothermal stability, free radical, degradation, vanadium

1. Introduction

In vegetable tanned leathers, tannin molecules form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The shrinkage temperature (T_s) of vegetable tanned leather is in the range of 70-85°C (Covington, 2009). By retanning with metals such as aluminium the T_s of vegetable tanned leather can be elevated considerably in a process that is commonly known as semi-alum tanning. Similarly, retanning of vegetable tanned leather with metal salts has been referred to as semi-metal tanning (Lampard and Covington, 2004).

In combination tanning using metals and vegetable tanning agents, the order of tanning is important with respect to hydrothermal stability of the leather. Retanning of metal-tanned leather with vegetable tannin confers lower shrinkage temperature, while retanning of vegetable tanned leather with metal salt results in a synergistically increased shrinkage temperature (Kallenberger and Hernandez, 1984). In regards to the mechanism of semi-metal tanning, Slabbert (1981) suggested that aluminium ions form complexes with the already bound tannin molecules and form covalent links with the carboxyl groups of collagen. However, another study later showed that semi-aluminium tanned samples of normal and methylated hide powders have similar T_s , so blocking of carboxyl groups by methylation did not affect the final shrinkage temperature (Kallenberger and Hernandez, 1984). Furthermore it was demonstrated that even metals that are known to have weak interaction with carboxyl groups of collagen can significantly increase the shrinkage temperature of vegetable tanned

leathers (Kallenberger and Hernandez, 1983). The results indicated that the collagen-metal interactions are not critical with regards to the creation of the high hydrothermal stability. The accepted model of the principal interaction in semi-metal tanning (illustrated in Figure 1) is based on complexation of metal ion by the metal-polyphenol. The chelated complexation of the metal centre creates crosslinks in the polyphenolic tanning matrix resulting in the formation of an extended supramolecular tanning matrix around the collagen. Subsequently, the shrinkage temperature is increased considerably (Covington, 2008).

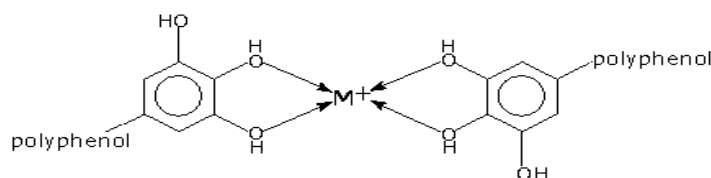


Figure 1. Schematic model of the semi-metal tanning interaction (Covington, 2009)

Sykes and Hancock *et al.* (1980) showed that phenolic compounds having one or more pyrogallol (3,4,5-trihydroxybenzene) or galloyl groups (3,4,5 trihydroxy benzoate) in their structure are more reactive towards aluminium compared to catechol (1,2-dihydroxybenzene) derivatives. The presence of the third hydroxyl group in the pyrogallol/galloyl groups increases deprotonation of the adjacent ortho-dihydroxyl group because by its inductive effect.

In contrast to the synergistic hydrothermal stabilisation through ‘the alliance of structure making’ by metals and polyphenols (Lampard and Covington, 2004), there are also metal-polyphenol interactions that lead to destabilisation of the tanned collagen and subsequent deterioration. Commonly, iron tanned leather is vulnerable to oxidative degradation (Heidemann, 1993). Unmasked iron that originates from buffing, shaving or splitting operations causes grey/blue spots and if the quantities are greater the leather could actually deteriorate rapidly (John, 1997). The presence of iron and copper are known to act as catalysts in enhancing deterioration of historical leathers (Kite and Thomson, 2006). In a review of semi-metal tanning, Lampard and Covington (2004) mentioned that the Ts of vegetable tanned leathers retanned with vanadium(IV) salt was found to have declined from 100°C down to 60°C under ambient condition of storage for more two years. This peculiar phenomenon has been described as reversal of tannage caused by a degradative mechanism that involves redox interactions with the metal playing the role of a catalyst. Similarly, a reduction in shrinkage temperature of vegetable tanned leather by 17°C was also observed after treatment of the leather with sodium molybdate (Kallenberger and Hernandez, 1983).

This paper describes a comparative study on metal tanning and semi-metal tanning potency of the first row transition metals (excluding scandium). The results of periodic analysis of hydrothermal stability have shown that some semi-metal tanned samples undergo degradative changes progressively under normal conditions of storage. The extent of these autodegradative changes and the mechanism of the process are discussed.

