

INTRODUCTION TO THE 52ND JOHN ARTHUR WILSON MEMORIAL LECTURE

by

LUIS VELEZ

Leather making has been for ages a very delicate balance between empiric knowledge, scientific based principles, engineering and of course the aesthetic ingredient — “The artistic touch”. John Arthur Wilson dedicated together other titans of leather tanning erudition, his professional life to “land” deep and dense scientific concepts on leather Chemistry and reconcile them with practical applications on the daily tannery operations: his contribution partially condensed in his now classic *The Chemistry of Leather Manufacture*, opera prima in 1923, is now one of the scarce textbooks on the subject; used by many students, like I did to unveil the secrets of the old tanners.

Today I have the privilege and pride as fellow Colombian and personal friend to present you the recipient of the 2011 John Arthur Wilson memorial lecture responsibility.

Dr. David Ravinovich is considered by many experts in leather and tanners all over the world as one of the brightest minds in the industry; graduated in Chemistry from Berkeley he

became well respected in Colombia and all South America as the “out of the box” thinker on leather tanning/retanning. Then after an obligated exile he has been a constant investigator and writer of leather science papers in many diverse topics as Thermodynamics, environmental issues, reaction mechanisms and modified reactivity of collagen. In 2009 he was awarded with the Fred O’Flaherty service prize recognizing his significant contribution to the ALCA.

Finally on a personal note: I met him 25 years ago at my first lecture to the Colombian leather chemist’s association when he found a typo on one of the thermodynamics equation I was showing. He was the only one in the audience not sleeping or bored to death with my presentation.

Ladies and gentlemen Dr. David Ravinovich.

EVERYTHING YOU WANTED TO KNOW ABOUT COLLAGEN MODELS — BUT WERE TOO AFRAID TO ASK!

by

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ABSTRACT

Collagen is a wonderfully complex starting material for making leather, which we are now only beginning to understand! Practical tannery recipes arose out of the craftsmanship developed by multiple successive generations of artisan tanners that obtained, by trial and error, the rules of thumb that eventually converted into a technical folklore. Leather chemists then tried to interpret this technology according to the scientific theories of the day, whereas tanners retained the technology that seemed to work best. Although Colloidal Chemistry has developed tremendously in the last century, some of its principles are not any longer agreeable to the leather sector in general, and are regarded with great mistrust. Some of these colloidal concepts can be very useful if properly applied and can be used to produce better leather in better ways; such then should be the ultimate goal of any working chemical model employed by tanners to be guided in the actual processing of leather.

RESUMEN

El colágeno es una maravillosa, pero compleja, materia prima para la elaboración del cuero que solo estamos empezando a comprender. Recetas empíricas surgieron a través de múltiples generaciones de curtidores artesanales que dieron a luz por fuerza de prueba a unas reglas que se fueron convirtiendo en un folklore técnico. Químicos curtidores entonces trataron de interpretar esta tecnología en términos de teorías científicas del día, mientras los curtidores retuvieron las tecnologías que les parecieron que dieran los mejores resultados. Aún que la Química Coloidal ha tenido tremendos desarrollos durante el último siglo, algunos de sus principios ya no son bienvenidos por el sector del cuero en general y son considerados con mucha desconfianza. Muchos de estos conceptos coloidales son útiles y aplicables a la producción de mejor cuero con mejores procedimientos. Tal debería ser el objetivo de cualesquier modelo químico empleado por curtidores deseando ser guiados en el procesamiento del cuero.

INTRODUCTION

In providing a working chemical model useful for the tanner, perhaps one needs to define at first what the model is not intended to be! This is not a “*unified-field-type*” theoretical model that will elegantly and succinctly *explain all* the ultimate and intimate nature of what *tannage* is all about, in terms of very basic fundamental principles. Leather and leather-making material science is still far too much of a complexly evolving *art* for that! Hopefully, as well, this will also *not be* the very last model you will use to devise tannery processing strategies, as our leather field should continue to rapidly evolve with the creation of not only new, but different chemical unit processes, as well as different mechanical means to accomplish them. In the near future, perhaps even drums might disappear! In any case, the adept tanner must always consider which are *the active* chemical groups on collagen/leather that react with the *offered tannery chemicals* and how to offer such chemicals at as low of an astringency as possible, but at as high a concentration (thus low floats!), such as there results at first the desired penetration and distribution through the cross-section, and then and only then, by allowing, or actively changing the reaction conditions, increase the astringency involved to get the best fixation and optimum chemical exhaustion efficiency. In most cases, we at least do know which of collagen’s reactive groups are involved in the initial reactions, although the ultimate chemical course that follows may be as of yet, unclear.

This last reasoning to get adequate penetration of chemicals is in accord with concepts used successfully in dealing with chemicals involved in the use of amphoteric ion-exchange resin systems and predicting their transport characteristics through such columns. An old-time leather chemist, Prof. Dr. W. Grassmann¹ had even proposed the use of the R_f value concept from ion-exchange resin separation technology, as a parameter applicable to deal with penetration/astringency issues for leather chemicals coursing through a biological matrix, as comparable to such an analogous *ion-exchange* column that collagen/leather would then resemble. Dutta² had

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made parallel analyses of the problem, and refers to *resistance [to penetration]* as being due to *High Degree of Reactivity of Collagen*, which would then be in accord with this point-of-view, namely that the *astringency* is inversely related to the *rate of penetration* for a leather chemical coursing through the cross-section, hereby being proposed. The analogy between collagen/leather acting like an amphoteric ion exchange resin in an aqueous medium, equipped mainly (but not only) with anionic carboxyl and cationic amino side-groups attached, is thus incorporated into this particular collagen/leather chemical model. The effect of pH values as well as of the chemical conditions required, such as *ionic strength, dielectric properties* of the medium, etc. can be also considered. Built-in also is how to consider “masking”, both by classic coordination and by just simple electrostatic blockage, to achieve our objectives. Specific Hofmeister Series ions effects are causing the three collagen’s peptide strands side-groups to be, or not to be, as reactive to the added chemical at that particular processing stage must also be dealt with. Thus the manipulation of the *chemical reactivity* (astringency) of collagen’s reactive side-groups, that is, the actual control of the *effective pKa* values for the amino and carboxyl side-groups of each of the individual polypeptide strands involved in conforming tropocollagen, is of paramount importance to be able to achieve tannery processing objectives.³ To summarize: *high astringency* (reactivity) causes *poor penetration* and vice versa, *low chemical affinity aids penetration* for those charged chemicals as mostly used in the tannery.

An array of interconnected chemical equilibria arising out of the classical biochemistry based on work by Hofmeister, Sørensen, Levy and others, in combination with colloidal chemistry concepts, give rise to a chemical model useful for the tanner considering the appropriate strategies for offering chemicals based on manipulating the *reactivity* of collagen. The different tautomers of an amino acid (as well as for simple peptides, polypeptides and even insoluble fibrous proteins such as wool and collagen!) are considered by the classical Sørensen’s Formol Titration scheme explanation.⁴ These interconvertible, but differing peptide structures, represent a chemical model that can be used to consider the reactivity of collagen and leather. The classical equilibrium [see chemical model detailed later] involved in the array have been slightly expanded by two added items: to equilibrium **A** (left), the uncharged tautomer, and at **F**, the water-micelle (above); to be able to describe how beam-house chemically purified collagen⁵ reacts as it is being further processed. The non-charged (often referred to as “canonical”) tautomer availability on the left side of equilibrium **A** can be encouraged to increase, at the cost to the *Zwitterion* (charged, but overall neutral!) *tautomer* fraction available on the right side. A *less polar* medium (including the gas phase), dehydration, higher temperatures (as it is less stable) etc. can encourage formation of the non-charged tautomer species, whereas the *charged*

(groups) *Zwitterion tautomer* on the right is more stable under *aqueous and polar* solvent conditions. There is a great *decrease* in entropy when the *Zwitterion tautomer is formed*, that is *increased* self-organization takes place, which has been attributed to *low-entropy water polymers* interacting with the peptides involved.⁶ When a *solvent fatliquor* is used under very low float conditions, the reverse is true and the formation of the uncharged (canonical) tautomer is then favored some more, *encouraging* the individually charged chemical’s penetration. This technique is often employed in the retannage of wet-blue, to aid the penetration of large molecules such as *anionic* vegetable tannins at relatively low pH values, and such is required in order not to strip-off other previously-added *anionic* products, such as dyes. The fish-oil tanning process for making *Chamois* also uses carefully controlled *higher temperatures, dehydration measures* (salt added at a diminished float!), addition of *powdered alkalis* (discharges cationic amino groups), and the use of a *non-aqueous solvent* (cod- oil!) in order to *encourage acrolein*, an air-oxidation formed aldehyde product, to initially react with the *uncharged amino* (–NH₂) side-group present. As in the case of *all* aldehydes, acrolein will *not react* with the charged amino (–NH₃⁺) group such as present in the *Zwitterion* tautomer configuration. The similarity with how *keto-enol* configuration equilibria can be willfully manipulated to obtain desired chemical objectives, is just barely being mentioned, but it serves to make the leather chemist aware of the potential benefits to leather processing by the manipulation via ionic strength and dielectric properties of the medium, of the *equilibrium labeled as A* in the proposed chemical model.

