

Science and Technology of Chrome Tanning

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The element chromium discovered in 1797 by the French Chemist, Louis N. Vanquelin, has found applications in the form of its compounds in various industrial processes from electroplating to tanning. Ever since the first report of Friederich Knapp in 1858 that chromium chloride converted raw skins into leather, the chemistry and technology of chrome tanning have been well documented¹⁻⁷. Several reviews appeared on the chrome tanning methods prior to 1974⁸⁻¹⁰. An attempt has been made in this review to highlight the recent trends in the chemistry and technology of chrome tanning, including the modifications in the pretanning processes.

Pre-tanning Processes

Tanning is the process by which the putrescible proteinous matter, hide or skin, is made non-putrescible. However, in leather making, for ensuring optimum physical and surface characteristics, several pre-tanning operations, which influence the reactions involved in tanning, are carried out. The pre-tanning processes may be described as follows: (a) The rehydration or soaking of the raw skin which had been preserved; (b) the loosening up of hair and flesh through a liming operation, consisting of a treatment with infusions of calcium hydroxide and other nucleophilic reagents like sodium sulphide to break the disulphide bonds in the hair protein; (c) neutralization of alkali during a deliming operation by treating with an acidic salt, such as ammonium chloride or ammonium sulphate; (d) solubilization of unwanted proteinous matter by an enzymatic treatment during bating; and (e) preconditioning of the acidity for mineral tanning through treatment with a mineral acid like sulphuric acid and a neutral salt (say NaCl) in pickling.

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Tanning Methods and Chrome Tanning

Tanning or permanent preservation may be effected by one of the following methods, depending upon the end use of the leather:

(i) Vegetable tanning using aqueous infusions of polyphenolic type (such as leucoanthocyanidins, glucogalloyl esters, etc.) materials of plant origin for heavier and filled up leathers, such as sole

(ii) Chrome tanning using sufficiently basified salts of Cr(III) for light leathers like upper, glove, etc.

(iii) Tanning with aldehydes or oil tanning using the oxidation products of an unsaturated oil like fish oil for speciality leathers

(iv) Aluminium or zirconium tanning, using sufficiently masked salts of Al(III) and Zr(IV) for white leathers like hockey ball

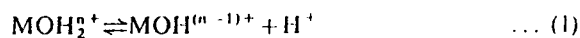
(v) Combination tanning methods in which a judicious combination of the methods described under (i) - (iv) above is used, so that the advantages of various tanning methods may be utilized fully.

Recent advances in the science and practice of chrome tanning reviewed in this work include (1) determination of the composition and characterization of chrome tanning solutions, (2) methods for preconditioning of proteinous raw material to control the reactions of Cr(III) complexes with the pelt, (3) imparting further stabilization of chrome collagen compound against wet and dry heat, bacteria, sweat, etc., improving qualities like vulcanizability, water resistance, built in lubrication, dyeing characteristics, mellowness, fullness, etc., and (4) devising newer methods of application, with particular reference to saving in time and energy, and increased exhaustibility to decrease the pollution load of chrome leather industry.

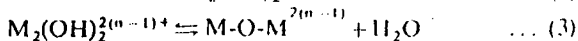
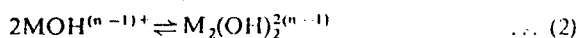
Composition and Characterization of Chrome Tanning Solutions

The chrome tanning liquor, usually obtained by the reduction of Cr(VI) with reducing agents like sulphur dioxide, glucose, molasses, etc., does not constitute a

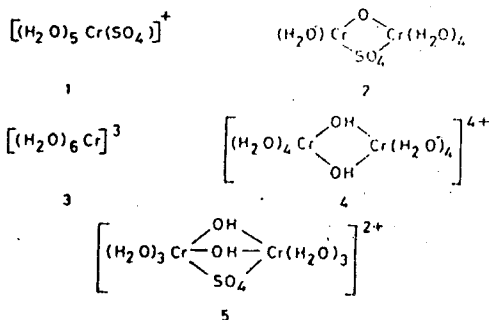
single active species, but contains a mixture of species, varying in structure and properties. The different mechanistic pathways involved in the reduction of Cr(VI), such as the one- or two-electron equivalent step, aqueous chemistry and the ligand capturing abilities of the transient intermediates, such as Cr(IV) and Cr(V), and the hydrolytic behaviour of Cr(III) products, depend on the nature of the reducing agents, acidity, temperature and other conditions. The acidity of the aquo and other ligands coordinated to Cr(III) ion gives rise to hydrolytic equilibria of the type shown in Eq. (1) in the $[H^+]$ region $(1.0 - 0.1) \times 10^{-3} M$,



and dimerization reactions (2) and (3), depending on the metal and hydrogen ion concentrations.



Since most of the commercial tanning liquors are prepared in the presence of coordinating type of ligands like SO_4^{2-} in aqueous solutions, sulphatochromium(III) species are also present. Although different species in the tanning liquors can be considered to exist in equilibrium, the relatively slow rates of re-equilibration help in the separation of various constituents in Cr tanning liquors. Since 1974, there have been a number of studies on the isolation and characterization of various active constituents from Cr tanning liquors¹¹⁻¹⁸. By gel filtration and ion-exchange chromatographic techniques, laboratory prepared Cr tanning salts have been separated, using SO_2 reduction and glucose reduction and the constituents have been obtained in pure form. As many as seven cationic and six non-cationic species were isolated from SO_2 reduced liquors^{12,13}. Glucose reduction, in the presence of SO_4^{2-} , also gave some species which were same as the ones obtained from SO_2 reduced liquors. Monomeric, dimeric and trimeric complexes with charges ranging from +1 to +5 were obtained. Characterization studies showed that SO_2 reduced liquors, after basification to pH 3.0, gave species 1 - 5 (ref. 18).