2. Materials and methods

Hide powder samples were prepared according to the method described by (Brown and Latona *et al.*, 2010). Unmodified tanning extracts (mimosa, myrobalan) were obtained from Silvateam Spa., (Italy). The following analytical grade metal salts of the first row of the

transition metals (excluding scandium) were sourced from Fisher Scientific Ltd. (UK) were used as tanning/retanning salts in the experiments: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, $\text{Ti}(\text{SO}_4)_2$, $\text{VO}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, NH_4VO_3 , $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{Mn}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ and $\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$.

Preparation of metal-tanned hide powder samples

Dry hide powder samples (2g) were rehydrated with 15mL of 5% NaCl solution and equilibrated to pH 2.8 using dilute acetic acid. Tanning was carried out by stirring 5mL of 1M solution of the metal ion into each sample, after an hour of stirring the pH of the all samples was adjusted to 5.0, except the for the Ni(II), Co(II), Cu(II) and Zn(II) samples that were adjusted to pH 6.5, close to their precipitation point. Then the samples were heated at 35°C for another 1hour. Finally, filtered samples were dried and stored at 21°C and 65% relative humidity.

Preparation of vegetable tanned hide powder samples

Separate batches of hide powder (5g) were rehydrated for 12 hours with 50ml of 5% NaCl solution and adjusted to pH 6.5. Tanning was carried out with a total of 10% (w/w), four equal aliquots of a 1:10 predissolved solution of the tanning powder were added at 30 minute intervals with continuous stirring. Then the pH was adjusted to 4.0 and the tanned hide powder samples were filtered and dried at room temperature.

Preparation of semi-metal hide powder samples

Dried vegetable tanned hide powder samples, each weighing 2g, were rehydrated in 15 ml of 5% NaCl solution for 2 hours and adjusted to pH 2.8 using 0.1M acetic acid. Then 5ml of 0.1M solutions of the metal ion was stirred into each sample, stirring was continued for 1 hour. The samples were heated at 35°C for 1 hour and the pH was adjusted in the same manner as mentioned above in the preparation of the metal-tanned hide powders. The samples were suction filtered and rinsed with 10ml of deionised water, then dried at 21°C and 65% relative humidity. Control samples of vegetable tanned hide powder were processed in the same way but without addition of transition metal salt.

Shrinkage temperature (T_s) and enthalpy (ΔH)

Shrinkage temperature measurement was carried with a differential scanning calorimeter (DSC, Mettler-Toledo 822e). Wet samples (2-5mg) were placed in standard aluminium pans (40 μ l) and hermetically sealed. Measurements were carried out in dynamic mode from 20°C to 140°C heating the heating rate of 5°C/min with an empty pan used as reference. The thermogram outputs were analysed using the Mettler STARE software and normalised values of enthalpy of shrinkage were calculated. Measurements were carried out immediately after completion of the sample preparation followed by measurements after 2, 8, 32 and 64 days of storage at 21°C and 65% relative humidity.

Metal content

Analysis of metal content was carried out according to the official method IUC-27/ISO 17072-2:2011 using ICP-OES (IULTCS, 2011).

3. Results and Discussion

Metal tanned tanned hide powder samples

As shown in Figure 2, the Ts of samples tanned with acetate masked metal salts is lower than 75°C, with the exception of the chrome tanned sample. Studies on aluminium tanned pelts indicate that the tanning interaction between the metal and carboxyl groups of collagen is a complexation reaction with a predominantly ionic character, transition metals are also likely have similar type of interaction (Covington, 2009). The samples tanned with aluminium, titanium and vanadium showed slightly greater Ts between 70-74°C. Chakravorty and Nursten (1958) carried out a screening experiment on the tanning potency of transition metals and found out that the highest possible Ts of transition metal tanned collagen can be obtained by tanning near the precipitation point of the metals; nevertheless because of the weak interactions with collagen the leathers have low hydrothermal stability.