MICELLE STRUCTURES

The colloidal (*water*) *aggregate* at the top of equilibrium **F**, that represents the tropocollagen triple helix structure, has also been added to introduce to the reader the concept that the triple helix results from three polypeptide chains, mainly held together by (water-aided) H-bonds between imino and keto “backbone” elements of the different linked alpha amino-acid strands, as a consequence of peptide bond formation and resulting in increased helicoidal *hydrothermal stability*. Augmented stability also occurs in the case of mammalian collagen and associated intimately with the hydroxy-bearing, hydroxyproline and other amino acid components *favoring H-bonding*, between each individual, long “Jello” polypeptide strands (–R–), that are intertwined into a right-handed twisted rope-like trimer” that is the triple helix. Collagen, however, is also *additionally thermodynamically stabilized* by *electrostatic saline links*⁷⁻⁹ which have key consequences on its chemical reactivity in the tannery,¹⁰ as well as by *highly-ordered* water polymeric sheaths possibly physicochemical analogous in role, to the waters involved in creating surfactant-type micelles, *also* a colloidal-realm phenomenon related to the schizophrenic concurrent hydrophobic/hydrophilic

behavior of large amphiphilic molecules, which tanners will surely need to better understand their hydration and dehydration properties.

The distinction between tannage and retannage is really just only a *traditional* administrative tannery convenience, rather than a truly *relevant* chemical distinction in the fundamental chemical processing of leather, thus is irrelevant to the chemical model. The fact that shaving is traditionally done before “retannage” as not to waste any of such chemicals in shavings, greatly limits our thinking as tanners regardless of actual material cost options involved! In the year 1931 J. A. Wilson presented a lecture titled: “*Leather, Sanitation, and Colloid Chemistry*”.¹¹ It clearly describes the operational reasons for practicing tanners to mistrust leather chemists! Wilson proposed then that the concepts of colloid chemistry might yield a better outlook required of the chemist for compromises; such as to be able reconcile the *differing viewpoints* between the practical tanner and the theoretical based leather chemist. Whether this is feasible, the author hopes that the practical use of this model will help at least, to diminish this philosophical approach gap mentioned by Wilson. When vats and then drums were introduced to the tanner in the early 20th century, many of the traditional recipes continued in their *fundamental design* to be still suited better for pits, and only slowly and more recently, has the drum been better employed, *at low floats*, to its full potential as a *chemical reactor* in the tannery.

THE CHEMICAL MODEL

F (above) includes the so called supramolecular water-structure ($n=3$ for *tropocollagen*); each of the intertwined (not necessarily *exactly* identical) peptides, or alpha-helix strands represented as $-R-$, that is then, a long “Jello” (gelatin product) type strand of peptide-bond joined alpha amino-acids with multiple amino and carboxyl side groups attached. These side-groups appear also distinctly in (the separated by the process of denaturation) gelatin individual-strand titration curves, whereas $x^{(\text{footnote a})}$ mysteriously represents very complicated chemical functions; yet to be really understood, and not just simply “*waters of (organic) crystallization*,” for there are several types of waters involved very differently in such structures.¹² Multiple types of complexly associated *water* is the real and *effective distinction* between leather and the usual leather substitution plastics.

The Colloidal (?) Aggregate with Water is thus a Micelle when above an equivalent critical (minimum) micelle concentration

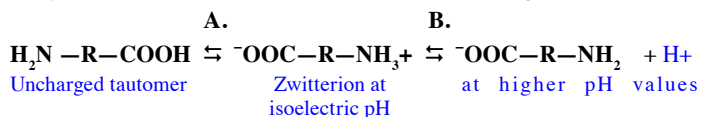
(CMC) value. Excessive hydrotropic (Hofmeister) intimate swelling of the tropocollagen triple helix brings about the irreversible denaturalization by “peptide dilution” below CMC, and unraveling into randomly distributed coils in the solvent; that is completely separated, (“Jello”) alpha-amino acid strands.



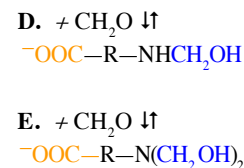
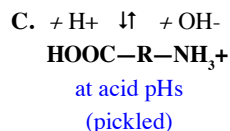
F. ↑↓

(← “Salting-out”)
Dehydration

B is driven to
right as basified



(“Salting-in” →)
Hydration



DISCUSSION

These equilibria (**B** through **E**, with their associated double arrows) are employed in classical biochemistry for the descriptive mechanism behind *The Sørensen Formol Titration* results, extensively observed in *proteins, amino acids, and peptides*; a phenomenon, by which the *mere presence* of formaldehyde, causes that the value of the *pKa for the amino group* in **B** to drop from 2 to 5 pH units! The explanation traditionally offered, is that added aldehydes will *displace* the whole sequence of series towards **D** and **E**, making an amino side-group proton ($-\text{NH}_3^+$) in **B** much easier to remove, that is for the peptide species to *charge negatively*, thus making the resulting net *anionic peptide* configuration; *more reactive* to *cationic* chemicals (such as chrome tannins or aluminum cationic multinuclear complexes), and the system as a whole then finds itself less likely to return back towards the Zwitterionic, *multiple-charged, but overall neutral*, isoelectric condition, through reversal of the formation of the resulting *methyl* derivatives. These *methylol anionic* derivatives are just the initial (“snapshot”) reaction products that will probably continue to react in complicated, covalently linked, but leather-stabilizing, ways. It is, however, the additionally exposed (“unburied”) anionic collagen *carboxylic* side-group; the one that is involved in the cationic chrome tanning process. This disablement of a saline bond between amino and carboxyl

(a) x obviously should deal with several different types of waters, hence the *interhelix* water involved in Hofmeister lyotropic effects is most likely different from supramolecular “sheath” waters involved at other dimensional hierarchies and processes, such as in hydration Zwitterion stabilization leading to “peptization”.

side-groups of collagen/leather by discharging through an aldehyde reaction, that causes important chemical processing consequences for the tanner. Aldehyde, then is effectively “unburying” the previously somewhat *un-reactive* carboxylic groups present in the Zwitterion tautomer, as they are themselves involved in *longer-ranged*, saline links with cationic amino side-groups in the cases of *proteins, amino acids, and peptides*. This *Sørensen Titration* aldehyde effect on the *observed pKa* value of the amino-group in the titration curves, it must be emphasized, occurs as well in even *ordinary amino acids* (-R- would be then a small group) dissolved in aqueous solution! Thus the saline-bond interactions between *solvent-separated Zwitterions* evidently still occur, and *are active*, even at the very long distances (on a chemical-molecular scale) between the *individual* amino acid Zwitterions dissolved in aqueous solutions! This would imply coulomb interactions are still taking place in-between the solvent-separated Zwitterions. Moreover, these ordinary alpha amino acid solutions, also display the characteristic clockwise rotation (*steepening*) of their titration curves about the isoelectric pH point, as ionic strength (salinity) is significantly increased above the optimum “peptization” value. Such as was previously suggested,³ as being caused by a greater neutral salt addition causing a colloidal realm “*protein dehydration*” process occurring in the *immediate surrounding environment of the saline links* with a corresponding *decrease of the Zwitterion* fraction present. Even though there are alternative or additional possible explanations for this obviously extremely complicated effect,¹³ the “*steepening*” of the successive titration curve of *proteins amino acids and peptides* at higher salinities, has been attributed by respected scientists as due to the peptide’s dehydration⁴ by the salt (footnote1). ‡ These opposite-sense changes in their observed pKa values, as per titration curves, for *either of the components of the saline bond*, just as it also occurs with more complex peptides and fibrous proteins¹⁴ as well, and can be controlled when subjected to varying ionic strength. It is to be mentioned that that the effect on the *peptide’s amino pKa* values by the *action of aldehydes*, is in the same sense and fairly similar to the changes brought about by the larger increases in ionic strength, that is, its displacement towards lower pKa values, such as perhaps, attributable to *Zwitterion* concentration decrease through dehydration caused *reversal of A*. The pKa change of the *carboxylic* functions as *being nil by the peptide’s reaction*

with aldehydes (which would hint then that the inductive effects through the hydrocarbon structure are likely minimal), but it is shifted towards *higher values* by the *increased ionic strength* induced high-salinity dehydrating effect. That is, in an *opposite sense* to the amino group pKa displacement by the same saline dehydration effect, resulting in an overall clockwise rotation about the isoelectric pH point of the titration curves as salinity increases beyond the maximum ionic strength at the *optimum salting-in point* at about 5 β NaCl salinity for tannery beam-house treated collagen. Manipulation of the *effective Pka values* of reactive groups (astringency) in collagen is the basis of achieving not only more efficiency in chemical usage, but for also making better leather!