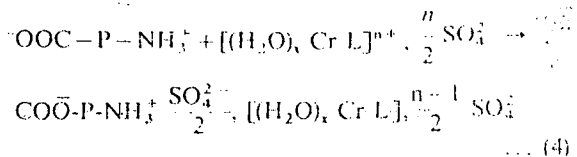


Besides, species of the formulations $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ (6) and $[Cr(OH)_2(S_2O_8)_2]^{2+}$ were also obtained from the SO_2 reduced liquors.

Glucose reduced liquors have formate, acetate and oxalato complexes as well as *p*-hydroxy dimeric and trimeric complexes¹³. The solution chemistry of Cr(III) complexes isolated from chrome tanning solutions is influenced largely by the structure and charge characteristics. When chrome tanning was carried out using a mixture of species for 2-2.5 h (as normally practised during chrome tanning), only constituents with a suitable thermodynamic binding constant and kinetic lability were taken up by the pelt, leaving other constituents in the effluent¹². The relative uptake of the various constituents from an SO_2 reduced chrome liquor has been studied by determining the composition of chrome tanning liquor and its effluent. Since a higher degree of aggregation and greater cationic charge give rise to higher exhaustibility of chrome liquor, the addition of long chain dicarboxylic acids was found useful during the preparation of chrome tanning liquors^{12,16-17}. The aggregation tendency is also influenced by the concentration and method of preparation of chrome liquors. However, in chrome tanning practice, kinetic factors led to the use of Cr liquors that had been premasked by the addition of anionic ligands like formate, acetate, oxalate, etc.

Kinetics and Mechanism of Chrome Tanning

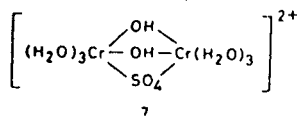
The factors governing the uptake and fixation of chromium by skin or hide are very complex. Dealing with the three-dimensional matrix, viz. skin or hide, the diffusion of chromium tanning materials is the primary process. The diffusion time limits of $\approx 10^{-12}$ s that are characteristic of reactions in solutions of low viscosity cannot be assumed for the hide proteins. Factors like surface charge of the pelt, basicity, degree of aggregation, masking, etc. influence the relative ease of uptake and penetration^{18,19}. On treatment with the basic chromium salt, the pickled pelt may form ion pair, as shown in Eq. (4).



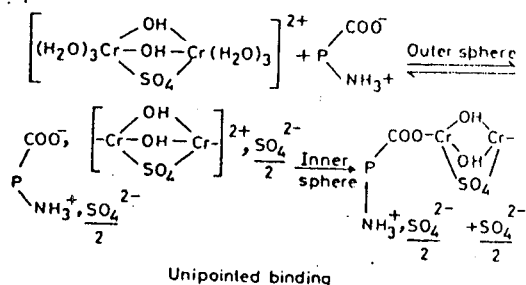
where *P* refers to the collagen backbone; *x* is the number of coordinated aquo ligands; *n*, the charge; and *L*, ligands other than water.

Basification to increase the number of ionized carboxyl groups and prolonged treatment may then lead to the inner-sphere complexation of protein carboxyl groups with Cr(III), giving rise to unipointed

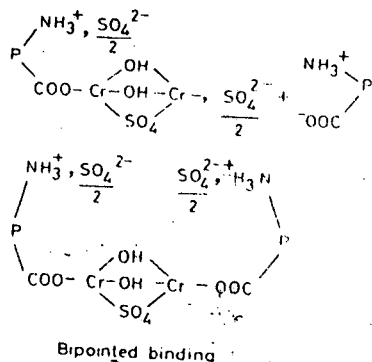
fixation of the metal ion. Considering the example of the chief constituent of 33% basic chromium sulphate (7),



the following inner-sphere complexation reaction may be visualized to give unipointed binding¹⁸.

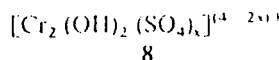


Depending upon the spatial orientation of the carboxyl groups in the protein chain and the size of the Cr(III) polynuclear complexes, bipointed fixation or crosslinking of the following type might occur.



The inference that the carboxyl groups are active sites in chrome tanning was drawn from indirect studies. The chromium uptake was lowered drastically when the hide powder was decarboxylated. The side chain carboxylic acid groups of aspartic and glutamic acids are believed to be the Cr(III) binding sites in collagen⁵. However, the outer sphere complexation and the diffusion of chrome tanning salts into the pelt being the primary steps, the greater the charge *n* on Cr(III) complexes and the more negative the surface of the pelt, the higher is the surface fixation of Cr(III). In such cases, the penetration of chrome tanning salts is hindered and the resulting leather surface is coarse. Therefore, masking of Cr³⁺ complexes by inner sphere complexation of anionic ligands is done to achieve better leather characteristics. Masking also helps in stabilizing Cr(III) tanning salts against hydrolysis and

precipitation as metal hydroxides by rendering Cr(III) complexes as weaker acids. Solutions of basic chromium sulphate at high concentrations behaved like masked chrome liquors due to the inner-sphere complexation of sulphate groups, typically (8). On dilution, due to the low equilibrium constant for SO₄²⁻ complexation, these undergo aquation to give the *μ*-sulphato-*μ*-hydroxo species of the type (5), which give rise to multipoint fixation of Cr(III). Chrome tanning imparts to the resulting leather the highest shrinkage temperature of all the tannages known and practised commonly.