Semi-metal tanned hide powder samples

As shown in Figure 2, all of the semi-metal tanned hide powder samples show significant increase in shrinkage temperature. The myrobalan samples retanned with Al(III), Ti(IV), V(IV) and Cr(III) show the highest rise in Ts or ΔT_s by 23-32°C relative to the Ts of the vegetable tanned sample. The actual Ts of these samples was 100°C and above, except for myrobalan-V(IV) sample that showed 95°C. Similarly, moderate ΔT_s of 18-20°C was attained by the myrobalan-Fe(II) and myrobalan-Ni(II) samples, the myrobalan based semi-metal tanned samples of Cu(II), Zn(II), Co(II) and Mn(II) showed significant elevation of Ts by 5-10°C.

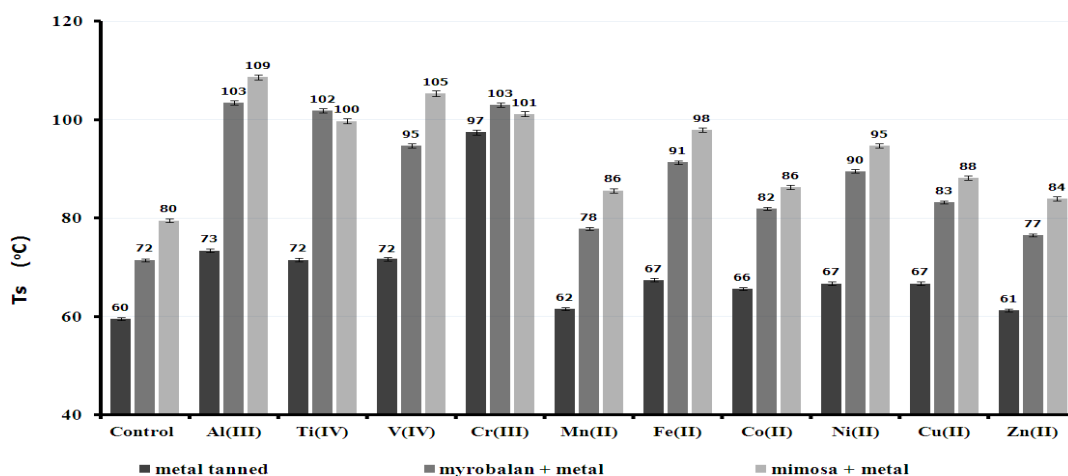


Figure 2. Shrinkage temperature of semi-metal tanned hide powder samples prepared by retanning myrobalan and mimosa tanned samples with sulfate salts of the first row transition metals

The mimosa based semi-metal tanned samples showed similar pattern of ΔT_s . With the exception of Ti(IV) and Cr(III) retanned samples, the Ts values of mimosa based samples is slightly higher than the corresponding myrobalan based samples. However, in most of the cases, the myrobalan samples that initially have lower Ts than mimosa, have shown greater net increase of Ts as a result of retanning, with the exception of the myrobalan-V(IV) samples that gave Ts value 10°C less than the corresponding mimosa based sample.

The change in Ts as a result of retanning with the different metals is highly varied. Nonetheless, the results show that even metals such as manganese and zinc that hardly have

tanning effects on collagen, are capable of elevating the Ts of vegetable tanned leather appreciably (Morera and Bartoli *et al.*,1995), (Kallenberger and Hernandez, 1984).

Synergistic hydrothermal stabilisation

The temperature of temperature of synergistic hydrothermal stabilisation (denoted as S) of the semi-metal tanned samples was calculated as $S = \Delta T_{sm} - (\Delta T_m + \Delta T_{veg})$; where ΔT_{sm} is the total rise in Ts of the semi-metal tanned sample with respect to the Ts of the untanned material, ΔT_m is rise in Ts in metal tanned samples and ΔT_{veg} the corresponding value for the vegetable tanned samples (12°C for myrobalan and 19.5°C for mimosa). The S values of the semi-metal tanned samples in this experiment are shown in Figure 3.