These then are presumably *colloidal effects* that occur at dimensional hierarchies *greater* than the usual chemical-molecular scales of dimensions. The dissolved ordinary alpha amino acids also behave similarly to more complex peptides and proteins, as to the effects caused by Debye-Hückel ionic screening processes followed by “*dehydration discharge of the Zwitterion*”, as inferable by their parabolic (as they salt-in and then out!) solubility curves vs. ionic strength graphs. These characteristic solubility curves display effects that are occurring even to dissolved alpha amino acids, again suggesting that amino acids *Zwitterions* and are still somehow significantly electro-statically associated even when present in *ordinary solutions*, in order to exhibit the aggregation and disaggregation effects reflected by their solubility characteristics under changing salinity, as described by A. If the separated alpha amino-acids in solution, display these saline-bond (*peptizing*) character properties due to *Debye-Hückel shielding* by the dissolved salts; it should not be surprising then that amino acid side-group components in the triple helix individual gelatin strands, locked into the triple helix configuration at relatively close (at colloidal dimensions) separations by H-bonding, should also display the characteristics of columbic electrostatic longer-ranged interactions occurring between anionic carboxyls and cationic aminos side-groups, also likely between each of the separate strands conforming (interhelically) the same triple helix! Certainly *intrahelical* and even *intrafibrillar* saline bonds and at even higher colloidal dimensional hierarchies still would be possible, as well to also occur at even lower salinity values

(1) Edwin J. Cohn in a milestone ACS Monograph #90 of the mid-twentieth century, in “*Proteins Amino Acids and Peptides*,” see Ref #4 pgs. 608-609: “...Hofmeister emphasized an important element of the truth in suggesting that the phenomenon was due to the “*dehydration*” of the protein by the added salt. This conception, couched in more explicit and quantitative terms, forms the basis of Debye’s theory of salting out. The specific influences of different salts, as enunciated by Hofmeister in his studies, are found also in the actions of salts on amino acids, and indeed on the simplest gases. The striking qualitative similarity in the action of salts on the solubility of cystine and hemoglobin should be stressed. *The salting out effect* in the action of salts on amino acids is apparent even in very dilute solutions; in proteins, likewise, its significance probably will prove to be even greater than earlier investigators were led to suspect. The elucidation of the nature of the effect is not a special problem confronting the colloid chemist only; it is rather a problem of extraordinary wide scope in the general theory of solutions.”

than the closer ranged interhelical saline bond disruption by higher salinity values as required by the Debye-Hückel electrostatic screening at the much shorter interhelical dimensions. Distances between opposite charges are very important then in Debye-Hückel screening analyses. This *salting-in* colloidal effect, due to ionic-strength charge shielding action, has been called “*Peptization*” in classical colloidal terms and is paramount in determining the *chemical reactivity* (astringency) of proteins, amino acids, and peptides, towards the mainly *anionic* and *cationic* tannery used chemicals, as well as the peptide’s increased swelling/solubility in and by water, through the *salting-in* action.

These *compound* salt-bonds (for they also could possess *potential* H-bonds) interactions in the triple helix water-micelle, should contribute to additional hydrothermal stability to collagen.¹⁰ The characteristic protein salting-in/out effects as is reflected by their solubility curves being parabolic and are not only displayed by *ordinary* amino acids and more complex peptides as well, but are also displayed by the surface physicochemical characteristics of an *otherwise insoluble* fibrous protein in contact with water! An aqueous *gelatin* solution, that is: the peptide products resulting out of *denatured triple-helices*, after the organizing *H-bond structures* are destroyed (by “denaturing” through interhelical Hofmeister lyotropic swelling accompanied by a large *entropy increase*), also display *the rotation* of the titration curves about the isoelectric point at increasing salinities, indicating that the *Zwitterionic* saline interactions remain even in the “Jello” solution, that is, *after* the triple-helix itself is no longer in existence. Remnant equilibrium **A** features *can then still be manifested* in the solvent *separated (randomly) gelatin strand individual components* of the triple helix, because of the much longer characteristic distance effective range of saline-link interactions compared to other short-acting linkages in the molecular-chemical realm. Thus gelatin salting-in/-out is similar to that of collagen fibrils and even in wool!

When we assert that the reversal of **A** occurs because of *dehydration* as being opposite to the mysteriously complicated *hydration* that gives rise to the *Zwitterion stabilization*, as established by spectroscopic evidence in amino acids and simple peptide systems,¹⁵ we are obviously speaking of dehydration effects on highly organized complex H-bonded polymeric water systems comprising a mysterious (colloidal micelle ?) supramolecular water self-organizing structures at the top of **F**, most likely involving also the saline bond’s additional potential H-bonding capacity of the amine’s hydrogen’s, with electronegative component-elements of the supramolecular water-sheaths present in the lowered entropy (self-organizing) micelle structure. The tauntingly complex colloidal effects behind the displacement of equilibrium **A**, need not philosophically overwhelm us into complete inaction, but we should humbly accept our obvious current ignorance, *when working as tanners*, as long as we can get the

desired salting-in/-out effects and make charged reactive side-groups to discharge and recharge at our will! We should use the benefits of variable ionic strength and dielectric properties based methods affecting effective Pka values of side-groups in processing leather, for astringency control purposes, both for enhancing penetration as well as, for reaching our ultimate fixation/efficiency goals.

The *Sørensen Formol* titration scheme then similarly explains why formaldehyde (or better yet, work-place preferable Glyoxal, Glutaraldehyde or Glyoxilic Acid!) in the pickle helps to chrometan better and fix *more* chrome on leather (with up to 96% efficiency!) as so stated by the late Umberto Sammarco in the 2006 IUCLTS Congress in Istanbul.¹⁶ “*Unburying*” anionic carboxyl’s (by their effective “demi-peptization” as corresponding saline links amino side-groups are blocked by the added aldehyde) that were previously involved in said saline links with cationic amino collagen side groups, present both in *inter* and *intra* linked tropocollagen helices, and would logically cause more appropriate *reactive sites* for cationic metal tannage (co-polymeric-hetero-coagulation?) to be made available in collagen, at several differing dimensional hierarchical levels.

C (vertical) down describes the peptide species in equilibrium under acid conditions, such as when pickling (or even when **B** is reversing to the left and then down through **C** when an anionic re-tannage product is being fixed by the use of formic acid!). Hence this *cationic* protein species would be expected to be clearly *less reactive* to cationic metal tannins— at least as not until the actual basification is initiated! For didactic purposes only, this *micelle structure* in the top of step **F** is depicted with much more structural detail as the triple helix, differently from those others, really also trimeric structures, but simplified in the rest of the series. Obviously all the tautomers of collagen that are already aggregated into *trimeric* colloidal triple-helix “micelles” (unless they were previously and irreversibly denatured into separated “Jello” strands randomly distributed throughout the solvent!) are thus not depicted as conforming triple helices, but just for clarity sake! This seemingly outlandish affirmation that collagen, a fibrous protein, (equilibrium **F**, vertically up) as being thermodynamically analogous in a structural physicochemical sense to *colloidal* water-surfactant micelles, is not just by any means the author’s original idea. It has variously been suggested as an insight by well known leather scholars such as McLaughlin-Theis,¹⁷ Bienkiewicz¹⁸ and the much respected modern chemist Vollhardt in his “Organic Chemistry” text.¹⁹ The colloidal concept of *supramolecular* water structures (clathrates?) or aqueous-sheaths surrounding proteins at *colloidal supramolecular dimensions*, is commented upon by Dr. A.D. Covington²⁰ as well. The relationship between Hofmeister Series hydration/dehydration effects occurring there;²¹ between the polypeptide strands associated through colloidal structured waters in tropocollagen, rather than in the

free “bulk water” of the true solvent phase involved. **Salting-out** in equilibrium **A** is probably a much different phenomenon to the Hofmeister lyotropic coagulating (de-swelling) effects occurring at the triple-helix internal dimensions and always results in increased hydrothermal stability as H-bonding becomes then better oriented. This will surely be a difficult, but an interesting subject to still preoccupy us. Collagen chemists need undertake many future studies, but it is perhaps too premature yet, as tanners; for we are being currently considered as ecological-political scapegoats in so many countries. We must defend ourselves *here and now*, through effective increased-efficiency results that need not require us yet completely delving into detailed and long standing unresolved controversial colloidal theories on solvation of proteins, amino acids and peptides!

ACTUAL PRELIMINARY TRIALS FOR INCREASING CHROME TANNAGE EFFICIENCY

In several Latin American tanneries, recent chrome tannage trials were undertaken in which relatively small amounts of an aldehyde agent and an aluminum salt product were added *at the pickling stage*. This caused a significant increase of *chrome utilization efficiency* compared to the usual conventional processes. Appendix A, at the end of this paper, shows the results obtained. (A sample representing the resulting leather was made available to the lecture attendees.)

IS CROSS-LINKAGE INVOLVED IN TANNERY PROCESSING? WHAT TYPES OF CROSS-LINKING?

