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Sustaining tanning process through conservation, recovery and better utilization of chromium

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Abstract

Leather is a unique material unmatched in properties by synthetics. Leather making is an environmentally challenged process. Tanning is the key process that renders stability to the skin matrix against microbial degradation, heat, sweat etc. Chromium(III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. The reported toxicity of chromium compounds coupled with poor uptake of chromium during tanning process has challenged the continued use of this process. Problems associated with tanning have been classified as avoidable, controllable and unavoidable. Technological developments in avoidance and control of pollution in leather processing have come forth. There are both in-plant and end-of-pipe treatment solutions. This paper surveys the development of technologies that have rendered the tanning process eco-sustainable. A call for further understanding of the chemistry of tanning and need for cross-fertilization of ideas is made for enabling the greening of the tanning industry.

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1. Introduction

Modern society is dependant on several materials. The production systems of consumer products have become both material and energy intensive. Such intensive production systems lead to the generation of a significant amount of industrial

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wastes (Durning, 1994). In some cases, the amount of wastes generated exceeds the carrying capacity of the region (Postel, 1994). This in turn leads to adverse effects on eco-systems.

The abatement of industrial pollution is now of high and immediate priority. There is an urgent need to render the production systems cleaner. Emission of wastes from industrial production needs to be reduced significantly, if the required rate of industrial growth is to be rendered environmentally sustainable.

Leather has remained a unique material for a long time. Visco-elasticity and pore size distributions are two important properties of leather that have rendered it a unique material. The ability to breathe and readjust to volume fluctuations of the foot has made leather a unique material of choice in footwear industry. These properties have not yet been matched. The processing methods in tanning industries have been dominated by traditional practices. From an eco-product, the public perception of the industry has changed to negative, on account of the ecological threat emanating from the tanning activity.

Tanning as a process has evolved over time. The practice and skill evolved first, understanding of the underlying chemical principles followed later in the development of the art and science of tanning. The discovery of tanning with plant and organic materials may have been accidental. With increasing demand for aesthetic appeal and softer types of leathers as well as the need for reduction in process time, alternative tanning methods and post tanning operations had to be developed. The discovery of chromium tanning in 1858 is a landmark in leather processing. Although many alternative mineral tanning materials have been explored, chromium based tanning methods in the manufacture of light and softer types of leathers have stood the test of time. The uniqueness of chromium based tanning materials in leather processing has been much discussed.

Stabilization of collagen derived matrix proteins in the skin/hide against (a) wet heat, (b) dry heat, (c) thermo mechanical stress and (d) enzymatic attack forms the basis of leather making. Such a stabilization is attributed to the formation of new chemical crosslinks in the matrix proteins. Different theories have been advanced to describe the observed effects of tanning. They include (a) coating, (b) intra- and inter-molecular crosslinking, (c) dehydration, (d) fiber separation capacity of tanning agent, (e) reduction of number of reactive groups leading to decreases in adhesive tendency of fibres and (f) metal induced long range order coupled with changes in surface charges.

Tannages are broadly classified as (a) mineral, (b) vegetable and (c) aldehyde. When the stabilization of skin is achieved by the use of a suitable inorganic salt, the process is known as mineral tanning. The most commonly used mineral tanning salt is the basic chromium sulfate (BCS).

A broad understanding of tanning with regard to fixation at carboxyl sites and elsewhere in collagen has been obtained. Speculations on the nature of crosslinking have been made at various times. Whereas binding of chromium by functional sites in collagen may participate in fixation of the metal ion, the chemical stability of chromium–collagen compound may well arise from the specific interactions, many of which have not yet been understood.

Tanning is more easily described than defined. The need for a better understanding of the structural changes involved in the chrome tanning process has been stressed.

2. Global leather industry: environmental concerns

Leather is the major industrial product made from a natural fabric, the skin. Leather processing has evolved from a traditional artisanal practice to an industrial activity. Intensive production of leather in small clusters has caused environmental concern (Ramasami et al., 1999). Leather processing activities subjects a skin or hide to a wide range of pH changes. It involves the use of copious amounts of water. Environmental challenges from leather processing arise from the nature and quantity of chemicals used as well as the amount of wastes generated and discharged (Prasad et al., 1981).

The raw material for the leather industry namely salted hides and skins, carries with it common salt, which later forms a disconcerting source of pollution (Kronick, 1995). Other major polluting chemicals used in tanning industry which cause pollution are lime, sodium sulfide, ammonium salts, sulfuric acid, chromium salts and vegetable tanning materials (Schramm, 1997). About 30–35 l of water is employed for every kilogram of hide processed (Ramasami and Prasad, 1991). Typical emission factors expressed as wastes generated for every ton of leather processed at various stages of processing are presented in Table 1. Typical levels of utilization of chemicals in leather processing are indicated in Fig. 1.

3. Aqueous chemistry of chromium(III): its relevance to tanning

The ground state electronic configuration of chromium(III) is $3d^34s^0$. In an octahedral environment of ligands, the metal centred electrons populate d orbitals of the t_{2g} subset (Kettle, 1975). Inter electronic repulsion expected between the metal centred electrons and lone electron pairs of incoming ligand renders nucleophilic substitutions difficult. The stability of an octahedral ligand field of a d^3 ion is considered as the cause for the substitution inertness of chromium(III) (Orgel, 1967; Swaddle, 1983).

The electronic configuration of Cr(III) supports the hybridization of $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals. Such $3d^24s4p^3$ hybrid orbitals as well as the tripositive character of the metal ion enable the formation of thermodynamically stable coordinate covalent bonds. The tanning phenomenon is influenced by thermodynamic and kinetic factors associated with the reactions of chromium(III) (Santappa et al., 1982).

Chromium tanning salts are reported to contain a large number of Cr(III) species varying in (a) degree of polymerisation (b) charge (c) number of coordinated aqua and hydroxyl ligands and (d) ligand field stability (Chandrasekaran et al., 1999). The kinetic lability of the species contained in chromium tanning salts varies (Ramasami

Table 1
Typical waste emission factors associated with leather processing

	Soaking	Liming	Deliming	Pickling	Chrome Tanning	Dyeing & Fatliquoring	Composite (incl. Washing)
BOD ₅	8.3–18.8	17.5–35.0	1.5–4.5	0.3–0.5	0.5–1.2	1.5–3.0	35.0–105.0
COD	22.5–45.0	35.0–87.5	3.8–10.5	0.8–2.3	1.5–3.8	3.8–10.5	87.5–280.0
Total solids	262.5–415.5	105.0–175.0	6.0–15.0	26.3–52.6	45.0–90.0	6.0–15.0	528.0–875.0
Dissolved solids	240.0–360.0	84.0–105.0	3.8–9.0	25.5–50.3	43.5–86.3	5.1–13.5	455.0–735.0
Suspended solids	22.5–52.5	21.0–70.0	2.3–6.0	0.8–2.3	1.5–3.8	0.9–1.5	70.0–140.0
Chlorides as Cl ⁻	112.5–225.0	14.0–28.0	1.5–3.0	1.5–3.8	23.0–38.0	0.8–1.5	210.0–332.5
Chromium (total) as Cr	–	–	–	–	3.0–7.5	–	3.5–8.8

All values expressed in kg/tonne of hide processed.