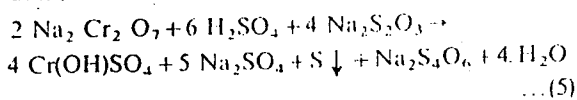


The high shrinkage temperature (*T_s*) of chrome leather is generally attributable to bi- or uni-pointedly fixed chromium. Several factors such as concentration of chrome liquor, masking effect of the complexing agents, temperature of tanning, presence of neutral salt, nature of chrome tanning complexes, *pH* of tanning and the ease of hydration of chrome collagen compounds, etc., seem to influence the shrinkage temperature. Although shrinkage temperature is used as a measure of the degree of crosslinking, the exact structure of Cr(III) complexes with protein in bound form or the mechanism by which the bound Cr(III) confers resistance to collagen against the action of collagenase (a collagen-specific enzyme) and proteases has not been established. Chrome tanning may result through any of the following mechanisms: (i) toxicity of Cr(III) salts to the enzymes, (ii) competitive inhibition of the enzyme-specific functional groups in the collagen and (iii) conformational changes in the molecular structure of collagen following Cr(III) protein interaction. Attempts to cleave the chrome tanned collagen molecule selectively, retaining the Cr-collagen crosslinks, have not been successful¹⁹. Nevertheless, the preconditioning and the chrome tanning procedures for optimum effects have been standardized.

Science of Preconditioning and Chrome Tanning Methods

Two-bath chrome tanning^{1-3,20-22} Although the ability of Cr(III) to tan hides/skins had been known earlier, in the absence of proper preconditioning methods, Schultz in 1884 evolved the concept of two-bath chrome tanning. The process consists essentially of two steps, viz. treatment with chromic acid and *in situ* reduction of Cr(VI) with thiosulphate in acidic media. A bated or pickled pelt may be treated with a solution of sodium dichromate, sulphuric acid or hydrochloric acid and sodium chloride, when the chromic acid formed is distributed uniformly over the

skin. Treatment with an acidified solution of the reducing agent, $\text{Na}_2\text{S}_2\text{O}_3$ or NaHSO_3 in the second bath, results in the following reaction:



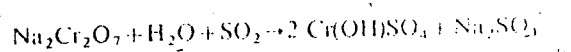
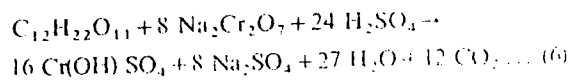
In this type of chrome tanning, a uniform distribution of chrome and fullness of the leather may be achieved due to deposition of colloidal sulphur. Though this method is particularly useful for kid and glove leather, it is time-consuming and involves excessive use of chemicals which increase the pollution load.

Partial two-bath chrome tanning - To overcome some of the disadvantages of the two-bath chrome tanning process, a modified method in which both Cr(VI) and Cr(III) were used successively was evolved. The main features of this type of process are treatment of the pickled stock first with a dilute solution of sodium bichromate (0.25 - 0.5% Cr_2O_3 on pelt weight basis) and then with a basic chromium (III) tanning salt and finally reduction of Cr(VI) with a suitable reducing agent like sodium thiosulphate, sodium bisulphite, etc.²².

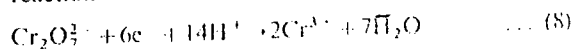
In all such treatments wherein a mixture of $\text{Cr}_2\text{O}_7^{2-}$, Cr(III) tanning salts and sodium bisulphite is employed to effect tanning, the chemistry of oxoanions has a large role to play. It is known that both the oxoanions, $\text{Cr}_2\text{O}_7^{2-}$ and SO_3^{2-} , undergo complexation with $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ instantaneously, with metal oxygen bond retention to give rise to anionic complexes^{23,24}. Therefore, a certain degree of masking effect and more uniform distribution of chromium may be effected. A suggested modification of partial two-bath process involves treatment of the stock pickled with formic acid and salt with sodium dichromate and a fat-liquor, that may contain a certain emulsifier²². The reduction of chromic acid in the skin is carried out at pH 3.3 with sodium bisulphite acidified with sulphuric acid. It is claimed that the fat gets fixed firmly after the reduction of chromic acid by this method²². The formation of Cr(III)-fatty acid complexes in this process cannot be ruled out. It is also believed that the use of chromic acid results in a more uniform distribution of chrome in the leather.

Single bath chrome tanning: Various improvements in pre-conditioning and tanning methods

*Preparation of chrome tanning salts*²⁵⁻²⁹ - The commercial exploitation of basic chromium salts for tanning pelt by Martin Davis and supported by Procter involves the preparation of chrome liquor through the direct reduction of dichromate with sugar-sulphuric acid mixture (Eq. 6) or by SO_2 (Eq. 7).



Although stoichiometric equations, such as Eqs (6) and (7) show the formation of Cr(OH)SO_4 along with CO_2 and SO_4^{2-} , the concentration of the reactants and the order in which they are added affect the formation of the products. For example, reduction of sugar or molasses leads to different products depending on whether (i) sugar or molasses is added to the solution of dichromate and sulphuric acid or (ii) sulphuric acid is added to a solution of dichromate and sugar⁴⁰. The reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr(III) products requires $[\text{H}^+]$ (Eq. 8) to form the transition states involved in the reaction⁴¹.



Therefore, in the first case, wherein $\text{Cr}_2\text{O}_7^{2-}$ and H_2SO_4 have been premixed, the sugar or molasses enters a strongly oxidising system and gets oxidised to form CO_2 in the initial phases of reduction. Later, when the concentration of Cr(VI) is depleted, the reduction becomes slow and gives rise to partially oxidised or free sugars. In the second case, the low acidity in the medium during the initial phase of the reaction renders the oxidation of sugar milder and leads to intermediate products like formic acid and highly masked formate complexes of Cr(III). If the chrome liquor reduced by sugar or molasses contain some free sugar, leathers produced show red pigmentation, particularly in tropical countries because of the development of mould on the leather^{42,43}. Further, free sugars may also create problems in drying due to their hygroscopicity. The problems of mould formation and drying can be avoided by replacing 5-10% of molasses by other reducing agents like sodium sulphite at the final stages of reduction⁴⁴. Studies have also been made to identify the bacteria and mould that can grow on chrome tanned leathers, so that protection may be rendered^{45,46}. In both methods (i) and (ii), the higher the temperature, the faster is the reaction and more extensive is the oxidation of sugar/molasses.