Many tanners and leather chemists are very predisposed to consider the concept of *cross-linking* by chemical means as being at the heart of all tannery processes. However, they prefer to accept high-energy *covalent* cross-linking as the really the “politically correct” explanation, because of its higher individual energetic characteristics (as compared to a weaker, but much longer-ranged *saline* links), although paying some lip service to hydrogen bonding concepts as being very “modern” and thus somehow ought to be included in any discussions of real scientific value! So there are then *some theoretical topics* of co-agreement between tanners and leather-chemists even if not quite understandable to all!

SEVERAL RELEVANT CHEMICAL STRUCTURAL LINKAGES THAT CAN APPLY TO COLLAGEN/LEATHER

It is useful at this point to make some very succinct and elemental remarks on the properties of various applicable chemical links as that will help guide us on how to understand

the workings behind this model being presented for operating under actual tannery situations. Of all the chemical links, the salt-bonds primarily caused by electrostatic (coulomb) forces, are the longest-ranged and thus are the *more relevant* in the regimentation of supramolecular (nanometer-colloidal) dimension processes as opposed to smaller yet, chemical-molecular scales of dimensions, where *some* covalent bonds can be involved (such as with aldehydes) in the tannage of collagen. The *inverse square force* attractions (or repulsions for like charges) are generally the first step involved in most tannery chemical processing, because of their longer range. In dyeing, for example, where anionic dyestuffs are attracted, through their anionic sulphonic groups, to the cationic amino groups of collagen/leather at typical colloidal-range of dimensions, but generally only later, are the dyes affected by other, closer-ranged, usual chemical-bond forces such as covalence, coordination, hydrophobic attractions, Van-der-Waals attractions, H-bonding, etc. etc. that are typically ruled by various -6 through 12 *exponential* force laws acting only *at much shorter distances* than does the coulomb inverse square (-2) exponential law (footnote 2). These later types of chemical *short-ranged* forces are generally the ones involved in the *final* fixing of a dyestuff, as the leather is drying and the distances between reactive groups shorten to those then involved in typically chemical, rather than colloidal dimension events. Repulsions in the cases of other forces than inverse square coulomb forces involved need not to be even considered yet by ordinary tanners, thus reemphasizing the fact that saline bonds are really very different fundamentally in their nature from all the other chemical shorter-range bonding that can be involved. One of the characteristic consequences of these electrostatic inverse square forces, is that collagen's saline links can be broken-down by starting to decouple saline bonds, at first at the largest dimensional ranges between layers of fibers, by the shielding attenuation on charge interactions caused by ever increasing concentrations of dissolved ions (such as those resulting from mid-series, relatively non-swelling/non-coagulating, Hofmeister ions such as resulting from KCl, or NaCl), and as described by the *Debye-Hückel theory of solutions*. Dr. Covington refers to this colloidal-dimension phenomenon as the “*smearing-out of charges*” when referring to the presence in collagen of salt-like links.²¹ Saline links in collagen can then occur (as well as decouple!) at different hierarchical dimensional levels depending on *ionic strength* (and of course pH!) of the of the gross aqueous medium (bulk solvent) surrounding the proteins. Thus ionic strength control becomes a very important factor in seeking the somewhat mysterious colloidal state of maximum “**peptization**” (at relatively lower ionic strengths, or “**salting-in**”) by breaking apart by “*ionic screening*” the longest-ranged saline links first, with a resulting increase of available reactive (water-dipole separated, that *is swollen*) charged sites available to tannery

(2) Since force times distance is the energy involved in linkages, then force and energy will always differ by one r exponent unit.

chemicals, but the basic tropocollagen structure, although maybe somewhat weakened by this gentle distortion from its fully helicoidally most-stable geometry, remains essentially intact. Thus saline links can be uncoupled by the electrostatic screening effect on the opposite charges between the intra and inter strand bridging bonding sites on collagen and the appropriate charged amino or carboxyl collagen side-groups present. In this case, it is the ionic strength as a property of *the bulk solvent* that is important. The primarily electrostatic saline-link can also essentially vanish through use of stronger yet saline medium, as a *strong* colloidal level **dehydration** eliminates the very formation of Zwitterionic individually charged groups (“**salting-out**”). In this last case, uncharged tautomer canonical configuration at the left in equilibrium **A** more favorably occurs; the resulting bio-structures will also lose the additionally stabilizing saline bonds. Though these two phenomena appear closely inter-related, as salts can be involved in both cases, the nature of **peptization** breaking-apart of saline bonds through charge shielding by ionic strength of the *bulk solution*, and thus results in *enhanced reactivity properties of collagen* towards charged chemicals; is completely different from the saline bond absolute disappearance because of the **severe dehydration** caused discharge, as a proton re-migrates from amino to carboxyl, and thus minimizing the proportion of Zwitterion tautomers present. This effect is not due to the *bulk solution solvent* ionic strength properties, but by *specific effects of lyotropic de-swelling Hofmeister chemicals* affecting the *waters in between the individual tropocollagen alpha amino strands*, that is, at the micelle-colloidal level of dimensions. As a matter of fact, **solvent dehydration** can cause equilibrium **A** to reverse to the left without any salt even being present! The different natured **salting-in** and **salting-out** colloidal effects are inherently, but somewhat simplistically (elegantly?), described by equilibrium **A**. The first (**toward the right**) involves just a little salt added, whereas the second (**towards the left**) involves lots! It must be further emphasized that the placement inside the triple helix of either of Hofmeister Ion Series (at either extremes of lyotropic swelling or de-swelling character) should affect not only the state of internal hydration of triple helix specifically,¹⁸ but in addition these ions could also contribute to the *gross solution's bulk ionic strength* electrostatic shielding (at specific larger distances) by the **Debye-Hückel salting-into solution** effect. This should hint at the exasperating difficulties involved in stating quantitative expressions describing the differences between these two types of colloidal events, perhaps both could be occurring concurrently *at different* dimensions, but at the same overall salinity! At really higher concentrations of salinity (about 15 βe NaCl and higher!), the electrostatic shielding begins to affect links spanning shorter distances still, but eventually the strong dehydration of the Zwitterion H-bonded structure conforming the supramolecular water sheaths, but not the bulk solvent, causes the saline links to vanish substantially in collagen, as it turns towards being **pseudo-leather**!

The skill required of a tanner is how to use salt-addition wisely, by use of appropriate float size depending on the need by such action, and minimize excessive and unnecessary salinity from that resulting in the combined tannery effluents, but obtain the required astringency control required for best tannery chemical utilization efficiency, as related to the real and current pollution issues!

SALINE-LINKS DO ALSO AFFECT MANY OF THE MACRO-PROPERTIES OF LEATHER

The “hardening” of leather/collagen upon drying is related to compound saline links forming between fibers and layers of fibers at higher dimensions. Water can act as a “fiber lubricant” by dissolving salt bonds, thus separating charges while water is present in excess, but water removal by severe dehydration, such as by successive acetone washes, then bars the saline link formation for lack of *Zwitterions present*, as the relevant equilibrium **A** is substantially reversed towards the left by such an extensive solvent dehydration method, and collagen then becomes *pseudo-leather*. This is the theoretical interpretation of Dr. Azdet's visionary ecological processing project proposal that might even eventually eliminate (re) tanning drums.²² Pseudo-Leather dries soft (but remains very avid for water) rather than the hard, horn-like, but not easily wettable parchment(?). An anionic fat-liquor fixing on the charged amino-end of the saline link, disables it from re-coupling by electro-statically “masking it”, and thus avoids the reformation of the extended hardening saline-links between fibers, while the hydrophobic, non-polar, “other end” of the oil chain is said also to “lubricate the fibers” as the non-polar, solvent-like organic character of the oil also does deter electrochemical saline bonds from effectively reforming because of the lack of Zwitterion charged configuration available, needing a polar aqueous medium present in order to form! In other words a non-polar, *organic other-end*, of a fatliquor chain can similarly solvent-dehydrate collagen thus *appearing* to lubricate fibers! Aldehydes by blocking-off uncharged amino groups and preventing them from recharging, then also *tend* to yield *softer* leather, in general, because of the disabling of their cationic charges required to make the “hardening” extended-range salt-links. For these reasons aldehyde tannage, in general, also tends to loosen the grain-break as well and can be very useful for achieving the more dramatic grain-milling effects sought by tanners to camouflage certain defects, in lieu of leather-hardening (printed) embossing. Thus fat liquors provide “*half*” of the required effect for turning collagen/leather towards the *pseudo-leather*, defined by: “as lacking too many extended saline links”. Actual “*Leathering*” thus also involves some “**dehydration**” *caused by the prevention* of such hardening, very long-ranged, saline links! Thus deep application of waterproofing hot wax applied in the finishing, affects the temper of the resulting leather by decreasing Zwitterion tautomers present as the hot wax displaced water.