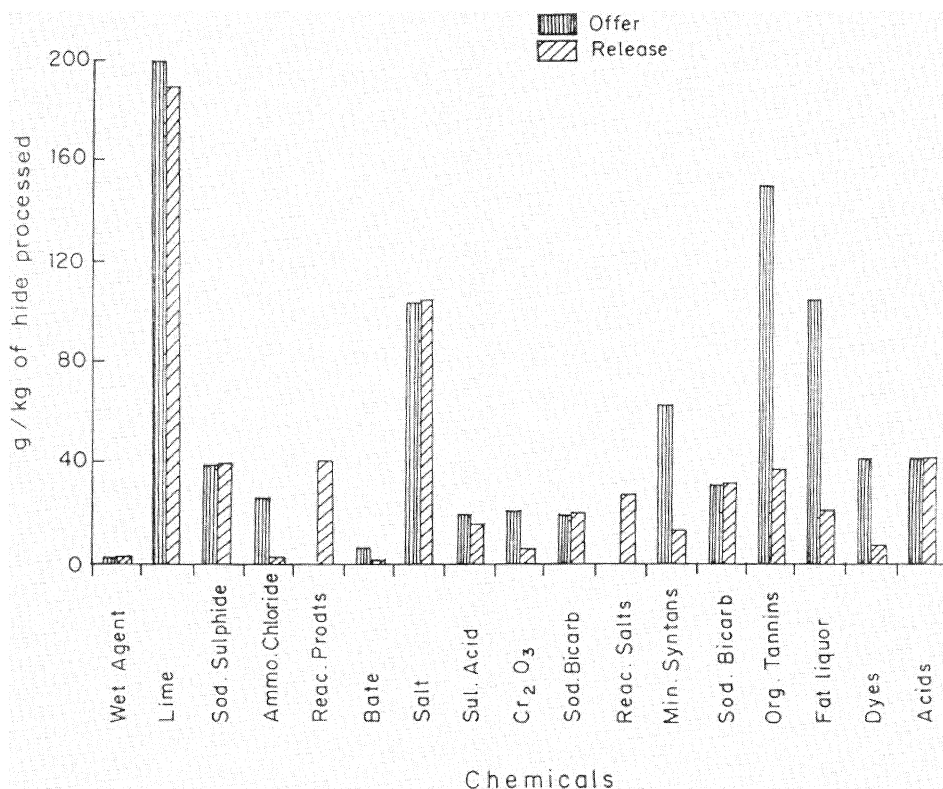


Fig. 1. Typical levels of utilization of chemicals employed in leather processing.

et al., 1987). The affinity of various species contained in chromium tanning salts to the binding sites of collagen is widely different (Gayatri et al., 1999). In general, the replacement of coordinated ligands from the first coordination sphere of the chromium(III) environment is a slow process. Typically, the half-life for the water exchange in hexaaquachromium(III) is over 100 h at 30 °C (Swaddle, 1974). The equilibrium constants for the binding of unidentate ligands like acetate with aquochromium(III) complexes are low (Hamm et al., 1958).

The uptake of chromium by collagen during tanning may be limited by factors such as (a) problems of transport of the chromium compounds into the fiber structure and molecular aggregates of collagen (b) kinetic inertness of chromium(III) ions (c) lower thermodynamic affinity of some species for complexation with functional sites in collagen and (d) inappropriate conditions viz. pH, temperature, liquid–solid (float) ratio etc. employed for tanning (Chandrasekaran et al., 1999).

Aqueous chemistry of Cr(III) ion is well understood and extensively reviewed (Larkworthy et al., 1987). Since the reaction of chromium(III) with collagen is carried out in water media, aqueous chemistry of the metal ion is most relevant in understanding the exhaustion behavior of the chromium tanning salt.

4. Chromium tanning: environmental concerns

Varied nature of chromium salts and application methods employed result in an average level of absorption of 40–70% of Cr_2O_3 used in tanning. In the absence of adoption of suitable technological methods, typical concentrations of chromium in sectional waste streams of chromium tanning yard are in the range of 1700–2500 ppm (Ramasami, 1996).

The biotoxicity of chromium has been a subject of active discussion. The biological implications of chromium are known to vary with the oxidation state of the metal ion (Dartsch et al., 1998). Chromium(III) is included among the essential trace elements. The implication of chromium(III) in glucose metabolism has been considered beneficial (Mertz, 1998) while oxyanions like chromates are well-established human carcinogens (Costa, 1991). Some Cr(VI) salts are potentially genotoxic at a number of *in vitro* and *in vivo* end points (Singh et al., 1998). The oxyanions are actively transported into the cell by sulfate transport systems. They react with a number of reducing agents in cells and are eventually reduced to Cr(III) (Arslan et al., 1987). The ability of Cr(III) to (a) crosslink DNA and proteins (b) participate in non-enzymatic phosphorylation and (c) influence calcium transport channels has been discussed (Salnikow et al., 1992; Tsou et al., 1997; Balamurugan et al., 1999).

A dynamic equilibrium among Cr(III) and Cr(VI) forming under the influence of soil bacteria is not unlikely. The naturally occurring form of chromium in ore is oxides of chromium(III). The chromium content in the earth's crust is 122 ppm but the metal ion is contained in an insoluble form (Hartford, 1979). The mobilization of the metal ion into the flora and fauna is limited by the poor solubility of the Cr_2O_3 form present in the chromite ore. When a soil contains large amount of soluble and biologically assimilable forms of chromium, effects of soil pollution by the metal ion are observed (Bartlett, 1991). Although nature presents chromium in trivalent state, mining of the chromite ore leads to the formation of Cr(VI) (Palmer and Wittbrodt, 1991). Usually part of any Cr(VI) added to a soil may be reduced by soil reductants, especially under acidic conditions (Bartlett and Kimble, 1976). When the reducing capacity of soil is exceeded, chromium(VI) may persist for years without change of oxidation state. When soluble Cr(III) is added to soil, manganese oxides present in the soil may cause oxidation (Bartlett and James, 1979). When not oxidized to Cr(VI) form, Cr(III) may remain immobilized in the soil. A portion of chromium(III) in soil is mobilized through the formation of complexes with organic ligands. Chromium in soil may be subjected to redox cycles (Bartlett, 1991).

In view of the potential toxicity of some forms of chromium, the environmental regulatory norms stipulate that the levels of chromium in wastewaters be controlled. The discharge norms for industrial wastewaters in different countries specify permissible concentrations of chromium in the range of < 0.3–2 ppm (Ramasami et al., 1999). Such strict norms demand technological interventions for abating chromium pollution.