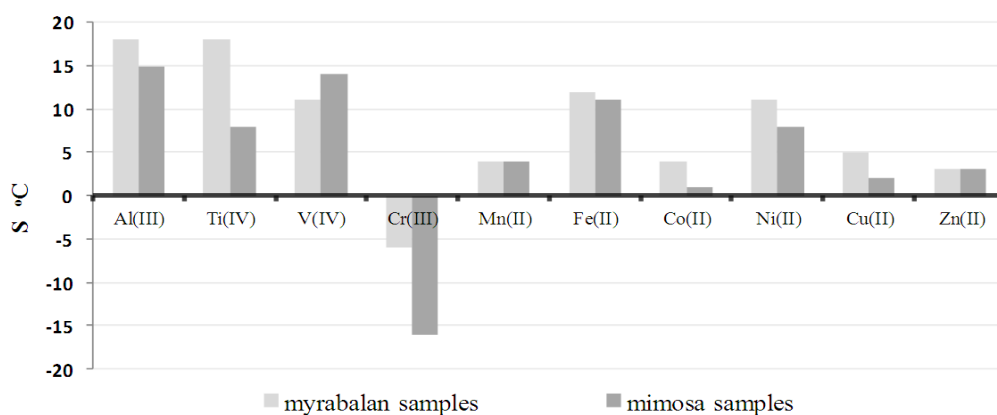


Figure 3. The temperature of the synergy (S) of semi-metal tanned hide powder samples prepared by retanning myrobalan and mimosa tanned samples with sulfate salts of the first row transition metals.

Despite the high Ts of the semi-Cr(III) samples, the S value of chromium(III) is negative. This might appear to be an antagonistic mode of interaction between polyphenols and the metal. However, the mode of interaction of Cr(III) and vegetable tannins is practically independent: semi-Cr(III) tanning appears to be similar to chrome tanning with regards to hydrothermal stabilisation. The correlation graph of the change in Ts by metal tanning (ΔT_m) with the average values of temperatures of synergy (S) of the metals is shown in Figure 4.

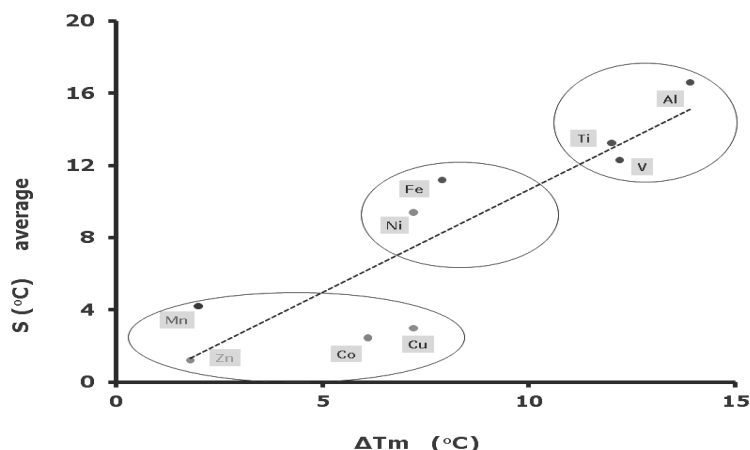


Figure 4 – Correlation graph of change in shrinkage temperature because of metal tanning with the average values of temperature of synergy(S).

There seems to be a linear relationship between the metal tanning effect (ΔT_m) and the semi-metal tanning effect (S). Based on the result of this experiment, the transition metals fall in to three nearly distinct clusters of synergy. The high synergy group includes Al(III), Ti(IV) and V(IV) having average S values in the range of 12-16, while the low synergy group (average S between ranging 1.2-4.0) is consists of Mn(II), Zn(II), Co(II) and Cu(II). Iron and nickel have moderate show moderate synergy of 9.0-11.0.

An important aspect that can be related to the strength of metal-polyphenol complexation is the charge density of the metal ions and the tendency to act as a Lewis acid in complexation reactions. The highest value of S belong to Al(III) and the d^0 and d^1 ions Ti(IV) and V(IV), that exist in aqueous solution normally as oxo-cations, namely titanyl $[TiO]^{2+}$ and vanadyl $[VO]^{2+}$.

Metal contents of semi-metal tanned samples

Myrobalan based semi-metal tanned samples showed metal uptake in the decreasing order of Ti(IV)>Cu(II)> V(IV)>Al(III)>Fe(II)>Ni(II) with the values ranging between 0.6-2.44% as shown in Table 1. On the other hand, the temperature of synergy (S) in decreasing order is Al(III)>Ti(IV)>V(IV)>Fe(II)> Ni(II)>Cu(II). The difference reveals that the effectiveness of semi-metal tanning does not necessarily depend on the amount of metal ion offered but on the strength of the particular metal-tannin interaction.