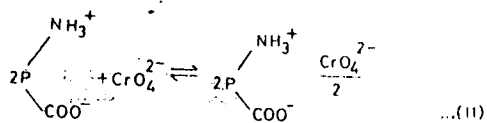
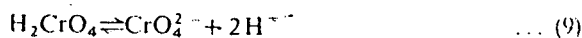
The present trend is to carry out the reaction at higher temperatures and minimize the degree of masking, so that exhaustion of the bath is easier. Using sugar or molasses as the reducing agent, there is considerable effervescence in the reaction kettle at higher temperatures; it can be controlled by 'silicone' defoamers^{47,49}.

When SO_2 is used as the reducing agent, depending upon the order of addition, rate of flow of SO_2 , etc.,

the formation of dithionato complexes is possible if one electron oxidation of SO₂ may generate SO₂ radicals¹². Since readjustments in the final equilibrium condition of the constituents in chrome tanning liquors occur slowly, the chrome liquors prepared by any reduction process are allowed to age for a week before either using as such in the liquor form or converting them into powder extract. Ageing also results in homogeneity of the chrome liquor.

Preparation of pelt⁵⁰⁻⁶⁸—The normal feedstock for single-bath chrome tanning is the pickled pelt in which pickling renders the protein carboxyl groups unionized and unavailable for chrome binding⁵. Pickling is carried out in a solution comprising 1-1.4% H₂SO₄, 4-8% NaCl and 60-80% water of the wet (pelt) weight of hide/skin for a period of 6-10 hr. The primary function of pickling the stock prior to chrome tanning is to adjust the pH of the skin and the degree of swelling, particularly of the outer zones of the skin. To achieve this, the use of a 'buffered pickle' comprising sodium and calcium salts of formic acid has been suggested. However, leathers tanned after such pretreatments lack in fullness and the tanning period is increased considerably. To overcome the difficulties of both 'equilibrium' and 'buffered' pickles, dry deliming or treatment with amino resins has been suggested^{54,55}.

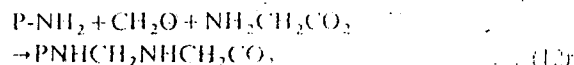
For dry delimiting, skins are treated with non-swelling acids like aromatic sulphonic acids (such as naphthalene sulphonic acid), chromic acid, sulphophthalic acid or polyphosphoric acid. These pretreatments are done with a view to complexing Cr(III) and rendering the chrome tanning salts less cationic, so that more uniform fixation of Cr may result. When chromic acid is used as the non-swelling acid, equilibria (9), (10) and (11)



result giving a uniform distribution of basic chromium sulphate after reduction.

One limitation in the use of non-swelling acid for delimiting is the difficulty in carrying out the bating operation due to the acidity. This may, however, be avoided by pretanning the surface of the pelt with an amino resin or chrome alum under alkaline conditions^{56-59,69}. In the case of chrome alum, the sulphato coordination renders the complex neutral, facilitating penetration into delimed pelt. Alkaline hydrolysis of Cr(III) salt gives rise to cationic Cr(III) *in situ*, leading to a tanning effect. A subsequent

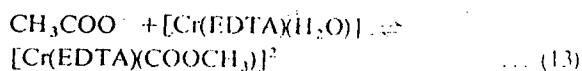
treatment with cationic chromium in the presence of cationic fat liquor has been reported to be beneficial for better distribution of chromium and uptake of dye⁷⁰. Amino resins which are methylol compounds of nitrogen bases, such as urea melamine or dicyanodiamide may also be used⁷¹. Such a resin tannage may be achieved by either impregnating the skin with a monomer followed by polymerization within the skin or treating the pelt with an amino resin of small molecular size. The amino resins bind the amino groups of collagen and do not compete for the Cr binding groups of protein. They tan collagen at pH 4-5 and have a tendency to form Schiff bases of the type R-CH=N-R⁵⁹ and to form polymers⁵⁶. Pretreatment with amino resins prior to chrome tanning produces a fuller, soft and supple leather, because the methylol compounds get deposited. Protection of the surface prior to Cr tanning by means of syntan and quinone tanning has also been recommended, but the cost, colour and toxicity prohibit commercialization of quinone pretreatment. It has been suggested that glycine and protein hydrolysates may be condensed with the amino group of collagen through Mannich condensation (Eq. 12), producing enhanced number of carboxyl groups for Cr fixation⁶⁴.



The guanidino and ϵ -lysine amino groups of collagen may provide sites for such Mannich base condensations. Although indirect evidence for such Mannich base condensation, involving protein amino groups, formaldehyde and active hydrogen compounds like malonic acid was obtained in the form of increase in shrinkage temperature of Cr leather⁷², a chromatographic separation of the hydrolysates provided direct evidence for the formation of R-NH-CH₂COO⁻ (ref. 73). Although this activation of the protein towards chrome binding may facilitate the uptake of Cr(III), the Mannich reaction prior to Cr tanning may create Cr(III) penetration problems. Such treatments are best done in a sandwich process, where Mannich base condensation helps the Cr build up during Cr retannage. Long chain decarboxylic acids, which have a tendency to form μ -carboxylato complexes of Cr(III) also help in building up chromium during Cr retannage. On the other hand, for the application of non-cationic Cr(III) salts for Cr tanning, the delimed pelts have been recommended. Such non-cationic complexes may be obtained by highly masking the Cr(III) salts with chelating ligands like lactic acid, EDTA or monoethanolamine⁶⁵⁻⁶⁷.