5. Technological interventions for management of chromium

Several technologies for better management of chromium in tanneries have been forthcoming. Some of these technologies are grouped in Fig. 2. In general, such technologies can be classified based on different approaches such as (a) higher exhaustion (b) recovery and recycle (c) alternatives to chromium and (d) safe utilization and disposal of chromium bearing wastes.

5.1. High exhaustion systems

The uptake of chromium from tanning bath under normal conditions of tanning is of the order of 40–70% of chromium used. It is now possible to increase the absorption levels of chromium in the tanning bath (Kedlaya, 1974; Prasad et al., 1987). These strategies include (a) changing conditions of tanning (b) use of exhaust aids (c) modifying BCS salts and (d) modifying protein substrate.

5.1.1. Towards higher exhaustion: changing conditions employed for tanning

5.1.1.1. *Mechanical action.* The irreversible binding of chromium to skin is limited by the nature of interactions between the metal ion and binding sites in the protein (Santappa et al., 1982). The access of the metal ion to the sites in the protein is a fundamental requirement. Transport of chromium ions into the fiber structure is an

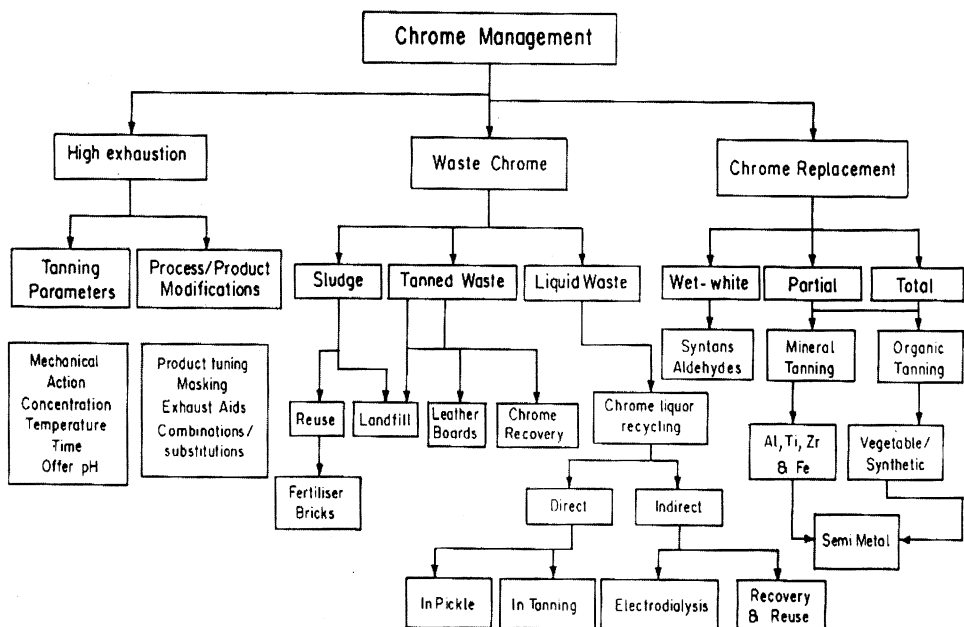


Fig. 2. Technological options for better management of chromium in leather industry.

important pre-condition prior to tanning (Germann, 1995). Mechanical action serves to flex the skin and create forces required to pump chromium liquor into the fiber structure, primarily through pressure alternations within the connected pore structure of the matrix. The rate of penetration depends on the speed of agitation that in turn is influenced by the geometry and speed of the drum as well as cascade ratios (Lhuede, 1969; De Simone, 1986). The faster the rate of penetration of chromium, the higher the time available for chemical reactions between the metal ion and the protein sites.

5.1.1.2. Concentration of solutions. BCS used in tanning is a mixture of several chromium(III) species, which exist in a dynamic equilibrium (Chandrasekaran et al., 1999). Concentration of chromium forms an important parameter influencing the equilibrium composition of BCS. Sulfate ion contained in BCS plays an important part in tanning (Gustavson, 1956; Hormann, 1974). At high concentrations of BCS, sulfate remains coordinated to chromium rendering Cr(III) species non-cationic thereby (Gustavson, 1956). The ionic character of chromium species influences the rate of penetration. The higher the concentration of chromium(III), the faster the rate of penetration of chromium into the fiber structure. Model studies conducted have shown that rate of penetration is first order on Cr(III), or in other words, rate of penetration is directly proportional to chromium concentration (Covington, 1997).

5.1.1.3. Temperature. Temperature is a parameter that influences many factors in the reaction of chromium with protein (Gustavson, 1956; Heidemann, 1993). Factors which are known to be influenced by temperature of the reaction medium are (a) viscosity (b) equilibrium composition of various species (c) protolysis of chromium(III) species (d) polymerisation (olation and oxolation) of chromium and (e) lattice ordering of skin matrix (Chagne et al., 1996). At higher temperatures, acid–base dissociation of aqua ligands in chromium(III) complexes increases. The rate of diffusion of chromium species into hide structure increases with temperature, when T is less than 50 °C (Bickley et al., 1967). The pickled pelt undergoes major changes in lattice order at temperatures above 50 °C. Chemical reactions of chromium with collagen are subject to thermal activation. Temperature, therefore, influences chromium tanning by changes in the rates of penetration as well as in the fixation of chromium (Covington, 1991).

5.1.1.4. Reaction time. Contact time between the reaction mixtures has direct bearing on the extent of reaction when the reaction rate rather than diffusion controls the process. It has been found that chromium fixation increases with longer process time, say up to a period of 24 h.

5.1.1.5. Hydrogen ion concentration. The reaction of chromium with collagen involves ionized side chain carboxyl groups of aspartic and glutamic acid residues with pK_a values 3.9 and 4.3 respectively, at a temperature of 25 °C (Stryer, 1975). The rate of reaction depends on the number of ionized carboxyl groups on the

collagen. It can be calculated that at pH 2, 3 and 4, the percentage of protein carboxyl groups remaining ionized is of the order of 1, 9 and 51% of the total respectively (Covington, 1986). In tanning practice, best results are generally obtained by beginning at a lower pH and finishing at a pH around 3.8–4.0.

5.1.1.6. Masking. Masking is a process through which the reaction of chromium with protein sites is moderated. By the coordination of some ligands to chromium, it is possible to alter the precipitation behavior of the metal ion. Masking may also influence the degree of polymerisation and solubility of various molecular ions of chromium(III) contained in BCS. Masking is used as a convenient tool in tanneries to influence chromium tanning.