The Zwitterion conformers are the ones ultimately causing extended, leather hardening, salt-links. Sometimes for these reasons, a resulting loose-grained crust leather can be substantially salvaged by a slightly acid (pH 4.5-5) water and formic acid wash or spray, followed by careful mulling and re-drying, because it causes some saline-links to reform as some previously discharged amino groups are made cationic again, and tend to re-couple with relatively more distant still existing anionic carboxyl sites, thus strengthening of the multiple very long range, but weak saline links between the grain and corium layers that can often critically determine the “break” character of leather. This “first aid” treatment, however, does tend to harden (that’s why it works at all!) the crust a little upon drying. This, however, can save the day for a harried tanner because of a VIP customer wanting his particular leather’s break repaired by “a supposedly competently” adept tanner that “should know what he is doing”, rather than solving the defective break problem by just conveniently selling-off the misbehaving leather to a potential competitor, at a discount to boot! This type of “art” is what makes a tanner into “a real scientist” in the customer’s eyes! Any mischievous boy that has wet his shoes by purposely walking through a slightly acid (CO₂ containing) rain-water puddle, is aware of this *advanced grain-tightening* technique, especially if he dries-out his leather shoes very quickly, before his parents come home, and keeps quiet about resulting blisters caused by having to “break-in” his shoes all over again!

The purification of raw collagen from presumably electrostatic-attached impurities such as proteoglycans, décorin, etc., is performed usually by a 10 βe common salt (10% b.w.) solution in early soaking (5 hours). As collagen starts to lightly de-swell at slightly higher salinities after saline bonds to these impurities have been decoupled by slightly higher ionic strength Debye-Hückel shielding of the linking charges, and thus long-chained, previously saline-linked impurities can then be easier washed-out than at the 10 βe salinity level when collagen is also slightly additionally de-swollen from the fully neutral “**maximum salt swollen-in**” (peptized) state, occurring at approximately 5 βe salinity. Then, as the ionic strength of the medium increases after early preliminary rinse-washes, we get at first the decoupling of the longer ranged saline-links of the actual already purified collagen components (rather than of the un-removed impurities) as between fibers, in differing layers, and even perhaps some Debye-Hückel shielding decoupling between still at some more distant interacting fibers, in specific layers. The resulting uncoupled, but still charged amino and carboxyl groups, remain protruding out into the solvent water (thus making the peptide more soluble and tanning reactive!), but much too electro-statically shielded from their further-away opposite charged “targets”, to be able to reform the longer-ranged intracollagenic saline-links at the highest of leather’s hierarchical dimensions. Collagen then becomes more chemically reactive towards anionic or cationic chemicals in its optimum “salted-in” or “peptized”

condition. Thus the “peptized configuration” version of fibrous collagen is a direct consequence of Debye-Hückel shielding of electrostatic attractions comprising saline links being uncoupled at bulk-solvent action at lower ionic strength regimes. Then, at higher ionic strengths still, such as occur during the *dehydrating pickle at early tannage* stages, some compound saline links between triple helixes themselves might be completely split-apart, but many in this case just simply vanish because the stronger dehydration ends the possibility of saline link existence because of substantial reversal of the Zwitterion formation equilibrium A that actually eliminates most opposite charges! *Dehydration*, however, many times will actually increase hydrothermal stability as *interhelical* H-bonding reorients their action. This type of Zwitterion discharging should also affect the ease of diffusion of charged tannins through the collagen fibrous bio-maze. Nevertheless at these higher ionic strengths some closer ranged intra tropocollagen saline links would be expected (at least intuitively!) to decouple, but detailed Debye-Hückel effective distance-of-shielding calculations based on tropocollagen intimate dimensions, need to be carefully made with the collagen’s structural knowledge now available.¹² Some charged amino side-groups can remain, as carboxylic groups are immediately blocked and discharged by the excess of protons at pickle pH’s. The remaining few cationic amino groupings from the fewer Zwitterions left under the extreme saline dehydrating conditions, are “masked” (that is blocked) by the excess anionic sulfate ions present, because sulfate as a Hofmeister (dehydrating at the tropocollagen internal dimensions) coagulating divalent anion that would bridge electro-statically, cationic amino groups attached to the triple helix structure, forming saline bonds and even providing *some additional hydrothermal protective stability* to the delicate collagen structure under such harsh acid pickle conditions. These arguments are not being given to negate, in order to just be able to ignore, the occurrence of severe osmotic swelling by like-charge repulsions at somewhat higher dimensional hierarchies (at a *virtual membrane* level?), caused by acids and bases as *Donnan Forces* are also easily controllable by salt presence as well; but rather to place specific Hofmeister lyotropic swelling/deswelling effects of the triple helix itself into a proper dimensional hierarchy perspective! This is why *basic chromium sulfate*-containing (Hofmeister coagulating and dehydrating SO₄²⁻) tanned collagen yields “linked-and-locked” by saline-links, superior tanned leather (Ts~115°C), whereas *ordinary chromium chloride* (without the extra sulfate amino-bridging) treated collagen yields *rather ordinary* Cr tanned leather (Ts~85°C) that is “locked”!

Paying attention to fur processing can be illustrative as to how collagen behaves to hydration/dehydration phenomena under approximately neutral conditions, as the lack of required mechanical removal of keratin skin components in early processing of fur,²³ without alkali present, yields obvious and much simplified clear-cut neutral swelling interpretation of

the soaking processes, although the key (limiting/enabling) salinity values are probably somewhat different to those affecting the usual purified collagen, that has gone through the usual alkaline beam-house processing. Initial neutral fur soaking under increasing saline conditions yields a maximum swelling, as determined by weight, at about 4.8 β e salinity. Presumably this salting-in colloidal process yields some multi-charged “peptized” zones where the solvent water interacts by separating charges due to salting-in and is taken-up by the electrostatic charged pelt, as equilibrium **A** is displaced towards its Zwitterion configuration that had initially caused charges to form. As ionic strength then exceeds equivalent salinity values given by about the 10-12 β e zone, the upper limits for some of the residual neutral swelling to be still present, and then at higher salinity still, collagen begins to de-swell because of salt-caused dehydration (affecting equilibrium **A**) towards and past the base weight obtained in salt-free water under no-salt added, equilibrated, minimal peptization conditions. Eventually because of increased dehydration and discharge of the *previously peptized* side-groups that had interacted with the solvent, actually then collagen de-swells below the base intermediate weight, to display negative (more dehydrated still) weight values (at the right side of the maximum swelling peak occurring at about 4.8 β e), at about 15 β e and higher salinities. This implies that Equilibrium **A** then starts to reverse towards the left because of the *colloidal* “salting-out” dehydrating action on collagen’s *water-stabilized Zwitterion* configuration and thus becomes less reactive still to the water as the solvent and, of course, less astringent to any charged chemicals being offered, aiding their penetration through the *less polarized* amphiphilic bio-matrix maze. Hence for better penetration of *any charged chemical*, low-float with a relatively *high gross ionic strength* (15 β e plus NaCl equivalent) is recommended. Heidemann gives this recommendation for accelerated penetration for highly cationic multinuclear aluminum²⁴ tannins that are not as readily “sulphate-maskable” into anionic species such as regular chrome sulfate *is* at pickle pH’s, under higher sulfate concentrations! Similarly, since aldehydes *react only with discharged amino* side-groups, higher salinity makes the non-ionic aldehyde tannins more astringent towards collagen, although aldehydes are traditionally and widely considered by *most tanners* as being *anionic* chemicals! This idea probably results because of the blocking of the uncharged amino groups by aldehydes towards the uptake protons, is thus limiting the maximum cationicity possible in aldehyde-treated collagen/leather. This gives an erroneous impression of inherent anionicity contributed to collagen by aldehydes. Thus collagen/leather, under stronger, dehydrating, saline conditions, becomes a much better avid scavenger of *unfixed aldehydes*, than that as with no salt present, pH conditions being equal! This would be a case where a little extra salinity at very low floats would help greatly to eliminate unfixed (free) aldehyde discharges in wet-white processing into the effluents; — which case, some salt or excess free-aldehyde presence

— would be considered ecologically worse? Thus salinity control should be employed as well to better exhaust toxic aldehydes employed in metal-free tannages. Thus reversing peptization (**A** to left) fixes more uncharged aldehydes as its action is chemically different from most ordinary anionic/cationic tannery chemicals.

The often heard, and reckless requested “*suggestion*” made by not too well informed tannery administrators (some times as owners!), to diminish all salt offers drastically, in all processing recipes, in order to attempt to obtain ecological good-will and acceptance by the chemically *not-too-sophisticated* pollution control authorities, by this action; this could possibly cause much *more harmful* pollution (as well as possible destructive osmotic swelling in pickling!) due to wasted offers of more environmental sensitive chemicals of higher toxicity, than really common salt should really be considered, because of the decrease in collagen’s specific reactivity, due to the lack of salt-induced discharged aminos extent! By the very use of very low floats in good drums, with the possible use of a grain-protective slipping agent, if so required, the salinity levels needed for the required decoupling of saline links, as well as if needed to diminish the Zwitterion tautomer fraction for penetration enhancement purposes, can be obtained without ever over-loading the combined global effluents with the salts required at higher conventional usage floats. The intentional use of Glaubber salt in dyeing processes, such as wool and fur dyers customarily do, would at least produce a salt-anion greatly precipitated by lime (from the usual associated beam-house waste) instead of the much too difficult to remove chloride anion! The *hydration* of *peptides, amino acids and proteins* under the proper saline ionic strength *encourages the Zwitterion formation* and gives rise to the *chemically charged (peptized) side groups*, the ones mainly reactive to most of the usual tannery chemicals, such as dyes, etc.