A ready complexation between protein carboxyl and anionic species such as [Cr(EDTA)(H₂O)]⁻ may be

expected on the basis of the model reaction between acetate and the monoanion as in Eq. (13)^{74,77}.



The coordinated carboxyl groups in the EDTA and other carboxylate ligands are believed to catalyze the rates of aquo ligand displacements by foreign carboxylate anions (in this case protein carboxylates) by way of anchimeric assistance. However, the binding constant in such cases may be relatively low⁷⁴, explaining thereby the poor ability of anionic complexes to tan and give high hydrothermal stability.

Tanning procedures It has been observed that the highest hydrothermal stability is obtained when cationic Cr(III) complexes are used⁵. Therefore, the common practice in chrome tanning is to use cationic Cr(III) complexes and start the tannage at pH 2.5, where protein carboxyl groups remain unionized and complete the tannage at pH 3.8, where carboxyl groups ionize and form complexes with Cr(III). Basification to pH 3.8 leads to hydrolysis and further aggregation of Cr(III) tanning complexes. However, the extent of basification is varied, depending upon the end use of the leather. Whereas light leathers with a high stretchability, to be used for gloves, etc., receive a low percentage of chrome (1.5%) at a low basicity (33%), fullness in upper leathers is obtained by tanning with 2.5% Cr₂O₃ at a much higher basicity (40-60%).

The final basicity of the Cr(III) complexes in the pelt may be increased by tanning with a less basic Cr salt and basifying with a dilute solution of borax, Na₂CO₃ or NaOH or by prebasification of the Cr salt, prior to tanning to different degrees. Several variations in the procedures have been suggested, the simplest being to tan initially with 33% basic liquor and adjust the basification operation suitably. Since the alkaline hydrolysis of Cr tanning complexes to give chromic hydroxide precipitate is relatively rapid, the use of masking salts like formate or acetate in the basification step along with alkali is also suggested^{78,79}. However, to ensure complete equilibration, the leathers are allowed to age for 4-8 hr after chromic tanning and basification, prior to neutralization of the quaternized amino groups of the protein and mineral acids used in chrome tanning. Depending on the nature of leather, neutralization⁸⁰ may be done to pH 4-5.5 using a mild alkali like Na₂CO₃, borax or salts of weak acids (masking salts) or deacidifying syntans. The purpose of neutralization is (i) to avoid the deleterious effects of mineral acids, if any left in the leather, and (ii) to facilitate the treatment with oil emulsions for lubrication and acid dye solution for colouring. The introduction of self-basifying agents^{81,82} is one of the major developments in this area. A self-basifying

mixture contains dolomite, calcium carbonate, sodium sulphite, syntans, bisulphite, sodium bicarbonate, sodium polyphosphate and sodium formate. A suitable self-basifying mixture can be added to the chrome bath and the masking effects of formate, polyphosphate as well as the alkalinity of dolomite, provide the desired conditions. The requirements of the eighties have shown that chrome tanned pelts may have to be retanned suitably to suit the characteristics required of chrome leather for various considerations in the retanning of chrome leather including the ecological standpoints, have been reviewed earlier^{83,84}. Treatments with parent 2-oxazolidines have been suggested for chrome retanning of chrome leather⁸⁵. Combination of other mineral tannages have been suggested for imparting qualities like fullness and scuff resistance to chrome leathers using zirconium or zirconium-aluminium combination methods. It is claimed that basic chromium sulphate⁸⁶ prepared by the reduction of Cr(VI) with aluminium gives improved dyeability, resistance to hydrolysis and fullness. In combining the chrome tanning methods with the easily hydrolysable tannages, such as aluminium, the masking salts have been found of much use; the formation of intermetallic complexes has been suggested in this case^{87,88}.

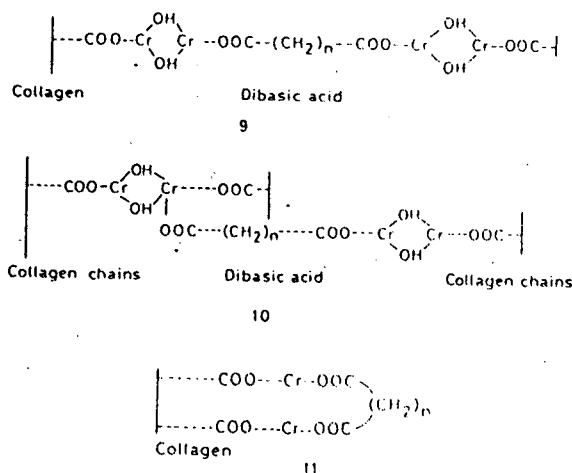
Use of masking salts in chrome tanning Masking is the process in which the basic chromium salts are rendered less cationic through coordination to anionic ligands like formate, acetate, propionate, sulphite, phosphate, etc., so that a greater resistance to hydrolysis and uniform distribution of Cr may be obtained. Although it is stated that masking salts raise the precipitation point⁵, it is not always true. For example, aromatic carboxylic acids which have a tendency to form *gc*-carboxylato-poly-nuclear complexes of low solubility tend to precipitate readily. Similarly, polyphosphates also tend to precipitate Cr complexes. Such masking agents, however, find extensive applications in 'high exhaust-low waste' chrome methods. Barring a few exceptions, the tool of masking is used widely to attempt the simplification of chrome tanning and to impart many special characteristics. The masking agents may be applied at an appropriate stage in the tanning procedure or used during the preparation of the basic chrome salt itself. The special characteristics that could be imparted include (i) built-in lubrication, (ii) vulcanizability, (iii) shower or water proofness, (iv) wet heat resistance, (v) sweat proofness, (vi) fullness and mellowness, (vii) intense dyeing, (viii) level dyeing, (ix) shrunken grain effect, (x) wettability, etc.