5.1.2. Towards higher exhaustion: use of external exhaust aids in chromium tanning

5.1.2.1. Tanning at a high pH. Aqueous chemistry of Cr(III) is well understood. At relatively higher pH conditions, chromium(III) displays a tendency to aggregate and form hydroxo bridged oligomers of relatively lower solubility (Gustavson, 1956). There have been approaches to carry out tanning at relatively higher pH conditions such that chromium contained in unspent chromium liquor is modified and their deposition into skin structure increases (Dasgupta, 1998). Several modifications of this approach including direct recycling of spent chromium tanning solution as pickle bath have been adopted and used in commercial practices (Davis and Scroggie, 1980; Chandrababu et al., 1995; Money, 1999). Recently, a synthetic tanning agent based on chromium which is devoid of formaldehyde and offers high uptake of chromium has been reported (Suresh et al., 2001).

5.1.2.2. External exhaust aids. Spent chromium tanning solutions contain Cr(III) species of relatively poor affinity to the protein matrix. Therefore, external aids to improve the exhaustion and uptake of chromium need to modify either the chemical species of Cr(III) or the reaction mode involved in the binding of the metal ion by skin protein. It is now possible to increase significantly the exhaustion levels of chromium through the use of external aids (Rao et al., 1999). Many chromium exhaust aids are already available in the market. Some of them work on ion exchange principle while some others are based on complexing agents that reduce the solubility of chromium(III). Known external chromium exhaust aids are based on (a) polyhydroxy aluminium chloride gels (b) polyamides (c) polycarboxylates (d) long chain alkanolamines (e) polyelectrolytes and (f) ion-exchange resins of suitable particle sizes. These exhaust aids may help in fixing more chromium by creating additional sites for the interaction of chromium. Exhaustion levels of the order of 85–95% have been reached by making use of exhaust aids.

5.1.3. Towards higher exhaustion: product modification of BCS

5.1.3.1. Modified BCS. A true scientific approach to increasing the exhaustion levels of BCS rests in (a) identifying the nature and molecular structures of major Cr(III)

species not being absorbed during tanning and then (b) evolving methods to avoid the formation of low affinity species through directed synthesis strategy for the manufacture of BCS. The benefits of this approach have already been demonstrated (Rao et al., 1998). The utility of the method has gained commercial recognition.

In the manufacture of BCS salts, several reaction parameters gain importance. The constitution and composition of BCS varies as a function of manufacturing conditions. The amount of a low affinity tetrapositive tetrameric species present in BCS is known to influence the exhaustion behavior of the tanning salt (Rao et al., 1997). Processes employed for the preparation of BCS may now be modified suitably to minimize formation of such low affinity species. A modified BCS salt which shows an exhaustion level of 85% of chromium offered has been reported (Rao et al., 1998).

5.1.4. Towards higher exhaustion: modifying the skin substrate

5.1.4.1. Increasing the number of metal binding sites in collagen. Increasing the number of metal binding sites in collagen can increase reactivity of the protein in chromium tanning. The simplest method to increase the number of carboxyl sites in collagen is to subject the amide side chains of asparagine and glutamine to alkali hydrolysis as in the case of liming (Germann, 1999). Another way of increasing the number of carboxyl groups is to condense active hydrogen compounds containing carboxyl groups with the side chain amino groups of collagen using the Mannich reaction (Bowes and Elliott, 1962; Ramasami and Ramaswamy, 1975). Some significant improvements in metal binding capacity of collagen have also been reported by exploiting Michael reaction, where β -carboxy ethyl acrylate is covalently bonded to free amino side chains (Scholnick et al., 1991).

5.1.4.2. Catalysis. Some molecular species of Cr(III) contained in BCS may be substitutionally inert. Catalyzing the reaction of inert species is potentially useful. It has been proposed that the improved exhaustion of chromium observed by the use of monoethanolamine during tanning may be because of its ability to involve in hydrogen bonding with carboxyl groups (Covington, 1997). A catalytic cycle mechanism has been proposed to explain the experimental observations. The system based on monoethanolamine enables greater than 90% exhaustion of chromium (Prentiss and Prasad, 1981; Chandrababu et al., 1995).

5.1.5. Towards higher exhaustion: chromium saving and replacement approaches

5.1.5.1. Combination tanning and chromium savers. Combining chromium with other tanning agents like aluminium, zirconium and titanium compounds or glutaraldehyde or its derivatives, has been found to be an effective approach to decrease chromium content in spent tanning solutions (Celades et al., 1990; Guo et al., 1992). These systems have the added advantage of imparting desired physical and chemical properties (Mitchel, 1981; Covington, 1998).

One of the popular chromium saving systems is aluminium–chromium combination tanning approach. Several practical methods of combining aluminium and

chromium have been explored. One standardized method is based on the use of Alutan (an aluminium based tanning salt capable of binding irreversibly to leather) and BCS. Alutan is based on a polymeric network (Kanthimathi et al., 1985). It carries suitable liganding sites to increase chromium fixation when used in combination with BCS. A combination tanning system with 1.5–2% Alutan and 5% BCS has been shown to offer chromium exhaustion of above 95% (Chandrababu et al., 1995).

The use of monoethanolamine in combination with a modified pickling method has opened up new possibilities for saving chromium. In this method, after delimiting, the pelts are rinsed with acetic acid and then treated with monoethanolamine that provides a buffering system. When the pelts are tanned with BCS in the presence of monoethanolamine, chromium exhaustion levels are raised to >95% of the chromium used. Therefore, the method provides an opportunity to reduce the use of chromium by about 30% (Chandrababu et al., 1995). Chromium saving approaches are gaining commercial significance.

5.1.5.2. Closed pickle-tan loop. The use of tanning methods based on Alutan–BCS or ethanolamine–BCS lead to spent chromium liquors with chromium concentrations in the range of 200–500 ppm (Chandrababu et al., 1995). The direct reuse of such chromium solutions in pickling opens up the possibility of developing a near-zero waste tanning method. When the concentrations of chromium are as low as 200–330 ppm, it is possible to reuse the spent bath for pickling without any danger of coarsening of grain of leather. Such a closed pickle-tan loop system has been proved to be a commercially viable and successful process with many advantages. Recently a two-bath process with pH static approach has been developed. In this process, chromium bath after tanning is recycled at its natural pH and the basification carried out in a separate bath. The advantages of the process have been examined thoroughly (Muralidharan et al., 2001).

5.2. Chromium recovery and reuse: various methods

5.2.1. Chromium reuse: recycling strategies

5.2.1.1. Basic approaches. Spent-tanning solutions from a chromium-tanning yard can be recycled if the liquor is segregated and chromium is reused in successive tanning baths. There are two fundamentally different methods of reusing the unused chromium remaining after tanning. Chromium can be reused by either recycling the spent solutions directly or after recovering the unused chromium as chromic hydroxide and regenerating as BCS for reuse (France, 1975).