Table1. Metal content of semi-metal tanned hide powder samples in % w/w of the dry weight

Metal	Myrobalan+metal	Mimosa+metal
Al(III)	1.9	1.3
Ti(IV)	2.3	2.2
V(IV)	1.9	1.8
Cr(III)	1.3	1.2
Mn(II)	0.7	0.9
Fe(II)	1.6	1.3
Co(II)	0.6	0.6
Ni(II)	0.9	0.6
Cu(II)	2.4	1.5
Zn(II)	0.8	0.6

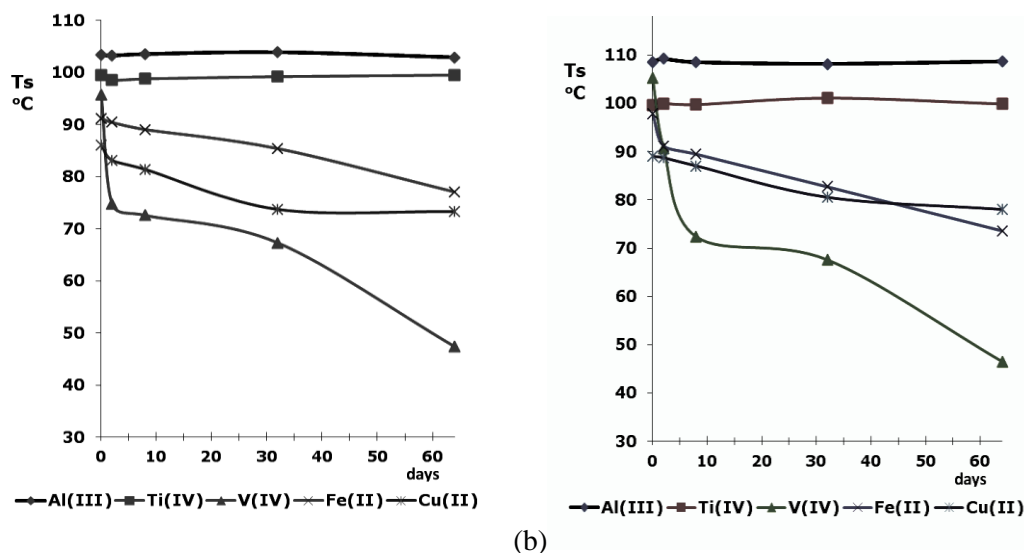
The high metal content of the myrobalan-Cu(II) samples and its relatively low temperature of synergy (Figure 3) indicates that most of the metal ions could be bound to the tannin compounds but did not create greater degree of crosslinking in the tanning matrix.

Changes in Ts of metal tanned samples

All of the metal tanned leather stored for more than 2 months maintained the initially attained Ts value, except those of V(IV) and Fe(II). As shown in Figure 5, iron(II) tanned samples showed slight increase in Ts by 3°C accompanied with change in color from white to yellowish orange. The Ts of the V(IV) tanned samples declined significantly from 72°C down to 58°C, the color of the samples also changed from light blue to sharp yellow color. These changes are related to oxidation of Fe(II) to Fe(III) and V(IV) to V(V). Hide powder sample treated with vanadium metavanadate has bright yellow colour and Ts of 58-59°C similarly tanning with Fe(III) sulfate also gave Ts of 73°C.

Change in T_s of semi-metal tanned powder samples

As shown in Figure 5, the semi-V(IV) samples of both type showed sharp decline of T_s within a day and the decline also continued further to the extent that T_s values went below that of the untanned hide powder (59.5°C). The overall reduction in T_s in myrabalan-V(IV) and mimosa-V(IV) over 64 days was 49°C and 60°C (respectively) that corresponds reduction by more than half of the original T_s values (95°C and 105°C). Similarly the T_s of myrobalan-Fe(II), mimosa-Fe(II), myrobalan-Cu(II) and mimosa-Cu(II) samples showed similar decline by 14°C , 24°C , 13°C and 11°C . At the same time, the T_s of all the other semi-metal tanned samples remained consistent.



(a)

(b)

Figure 5 - Changes in the shrinkage temperature of (a) myrobalan + metal tanned and (b) mimosa + metal tanned samples.