Imparting Special Properties to Chrome Tanned Leathers

Built-in lubrication—It has been observed that the

lubrication of a leather can be achieved through the incorporation of deposits in the interstices of fibre bundles⁹⁰. However, the lubricants based on raw oil may be extracted easily with the help of dry cleaning solvents resulting in harsh leathers⁹⁶. To ensure that the lubricants (or fat-liquors) are bound irreversibly, the use of fat liquors based on long chain alkyl sulphonyl chloride (such as Immergen) which react with the protein amino groups, has been suggested⁹¹. However, for application on chrome leather, the Cr complexes used for tanning provide additional active sites for the binding of leather lubricants. It has been reported that long chain mono- and di-carboxylic acids⁹²⁻⁹⁶ may be used for this purpose. The use of chromium stearatochloride and Cr(III)-hydroxystearic acid complexes for built-in lubrication is already known⁹⁹⁻¹⁰².

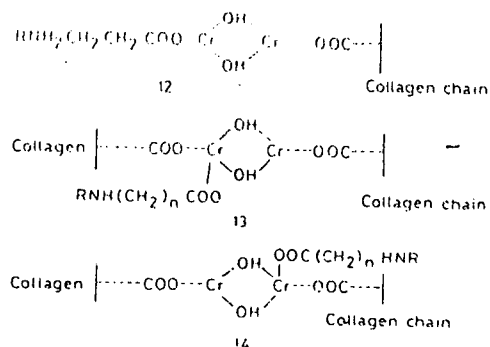
The ammoniacal salts of long chain dibasic acids ($C_{10}-C_{40}$)^{94,95} are also used as masking agents in which the dibasic acid may coordinate with one or more chromium centres, already bonded to collagen in a uni- or bi-pointed manner. Such a coordination may lead to inter- or intra-chain crosslinks through Cr centres, as show in compounds 9 to 11.



The long aliphatic chain gives the lubricating property as well as water-proofness and Cr-OOC bonds lend to built-in lubrication. Usually dibasic acid treatment is given to chrome leather tanned with 1-1.5% Cr_2O_3 which is then retanned (after dibasic acid treatment) with 1.5% Cr_2O_3 at 40°C. The penetration of dibasic acid is facilitated by the addition of 5% benzyl alcohol. However, such a treatment is attended by 5-10% loss in area and hydrophobicity creates problems in dyeing after crusting. Dyeing in such cases has to be carried out prior to drying or rechroming.

Built-in lubrication with improved dyeing properties^{97,98,103}—The dicarboxylic acid treatment has been shown to cause problems in dyeing with

anionic dyes due to lowering of the cationic surface charge and hydrophobicity of the final leather after crusting. Such difficulties can be overcome by treating the leather with a long chain amino acid, such as β -amino propionic acid or betaines¹⁰³. Whereas the carboxyl centre may serve to coordinate to Cr(III) to give substantivity, the aliphatic long chain and amino groups contribute to the lubrication and dyeing characteristics respectively. These amphoteric type of lubricants may have chain lengths up to C_{12} , typical examples being compounds 12 - 14 (refs 53, 54).



Water/shower proofing—Products like monoalkyl ester of phosphoric acid, having a long alkyl chain ($C_{12}-C_{14}$) and long chain fatty acids, impart water repellency as well as built-in lubrication. The coordination of Cr(III) to the anionic centres and the coating of the fibres/surface with long alkyl chains ($C_{12}-C_{20}$) impart water repellency. The phosphochrome complexes exhibit greater stability than chrome-fatty acid complexes. Several fluorinated compounds have also been suggested to impart fire retardation characteristics to the finish films on Cr leather.

Vulcanisability¹⁰²⁻¹¹⁰—It is established that for achieving sufficient softness and suppleness, leather lubricants are to be included in the process. These oils and fat-liquors, however, have a tendency to migrate to the surface when the leather is subjected to heat during processing, e.g. during vulcanization. In the vulcanisable leathers, the migration of leather lubricants is avoided through complexation with Cr(III). Application of esters of di- or polyfunctional acids, e.g. monododecyl ester of citric acid, monoalkyl ester of phosphoric acid, etc. where the long chain consists of $C_{12}-C_{18}$ units, is recommended for this purpose¹⁰⁹⁻¹¹¹. The use of polysulphides has also been suggested.

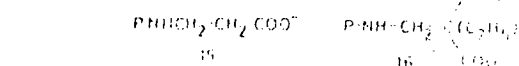
Wet heat resistance¹¹²⁻¹¹⁸—Whereas the hydrothermal stability (T_s) of leather is taken as a measure of the degree of crosslinking and chrome leather is known to exhibit high shrinkage temperatures, there has been much effort in further enhancing the wet heat resistance of chrome

leathers¹¹⁹. High temperatures (near boiling) may be used for operations such as dyeing, so that deeper shades and greater exhaustion of the dye bath may be obtained. One of the major developments in improving wet heat resistance is the application of 'ladder type' crosslinking agents^{112,113}. In a recent review, the utility of dibasic acids for improving wet heat resistance - has been emphasized¹²⁰. Aromatic dicarboxylic acids like phthalic acid undergo complexation with Cr(III) to give polynuclear complexes⁵ with decreased solubility. The use of such aromatic acids has been reported to improve wet heat resistance remarkably. Chrome leathers that can withstand the boil test for 27 hr have already been prepared successfully¹¹². Some other means of increasing heat resistance of Cr leathers have been reviewed by Herfeld and Endish¹²¹. Deposition of vinyl mixed polymers with antimony oxide in aqueous solutions or the impregnation of a fluoro elastomer as 5% solvent solution has been found to increase heat resistance¹²¹.