There are exceptionally homogeneous resulting and level-dyeing nubuck recipes (of the two-step kind) that obtain very rapid penetration of the anionic dye-stuff through the crust, in a very small, cool float, by the joint addition of commercial chrome tanning salt powder (about 1/3-2/3 of the dye-weight offer) and the *powder dye-stuff* (which traditionally contains substantial amounts of Glaubber salt as well!). Since the chrome itself is greatly anionic under the excess of sodium sulfate present (up to nearly 50% b.w. in many commercial chrome tanning products!) and since the sulfate anion, a specific Hofmeister Series coagulating (tropocollagen dehydrating) divalent anion, because it associates by salt-linking two cationic aminos (of which there will be few anyway at the usual higher initial dyeing pH conditions, as favorable initial crust dyeing conditions; would fit-in towards the right-side of equilibrium **B**). The weakly reactive (partially dehydrated at higher ionic strength because of low float and lot’s of sulfate acting on the collagen triple helix) as equilibrium **A** reverses towards the left to yield more of the non-astringent discharged canonical

tautomer; after the desired dye penetration is quickly achieved under these relatively un-reactive conditions. Following with a *hot, large (250-300%), formic acid containing* bath added to help fix just about all of the dye-stuff, by dilution, such as to produce low ionic strength conditions and switching the equilibrium **A** back towards the relative abundance of the Zwitterion tautomer, of much higher astringency towards an anionic dye. As the chrome complexes themselves become more cationic with time, temperature and the violent drop in sulfate-concentration caused salinity; the *dyestuff-colloidal anion-aggregates*, also *disassociate* from their own “surfactant micelle-like” aggregated-conditions, causing *increased dye* astringency as well. Many sulphonic-equipped dyestuffs often display colloidal-aggregation micelle behavior similar to surfactants as well! Chrome then contributes ever so gradually by its own astringency enhancement factor, as it rejects protons from re-fixing on ionized carboxylic groups by their chrome tannage, which then causes still more dye-astringent charged amino groups to occur. Chrome behaves thus; as a dual-action auxiliary (dye-astringency leveling initial action followed later as a dye-shade intensity enhancer!). Thus basic chrome sulphate tanning salt is in effect, a self-regulating dyeing auxiliary for best dyeing purposes, *if used properly without pre-dissolution*, to control desired course of charge changes. The considerable additional benefit of re-chroming the leather also helps the quality of the dyeing operation as well! These examples also demonstrates how to operationally use this proposed chemical model, even if you do not wish to believe in colloidal science applications in the field of tanning, because of previously held convictions.

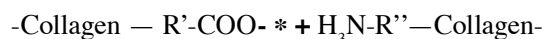
In Dr. Jaume Cot's highly sophisticated collagen model presented at the joint ALCA-IULTCS congress in 2007;²⁵ he clearly and emphatically states his opinion that the chemical forces affecting fibrils and the higher hierarchies of dimensions of collagen such as fibers, *are electrostatic in nature rather than covalent*. Thus the compound saline links between *collagen* carboxyls and cationic amino groups consist of an electrostatic bond probably augmented energetically as it is compounded by up to three (most likely, just two) possible H-bonds between the amino hydrogens and electronegative component elements that may or may not be present in the immediate neighborhood! But if there is a *colloidal supramolecular* water-sheath between the protein triple helix fibril-structures, different from the Hofmeister Series sensitive inter-tropocollagen water; it can be involved with the amino hydrogens through H-bonds as well, and electrostatically with carboxylic elements of saline bonds attached through and between the more hydrophobic remnants of the triple helix, that is, in-between the polar side-chains and the hydrophilic zones due to the more polar back-bone proper. The *Zwitterion formation* clearly involves intrinsically the transfer of a proton! The title of a very suggestive paper is hereby presented such that it might entice some readers into delving into more theoretical details, but taking nothing away from

the need of the expeditious application of this chemical model being presented, for solving the present day-to-day problems in the tannery:

“Thermodynamic Description of a Contact and Solvent-Separated Ion Pair as a Function of Solvation: A Model for Salt Bridges and Proton-Transfer Reactions in Biology”

This paper by Beeson and Dix²⁶ clearly stresses the importance of solvent polarity in not only affecting proton transfer in protein configurations, namely equilibrium **A**, but deals with H-bonding energetics in peptide stabilization as well. The question of *Zwitterion* formation and energetic, steric and thermodynamic factors that then clearly affect the shifting of equilibriae such as **A**, are discussed from a general point of view, in the M.Sc. degree thesis of Mr. Erik Tung-Lam Cheung²⁷ that makes special mention of the significance of the proton transfer reaction importance and thus the relevance for understanding better the *Zwitterion tautomer formation*, that is often just completely ignored by working tanners and some leather chemists. These last theoretical background considerations are being then presented for those interested in delving a little deeper into the topics of this presentation stressing *importance of saline links* as being vital in augmenting of the overall thermodynamic stability of the triple helix micelle and thus as an insight into the basis of the proposed concept by the author and referred to as “thermodynamic originated”²³ *steric hindrance* as being the cause for the various possible reasons for unreactive (“buried”, “unavailable”, “self-masked”, etc.) carboxylic and amino side-groups behavior as reported in the biochemistry²⁸ and tanning literature²⁹ (footnote 3). More reactive groups need to be made available by ionic strength control, saline-bond break-up, etc. in tannery reactions to help approach a more complete stoichiometric outcome, to not only avoid chemical waste, but to actually make *better* leather.

THE THERMODYNAMIC STABILIZING SALINE-BRIDGING (*) WITHIN THE VARIOUS HIERARCHICAL DIMENSIONAL STRUCTURES OF COLLAGEN CAN BE DESCRIBED AS:



The basic principle concerning enhancing reactivity of collagen to most tannery chemicals, is hereby being presented to the tanner: any offered chemical (including H⁺ and OH⁻!) that decouples this saline link, *very widely present throughout collagen*, by chemically fixing on either the anionic carboxyl or cationic amino, then frees gradually the remaining component of the electrostatic salt-link, denoted by the asterisk, to react with an opposite charged tannery chemical being, or to be soon, offered. Thus the well known beneficial action of a commercial syntan-masked chrome tanning products³⁰ is due to the anionic sulphonic aromatic syntan component fixing on

to the cationic amino, as it then frees then the corresponding anionic carboxyl of collagen, to react with any chrome present, as it rapidly turns into cationic tanning complexes from the supposedly *freshly-dissolved* highly masked sulphonic anionic complexes formed. Sulphonic syntans can be also considered to be as specific Hofmeister Series coagulating (tropocollagen dehydrating) weakly tanning anions. Even when so called masked-chrome syntan preparations are added in the presence of ordinary basic chrome tanning sulfate salt, an increased *total chrome* absorption by collagen results and the produced leather itself is much superior to that obtainable by adding only ordinary commercial chrome alone. This is often being reputed as being because of the “combined” action of the dual tannage concurrent processes occurring, that it is both a sulphonic aromatic syntan *anionic tannage* and that of *cationic chrome tannage* itself. The beneficial aspects of the effect are also often attributed as well, to the “masking effect” of the syntan on the chrome (footnote 4), but it should be made perfectly clear that in cationic aluminum tannage as well, is improved by the concurrent addition of such an anionic sulphonic syntan, even though in the case of aluminum, the much weaker metal masking occurring, because of its lesser coordination capacity, is probably then not too much of a real factor at all! Certainly the co-use of aldehydes to effectively disable the aforementioned saline links through more permanent discharge of cationic amino groupings, also exhibits better chrome uptake in tannage as proposed by Umberto Sammarco and many others, and is also due to the synergistic effects of decoupling the saline link primarily, as described by the previously discussed Sørensen Formol titration effects on chrome fixation, and in that particular case, there is certainly *no additional coordination chemistry advantage* involved! Certainly the remarkable increased chrome efficiency effects by offering during pickle Glyoxilic acid (HOOC-CHO, Hoechst’s Feliderm CS™) are explainable as the aldehyde function blocking amino-side groups against salt-links with carboxyls.