The enthalpy of shrinkage transition per dry weight (ΔH) of the samples showed that with the exception of the cases of semi-V(IV) samples, all ΔH the values remained relatively constant falling in the range of 11-14 J/g. As shown in Table 2, the ΔH of the semi-vanadium samples showed decline after 32 days, at the same time the T_s was lowered considerably below that of untanned collagen. The changes in semi-vanadium tanned leather were observed by earlier by Lampard and Covington (2004) and the peculiar phenomenon was considered as reversal of tannage. In this experiment it has been proved that the autodegradation caused by vanadium(IV) does not merely destabilise the tanning matrix, but also proceeds further into affecting the structural integrity of the collagen, the triple helical structure is partially destroyed and the shrinkage transition requires less energy to occur.

Table2 – Changes in enthalpy and shrinkage temperature of mimosa-vanadium(IV) tanned samples

Time	T_s ($^\circ\text{C}$)	ΔH (J/g)	Colour
0	94.6	12.11	blue
2	77.3	11.31	green
8	73.3	11.86	green
32	60.9	11.27	dark green
64	43.4	7.48	dark green

Mechanism of metal induced autodegradation

The interaction of vanadium(IV) collagen with vegetable tanned leather dynamically changes from the phase stabilisation (i.e. semi-metal tanning) to destabilisation or reversal of tannage (i.e. decline in Ts) and eventually to complete denaturation of the collagen. On the other hand, the change in its interaction with collagen is limited to shift from stabilisation to reversal of tannage as a result of oxidation of vanadium, as no apparent denaturation has been observed. Hence the main cause of the observed autodegradation in the semi-metal tanned samples is not related to the collagen-vanadium(IV) interaction but rather to that of vanadium-polyphenol interaction.

In aqueous solutions, vanadium(IV) of the oxovanadium(IV) ion $[\text{VO}]^{2+}$ is slowly oxidised in aerobic conditions into the vanadium(V) or the dioxovanadium $[\text{VO}_2]^{1+}$. A Review of studies on the interaction of dioxovanadium $[\text{VO}_2]^{2+}$ ions with phenolic compounds and ascorbic acid has shown that the dioxovanadium can be reduced to the oxovanadium $[\text{VO}]^{1+}$ by phenolic compounds such as catechol and pyrogallol derivatives. The occurrence of organic free radicals in the process of reduction has been detected. (Kustin and Nicolini *et al.*, 1974; Ferguson and Kustin, 1979; Bains and Arthur *et al.*, 1969)

Hence, the process of autodegradation in the vegetable tanned leather treated with vanadium could be a cyclic redox process as shown in Figure 6. The presence of air to oxidise the metal and subsequent reduction of initially chelate forming ends of the polyphenols by the vanadium(V) causes progressive decline in the composition and size of the polyphenolic matrix. Furthermore, the potential involvement of organic free radicals makes the reactions with the surrounding organic matrix rather non-specific.

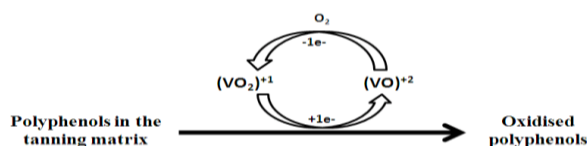


Figure 6. Schematic representation of the mechanism of polyphenol oxidation by cyclic redox reactions of vanadium(IV/V)

The change observed in the decline of shrinkage temperature in the first few days as a result of destabilisation of the polyphenolic matrix are merely the initial phase of the process. The autodegradation process extends further and eventually becomes a case redox denaturation of collagen.

4. Conclusion

One of the basic characteristics of leather is considered to be the degree of permanence of tanning interactions and hence time-dependent consistency of its properties. However, we have shown that the properties of leather can be altered as a result of changes caused by redox interactions, when metals can act as catalytic agents and cause deteriorative changes under normal conditions.

Metal induced degradation of vegetable tanned leather is non-selective because of the involvement of organic free radicals. The degradative process starts with destruction of the polyphenolic tanning matrix and extends further into breakdown of the collagen itself. The

presence of traces of redox active transition metals in historical leather could be one of the factors that have enhanced the deterioration process.

5. Acknowledgement

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