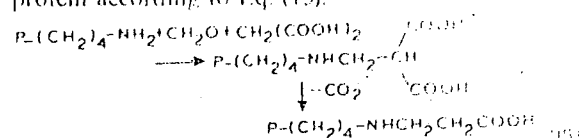
Sweat resistance - The effect of sweat on chrome leather has been attributed to the presence of strong complex forming ligands, viz. lactate, hydroxide, phosphate, etc., as well as to the action of moist heat¹¹⁹. It has been observed that the resistance of chrome leathers to the action of sweat is poor^{122, 125}. It is believed that the constituents of sweat, such as lactate, hydroxide or phosphate form stronger complexes with Cr(III) than the protein carboxyl groups. Therefore, the constituents of sweat lead to the leaching of Cr(III) from the leather. Several attempts have been made to stabilize the Cr-collagen compound against sweat¹¹⁹. One of the studies involved the functionalization of collagen for stronger binding with Cr(III). Active hydrogen compounds like malonic acid, ethylmalonic acid, orthophosphoric acid, catechol and resorcinol were coupled to the protein amino groups through Mannich reaction, using formaldehyde, as shown in Eq. (14).



In the case of chrome leather, the additional Cr(III) binding sites introduced through the active hydrogen compounds are believed to stabilize Cr(III) against the leaching influence of sweat. This coupling of active hydrogen compounds through Mannich reaction showed a decrease in the loss of Cr(III) when the leather was treated with synthetic sweat. However, it was also observed that the introduction of Cr(III) binding sites and crosslinks alone was not sufficient for the stabilization of chrome leather matrix against the action of sweat¹¹⁹. Whereas Mannich bases of the type 15 and 16 did not reduce area on sweat treatment, resorcinolformaldehyde treatment led to a decrease in



both area and Cr(III). It was, therefore, concluded that the dimensional stability of chrome leather depends on factors like fibre swelling, hydration energy, etc. of fibres, etc., in addition to crosslinking. The treatments also gave enhanced wet heat resistance and shrinkage temperatures as high as 127°C using high pressure steam. Treatments with HCHO and malonic acid led to the reaction of ϵ -lysine amino group of the protein according to Eq. (15).



The additional carboxyl groups introduced not only helped the uptake of chromium on retannage but also increased wettability due to hydrophilicity and levelness in dyeing. Nevertheless, the intensity of shades obtained using anionic dyeing procedures may be affected due to the lowering in the surface cationic charge. Resorcinol-formaldehyde treatment is, however, free from such problems and gives soft leathers even with low degree of fat liquoring, though darkening of shades due to oxidation of phenolic groups is disadvantageous. On commercial level, sweat proofing treatments are not given generally.

Fullness and mellowness - Chrome tanning, in general, is an empty type of tannage; though dibasic acid treatment is claimed to give full leathers¹¹². The non-filling character of chrome tannage led to the finding of proper combinations of tanning methods. Retannage with vegetable tannins, higher basic chrome, acrylic syntans, amino resins and treatment with other impregnating materials have been suggested¹²⁶⁻¹³². The products based on the copolymers of castor oil and acrylic monomers as well as melamine formaldehyde resin are being marketed¹³³⁻¹³⁵. Some of the acrylic polymers can be complexed with basic chromium chloride in an alcoholic solvent like isopropanol and be used for filling of chrome leathers¹²⁸⁻¹³². It is claimed that the filling up of leathers by either the application of acrylic salts or retanning with chrome acrylic complexes is superior to other modes of filling with acrylics, such as impregnation with acrylic solutions or emulsions¹²⁸⁻¹³². The use of alginate has also been recommended^{136,137}.

Achieving intense shades^{99,138} Dye affinity of chrome or semichrome leathers may be enhanced by (i) treating with reagents like β -amino propionic acid, (ii) incorporating 4,4'-diamino stilbene-2,2'-disulphonic acid in a sandwich process, or (iii) using alginate^{99,138,139}.

Shrunken grain appearance—The popular shrunken grain effect on chrome leathers may be obtained by a suitable reaction product of diphenyl-oxide sulphonic acid, hydroxybenzoic acid and formaldehyde. The polymeric product resulting from such a reaction has several active sites for ready chrome binding and this astringency has been shown to produce the shrunken grain effect^{140,141}. The shrunken grain leather, starting from wet blue stock, produces leathers of much higher strength than the commercial leathers from the delimed stock.

Wettability¹⁴²⁻¹⁴⁵—Wettable type of chrome leathers may be obtained by any one of the following methods: (i) by partially stripping the chrome of crusted skin by heavy pickling and retanning with chrome¹⁴², (ii) by treating the chromed skin with a long chain dibasic acid under neutral conditions, (iii) by treating the chrome tanned skin with a hydrophilic chrome complex before crusting^{143,144}, and (iv) by treating with complexing wetting agents and lubricants before crusting the leather¹⁴⁵.

Recent developments in methods of chrome tanning¹⁴⁶⁻¹⁸⁸—Recent approaches in chrome tanning have two major aims: (a) time and energy saving methods¹⁶⁶⁻¹⁷¹, and (b) controlling the pollution due to chrome tanning methods¹⁷²⁻¹⁸⁷. For this purpose, the rationalization of chrome tanning has been attempted.

Rationalization of chrome tanning—It aims at saving in time and labour by decreasing both the number and duration of operations. One of the methods of such rationalization is to pretan with chrome alum at the delimed stage, prior to tanning with basic chromium sulphate. Prolonged 'equilibrium pickle' operation may be avoided by using Cr(III) complexes masked highly with lactic acid, EDTA, etc. It is believed that highly masked complexes while penetrating into the leather at nearly neutral pH may undergo alkaline hydrolysis to basic Cr salts and cationic Cr tanning in a reduced number of operations⁶⁵⁻⁶⁷. The rapid processing methods for chrome tanning have been reviewed recently¹⁸⁰.