There is a favorable dye-leveling effect involved by the blocking action by aldehydes of charged amino formation, especially those in scar tissue! Scar tissue being somewhat of nature’s emergency “rush-job” for repairing disrupted normal collagen tissues, perhaps then has less cationic aminos favorably placed such as to be properly involved in the additionally stabilizing saline-links, and thus scars will naturally dye more intensely because of having more *uncoupled cationic amino* groupings than, the slowly-growing,

more stable, standard, highly helical character, collagen! The combined use in the pickle of aldehyde and a cationic Hofmeister lyotropic swelling agent (such as an aluminum salt!) that lowers the hydrothermal shrinkage temperature of pickled collagen by about 20-25°C, and has certainly been shown to improve chrome uptake and results later in more intense dyeing as well (see appendix A). If a neutralized naphthalene sulphonic syntan product is part of the subsequent basification as well, fuller chrome-use efficiencies even surpassing the Sammarco’s 95+ percent fixation are possibly achievable, even without reaching the recommended basification temperatures for better chrome exhaustion at 48-50°C, because of the traditional lack of adequately powered drumming equipment at most tanneries! The fact is that gentle and controlled destabilization of the triple helix itself by mechanical *energy inputs* such as described by the Hinsch mechanical drumming effect³¹ analysis, ultrasound energy input, *generalized* temperature increase, lyotropic swelling agent pretreatments by Hofmeister Series swelling ions (or similar acting chemicals, such as urea!) that gently destabilize thermodynamically the triple helix by the straining of the helicoidal structure (to more resemble and act as scar-tissue does!) as it lyotropically swells and some saline links probably become undone, and are presumed to make collagen more chemically reactive. Ionic-strength induced “peptization” by Debye-Hückel extensive shielding of the saline bond charged components, also has in common, an observed associated increased chrome tannins uptake upon basification dilution, which would seem congruent, at least, with a partial additional decoupling of the saline bonds being hereby proposed as an explanation for all these well known effects,³ and thus allow us a closer approach to the achievement of nearer stoichiometric goals in the tannage reaction (regardless whatever it’s “true nature” might be!) to yield better leather and waste less chrome. Thus overcoming *thermodynamic-stability originated steric hindrance to chrome-tannage* by decoupling additional collagen stabilization by saline links (such as heat-denaturing also does!) will increase the availability of reactive carboxylic groups on collagen. This tried and seemingly successful improvement philosophy needs to be practically implemented to effectively demonstrate to the pollution control authorities, that we, as tanners, are doing something tangibly real about unnecessary chromium pollution, even at the commercial risk of having to give-up some possibly now fashionably-current sales of metal-free leather!

(3) A.D. Covington makes the surprising calculation that only about one in six carboxyl’s available in collagen actually reacts with chrome tannins offered! Thus a small increase in the number of reactive, towards chrome, carboxyl side groups could appreciably improve chrome exhaustion efficiency.

(4) Sharpouse³⁰ downplays the coordination aspects about the action of this type of chemicals by stating that the syntan component probably reverts to the usual anionic tannage of collagen’s cationic amino groups.

One lyotropic Hofmeister cationic tropocollagen-swelling exemplary agent⁸ often employed in these high efficiency chrome tannages is a small amount of a soluble aluminum salt in the pickle! This will actually lower the Ts by about 20° C.³¹ There has been extensive discussion of the benefits of combining chrome tannage with an aluminum pre-tannage³² to better utilize chrome. Covington³³ refers to it as a “*catalytic*” effect of aluminum on the chrome tannage reaction, resulting in the development of the aluminum-containing ChromesaverTM family type of tannery chemicals, but not with much actual usage for shoe upper leather manufacture has occurred because of the tanner’s reluctance to change from the accepted practice for a mixed mineral tannage; such as aluminum when used as a substantial component of (re-)tannage, requires a much higher end-pH of basification than that of chrome.³⁴ This fear that ending basification at higher pH (5.8-6.0), is considered by most tanners as being a sure way for causing loose grain, and unfortunately, as well, the tanner’s perception that one should not expend even inexpensive and relatively ecologically perceived-harmless chemicals such as inorganic aluminum, in the making of shavings. This causes tanners to mistrust these recipes from the very beginning, although *they are known* to appreciably increase chrome-tanning efficiency. There appears that no objection is found in using excessive and fairly toxic aldehyde combinations in some wet-white-type production, to yield all-metal-free leather!

The colloidal concept of “**peptization**” (**salting-in**) of collagen caused by mild salinity, as well as the decrease of astringency by the use of much higher ionic strengths (**salting-out**) have all but disappeared after WWII from most tanner’s repertoires of conceptual tools. Probably because of the difficulties in clearly understanding the application of these concepts, but the mastery of these, is essential to the use of this chemical model being proposed (especially in the application of manipulating equilibrium **A**) for the intelligent offering of chemicals to collagen/leather; hopefully this presentation will help the tanner remedy this situation. Perhaps more enlightening research will soon arise to help explain these somewhat mysterious appearing and mistrusted colloidal processes better to the tanner.

The technology evolved from the use of pits to that of drums, where ionic strength control, mechanical effect control, temperature control, float size control, etc. are more feasible. Thus a drum should be as thought of being more of a chemical reactor, instead of just an “improved” motorized pit. Unfortunately most processing recipes remained still heavily influenced by classical pit-technology-thinking, and need to be better adapted to more modern conditions. It is hoped by the author that the use of this model based on “expected astringency” will so help.

APPENDIX A

Estimated Improvement in Chrome Uptake Efficiency:

Normal Tannage 6.5% BCS offer:

Average according to SENAI, nine samples=
5.18% Cr2O3 contents

ABC reduced chrome tannage 5.0 % BCS offer:

Average according to SENAI, nine samples=
4.68% Cr2O3 contents

Difference in ratio offer: $6.5\%/5\% = 1.30$

Difference in ratio results: $5.18\%/4.68\% = 1.11$

Estimated increase in efficiency by addition of 0.3% of $Al_2(SO_4)_3$ and 0.5% aldehyde tanning agent at 40%, to pickle at reduced chrome offer tannage:

~19%

Full production trials of about 10 metric tons of unsplit limed hides. Chrome stratigraphic contents performed on wet-blue by the Brazilian Leather Institute, SENAI. The data obtained seemed to have little dispersion and standard deviation information can be made available to any interested party.



Waste Baths: left ABC process, right normal tannery processing.

ACKNOWLEDGEMENTS

- I wish to thank my faithful suppliers, clients past, J.H. Lowenstein, and present for allowing me to try in the field somewhat unconventional formulations. Especially, Moyle Mink and ABC Leder Grupo Andino S.A. (CEO I.Q. Héctor Mario Agudelo) that is undertaking this project of minimizing tannery effluents through increased efficiency in chemical usage.
- The many people that provided helpful discussions are just too numerous to list!

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PRESENTATION AND ACCEPTANCE OF THE 2011 O'FLAHERTY SERVICE AWARD

by

DAVID OUELLETTE AND LORI HYLLENGREN

David Ouellette

The Fred O'Flaherty Service Award originated in 1974 in memory of the late Fred O'Flaherty for the high standard of service he gave to the American Leather Chemists Association. This award is given annually to honor an individual who over a period of time has made a significant contribution to the Association and the industry in general.

This year's selection committee consisted of Chairman Rob Harvey, from Hermann Oak Leather Company, Shawn Brown from Quaker Color, and Roar Solberg of BASF Corp.

When Rob Harvey, asked me to make this presentation I was quite please to do so even though I was not on the selection committee. I have had the pleasure to work on committees with this year's recipient and know first hand how truly deserving she is of this honor. Part of the criteria for selection is length and quality of service as well as contribution to the leather industry. This year's recipient has more than met these qualifications. When asked for a short synopsis she replied "Busy" and she truly has been busy working in various capacities for this organization and the industry in general. After graduating from the Rochester Technical College in 1975 she went to work for S.B. Foot Tanning Co. and is still there today. She is currently their lab manager. She oversees both the tannery lab and the footwear testing lab at Red Wing Shoe.

For the ALCA she has served as Councilor, Co-chair of the Technical Committee of Methods and Specifications and on the Research Liaison Committee. She is also the 2007 Alsop Award recipient. Since 1989 she has been active on the ASTM D31 Committee on Leather. She has served as the Secretary and two terms as the Chairman. It is on this committee that I had the pleasure of serving with her and can testify from first hand experience of how deserving she is of this award. In every organization there is someone who can best be described as the glue of the organization and from my time on the ASTM D31 committee I can tell you she was the glue. She insured that minutes were kept, meetings were organized, testing was coordinated and on and on. Her accomplishments are multinational in that she serves on the Canadian Standards Association technical committee for methods development for protective footwear used in Canada. She has also managed to serve on the European Committee for Standardization' Technical Body for Foot and Leg Protectors as the representative from Denmark. I'll let her explain how she managed to represent Denmark. She also participates on the Department of Defense Footwear Committee. There she assisted in the conversion of the Fed 311 methods to ASTM methods as well as co-editing the



David Rabinovich receives Wilson Plaque from Michael Bley.

current Military Specification MIL-PRF 3122J for leather in military footwear.

Beyond all this she still has found time to raise two children, Coty and Shelby and help run a farm with her husband, Steve, where they raise 1200 acres of corn and soybeans. As if that is not enough she is also active in her church serving on committees there.

The committee chairman as asked that I pass on the following words of thanks:

He says "I can't thank you enough tonight for your past and on-going service to the leather industry, but I will try. Your dedication to insuring that American Tanners have a strong and influential presence in world wide standard setting cannot be underestimated. We all appreciate the time and effort that you have invested to represent our industry on the world stage. On behalf of the ALCA and everyone in the American leather industry, thank you for all of your outstanding work."