5.2.1.2. Direct recycling of spent solutions. Spent chromium liquors have been reported to contain in addition to 0.15–0.50% chromium, about 3.3–3.5% NaCl, 2.8–3.3% of Na₂SO₄ (Prasad et al., 1987). When spent chromium liquors were replenished with fresh chromium and reused the percentage uptake of chromium was found not to increase. This has been attributed to (a) the structure and reactivity of

the poor affinity species remaining unaltered during recycling and (b) adverse influence of accumulated neutral salts on transport and uptake of the metal ion by skin (Rao et al., 1999). For direct recycling of chromium in the chromium tanning stage to be technically viable, concentrations of salt in spent tanning solutions need to be reduced below 1% from a total of 7%. Such reductions are not without cost implications. In view of the presence of large amounts of neutral salts, the reuse of spent chromium solutions in pickling rather than chromium tanning appears an attractive alternative. Reuse of spent tanning solution in pickling offers also the advantage of containing salt pollution from tanneries (Davis and Scroggie, 1980).

5.2.1.3. Recycling of spent solutions after membrane separations. Membrane based selective separation of neutral salts from chromium through electrodialysis is now technically feasible. The system couples the advantage of separation of the neutral salts contained in spent tanning solution from chromium and the use of neutral salt stream in pickling and chromium stream in tanning. A conceptual approach based on electrodialysis has been developed (Rao et al., 1989). The relative usefulness of electrodialysis concentrate stream as pickle and diluate as chromium tanning baths has been demonstrated. A loop, to renovate ground water from salt stream has also been examined (Rao et al., 1999).

5.2.1.4. Chromium recovery/reuse. The recovery and reuse strategy involves initially the separation of chromium from soluble neutral salts as chromic hydroxide (Covington et al., 1983). Chromium(III) is easily precipitated as chromic hydroxide by the addition of an alkali to spent chromium tanning solution (Hauck, 1972; Sreeram et al., 1999). Subsequently the precipitated chromic hydroxide can be redissolved by acidification. Technology packages for recovery/reuse method are readily available (Langerwerf, 1999). Relatively low solubility of chromic hydroxide permits the easy and secure removal of chromium salts from spent tanning liquors. Supernatant liquors from chromium recovery plants are relatively free of chromium and meet environmental standards for discharge viz. 0.3 ppm. Chromium uptake from regenerated chromium liquors from tanning is comparable to the uptake from fresh batches of BCS. This method of recycling does not help to overcome the problem of dissolved neutral salts in the effluent. The alkali used for precipitating chromium ultimately contributes additionally to the total dissolved solids (TDS) content in effluent (Ramasami, 1996). The reuse of supernatant solution from chromium recovery plants in various pretanning operations is one of the in-plant control approaches to contain TDS (Langerwerf, 1999).

Recently a semi-continuous method for the recovery of chromium(III) from tannery wastewaters containing the metal ion has been reported (Sreeram et al., 2000). In this system, sodium carbonate has been used as the alkali to precipitate chromium(III) as chromium(III) hydroxide, instead of magnesium oxide, which is preferred for batch type systems. The hydrostatic pressure built-up and turbulence within the reactor has been modulated to achieve online separation of chromium(III) hydroxide. Under steady state conditions, the inflow into the reactor and outflow

from it has been matched. The outflow from the reactor can be discharged without causing hardness to ground water.

5.3. Alternatives to chromium as tanning salt

5.3.1. Mineral tanning alternatives

There has been a continuous development in the understanding of technology of tanning. The search for alternatives to chromium has been both intensive and extensive. Viable alternatives to chromium have not yet been forthcoming. Many metal ions exhibit a degree of tanning activity. On application of objective criteria for the selection of technically as well as commercially viable mineral tanning material, metal salts suitable for tanning is restricted to those of Al(III), Si(VI), Fe(III), Ti(IV), Zr(IV) and Ce(III) or (IV) other than Cr(III) (Chakravorty and Nursten, 1958).

5.3.1.1. Non-transition elements. Two commonly known inorganic tanning agents from among non-transition elements are those from aluminium and silica. These salts do not enjoy the benefits of a partially filled d-orbital mixing to cause loss of degeneracy of d-levels. Although tanning methods based on silica and aluminium are known for several decades, commercial applications of tanning methods have, however been limited.

5.3.1.2. Aluminium tanning. The Romans employed aluminium for tanning of skins and fur some 2000 years ago. It is considered to be an incomplete tannage (Chambard, 1978). Unlike chromium(III), aluminium(III) does not form stable coordination complexes. The interactions of Al(III) with protein are predominantly electrovalent (Selvarangan and Nayudamma, 1964). Bound aluminium(III) salt is easily reversed. Formate or citrate masked basic aluminium sulfate salt has found better application in tanning (Selvarangan and Nayudamma, 1964; Montgomery, 1987; Takenouchi et al., 1997). With such masked salts, reversibility of the tannage is minimized.

The rate of exchange of solvate ligands is 10^9 times faster at Al(III) than at Cr(III) (Covington, 1997). The electronic configuration of Al(III) with unfilled third shell permits generally the hybridization of $3s\ 3p^3\ 3d^2$ which leads to the formation of labile complexes. In recent times, methods to render Al(III) behave like a transition element have been recognized (Taqi-Khan, 1987). Reversibility of aluminium(III) tanning is reduced when it is combined with vegetable tannins (Slabbert, 1981; Hernandez and Kallenberger, 1984; Gratacos and Marsal, 1990). Aluminium(III) mimosa tanning has been extensively investigated (Selvarangan and Nayudamma, 1965; Sykes and Cater, 1980; Slabbert, 1981). Combination of aluminium(III) with chromium does enable reduction in chromium offer in tanning. Aluminium(III) behaves as chromium saver.

Semi-alum leathers based on combination of condensed tannins and aluminium could exhibit a shrinkage temperature of ~ 90 °C while analogous leathers made from hydrolysable tannins resist hydrothermal shrinkage up to 115–120 °C

(Covington, 1999). Potentials for charge transfer reaction between Al(III) with phenolic constituents in vegetable tannin materials are now well known (Taqi-Khan, 1987). Aluminium based solid wastes from leather processing could be more easily converted into valuable by-products and managed.

5.3.1.3. Wet-whites. As a process intermediate in place of wet-blue: Although several limitations have been recognized for the wide spread use of aluminium as an alternative tanning material to chromium, the potentials for employing the method for obtaining a process intermediate have been actively pursued (Dunhill et al., 1991; Ward, 1995; Wren and Saddington, 1995). Aluminium tanning could stabilize the matrix sufficiently to permit splitting and shaving (Tonigold and Heidemann, 1985). Since aluminium tanned leather wastes are more easily managed and disposed, wet white is an interesting possibility. The concept of wet-white tanning is attractive. Nevertheless, commercial utilization has remained low.

5.3.1.4. Silicate tanning. Silica has long been examined as a tanning material. Some important additions to properties of leathers are made when sodium silicate is used. However, self-tanning potential of silicate is yet to be established. Sodium silicate has been used successfully more as a filler in chromium leathers than as a tanning material. Silicon(VI) under favorable conditions exhibits a tendency to form surface active colloids and hence it is possible to employ silicates as chromium exhaust aids and to a limited extent as a chromium saver (Gregorzewska and Staniewska, 1984). Tanning agents based on a combination of chromium and silica can provide good quality leathers with improved chromium uptake.