Powder chrome tanning is another method of rationalization of chrome tanning^{68,146,147}. A pickled or amino resin treated delimed-pickled pelt may be treated with basic chromium sulphate powder without any float, so that the penetration of Cr(III) is quicker. During subsequent flooding, the anionic form is hydrolysed in the drum to give cationic complexes and optimum tanning efficiency.

Another method of rationalization is warm chrome tanning in which the temperature of the bath is raised rapidly to 80°C, after carrying out the initial tanning at normal temperatures (20-30°C)¹⁴⁸⁻¹⁵³. However, in this method, if proper precaution to examine T_g of the

leather prior to warming is not taken, drawn grain may result. This may be avoided by tanning in a low float with an acidic salt and basifying at high temperatures. This method ensures efficient uptake of chromium and, therefore, has high exhaustion in short duration.

Chrome tanning using self-basifying products is another method of rationalization wherein a lightly pickled pelt is soaked in basic chromium sulphate, taken along with self-basification products consisting of masking agents⁸¹⁻⁸³.

Besides the conventional methods of chrome tanning, ultrasonics has also been tried with some success^{189,190}. Chrome tanning of delimed skins is carried out ultrasonically in mineral/spindle oil emulsion containing an alkyl phenol ethylene condensate type emulsifier. If bated skin in 60% float in a bath containing 4.8% Cr₂O₃ on pelt weight and spindle oil emulsion is subjected to ultrasonic whistle and tanned with basic chrome (1.8% Cr₂O₃), leathers with $T_g = 110^\circ\text{C}$ are obtained. The tanned leathers, after washing with the alkyl phenol ethylene condensate type of emulsifier, to avoid slipperiness during shaving, are neutralized with NaHCO₃. The requirement of sodium bicarbonate and fat liquor is reduced by 40% and 25-30% respectively. These leathers have good softness. Similarly, chrome tanning may be effected in solvents also¹⁹¹. Skins could be tanned with basic chromium chloride or basic chromium nitrate in alcoholic solvents. The completion of the tannages, however, requires water, though thiocyanato complexes of chromium do not require water for tanning action¹⁹². Use of these chrome tanning solvents which can tan in aqueous medium may not be a practical proposition at the present. It has been suggested that chrome tanning in non-aqueous media may become a reality in the near future. However, there is now a distinct trend to go back to water-based formulations. With the increasing realization of the need to save energy, low float methods are becoming popular. However, low float methods do not help in decreasing the pollution load; they only result in more concentrated effluents.

Effluent problems and methods for minimization¹⁹²⁻²⁰¹—The polluting nature of the tanning effluents had led to major difficulties for the leather industry in the advanced nations. One of the chief pollutants of the leather industry besides sulphide is chromium^{193,194}. It is believed that Cr(III) is in fact an essential element and is involved in the glucose metabolism¹⁹⁶; however, the insolubility of Cr³⁺ at body pH values and the kinetic inertness are to be considered. A systematic study on the toxic nature of Cr(VI) and Cr(III) reveals that though Cr(VI) is toxic at

neutral pH values, Cr(VI) is not reduced easily to Cr(III)¹⁸⁸.

One of the major approaches in meeting the stringent requirements of effluent water quality is the one adopted in the case of high exhaust and low waste chrome methods^{12,180}. Attempts have been made to correlate the structures of the Cr(III) species in Cr liquors and their affinity for proteins. Analysis of Cr(III) complexes in the effluent has shown that mononuclear and low charged species are the major constituents of the effluent^{12,13}. The use of dibasic acids like adipic, succinic, etc., in the preparation of chrome liquors was suggested as a means to produce 'low waste' chromium tanning solutions. Increasing amounts of such dibasic acids are now being used for achieving higher levels of exhaustion.

Several workers have suggested recycling of chrome liquors for improving the exhaustion¹⁹⁷⁻¹⁹⁹. Recycling procedures were shown to be commercially viable and the quality of the final leather may not be impaired by using recycled chrome liquors. The possible improvements of the tannery effluent from the point of view of the tanner have been discussed and the fundamentals of the exhaustion of chrome tanning process with improved chrome exhaustion have been reviewed²⁰⁰.

The use of aromatic dibasic acids and polyphosphates was also suggested for getting improved Cr exhaustion¹⁸⁸. In order to comply with the international standards of Cr content in the effluent, several treatment procedures and their economics were studied¹⁷⁷⁻²⁰¹. The methods for the recovery and disposal of the solid wastes from Cr tanning industry were also studied²⁰¹. Incineration of the solid wastes has been reported to be a very useful method for recovering Cr from the chrome wastes²⁰¹. However, further work is needed in this area to produce 'high exhaust-low waste' chrome tanning salts that do not give rise to surface fixation and drawn grain, while employing energy saving operations.

Conclusion

The century old chrome tanning methods are now undergoing major changes for the last ten years with R&D contributing to rationalization and development of rapid processing methods. With an increased awareness of the toxic effects of chromium, there is a greater emphasis on the need for improved Cr exhaustion methods. The challenges of the eighties to a chrome tanner are going to be in the form of making a full, soft, vulcanizable, heat-resistant chrome leather with improved dyeing and other characteristics but without affecting the ecological balance and using minimum amount of energy and labour. However, to a

chemist trying to understand the stabilizing forces of chrome-collagen compound, direct information on the manner in which chrome complexes are bound inside the leather will be evident only after a selective cleavage (without affecting Cr-collagen bond) procedure is standardized.

Summary

Recent trends in the chemistry and technology of chrome tanning including the modifications in the pretanning process are described.

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