Ladies and Gentlemen I present to you the 2011 Fred O'Flaherty Service Award recipient Lori Hyllengren.

Lori Hyllengren

Thank you Dave, for that "O'Flattering" introduction. Mr. President, officers, counselors, fellow ALCA members and guests;

To receive this award is a real privilege. There are many others in this room that are worthy, so being recognized amongst you is an honor, and doing so in my own backyard makes it truly

special. "I wrote two acceptance speeches for tonight, a long one and a short one. I'll give you the short one: 'Thanks.' But it seems there might be enough time for the long one as well, which is: 'Thanks a lot.'"

When I was asked for my bio, so that Dave would have something to talk about, I told him that my resume was pretty boring. I was born in Red Wing, went to school, got a job, been there since. It was 36 years ago today I was hired at SB Foot Tanning Co. The tannery was founded in 1872 and has operated in my hometown for 139 years. One quarter of those years I have occupied the laboratory. That is a very long time to spend in one place, especially in this industry, and I am proud of that. My long laboratory tenure also makes a convenient excuse for when people question my mistakes; I just blame it on all the fumes. Long before this casino existed, the Tannery took a gamble on me and the odds weren't in their favor. I knew absolutely nothing about leather, and only intended on working until I had children, who are now 25 and 30. Without the support of SB Foot and Red Wing Shoe, this award would not have been possible for me, so I am indebted to them and hope I made good on their investment. As a side note, in 36 years I have had 11 different bosses, for an average of three years apiece. Chuck, (pointing to my current boss), that means you've got about two years to go.

Although I was hired on June 11, I couldn't start for two weeks. At the time, Cliff Benrud, Dick Waite and Janice Barnes worked in the lab and were active members of the ALCA. It seemed they were going to be attending something called the ALCA convention, so I was told to wait until they came back. I had no idea what the ALCA was, but I knew it shorted me out of my first paycheck. For the next 14 years I looked forward to the ALCA convention, even though I never went. This meant for one week of the year I was "large and in charge" of the lab while the rest were gone. In 1989, I became the laboratory manager when Janice took a position at Wolverine. The best advice she left me with was to make sure I joined ASTM and ALCA, if for no other reason than to make contacts in the industry. I took her advice, and even before the Internet, email, Skype or Blackberries were invented, I was "Linked In."

As Dave said, I am currently involved on several committees that develop methods and write standards. He mentioned something about my organizational skills, but for anyone that has ever seen my office, they would have serious doubts about that. He kindly noted that I am the glue that holds things together on these committees, but I am not a committee of one. There are many other dedicated people involved and I am grateful that they have "stuck" with me. Standards development is not for everyone, as Craig can attest to. A few of the council members attended one of our ASTM meetings once, just to see what we do. After a short time they were looking for the nearest exit. Luckily, over the last century of tanning there have been many that share my passion to make leather better through testing and research. Between the ALCA and ASTM committees, we have published many methods that are used globally today.



Lori Hyllengren received O'Flaherty award from David Ouellette.

Speaking about committees, this is my chance to do a 30 second commercial and you can't turn me off with a remote. If you, or anyone in your company has an interest about the latest hide, skin and leather research being funded with your very own tax dollars, then join the Research Liaison Committee. We meet in exotic places, like Philadelphia. Or, if you or anyone in your company tests leather, wet blue, or tanning materials, you should join ASTM. We meet in exotic places, like Philadelphia, and eat at 5 star restaurants like *Chickies & Petes*. If you can't join ASTM, but want to keep informed about what is happening, then join the Methods and Specifications Committee of the ALCA. We meet in exotic places, like Red Wing, Minnesota. Many companies are thinking about succession planning these days. Send your younger technical people to these meetings. Invest in them and the payback could be rewarding.

In closing, I am truly humbled to be presented with the Fred O'Flaherty service award. Earlier today I bought one of those Scratch Off tickets. It said, "Sorry, you are not a winner." That couldn't be further from the truth. (L on the forehead) This doesn't stand for Loser, it stands for Leather, and I hit the jackpot. This award means more to me than double cherries or triple bars, and I want to share it with all of you. For me, this is not about my service, but instead about whom I serve. I am not here for what I have done, but rather for the opportunities that you and the leather industry have given to me. So again, thank you. I hope you have enjoyed coming to Red Wing this year. It was nice to see so many of you here and please have fun the rest of your evening. Just a word of caution: if you plan on trying your luck later, don't lose your shirt, this is Minnesota and winter's coming. On the other hand, if you lose your shoes, that's OK. We'd love for you to go buy another pair.

June 11, 2011

PRESENTATION AND ACCEPTANCE OF THE 2011 ALSOP AWARD

by

ELEANOR M. BROWN AND ANTHONY D. COVINGTON

Eleanor Brown presented by Craig Keyser
Mr. President, members and guests of the American Leather
Chemists Association:

The Alsop Award was established in 1939 in honor of William K. Alsop and to honor those who significantly promoted the knowledge of science and technology of leather for the benefit of ALCA members and the leather industry our Association supports. The award was established with the support of Tac Tannins and Chemicals, Inc. Since 2009, The American Leather Chemists Association has directly supported this annual prize to be awarded for outstanding scientific or technical contributions to the leather industry, under such terms as the Council shall deem proper. The Alsop Award is presented in recognition of outstanding scientific or technical contributions to the leather industry. This year's nominating committee consisted of Eleanor Brown, Chris Koeblinger and Gennaro Maffia as chairman. The committee selected, with the approval of Council, Anthony Covington as the 2011 recipient of the Alsop Award. Tony has been a member of ALCA since 1991, and has presented numerous papers at meetings over the years. Tony Covington, DSc. Emeritus Professor of Leather Science at the British School of Leather Technology (BSLT), at the University of Northampton, UK, has for more than thirty years dedicated his research, teaching, and publication to the science of leather.

In his recently published textbook "Tanning Chemistry: The Science of Leather" Professor Covington integrates the fundamental science with its application to the manufacture of leather. Because this book is written in a way that integrates the terminology used by tanners with the language of scientific publications, it enhances communication between the academic theorist and the tanning practitioner. This book introduces the reader to the structure and biochemistry of the hide, and through the many processes each with its own scientific basis that prepare it for the tanning step where the hide is transformed into leather. Currently, there are three classes of tannages, mineral, vegetable and aldehydic, each with a unique chemistry, in common use. Each of these chemistries and their applications are clearly explained. Typically, books of this scope are written by committee, with somewhat uneven results. It is a tribute to Professor Covington's scholarship, that based on the scope of his publication of original research in peer reviewed journals, he was qualified to write on all of the topics covered, thus producing a more cohesive and readable textbook than most. This book will undoubtedly become the standard text for leather chemists and technologists of the early 21st century.

Ladies and gentlemen, in recognition of his contribution to the science and technology of leather it is my pleasure to

introduce the recipient of the 2011 Alsop Award: Prof. Tony Covington, DSc

Tony Covington

When I received notice that the ALCA was to give me the 2011 Alsop Award, the first thing I did was to turn to my ALCA Directory to check the list of former recipients of this honor. After all, a chap needs to know with what sort of fellows he is being forced to associate. I found that the list is long, extending from 1939, and distinguished, including such luminaries as Bob Lollar (with whom I once had dinner) and Jean Tancous (a sort of transatlantic Betty Haines). Since the Award relates to scientific and technical contributions to the leather industry, not surprisingly the names of recipients reads like a list of references from a chapter of my book; currently available from The Royal Society of Chemistry and Amazon, but probably not from all good booksellers.

During my career of thirty-five years in the leather industry, and I should say in this company as a foreigner, of the 59 previous recipients of this Award, I have met 23. Among those these, there are several who became more than colleagues, I number them among my friends: Steve Fearheller, Bill Prentiss, Steve Shivas, Dave Bailey, Marcel Siegler, Hubert Wachsmann, Ellie Brown, Frank Rutland, Bill Marmer, to name but a few. I am happy to be number 60.

I have been an active member of the American Leather Chemists Association for 20 years, almost from my first visit to the United States. I accept this honors from my peers, with grateful thanks.

June 11, 2011



Dr. Anthony Covington receives Alsop Award from Craig Keyser.

CLOSING COMMENTS BY ALCA PRESIDENT ANDREAS RHEIN

Ladies and gentleman, it is an honor and a privilege to stand here tonight in this spot at this occasion to accept the responsibilities as your President. The ALCA has always been about Research and fellowship for its Members.

As President, my focus will be on,

- The Annual Meeting
- The Correspondence Course
- Attracting new members, and
- The *Journal*

These four goals have kept this group cohesive and vital for 107 years, and will continue so for as long as American Leather chemists and technologists have a need to belong to a professional group beyond their employer. In the coming year, we need your ideas and enthusiasm as we plan and carryout this task. I am looking forward to working with you, the council and members to achieve these goals! Thank you for your attendance this year and enjoy the rest of the evening.

Meeting adjourned.

June 11, 2011



President Andreas Rhein accepts gavel from past president Craig Keyser.

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