5.3.1.5. Iron tanning. The stabilisation of proteins by iron salts has been of academic interest partially because of the existence of iron–protein combinations in nature (Reife et al., 1997). Iron as a transition element enjoys similarities with chromium in many of its reactions. The history of iron tanning dates to the later part of the 18th century (Knapp, 1921). The application of iron tanning salts in leather industry has been limited. It has been reported that it is difficult to neutralize the acidity of leather without the precipitation of iron hydroxide (Kanagy and Kronstadt, 1943). The rapid deterioration of iron tanned leather was attributed to redox behavior of the metal ion (Jackson and Hou, 1921). Casaburi (1919) advocated the use of tartrate to retard acid–base hydrolysis of iron salts. Thorstensen and Theis (1949) found that upon addition of various masking salts to an iron tanning system, acid–base hydrolysis of iron salt could be reduced. It was shown that a shrinkage temperature of $\sim 87^\circ\text{C}$ was obtained using iron tanning (Tavani and Lacour, 1994). Comparative studies indicated that phthalate masked iron is a better tanning agent, than those masked with phosphate, adipate, tartrate and oxalate ions (Thorstensen and Theis, 1949).

Several researchers have examined chromium–iron combination tanning systems (Fleming, 1943; Gaidau et al., 1998). Iron pretannage and chromium retan affords an increased shrinkage temperature ($\sim 100^\circ\text{C}$). The mechanism involved in iron tanning is considered to be similar to that involved in chromium tanning. The

development of a tanning system based on mixed ligand complexes of iron with an aliphatic diamine and alkali metal salt of ethylenediaminetetracetic acid or of a pyrophosphate has been reported (Lauton, 1989; Balasubramanian and Gayatri, 1997). Gaidau et al. (1998) has reported the development of mixed metal complexes of iron and chromium. Recently a homogeneous chromium–iron complex with application potentials in leather processing has been reported (Thanikaivelan et al., 2000). Iron salts seem to offer the best scope for the development of an alternative to BCS provided the acid rotting of the final leather and redox instability of the tanning salt is overcome satisfactorily.

5.3.1.6. Titanium tanning. Aqueous chemistry of titanium(IV) is dominated by that of titanyl ion TiO^{2+} (McAuliffe and Basratt, 1987). The traditional use for titanium(IV) in tanning was in the form of potassium titanyl oxalate (Swamy et al., 1983a,b). The use of such tanning systems has been more useful in retanning of the vegetable tanned leathers than in mineral tanning with titanium (Ramasami, 1994). Hydrothermal stability above 95 °C is achieved only when the collagen is pre-treated with phthalate. Titanium(IV) is a d^0 ion with limited stability of the ligand fields. High cationic potential of Ti(IV) renders the ion acidic and in some cases the formation of titanium dioxide type structures is favored. A commercial product based on a mixture of titanium, magnesium and aluminium has been introduced in leather processing with limited success as a combination-tanning agent (Tate, 1989). The ability of titanium based salts to behave as tanning materials or chromium savers is yet to be established.

A recent report has shown that the use of titanium(III) sulfates masked with hydroxy ligands affords leather with a shrinkage temperature of ~ 80 °C (Covington et al., 1998). Pretanning with hetero complexes of Al–Zr–Mg has been reported (Gaidau et al., 1997) to result in wet-white leather, which can be converted into finished leathers using conventional products and procedures.

5.3.1.7. Zirconium tanning. Zirconium(IV) is a d^0 system and has no reported toxicity (Ghosh et al., 1992). The earliest report of zirconium tanning was in 1907 (cf. Ranganathan and Reed, 1958). Coordination chemistry of Zr(IV) in aqueous system is characterized by eight coordination geometry, high affinity for oxygen donors based ligands and oligomeric structures in which tetrameric complexes form the basic building blocks (Hock, 1975). Zirconium(IV) is not often used as a self tanning material. This is partly because of three reasons. They are (a) high acidity conditions needed for the tanning process rendering leathers weaker and developing drawn grain (b) lower hydrothermal stability of the product and (c) higher cost relative to chromium tanning. Masking of zirconium(IV) by addition of acetic, lactic, formic, sulfanilic and gluconic acids aids in increasing the pK_a of coordinated aqua ligands (Ranganathan and Reed, 1958a). Efforts have also been made to prepare complex salts of zirconium with oxo, hydroxy organic acids and sulfates as ligands (Erdmann and Miller, 1977). The use of arylsulphones, EDTA and lithium salts as complexing agents for zirconium has also been reported (Lauton and Puntener, 1993). Recently, the development of an organo-zirconium polymeric matrix—organozir as possible

alternative to chromium in tanning has been reported (Sreeram et al., 2000a,b). Since the cost of the zirconium product is higher, the utility of the salt as a chromium saver is limited.

5.3.2. Organic tanning agents as alternatives

5.3.2.1. Vegetable tannins. The use of plant materials containing polyphenols in the molecular mass range of 500–3000 is an age-old process. Traditional processes employed long process time. Modern vegetable tanning methods involve the use of mechanical equipment that reduce time of tanning. The use of appropriate pretanning processes help in avoiding pebbled and badly drawn grain due to rapid uptake of tannins (Bickley, 1992). One such method is the mimosa-cure process involving the use of anhydrous sodium sulfate (Slabbert, 1999). A modified vegetable-tanning process—the Liritan process has now been recognized as the most rapid pit tanning method. This method involves pretanning with calgon. It is believed that polyphosphates may form adducts with side chain amino groups (Shuttleworth and Ward, 1976). The method provides an opportunity to carry out vegetable tanning under warm conditions facilitating penetration of vegetable tannins. The system has advantages of sludge reduction, good tannin fixation, sequestering of iron by polyphosphates and light colors. The use of crosslinking agents like oxazolidine and acrylics has been reported to improve shrinkage temperature of vegetable tanned leathers (Dasgupta, 1977; Gill, 1985; Covington and Shi, 1998; Madhan et al., 2001).

5.3.2.2. Tanning with synthetic tanning materials. The goal in employing synthetic organic tanning materials is to simulate the properties of chromium tanned leather (Dasgupta, 1980). The application of polymers to tanning is well established. Polymers can be applied either by adding the prepared polymer or polymerize monomers in situ. The use of crosslinking monomers, such as resorcinol, pyrogallol and melamine, aliphatic active hydroxy compounds and aldehydic compounds and derivatives as in situ monomers has been reported (Dasgupta, 1977). Diffusion of syntans into the skin matrix is regulated by particle size of macromolecule, which in turn is controlled by the temperature of the reaction conditions. Commercially viable tanning methods based on syntans but free of the use of mineral tanning salts are yet to emerge.

5.3.2.3. Aldehyde based tanning methods. The reaction of hide with formaldehyde has been known for many years. Tanning with formaldehyde has been largely replaced by much stable tanning procedures, using longer chain, preferably bifunctional aldehydes (Wojdasiewicz et al., 1992). These aldehydes, such as glutaraldehyde, react with primary amines of the hide with elimination of water, to form Schiff bases. A reaction occurs mainly between side chain groups of the amino acids lysine, asparagine, glutamine, histidine and arginine. Crosslinks formed in collagen fiber through the reactions of glutaraldehyde are irreversible (Serra et al.,

1991). Natural polymers containing an aldehyde or a masked aldehyde group have also been employed for tanning.

Pretanning procedures with modified aldehydes afford leathers with shrinkage temperature of 70–80 °C. Such a stock provides a good intermediate for further tanning with syntan or vegetable tannins to obtain metal free leathers.

5.3.3. Criteria for designing an alternative to chromium as tanning system

While alternative materials to chromium(III) based tanning salts are being explored, commercial tanning technologies continue to be based on BCS. Therefore, in designing a system for replacing chromium(III) as a tanning material, alternatives need to meet some important criteria. They are (a) tanning efficacy (b) hydrothermal stability of leather (c) stability of resulting leather against weathering and discoloration (d) ease of addition of softness, color and compaction (e) treatability of wastewater streams (f) exhaustion level possible (g) cost effectiveness (h) disposability of the leather/products and (i) quantity and ease of disposal of solid wastes, if any.

5.4. Safe disposal and utilization of chromium containing wastes

5.4.1. Chromium from solid wastes

The discharge of chromium tanned wastes as landfill is forbidden. Detanning processes have aroused interest. Some of the methods used involve hydrolysis using lime, caustic soda or any other weak alkali or alkaline proteases (Heidemann, 1991; Rose et al., 1999). The processes have been designed to permit the recovery of protein hydrolysates as gelatine and hydrolysates from chromium bearing solid wastes. The gelatine recovered has found applications in photographic films, coating of textiles etc. (Taylor et al., 1997).

Chromium cakes obtained through leaching from chromium tanned leather wastes have been redissolved using sulfuric acid to generate chromium sulfate ready for reuse in tanning (Taylor et al., 1998). Detanning of chromium leather using strong oxidizing agents like hydrogen peroxide or chlorine under alkaline conditions has been reported (Heidemann, 1991). The oxidative leaching results in a mixture of Cr(VI) and protein. The process is expensive. Recently the use of chelating agents to release chromium gradually from protein matrix has been possible. Subsequently protein could be used in anaerobiosis and chromium in tanning (Chakraborty et al., 1999).

5.4.2. Leather waste utilization

Chromium leather wastes from tanneries and leather product units form an important class of by-products. Utilization of these by-products is crucial. Leather board provides a means to add value to waste products like leather trimmings, shavings etc (Miyakawa et al., 1992; Sykes, 1997; Germann, 1999). Depending on the method of manufacture these boards find use as soling, heeling boards, general heavy components, light shoe inserts and fancy goods (Sykes, 1997). The potential

use of chromium leather wastes as reducing agents for the manufacture of BCS has shown new avenues for the value added utilization of these wastes (Rao et al., 2002)

5.4.3. Utilization of chromium sludge from effluent treatment plants

Tannery sludge is essentially a solid waste contains organic materials to afford 40–60% of volatiles and 2–5% chromium. An effective and relatively safe method of disposal of chromium bearing tannery sludge is by its incorporation in a clay mixture and depositing in industrial ceramics (van der Zwan, 1994). Chromium sludge from tanneries can be mixed with clay in the composition of 5–15% by weight and used in brick manufacture under special firing conditions (Warrier et al., 1995). The manufacture conditions can be so adjusted to render chromium non-leachable (Merzagora and Paggi, 1999). This involves an oxidative firing and reductive cooling (Warrier et al., 1995; Ramasami, 1999). The use of chromium bearing tannery wastes as an additive in the manufacture of sodium chromate from chromite ore has also been reported (Kowalski and Walawska, 2001).

5.4.4. Bioaccumulation

Microbial reduction of Cr(VI) to Cr(III) has been one of the most widely studied forms of metal bioremediation of Cr(VI) bearing soils and solid wastes (Lovley, 1995). Many heterotrophic organisms have been reported to bring about the reduction of Cr(VI) to Cr(III) (Lovley and Coates, 1997). Though technologically viable bioaccumulation processes have not been developed to enable the removal of chromium from tannery wastes, some preliminary reports on the possible use of micro-organisms in the remediation of chromium(III) bearing solid wastes have appeared (Nair et al., 1985). Convincing technological solutions to the management of chromium bearing solid wastes from tanneries continue to be searched. A comprehensive technology and management approach to tackling environmental problems of chromium tanning industry is necessary.

5.5. Avoiding the formation of Cr(VI) in tanning process

In recent years, there have been reports that hexavalent chromium can be detected in leathers. While tanning process uses only chromium(III), the presence of chromium(VI) is due to utilizing processing conditions which oxidize chromium(III) to chromium(VI). Certain leather chemicals such as fish oil have been considered as the cause for the presence of Cr(VI) in leather. Various processing conditions required to enable Cr(VI) free leather have now been put forth (Fathima et al., 2001).

6. Chromium management: way forward

A comparative assessment of various high exhaustion technologies, chromium recovery/reuse methodologies and alternatives to chromium have been made and presented in Tables 2–4. Though not a complete assessment of current day technologies, these tables could serve as a lead for a general assessment of the

Table 2
Criteria for choice of high exhaustion tanning methods

Tanning method	Advantages	Disadvantages
With exhaust aids	Relatively marginal changes in process equipment and flow	May require additional chrome recovery approach to meet regulations. Could result in non-uniform distribution of chromium
Modified BCS	No change in process. Higher chrome exhaustion — ~ 85%. Reduction in BCS offer possible. Savings in post tanning chemicals	Effluent standards not met unless spent solutions are recycled
Monoethanolamine–BCS	Higher chrome exhaustion. Offer of BCS can be reduced. Recycling of spent liquors as tanning floats for subsequent batches possible. Pickling and basification can be avoided	Cost of ethanolamine needs to be considered. Modifications in process line required
Alutan–BCS closed loop pickle-tan loop system	Greater than 90% exhaustion of chromium. Economically beneficial for raw to finish. A closed loop system promises reduction in water usage, TDS, COD and BOD	Alterations in process line and additions to process equipment are needed

Table 3
Criteria for choice of recycling methods

Method	Advantages	Disadvantages
Chrome liquor recycling	Savings in chrome used	Build up of liquor volume
	Reduced levels of chrome in waste streams Reduced neutral salt requirement Simple and minimum capital cost No additional chemicals involved Indefinite recycling Flexible, not dependant on leather type	Quality of waste stream a primary concern Increased levels of process control Some changes in tanning process Different colour leather, usually darker Possibilities of surface deposition not ruled out
Chrome recovery/reuse	Savings in chrome used	Increase in discharge of neutral electrolyte
	Reduced levels of chrome in waste streams Closer to using fresher chrome than recycling liquor, minimum chemical change Minimum procedure changes in tanning	Increased level of process control required More complex plant needed, higher capital cost Additional chemicals and personnel needed, higher running cost
	Can be operated indefinitely	Current day system uses MgO, the quality of which is critical
	Flexible, can be applied to any type of leather No loss in quality of leather Wider economic benefits	Forms magnesium soaps when used for treating effluents with high oils and fats

Table 4
Comparison of alternative mineral tanning systems

Metal ion	Al(III)	Ti(III)	Fe(II)/(III)	Zr(IV)
<i>Extent of complex formation</i>				
Oxy complexes	**	**		***
Carboxy complexes	**	**		***
Amino complexes	*	**		**
Maximum Ts (°C)	90±2	96±2	87±2	97±2
Leather Quality	Detans on washing	Precipitates at pH > 2.5	Highly acidic, deteriorates on ageing	Drawn grain, pH < 1.5–2.0 required for tanning
Colour	White	White	Brown	White

More the number of * better the reaction.

present status of the research and development towards sustainable leather production.

BCS has enjoyed a critical role as a tanning material during the entire 20th century. During the last two decades, important questions have been raised regarding the environmental consequences of chromium based industries in general and that of chromium tanning industry in particular. At the end of the 20th century, questions are being raised as to whether chromium tanning as a technology needs to be phased out. Since the potential and negative consequences of uncontrolled discharge of chromium bearing industrial and trade wastes are likely to be serious, it is necessary also to examine the need for such a phase out of chromium tanning based on sound scientific assessment. The problems of chromium tanning activity as practiced widely in many developing countries can be categorized into three groups viz. (a) avoidable (b) controllable and (c) unavoidable, in the current technology scenario.

6.1. Avoidable

Whereas 35–45% of chromium used in tanning industry is not absorbed in tanning using currently employed conditions in many developing countries, it is entirely possible to adopt better exhaustion methods for chromium during tanning and avoid the problem of uncontrolled discharge of the heavy metal ion. Best practices in chromium tanning exist and are commercially viable. A typical example is chromium recovery/reuse. Batch processes of chromium recovery and reuse have been employed with success. Nevertheless, semi-continuous methods are necessary for managing large volumes of chromium bearing wastewaters. International experience in the application of continuous chromium recovery technology is growing (Young, 1976; Andres, 1985; Perrone et al., 1985; Sreeram et al., 2000). There are some critical gaps in the development of continuous chromium recovery methods to overcome an avoidable problem of discharge of sectional streams bearing spent

chromium liquor. The use of high exhaust chromium tanning, chromium recovery reuse, and chromium savers are the possible means to avoid the problem of chromium discharge from sectional wastewaters.

6.2. Controllable problems

Chromium tanning involves also the use of high amounts of neutral salts and sulfates. With environmental regulations stipulating levels of TDS at 2100 ppm, it is now necessary to evolve suitable technologies for controlling TDS discharge from chromium tanning systems (Ramasami et al., 1999). This may require a process rationalization and avoidance of pickling if possible. In this direction, technologies are emerging; but it is safer to classify that TDS in chromium tanning belongs to a controllable group of problems. The development of salt tolerant plants in areas surrounding tanneries could provide a solution.

6.3. Unavoidable

Chromium tanning, as an industrial process would generate some wastes containing chromium. Particularly, chromium leather wastes and sludge from wastewater treatment plants are unavoidable. These are solid wastes, which cannot be totally avoided. It is also a matter of concern that the currently used methods of disposal of used leather products including shoes are receiving negative perception of the public (Anon, 1993). The public perception of the chromium leather wastes is negative with regard to their ecological compatibility. Incineration of chromium bearing solid wastes is not without dangers. Therefore, replacement of chromium as a tanning material may then become necessary. Iron and zirconium form two potential possibilities to replace chromium.

7. Chemistry of tanning and environmental implications

Although chemical principles involved in chromium tanning have been extensively investigated and are well understood, an insight into the molecular basis of chromium tanning has just been gained (Gayatri et al., 2000, 2001; Ramasami, 2001). It has now been shown that different molecular species present in BCS salts afford to collagen varying degrees of dimensional stability against heat as well as enzymatic degradation by collagenase. A case for chromium induced long range ordering and assembling of collagen molecules has been made (Gayatri et al., 2001). A study involving reaction of dimeric, trimeric and tetrameric species of chromium(III) with rat tail tendon fibres reveals that the stability afforded by different species of metal ion varies with the structure of the complex. True scientific solutions to the problems faced by the tanning industry are feasible only if the science of tanning is better understood. For instance, a relatively lower degree of utilization of chromium in chrome tanning needs to be understood in terms of a correlation of molecular structure of chromium(III) species with its affinity to collagen under

tanning conditions. If such a structure-activity correlation existed, it may be possible to devise technologies for directing the synthesis of BCS towards the preferential formation of high affinity species.

Conventional wisdom of tanning technologies has mostly employed chemical approaches to long term preservation. If the long term preservation of collagen demands only changes in selected sites and changes in the conformation of the protein, in principle, it should be possible to make and break bonds to order within a collagenous assembly and stabilize using radiations. With the advent of modern technologies, viz., laser, it is not impossible to reorder collagen using irradiation methods. Thus a non-chemical route to tanning seems likely, though in distant future.

The use of chromium in tanning is likely to face further threats. More efficient processes of tanning with near zero concepts will be introduced, but the most significant challenge for the chrome tanning is likely to arise from the need to dispose used leather products without the danger of conversion of chromium(III) to chromium(VI). Total life cycle analysis of chromium tanned leather may indicate a posed threat. Future development may be focused on better management of chromium, based on a cradle to grave approach in tanning industry.

All the developments in chrome tanning would be sustainable only if technological upgrading in ore dressing is parallel to the advancements in down stream applications of chromium. Unless safe and secure solution to the problem of disposal of solid wastes generated by chromite ore processing industries are made available, chromium based tanning methods cannot be sustained (Sreeram and Ramasami, 2001). There is an urgent need to develop technologies for management of chromite ore processing residues and to develop alternate methods in leaching of chromium from ore.

8. Concluding remarks

An insight into the technologies available for better management of chromium in the leather industry is provided. Some of these technologies are in commercial practice while others are at their initial stages of development. For a sustainable development, there is a constant need to develop newer and cleaner processes. This paper is a call for cross-fertilization of ideas. What has been achieved by the leather chemists have been highlighted and a glance of what is needed presented with a hope that scientists from other areas of science and technology would be able to supplement towards sustaining one of the world's oldest technologies.

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